

# **ADHESIVES TECHNOLOGY FOR ELECTRONIC APPLICATIONS**

**Materials, Processes, Reliability**

by

**James J. Licari**

and

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## ***Dedication***

Dale Swanson is pleased to dedicate this book to his “Rolling Reader” students in Mr. Mike Heiner’s 3<sup>rd</sup> Grade Class and Ms. René Kopp’s 4<sup>th</sup> Grade Class (2001–2002) at Thomas Jefferson II Elementary School, Anaheim, CA.

### 3<sup>rd</sup> Grade

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# Preface

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Many books have been written on adhesives, but we believe this is the first that focuses entirely and comprehensively on the use of adhesives in the multi-billion-dollar electronics field. The rapid advancements that have been made during the past two decades in microelectronic devices and packaging have been the drivers for the major changes that have occurred in adhesive materials and processes. Polymer adhesives such as epoxies, silicones, cyanate esters, and polyimides have, to a large extent, replaced metallurgical and vitreous attachment methods for the very fine pitch, high-density flip-chip, chip-scale, chip-stack, and ball-grid array packages. Polymer adhesives have advantages over solder because of their lower cost, precision placement of devices, low-temperature processing, and ability to be reworked.

An understanding of the electrical, thermal, and environmental requirements of the electronic devices and circuits is important for materials and process engineers and for chemists in formulating and developing new adhesive compositions. At the same time, electrical design engineers require some understanding of the basic chemistry and properties of adhesives in order to select and specify a reliable adhesive for a specific application. Manufacturing engineers require knowledge of the various cleaning, deposition, curing, and rework processes and equipment. Finally, quality assurance personnel must be familiar with potential failure modes and mechanisms and the reliability aspects of adhesives.

This book brings together the entire technology of adhesives for electronics, starting with an Introduction that defines the various devices and packaging approaches, then progressing to Functions and Theory; Chemistry, Formulation, and Properties; Bonding Applications, Reliability, and Test and Inspection Methods. In addition to discussions on general applications such as die, substrate, and lid attachments, specific applications such as those for automotive, medical, space, and military are covered. Special

treatment has been given to relatively new developments including anisotropic adhesives, electrically conductive adhesives as replacements for lead-bearing solders, and underfill adhesives for flip-chip devices and ball-grid array packages. Mindful of current environment and energy requirements, we also discuss and compare formulations and curing methods that will meet these requirements such as UV curing, microwave curing, moisture curing, and 100% solids adhesives.

The reader will find an abundance of tables listing commercially available adhesives, adhesive properties, suppliers, equipment, and test methods that should save considerable time in selecting the most reliable material and process for a specific application. The tables provide examples, but are not intended to be comprehensive. The reader should consult each supplier for the latest product list and for the most recent data sheets. It is our hope that this book will be of value to a broad group of personnel working in the field of electronics including design engineers, materials and process engineers, chemists, quality assurance and reliability personnel, manufacturing engineers, and marketers.

*Note:* Throughout the book we have vacillated between the metric and English systems, especially for dimensions. At first, we wished to be consistent, but this was not practical because of the wide variation in dimensions from small-pitch devices to large circuit boards. Thus, mils or micrometers are used for the smallest dimensions while inches or millimeters are used for the large dimensions. For convenience, conversion tables are provided in the Appendix.

June 2005

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# 1 Introduction

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Adhesives are extensively used and are vital in the assembly and packaging of electronic devices, especially in the current proliferation and mass production of electronic hardware. Adhesives are used in assembling semiconductor die, both in single-chip packages and in multichip assemblies. Both bare-chip devices and prepackaged components are attached and electrically connected with adhesives to produce electronic circuits such as printed-wiring assemblies (PWAs), thin- and thick-film hybrid microcircuits, and multichip modules. Adhesives, as pastes or as solid films, are also used in fabricating high-density multilayer interconnect substrates, flexible circuits, flat-panel displays, and a host of other emerging applications including optoelectronics; high-speed, high-frequency circuits; sensors; and smart cards. Due to their low cost, ease of rework, and low processing temperatures, polymer adhesives have replaced many traditional interconnect materials such as solder, eutectic alloys, and wire, especially for most commercial and consumer electronics. However, because of the large number of adhesives available and the variety of polymer types, forms, and formulations, a basic understanding of adhesives and their properties is necessary in their selection and application to assure performance and avoid subsequent reliability problems. The prime objective of this book is to provide this basic understanding and define guidelines for selecting and qualifying adhesives based on the product and the conditions the adhesive is expected to meet.

## 1.1 ADHESIVE TYPES AND DEFINITIONS

Adhesives used in assembling electronic circuits may be classified based on their physical form, polymer type, molecular structure, formulation, curing method, function, or intended application.

### 1.1.1 Classification by Form

First, in terms of their physical form, adhesives may be either *pastes* or *preforms* (also known as films or tapes). Pastes are semisolid materials, easily dispensed through a needle or applied by screen or stencil printing. Film adhesives are solid sheets of thermoplastic or partially cured (B-staged) thermosetting polymers that can be cut to size and generally used to attach large-area components, substrates, and lids.

Paste adhesives, in turn, may be *single-component* or *two-component* types. A single-component adhesive is a one-part system in which the hardener or catalyst is latent, that is, although mixed with the resin portion, it will not react until a certain cure temperature has been reached. A two-component system consists of a separate resin portion, referred to as Part A, and a hardener or catalyst portion, Part B, either of which may contain filler. The two parts are packaged and stored in separate containers. When ready for use, the two parts are weighed, mixed, deaerated, dispensed, and cured. Two-part adhesives may be converted to one-part systems by quickly mixing Parts A and B, deaerating, freezing, and then storing the mixture at temperatures of  $-40^{\circ}\text{C}$  or lower. These one-part adhesives, known in the trade as *frozen adhesives*, may be purchased from several suppliers in tubes or syringes of various sizes and amounts. Frozen adhesives are generally epoxies and are highly desirable from a manufacturing standpoint since the electronics assembler obviates the risk of human errors inherent in the weighing, mixing, and processing of small batches of adhesive.

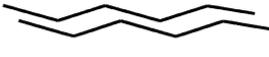
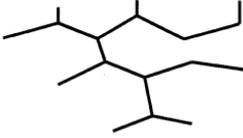
### 1.1.2 Classification by Polymer or Chemical Type

Adhesives are often referred to by their polymer type. The major polymer types used in electronics packaging are epoxies, silicones, acrylics, polyurethanes, polyimides, and cyanate esters. Some generic properties apply to each type but, in generalizing, one must be careful since there are hundreds of formulations of each type on the market, each with minor or major differences in properties. Even for a specific formulation, an adhesive's processing conditions, such as its cure schedule, can affect the final properties. Chapter 3 provides a discussion of the major polymer types and their properties.

Polymer adhesives may be further classified as either *thermoplastic* or *thermosetting*, depending on whether their molecular structures after curing are linear or crosslinked. The linear polymers may be straight chains

or branched chains (Fig. 1.1). Thermoplastic adhesives melt and flow at a specific temperature or within a narrow temperature range, then quickly resolidify on cooling. Thermoplastic adhesives are sometimes called *hot-melt adhesives* and are particularly advantageous in their ease of processing and reworking. Most polyurethanes and polyamides fall in this category. Although thermoplastic polymers are linear, not all linear polymers behave as thermoplastics. Many linear polymers have a high aromatic or heterocyclic content in their structures, thus increasing their thermal stabilities to a temperature that, instead of melting, char and decompose like thermosetting polymers. Among these are polyimide pastes. Other thermoplastic film adhesives that are fully polymerized, high molecular-weight resins behave in the same way; examples are polyetheretherketone (PEEK<sup>®</sup>, a trademark of Victrex), polyetherimide (ULTEM<sup>®</sup>, a trademark of General Electric), fluorinated ethylene propylene (FEP), polysiloxane imide, and some epoxies.

Thermosetting adhesives, on the other hand, soften as the temperature is increased to the glass transition temperature, but do not melt and resolidify. Instead, because of their highly cross-linked macrostructures, they decom-

<b>THERMOPLASTIC</b>	<b>THERMOSETTING</b>
 LINEAR CHAINS	
 BRANCHED LINEAR	<b>CROSS-LINKED MACROMOLECULES</b>
Soften and liquify at melt temp. Resolidify on cooling	Soften and decompose at temp. Irreversible
Easy rework, no clean	Rework difficult, char residues
Quick setting (seconds to minutes/no cure)	Long cures (minutes to hours)
High purity, low outgassing	Require hardeners/catalysts
Poor-to-marginal resistance to solvents, temperature, and radiation	High adhesive strength
	Resistant to solvents, high temperatures, and radiation

**Figure 1.1.** Representations of thermoplastic and thermosetting polymer structures.

pose and char on reaching their decomposition temperatures. Epoxies, cyanate esters, and phenolics are generally thermosetting types.

A unique adhesive type is *silver-glass*; a paste consisting of a glass matrix blended with silver particles, a polymer binder, and a solvent. Silver-glass adhesives are not polymer types. Although a polymer resin is added to the formulation to give the paste the thixotropic properties needed during dispensing or screen printing, the resin is subsequently burned off during final processing. Silver-glass adhesives are processed at much higher temperatures (400°C–450°C) than either polymer adhesives (75°C–175°C) or solders (180°C–300°C). These high temperatures are required to burn-off the polymer binder, melt the glass, and fuse the glass and oxides.<sup>[1]</sup>

### 1.1.3 Classification by Formulation

In many adhesives formulations, the resin portion is the same or similar and what determines its properties is the hardener or catalyst that is used to cure the resin. Thus, depending on the hardener, epoxy adhesives may be referred to as amine-cured, anhydride-cured, polyamide-cured, or novolac-cured. Polyurethanes may be polyol-cured or hydroxypolyester-cured.

Formulations may also be either *solvent-based* or *100% solids*. One-hundred percent solids adhesives contain no solvents and are rapidly replacing the solvent-based types because of environmental concerns over volatile organic compounds (VOC), government regulations restricting their use, and reliability concerns.

### 1.1.4 Classification by Curing Method

The curing process consists of transforming low-to-moderate molecular-weight resins (monomers or oligomers), generally liquids, into high molecular-weight solid polymers. Most curing mechanisms involve polymerization requiring a catalyst or hardener and are initiated by some form of energy.

**Heat-cured adhesives.** *Heat curing* by convection in box ovens is the most widely used and simplest method for curing adhesives. Heat is applied until a temperature is reached at which polymerization occurs and continues until the polymerization is complete. Time-temperature curing schedules are developed for each adhesive for which optimum properties are achieved. For each of their adhesives, suppliers provide several cure schedules that are considered equivalent relative to final properties. The user may also develop

his own curing schedule to achieve properties specific for his application and maintain production flow. This can be done experimentally by measuring a desired parameter such as electrical resistivity, dielectric constant, hardness, or bond strength as a function of cure temperature and time. Optimum cures may also be determined from the degree of polymerization as measured by infrared spectroscopy, thermomechanical analysis (TMA), or differential-scanning calorimetry (DSC).<sup>[2]</sup> The cure times and temperatures required are largely dictated by the hardener or catalyst used. With the rise in mass production of consumer electronics and the need to reduce energy costs, epoxy adhesives known as *snap-cured adhesives* have been developed that cure in less than one minute at temperatures of 160°C–170°C. Snap-cured adhesives are generally cyanate ester or modified cyanate esters that form high-temperature-stable triazine structures on curing.<sup>[3][4]</sup>

**Ultraviolet (UV)/visible-light-cured adhesives.** Adhesives that cure on exposure to UV radiation are also finding wide use because of their rapid cures (several seconds) and because they generally do not require heat energy. Their chemistry is such that exposure to UV light in the range of 2,000–4,000 angstroms initiates polymerization and effects cures in less than one minute. However, UV curing must often be followed by a short heat cure to fully polymerize portions of the adhesive that are shadowed from UV light by other components or portions of the circuit. Ultraviolet-light-curing adhesives are generally acrylics or include the acrylic, vinyl, or ethylene groups as part of the polymer structure. UV-cured adhesives are of particular interest in positioning and staking precision parts such as glass fibers in optoelectronic circuits or staking components on one side of a double-sided printed-wiring board (PWB) while the other side is being assembled, for example, by solder dispensing, attaching components, and reflowing solder.<sup>[5]</sup>

**Microwave curing.** *Variable-frequency microwave (VFM) curing* is yet another rapid curing method for adhesives. It differs from conventional microwave in using swept frequencies rather than a fixed frequency. The main advantages of VFM curing are cure times that are two to ten times faster than conventional heat curing and uniform heating of large sections because of an even distribution of energy.<sup>[6][7]</sup>

**Moisture curing.** *Moisture-cured adhesives* require only ambient moisture to cure. These adhesives contain functional groups that have been purposely blocked and rendered unreactive until exposed to humidity. Moisture reacts with the blocked groups releasing the functional (active)

group, allowing it to polymerize. Moisture-curing adhesives may take days to attain complete curing and may have to be supplemented with a short heat cure. Both silicones and polyurethanes are commercially available as one-part moisture-curing adhesives.

### 1.1.5 Classification by Function

Adhesives are often classified according to the function they are to perform. There are four main functions: mechanical attachment, electrical connections, thermal dissipation, and stress dissipation.

**Mechanical attachment.** Adhesives that are used to bond dissimilar materials must produce sufficient shear strength and tensile pull strength and maintain this strength for the life expectancy of the part and under the environmental conditions that the part will encounter. A reduction in bond strength generally occurs on aging at elevated temperatures and under moist conditions, but the reduced strength may still be sufficient for the intended application.

**Electrical connection.** Adhesives may substitute for wire or solder in forming electrical connections; for example, in connecting capacitors, resistors, or semiconductor devices to a printed-wiring board or to a thin-film or thick-film hybrid microcircuit. The best and most widely used electrically conductive adhesives are silver-filled epoxies. Because of the large amount of silver required in electrically conductive adhesives (60%–80% by weight), they also provide a high level of thermal conductivity, allowing components to dissipate heat and operate in their normal temperature range. Electrically conductive adhesives may be further classified as either *isotropic* or *anisotropic*.

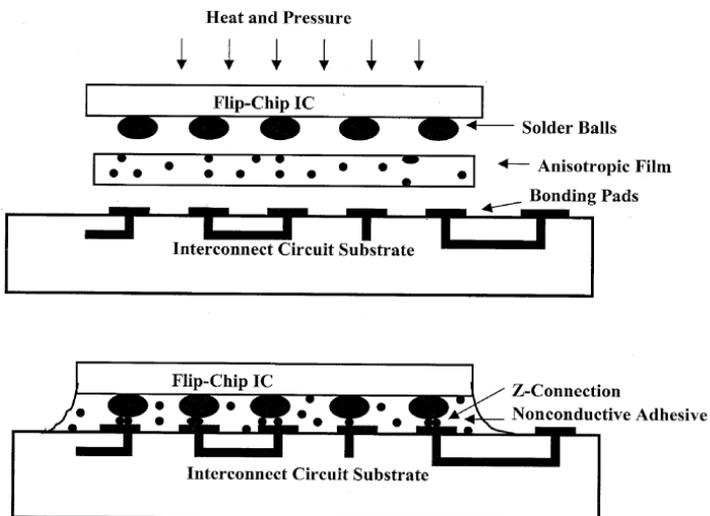
Isotropic adhesives conduct current equally in all directions and are the most common and widely used in industry. The anisotropic types, also referred to as *z-direction adhesives* or *anisotropic-conductive adhesives* (ACA), although filled with metal particles, are filled at much lower levels (0.5%–5% by volume) than isotropic types (filled 25%–30% by volume). The volume fraction of filler is well below the percolation threshold at which the adhesive becomes highly conductive in all directions. Because of the low volume fraction of metal particles, there are no continuous electrically conductive paths in the *x-y* plane. During the connection process, the anisotropic adhesive, either as a film or paste, is positioned between a flip-chip bumped die or a tape-automated bonded (TAB) die and the corresponding pads of an interconnect substrate. Pressure and heat are

applied so that the conductive particles contact and form  $z$ -direction connections. The connections are held in place by the surrounding nonconductive cured adhesive. The lack of continuous particle connections in the lateral direction provides electrical insulation around the connections (Fig. 1.2). Conductive particles, ranging in size from 5 to 20  $\mu\text{m}$ , may be pure metals such as silver, gold, nickel, or solder, plated-metal cores, or plated cores of plastic or glass.

Although dating as far back as the 1960s, anisotropic adhesives have only recently been rediscovered and advanced to a state where they are being used in place of solder to interconnect fine-pitch, high I/O-count flip-chip devices, TAB devices, and high-density interconnect substrates. Anisotropic adhesives are also used to interconnect edge connectors and flex cable to PWBs and flat-panel displays (FPDs). ACAs are commercially available in either paste or film form and as either thermoplastic or thermoset types.

Nonconductive or *electrically insulative* adhesives are used where electrical shorting may be a problem or where electrical isolation is required. Nonconductive adhesives are available in either paste or film form and are generally filled with silica or alumina to provide optimum flow properties for dispensing and to improve their thermal conductivities.

**Thermal dissipation.** *Thermally conductive adhesives* may be filled with metal, ceramic, or inorganic particles. Silver-filled epoxies have high



**Figure 1.2.** Representation of anisotropic conduction.

thermal conductivities, but may not be used where there is a risk of electrical shorting. In such cases, epoxies or other polymers filled with electrically resistive, but thermally conductive materials such as aluminum nitride, boron nitride, alumina, or beryllia must be used. Some applications for thermally conductive adhesives include attachment of power devices, heat sinks, large components such as capacitors and transformers, large ceramic substrates, and edge connectors.

**Stress dissipation.** Adhesives that reduce and dissipate stresses consist of low-modulus elastomeric types. Low-stress adhesives are required in attaching large die, large substrates, and flex circuitry. Low-modulus elastomeric adhesives are also used to attach and fillet large components to dampen vibration and shock.

### 1.1.6 Classification by Intended Use

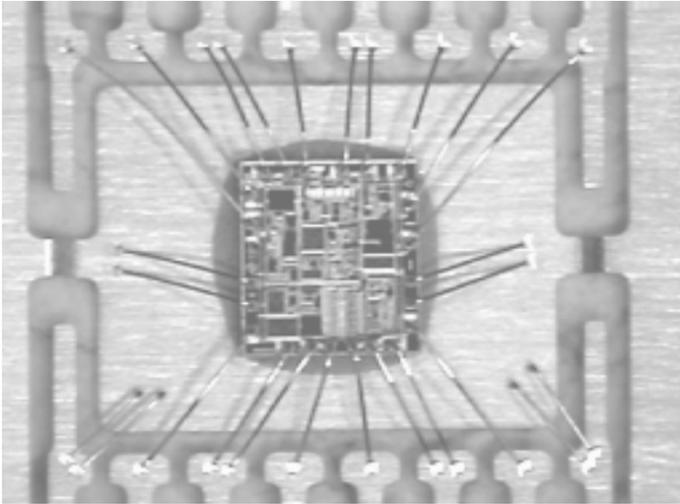
Adhesives may also be designated according to the electronic application for which they are intended and formulated. Some of these applications are discussed below.

**Die attachment.** Adhesives that are used to attach bare die\* (unpackaged semiconductors such as transistors, diodes, and integrated circuits) or chip\* devices (unpackaged capacitors, resistors) into a single package or onto an interconnect substrate are referred to as die-attach or chip-attach adhesives. They may be either electrically conductive, used where ohmic contacts are required as in connecting capacitors, resistors, and transistors, or electrically insulative, used in attaching ICs, stacked chips, connectors, heat sinks, and substrates. Die-attach adhesives are widely used to attach semiconductor die (chips) onto leadframes (COL: chip-on-lead) or leadframes onto die (LOC: lead-on-chip) prior to plastic molding or hermetic sealing in ceramic or metal packages (Fig. 1.3). Die-attach adhesives are also used in the assembly of hybrid microcircuits and multichip modules.

Bare die and other chip devices are attached with electrically conductive or nonconductive adhesives to ceramic substrates having defined circuit patterns produced by thin-film vapor deposition and photoetching of metals or by screen printing and firing of thick-film pastes.<sup>[8]</sup> With recent advancements in fine-line printed-circuit boards, adhesives are also finding use in attaching bare die to PWBs, a technology known as chip-on-board (COB).

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\* The words *die* and *chip* are often used interchangeably, although chip is a broader term that includes bare semiconductor die, but also chip capacitors and resistors.



**Figure 1.3.** Single chip, adhesive-attached and wire-bonded to leadframe. (Photograph courtesy of Analog Devices.)

**Substrate attachment.** In assembling hybrid or multichip modules, ceramic interconnect substrates fabricated using thin-film or thick-film processes are attached to the inside base of a ceramic or metal package. Generally, film adhesives that have been cut to size are used to attach large substrates (greater than one-inch square) while either paste or film adhesives may be used for smaller substrates. Substrates may be alumina, beryllia, aluminum nitride, or silicon.

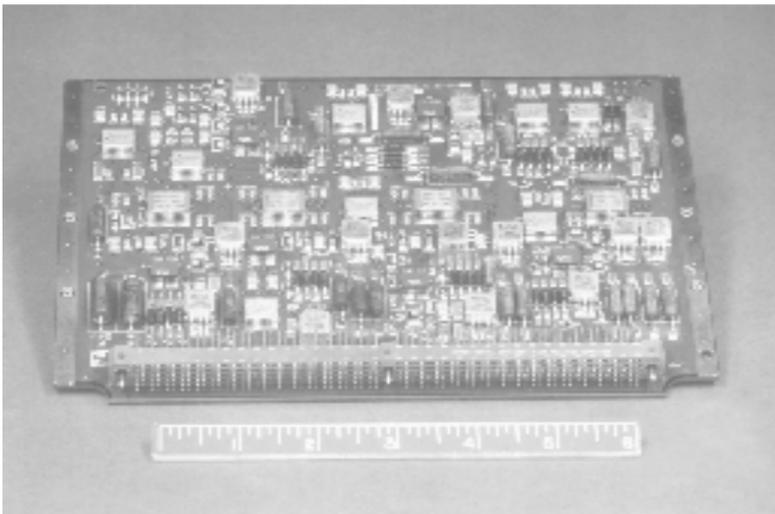
**Lid attachment.** Adhesives in both paste and film form have been used to attach and seal ceramic or metal lids to cavity packages that may also be ceramic or metal. These packages cannot be considered hermetic in the sense that seam-sealed, welded, or soldered lids are, but they are adequate for most commercial and consumer electronics where extreme moisture-temperature environments are not encountered. Packages sealed with epoxy adhesive have been reported to withstand 100 hours of 95% relative humidity.<sup>[9]</sup>

**Surface mounting.** Surface mounting of components onto PWBs is commonly referred to in the industry as *SMT* or *surface-mount technology*. It consists of the attachment of electronic components by automated dispensing or screen printing of solder paste and adhesive onto a PWB, placement of the components, then curing the adhesive and reflowing the

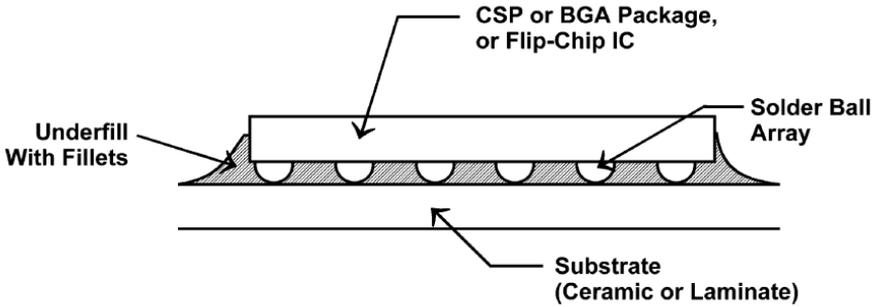
solder to form the electrical connections (Fig. 1.4). For SMT, the components are generally prepackaged as opposed to bare die and have pins, leads, or terminals that are solderable or can be connected using electrically conductive adhesives. Adhesives have been developed that will cure during the same operation in which the solder is reflowed, thus avoiding a separate cure step and accelerating production. Solder may also be replaced with an electrically conductive epoxy. Insulative adhesives may be used to reinforce large capacitors, inductors, or transformers.

Surface-mount technology replaces previous methods of inserting component leads into plated-through holes of PWBs, wave soldering from the back side to flow solder into the holes, and simultaneously forming both mechanical and electrical connections.<sup>[10]</sup> SMT is highly automated and currently the most widely used production process for the assembly of single-layer, double-sided, and multilayer circuit boards.

**Underfill for flip-chip-attached devices.** With the availability and increased use of flip-chip devices, a need has arisen to reinforce the connections and dissipate stresses resulting from mismatches in expansion coefficients among the solder, the substrate, and the device. This need has been met by underfilling the space between the solder connections with specially formulated underfill adhesives (Fig. 1.5). Underfill adhesives are



**Figure 1.4.** Printed-wiring assembly (4 x 8 in.) with surface-mounted components. (Photograph courtesy of the Boeing Company.)



**Figure 1.5.** Cross-section of flip-chip-attached die showing underfill.

electrically insulative epoxies or modified epoxies formulated to have good wetting properties and rapid flow and, once cured, to have low moisture absorption and stress-dissipating properties.

**Underfill for ball-grid-array (BGA) packages.** After attaching the BGA packages to a PWB and reflowing the solder, an underfill adhesive similar to that used for flip chips may be dispensed and allowed to fill the spaces between the solder balls, thus reinforcing the connections and relieving stress in the entire structure.

**Solder replacements.** Because of the toxic nature of lead in lead-alloy solders and health concerns from being exposed to hot solder fumes during circuit board assembly, interest has developed in replacing lead-containing solders with no-lead solders. Since most of the no-lead solders evaluated to date require higher reflow temperatures than the currently used tin-lead solder, a concurrent effort has been the investigation of electrically conductive adhesives as solder replacements. The feasibility of forming silver-filled epoxy bumps on the die at the wafer stage has been demonstrated for flip-chip devices, and adhesive formulations have been made commercially available.<sup>[11]</sup>

**Particle getters.** A minor, but in some cases, essential use of adhesives is to getter particles entrapped in a sealed microcircuit package. Some microcircuits have been found difficult to clean and to remove all metal and nonmetallic particles from their assembly prior to hermetic sealing. Others, even after cleaning and sealing, have been found to slough off particles during vibration. In these situations, a soft, tacky adhesive may be attached to the inside of the lid prior to sealing. Particle getters are primarily silicones.

## 1.2 SUMMARY OF PACKAGING TECHNOLOGIES

A brief description of the main electronic packaging technologies is provided to assist the reader in understanding how and where adhesives are being used. The large number of packaging approaches and variations for each approach precludes a thorough discussion here. The literature, however, is replete with hundreds of technical articles and several books for each approach.<sup>[8][12]-[19]</sup>

### 1.2.1 Single-Chip Packaging

After mechanical attachment to a substrate, a leadframe, or to the inside of a package, bare die or chip devices are electrically connected by one of five methods: wire bonding, flip-chip bonding, TAB, solder attachment, or attachment with electrically conductive adhesives. Figure 1.6 shows some of these methods.

*Wire bonding* is still the foremost method used. Aluminum or gold wire, generally 1-mil diameter, is used for most applications. High current power circuits require thicker wire up to 10-mil diameter. Die can be wire bonded at high speed with automatic thermocompression, thermosonic, or ultrasonic equipment.

In *flip-chip bonding*, the normal wire-bond pads at the perimeter of the die are replaced by solder or metal bumps. Solder bumps may also be formed throughout the die area (area arrays) to achieve up to 1,000 I/Os per die. The bumped die are flipped face down to mate with corresponding solder pads formed on the interconnect substrate that may be a PWB, a thin- or thick-film ceramic substrate, a chip carrier, or a ball-grid array package. The solder is then reflowed to form the z-axis electrical connections. Flip-chip bonding has major advantages over wire bonding in the large number of

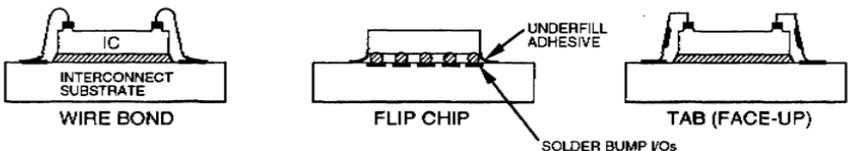


Figure 1.6. Cross-sections of basic die-bonding and chip-connection methods.

connections that can be made per unit area and their short electrical paths, important for high-speed, high-frequency circuits. Variations of flip-chip designs include flip-chip-on-board (FCOB), flip-chip-on-flex (FCOF), and flip-chip-in-package (FCIP).

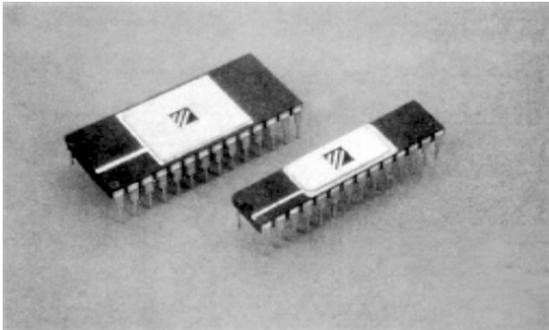
In *tape-automated bonding* (TAB), the semiconductor die, fabricated with bumped interconnect pads, are positioned in apertures of a polymer-film tape, generally polyimide (Kapton<sup>®</sup>, a registered trademark of DuPont), then gang-bonded to cantilevered beams that are formed by photodelimited metal pads on the tape. The tape (film) has sprocket holes along its sides similar to movie film and, like movie film, is handled on reels in automatic equipment for high-speed assembly.<sup>[15]</sup>

Once the die are attached and electrically connected, a large variety of packages and packaging approaches is available ranging from low-cost transfer-molded plastic or plastic-encapsulated devices to devices that are hermetically sealed in metal or ceramic packages. Initially, transistors were welded shut in small metal cans of various sizes referred to as transistor outline (TO) cans. With the introduction of ICs, followed by the progressive increase in functionality to large-scale integration (LSI) and very-large-scale integration (VLSI), increasing numbers of I/O connections (up to 1,000 per device) were required. To meet these needs, new cavity and non-cavity (plastic and ceramic) packages have been designed and built that have a higher number of leads of smaller pitch. These packages can be used for both insertion mounting and surface mounting. Among packages introduced were the dual-in-line packages (DIP), quad-flat packs (QFP), pin-grid arrays (PGA), and chip-scale packages (CSP) and, along with them, numerous variations and a host of new abbreviations and acronyms.

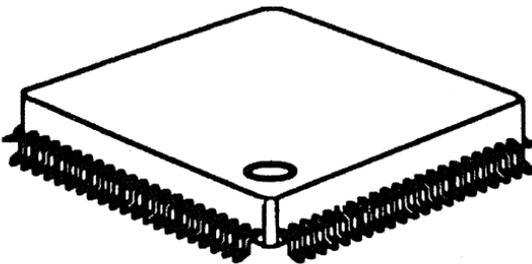
**Dual-in-line package (DIP).** The dual-in-line package is a very popular rectangular package in which the leads emanate from two parallel sides of the package (Fig. 1.7). DIPs may be constructed of molded plastic [plastic dual in-line package (PDIP)], primarily epoxy, or of ceramic [ceramic dual-in-line package (CERDIP)] and may have 8 to 64 leads with a pitch of 2.54 mm (100 mils). In one process, the die is attached with adhesive or eutectic solder to a leadframe, wire bonded, then transfer molded with plastic. The leads are formed (bent vertically), solder coated and then are ready for insertion in plated through-holes of a PCB. CERDIPs consist of a preformed ceramic body with one or two cavities containing the bonding pads to which the IC chips are bonded. The leads are brazed to connecting pads at the side edges.

**Quad-flat packs (QFPs).** Quad-flat packs may be metal or ceramic cavity types or plastic-molded packages where the leads emanate from all four sides (Fig. 1.8). Packages may be of various sizes with lead pitches as low as 12 mils and up to 370 leads. QFPs may be used to package either single chips or multiple chips in one package. The leads of QFPs may be formed in the shape of “gull wings” so that the packages can be surface mounted onto an interconnect substrate.

**Area-array devices and packages.** ICs, chip carriers, and packages may have their I/O connections formed throughout the surface area (area arrays) as opposed to peripheral I/Os as with wire bond pads on die or axial leads on packages. Area arrays include flip-chip, BGA, and pin-grid arrays. Area-array devices provide very high I/O counts per surface area, which are necessary for increased functionality.



**Figure 1.7.** Examples of dual-in-line packages (DIP).

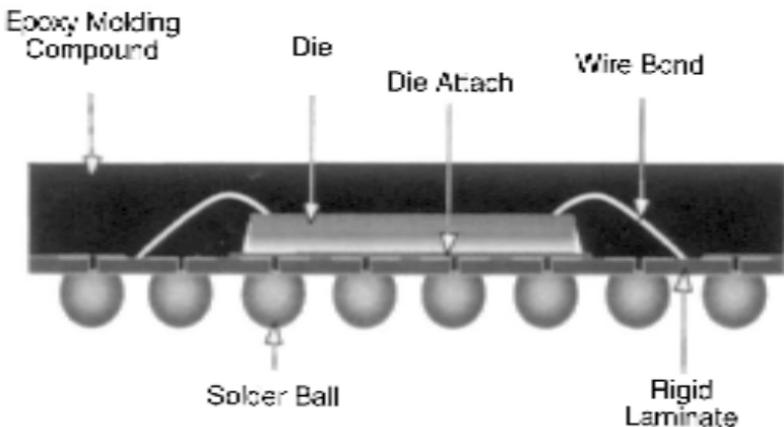


**Figure 1.8.** Diagram of a quad-flat pack (QFP) showing “gull-wing” leads for surface mounting.

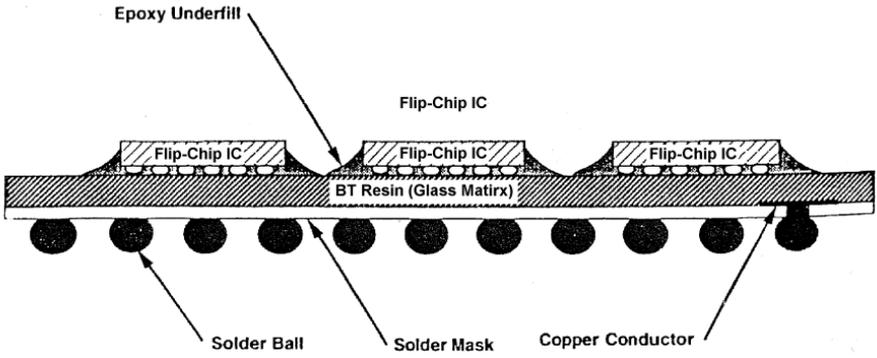
*Flip-chip devices.* Flip-chip devices have solder bumps, other metal bumps, or even conductive adhesive bumps on the face of the device for I/O connections. During assembly, the devices are flipped face down, then mated and bonded to corresponding solder or metal pads on the package or interconnect substrate. In the quest to eliminate tin-lead solders, electrically conductive epoxy adhesives are beginning to be used for the bumps.

*Ball-grid array (BGA).* Ball-grid arrays are analogous to flip-chip devices except that the solder balls are formed or attached at the next level: the package or the chip carrier (Fig. 1.9).<sup>[13]</sup> Thus, one can have flip-chip or wire-bonded devices or combinations in a BGA package. BGAs were developed because other packaging approaches such as the QFP had reached their limit in the number of I/Os that were practical and producible. Reducing the lead pitch for QFPs had increased the number of leads but, since the leads were at the periphery, such packages became quite large and risked damage to the closely spaced leads. With bumps spread throughout the area of a BGA package, even though the I/O pitch is greater, the overall size is smaller and up to 1,000 I/O bumps are possible. Figure 1.10 shows a flip-flip configuration where flip-chip die are attached and connected to a BGA interconnect substrate.

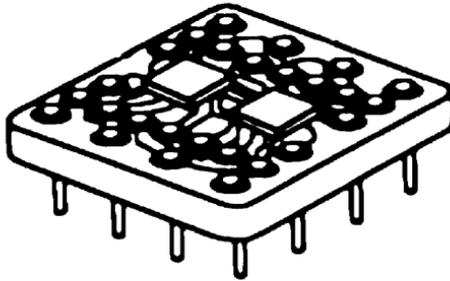
*Pin-grid array (PGA).* PGA packages contain vertical solder-plated or gold-plated Kovar<sup>®</sup> (a registered tradename of Carpenter Technology Corp.) leads on the bottom of a ceramic or plastic package (Fig. 1.11). Several rows of pins may emanate from the bottom perimeter of the package or there may be a full array of pins throughout the area. PGA packages have



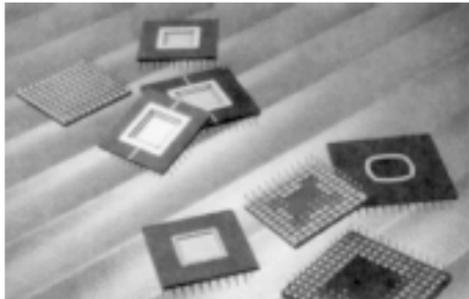
**Figure 1.9.** Ball-grid-array package. (Source: Amkor.)



**Figure 1.10.** High-density multichip packaging, flip-chip-attached die on ball-grid array substrate.<sup>[8]</sup>



(a)



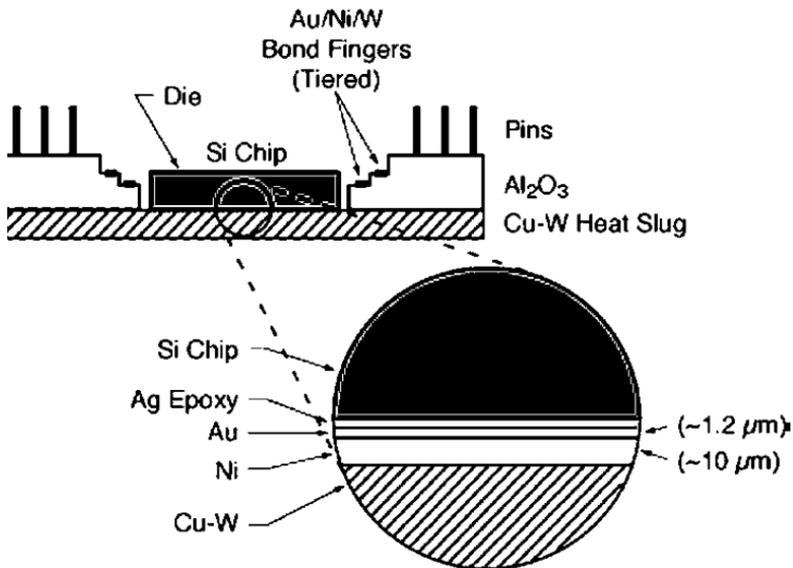
(b)

**Figure 1.11.** Pin-grid array: (a) construction, (b) examples.

a lead pitch of 100 mils and are designed for insertion mounting in PWBs. Figure 1.12 shows the construction of a ceramic PGA package (CPGA) whose base is a Cu-W slug that provides high heat conduction and heat dissipation from the device.<sup>[20]</sup>

**Chip-scale packages (CSP).** Bare die such as integrated circuits may be assembled in plastic or ceramic carriers, called chip-scale packages, whose dimensions are slightly larger than the chip. CSPs are often defined as packages that are no larger than 1.5 times the area of the die or no more than 1.2 times the width or length of the die.<sup>[21][22]</sup> If the carrier is a BGA type, an alternate definition is that the solder-ball pitch be less than 1 mm.<sup>[23]</sup> The pitch of interconnects varies by I/O count. Parts having fewer than 100 I/Os have pitches of 1 mm, decreasing to 0.5 mm as the number of I/Os increases to 500.<sup>[24]</sup>

Chip-scale packages have many advantages over bare chip attachments especially in their ease of handling, ability to be burned-in and electrically tested, and compatibility with automated soldering and epoxy attachment equipment. Chip-scale packages also have advantages over QFP and PGA packages in the higher levels of silicon density that are obtained. While the silicon density (ratio of silicon-to-package area) of a QFP is 10% to 60%,<sup>[25]</sup> that for a single chip in a CSP may be as high as 60%



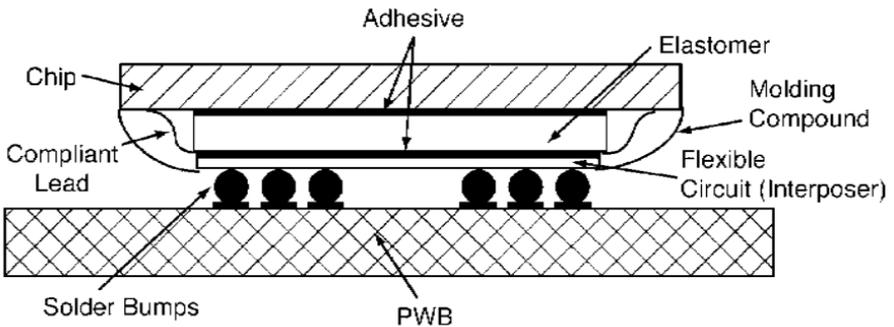
**Figure 1.12.** Silicon die, epoxy attached and wire bonded in a CPGA package.<sup>[20]</sup>

to 100%.<sup>[26]</sup> CSPs may be bumped for flip-chip connections or wire bonded. Adhesives are used to attach the chip to the carrier and the carriers to an interconnect substrate. In the past decade, there has been a proliferation of designs and configurations for CSPs, and they have become the preferred method of packaging ICs having up to 500 I/Os. One design is shown in Fig. 1.13. Chip-scale packages are classified as four general types.<sup>[22]</sup>

*Leadframe-based CSPs.* Leadframe CSPs are most closely related to conventional, single-chip packages. According to this approach, the die is attached and wire bonded to a copper leadframe using multiple rows of gold wire bonds. The completed assembly is overmolded, usually with an epoxy molding compound. Small size and weight as well as improved thermal and electrical performance are the key benefits of this technology.

*Rigid substrate-based CSPs.* The die may be attached and wire bonded or flip-chip bonded to a small rigid interconnect substrate such as a ceramic or a plastic laminate, for example, bismaleimide triazine (BT). Conventional wire bonding and overmolding processes, as in leadframe CSPs, are also used.

*Flex interposer-based CSPs.* This CSP type uses a flexible circuit having solder balls or metal bumps as an interconnect interposer between the chip and the next circuit board level. The bare chip is attached facedown and wire-bonded to the interposer. A thin elastomer, sandwiched between the chip and interposer, cushions the chip and the solder-ball interconnects, relieving stresses (see Fig. 1.13). The interposer generally consists of a metallized, flexible polyimide tape on which are formed electrical connections by photolithographic processes. As a final step, the exposed wire bonds and edges of the chip are molded with epoxy.

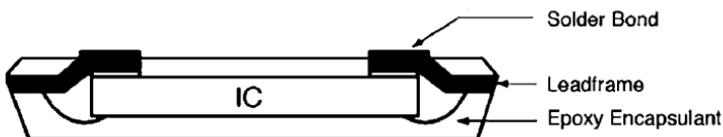


**Figure 1.13.** Construction of a flex-interposer chip-scale package (mounted on a printed-circuit board).

*Wafer-level CSPs.* CSPs can be batch fabricated at the wafer level by the semiconductor manufacturer resulting in lower costs and higher yields. In their production, through several more steps, the I/O bonding pads are redistributed to facilitate the formation of bumps. The bumped die are then encapsulated and singulated. In redistributing the pads and forming the bumps, photolithographic processes similar to those used in the original fabrication of the ICs are used. Cyclotene<sup>®</sup> (a benzocyclobutene dielectric coating developed by Dow Chemical Co.), polyimide, or other temperature-stable coating is used as an interlayer dielectric. A beam-leaded variation is also available.

**Lead-on-chip (LOC).** Lead-on-chip is a variation of CSP in which the leadframe is attached with adhesive to the face of the chip so that wire can be bonded within the chip area. The leadframes are attached to the chip with thermoplastic polyimide film or with a paste adhesive, and the metallized bonding pads on the chip are wire bonded to the leadframe (Fig. 1.14). Leadframes may consist of rigid or flex cable. Parts are subsequently epoxy molded on both sides of the leadframe except that the bottom surfaces of the bottom leads are left exposed so they may be solder plated. The leads are trimmed very close to the edge of the package. Advantages of LOC include high packaging density, ease of pretesting, improved power distribution, low parasitics, and high clock rates. Several variations of LOC have been developed that improve on the lead configuration for better standoff height, better heat transfer, increased compliance, and better inspectability of solder joints.<sup>[27]</sup> LOC chip-scale packages are used extensively for dynamic random-access memory (DRAMs) and other memory chips, providing packages with small form factors, high speed, and low profiles.

**Chip stacks.** A recent approach to increasing component densities is to connect the die or chip devices vertically as a chip stack instead of assembling them horizontally on a substrate. The silicon chips are first thinned to several mils (2–4 mils), then bonded together. Where the chips are of different sizes, such as an application-specific integrated-circuit (ASIC)

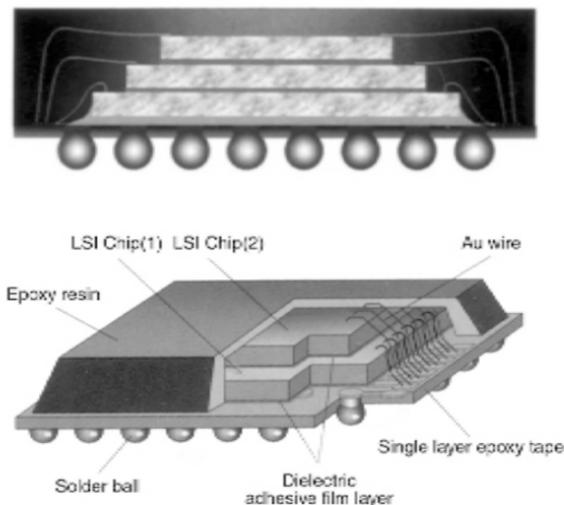


**Figure 1.14.** Example of lead-on-chip (LOC) construction.

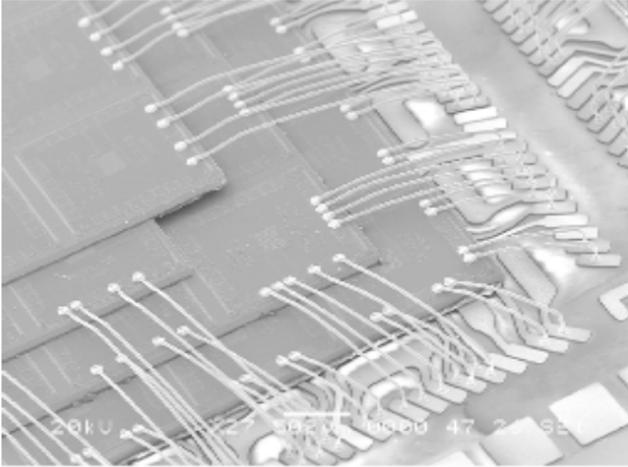
chip stacked on an static random-access memory (SRAM), the chips may be connected by wire bonding or flip-chip bonding, first to each other, then to a base substrate. Where the chips are of the same size, they must be staggered so that all the wire bond connections can be made from one side of each device to the base substrate. Cross sections of wire-bonded, two-chip and three-chip stacks are shown in Fig. 1.15. Chip stacks incorporating up to four chips having a height of only 1.3 mm have also been produced (Fig. 1.16). Chip stacks are widely used in cell phones.

### 1.2.2 Surface-Mount Technology

Surface-mount technology (SMT) is basically a component assembly technology related to printed-circuit boards wherein the components are attached and connected on the surface of the board using batch solder-reflow processes. SMT differs from other PWB methods where the component leads are inserted into plated through-holes and wave-soldered from the bottom to fill in the holes and interconnect the components. SMT has the advantages of achieving higher packaging densities, higher reliability, and reduced cost than the plated through-hole insertion process. SMT is currently the process most widely used for low-cost, high-production consumer electronic assemblies.



**Figure 1.15.** Cross-section diagrams of chip stacks.<sup>[28][29]</sup>

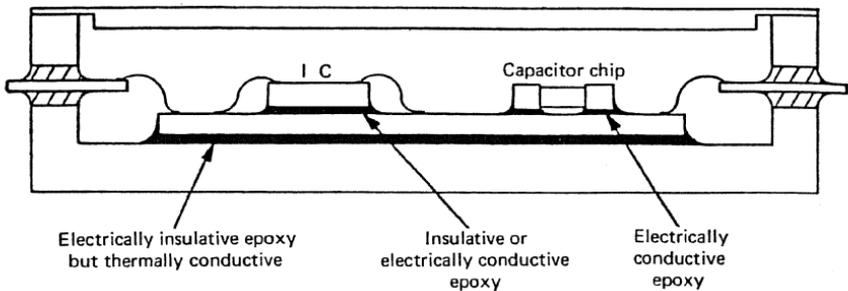


**Figure 1.16.** Stacked chip-scale package configuration. (Source: Amkor.)

### 1.2.3 Multichip Packaging

Multichip packaging involves the attachment and interconnection of a variety of chip devices on an interconnect substrate that may be single layer or multilayer. There are two basic types of multichip packaging: hybrid microcircuits and multichip modules.

**Hybrid microcircuits.** Hybrid microcircuits are high-density circuits produced by directly attaching and connecting bare chips to a fine-line interconnect substrate. The word *hybrid* derives from the large variety of devices, connection techniques, and interconnect substrates that can be used in their assembly. Bare semiconductor die (ICs, transistors, and diodes) and passive devices (chip capacitors, resistors, inductors, and transformers) may be mechanically attached with insulative adhesives and electrically connected using conductive adhesives, gold or aluminum wire, flip-chip soldering, or tape-automated bonding (TAB). The interconnect substrates may be constructed of single or multilayer thin- or thick-film circuits (Fig. 1.17). Additionally, prepackaged devices such as plastic-molded ICs may be assembled alongside the unpackaged chips. Because bare die, fragile wire bonds, and potentially corrosive thin-film metallizations are used, hybrid microcircuits must be well cleaned, vacuum baked, and hermetically sealed in an inert ambient. Packages may be gold-plated or nickel-plated Kovar<sup>®</sup>

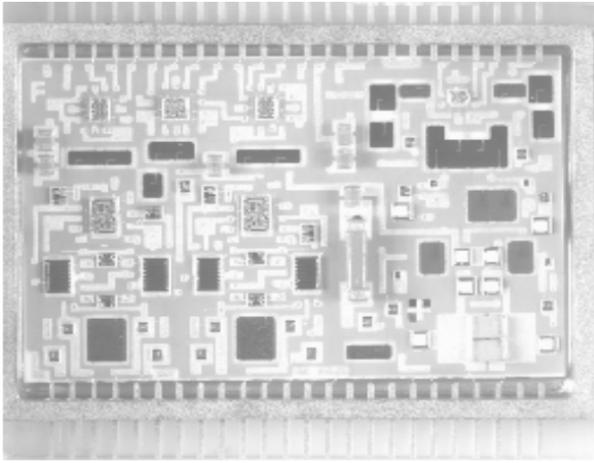


**Figure 1.17.** Cross-section of a hybrid circuit showing IC and capacitor attachments.

with glass-sealed leads emanating either laterally from the sidewalls or vertically as pins from the base. Packages may also be constructed from cofired ceramic in which the leads are formed as an integral part of the package.<sup>[8]</sup>

Thin-film hybrid microcircuits may be assembled on ceramic substrates such as alumina or beryllia where interconnect conductor lines and bonding pads have been produced by vapor depositing or sputtering thin films of metals, then etching the patterns using standard photolithography processes. Conductor metallizations are generally gold or aluminum. Conductor line widths and spacings are typically three to five mils. Thin-film resistor patterns may also be integrated with the conductors by depositing and photoetching nichrome or tantalum nitride. A key attribute of thin-film hybrids is the ability to produce precision resistors that, after laser trimming and annealing, have temperature coefficients of resistance (TCRs) as low as  $0 \pm 3 \text{ ppm}/^\circ\text{C}$  and resistor drifts of less than 100 ppm after aging 1,000 hours at  $150^\circ\text{C}$ .

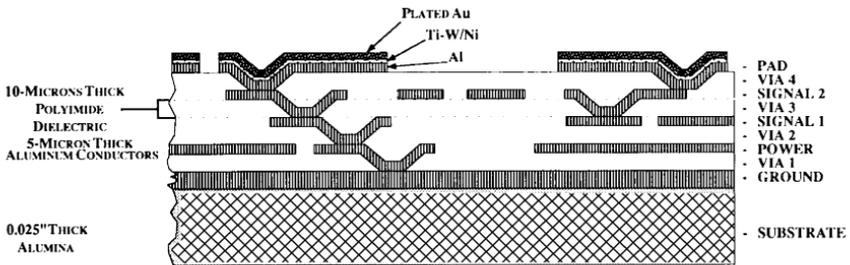
Thick-film hybrid microcircuits are also assembled on ceramic substrates such as alumina, beryllia, or aluminum nitride, but the conductors and resistors are applied by screen printing and firing conductor and resistor pastes (Fig. 1.18). Conductor line widths and spacings may be as narrow as 3–5 mils but, for high yields, are generally 10–20 mils. The ability to form multilayer circuits by screen printing dielectric layers between the conductor/resistor patterns and simultaneously forming vias in the dielectrics to interconnect the layers is a distinct advantage of thick films over single-layer thin films. A further advantage of thick-film over thin-film circuits is the lower cost of materials, processing, and equipment.



**Figure 1.18.** Thick-film hybrid microcircuit.

**Multichip modules.** Multichip modules (MCM) are basically extensions of hybrid microcircuits, the differences being in their higher degree of density and improved electrical performance. In general, an MCM is defined as a microcircuit that has a silicon-to-substrate density greater than 30%. Three basic MCM types, defined according to the process used in fabricating the interconnect substrate, have been developed. They have been classified by the Institute of Interconnecting and Packaging Electronic Circuits (IPC) as MCM-D (deposited thin film), MCM-C (ceramic thick film), and MCM-L (plastic laminate).<sup>[30]</sup>

MCM-D, the first MCM type to be developed, is produced by a vapor deposited or sputtered thin-film photoetch process similar to that used for hybrid thin-film substrates, except that multilayering has now been introduced. High-performance dielectric layers such as polyimide or benzocyclobutene (BCB) coatings are deposited over the etched conductors, the coatings are cured, and vias are formed by plasma or laser etching. On metallizing the dielectric and photoetching the next conductor layer,  $z$ -direction vias are also metallized and form electrical connections between the layers. Of the three MCM types, MCM-D provides the finest line widths and spacings (25  $\mu\text{m}$  or less), and smallest vias (25  $\mu\text{m}$  or less).<sup>[14]</sup> MCM-Ds may also be multilayered to form up to 8 conductor layers. Figure 1.19 shows the construction of an MCM-D interconnect substrate consisting of five conductor layers.

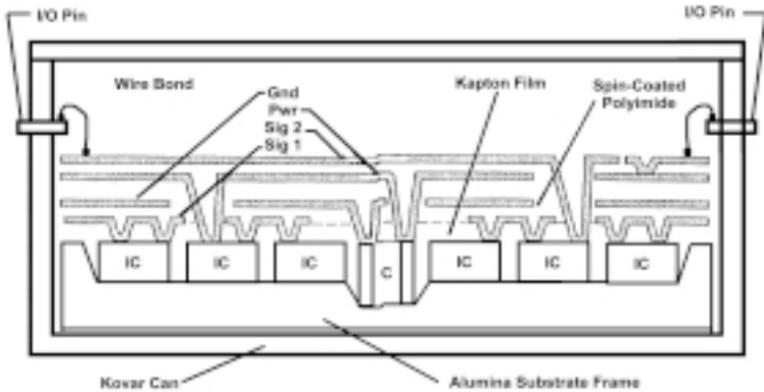


**Figure 1.19.** Cross-section of an MCM-D multilayer construction.

MCM-C interconnect substrates are produced from either low-temperature cofired ceramic (LTCC) or high-temperature cofired ceramic (HTCC). Either process can produce multilayer substrates having high numbers of conductor layers (up to 100), although for most applications 2 to 20 layers are sufficient. The fabrication of MCM-C involves thick-film processes that have wider lines and spacings (5 to 20 mils) than MCM-D, but are lower in cost.

MCM-Ls are multichip modules whose interconnect substrates are produced from plastic laminates similar to PWBs, but having much finer dimensions.

**High-density interconnect (HDI) overlay process.** The HDI overlay packaging process, developed by General Electric, is a unique variation of MCM-D. In it, the bare chips are attached first, face up, in a closely packed manner, to a bare substrate and the interconnect layers are then formed over the chips. A polyimide film is next bonded to the array of chips using a thermoplastic adhesive and vias are formed through the polyimide directly over the bonding pads on the devices using a programmed laser beam. The film is next metallized and photodelineated to generate the fine-line circuitry and  $z$ -direction interconnections. Subsequent interconnect layers may be formed by repeating the steps<sup>[31][32]</sup> (Fig. 1.20). A thermoplastic polyetherimide adhesive (GE's ULTEM<sup>®</sup>) was used to bond the devices to the substrate and also to bond the Kapton<sup>®</sup> film to the tops of the devices. The process has many advantages over the normal "chips last" approach used for hybrid microcircuits and most multichip modules. Among these advantages are the extremely short electrical paths (no wire, TAB, or flip-chip bonding required), high packing density of devices, and improved thermal conduction from the bottom of the die directly to the substrate which

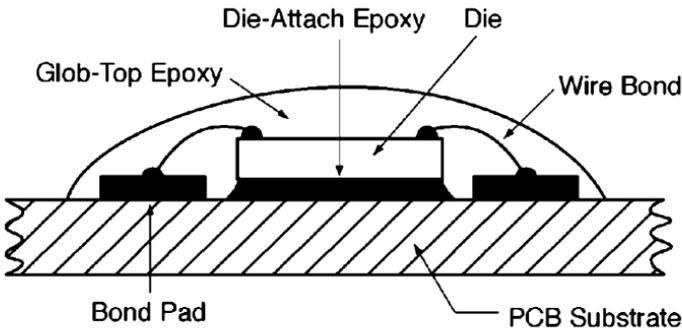


**Figure 1.20.** HDI overlay, “chips first” packaging.

may be alumina, aluminum nitride, beryllia, or other material having high thermal conductivity. Plastic substrates may also be used for low-cost applications.

**Chip-on-board.** Chip-on-board (COB), also known as chip-on-substrate (COS), is a relatively new technology that has evolved as a cross between high-density hybrid microcircuits and low-cost PWAs. Recent advances in producing fine lines and spacings and closely spaced bonding pads on PWBs have allowed the assembly of active and passive chip devices as in hybrid and multichip modules. Chip-on-board has resulted in much higher densities than PWBs that were assembled with prepackaged components. As with hybrid circuits, the chips are attached with electrically conductive or insulative die-attach adhesives, or they may be wire bonded or flip-chip attached with solder. Also, as with hybrid circuits, the bare chip devices must be protected from ambient moisture and other contaminants. For most commercial and consumer electronics, it is sufficient to selectively encapsulate ICs and other semiconductor die with a plastic encapsulant specially formulated for low moisture absorption and low stress. These encapsulants are known as *glob tops* and are mainly thixotropic epoxy formulations (Fig. 1.21).

**Flexible circuits.** Flexible circuits (flex circuits) are analogous to rigid printed-circuit boards except they are fabricated from a thin flexible dielectric film to which is adhesively bonded a thin copper foil. The copper is then photoetched to form a circuit pattern using normal photolithography processes. A plastic film (coverlay) is then adhesive bonded to the etched



**Figure 1.21.** Chip-on-board cross-section showing glob-top protection for IC chip.

copper circuitry except that open areas are left for subsequently attaching components. The coverlay provides moisture, contaminant, and handling protection much as a conformal coating does for a PWA. Dielectric films most widely used are polyimide, for example, DuPont's Kapton<sup>®</sup> H, polyester terephthalate (DuPont's Mylar<sup>®</sup>), epoxy polyester, and various fluoropolymers such as Teflon<sup>®</sup> FEP or Teflon<sup>®</sup> PTFE. Polyimide, because of its very high-temperature stability, is best suited where subsequent assembly involves solder attachments. A variety of adhesives may also be used including acrylics, epoxies, and epoxies modified with flexible resins such as phenolic butyral. Adhesives for flex circuits must meet several requirements, some of which are as follows:

- Retain adhesion while the circuit is flexed
- Wet and bond well to both the polymer film and the copper foil
- Have low moisture absorption
- Have good dielectric properties
- Have low or no-flow characteristics
- Be thermally resistant to solder-reflow temperatures

As with PWBs, flex-circuits may be single layer, double sided, or multilayer.

**Chip-on-flex (COF).** Chip-on-flex is similar to chip-on-board except that the die, chips, or CSPs are wire bonded, flip-chip attached, or epoxy connected to a flexible circuit instead of to a rigid interconnect substrate such as a PWB.

### 1.3 HISTORY OF ADHESIVES IN ELECTRONIC APPLICATIONS

The basic polymer resins used in adhesives formulations are not new. Epoxy resins, for example, now the most widely used in adhesive formulations, were first introduced in the late 1930s by Ciba.<sup>[2]</sup> Other early producers of epoxy resins included Shell Chemical Co., Dow Chemical Co., Union Carbide, Celanese, Reichold, and DuPont.<sup>[33]</sup> Polyurethane resins were introduced in the 1940s and produced by several large chemical companies including DuPont, Mobay Chemical Co., and Monsanto. Polyimides were developed by DuPont in the 1950s, and silicones, the newest of the second generation of electronic materials, were developed almost simultaneously at Dow Corning and General Electric in the 1960s.<sup>[34]</sup>

The assembly of devices and components started shortly after the invention of the transistor by using solder (primarily tin-lead), eutectic alloys (gold-silicon, gold-tin), and wire (copper, aluminum, or gold). In the early 1960s, polymeric adhesives and, in fact, any organic materials in hermetically sealed electronic packages, were not allowed in military programs, and rightly so, since adhesives first used were off-the-shelf commercial products not intended to meet the reliability standards of aerospace programs. Failures due to corrosion, metal migration, and outgassing initially gave organic materials a bad name. At the same time, the government and industry saw the need to use polymer adhesives because of their low cost, low processing temperatures, and ease of rework. During the next decade, with improvements made in purifying resins, reducing the amounts of ionic contaminants, and defining the requirements for qualification, polymer adhesives began to be accepted.

Although metallurgical methods are still widely used today, in the drive toward lower costs, higher densities, and further miniaturization, polymer adhesives have displaced them in many applications. Polymer adhesives such as electrically conductive epoxies have many advantages over solder, eutectic, or glass attachments<sup>[35]</sup> as listed in Table 1.1. However, the introduction of polymer adhesives in the 1960s was not without problems. Among problems encountered were: high levels of ions and other impurities that were present in the commercially available adhesives of the period; high outgassing in sealed packages; voids due to retention of solvents, absorption of water, or entrapment of air; and stresses due to mismatches in coefficients of thermal expansion (CTE). An awareness of

**Table 1.1.** Comparison of Metallurgical, Polymeric, and Vitreous Attachment Methods

Attachment/ Connection Method	Advantages	Limitations
Tin-Lead Soldering	<ul style="list-style-type: none"> <li>• Batch process</li> <li>• Automated dispensing or screen-printing</li> <li>• Automated reflow</li> <li>• Long history of use/mature process</li> <li>• Easy rework</li> <li>• Good electrical connections</li> <li>• Good thermal conduction</li> </ul>	<ul style="list-style-type: none"> <li>• Requires flux</li> <li>• Risk of flux residues and corrosion</li> <li>• Concern over toxicity of lead</li> <li>• Corrosion of solder in humidity, if not overcoated</li> <li>• Risk of voids under large components</li> <li>• Stress due to large CTE mismatches</li> <li>• High temperature exposure during solder reflow (220°C–240°C)</li> <li>• Limited wetting and adhesion to some surfaces (e.g., glass)</li> </ul>
Polymer Adhesive Bonding	<ul style="list-style-type: none"> <li>• Easy rework</li> <li>• Low cost</li> <li>• Low processing temperatures (&lt;165°C)</li> <li>• Automated dispensing or screen-printing</li> <li>• Application-specific formulations</li> <li>• Wide variety of commercially available products to choose from</li> <li>• Ability to relieve stresses</li> <li>• Excellent adhesion to most surfaces</li> <li>• Snap cure types cure in seconds (160°C–200°C)</li> <li>• Directional conductivity with anisotropic forms</li> </ul>	<ul style="list-style-type: none"> <li>• Risk of outgassing in enclosed packages and for space hardware</li> <li>• Most require moderate to long cures (1–2 hours)</li> <li>• Limited thermal stabilities</li> <li>• Finite absorption of water presents “pop-corn” problem during reflow soldering</li> </ul>

(cont'd.)

**Table 1.1.** (Cont'd.)

<b>Attachment/ Connection Method</b>	<b>Advantages</b>	<b>Limitations</b>
Silver-Glass Bonding	<ul style="list-style-type: none"> <li>• High thermal conductivity (50–90 W/m<sup>2</sup>K)</li> <li>• Good electrical conductivity</li> <li>• Suitable for single-chip packaging</li> </ul>	<ul style="list-style-type: none"> <li>• Long cure schedule to remove binder and fuse glass/oxide</li> <li>• Very high processing temperatures (up to 400°C)</li> <li>• Not practical to rework</li> <li>• Not suitable for multichip modules with temperature-sensitive materials and devices</li> </ul>

the requirements of the emerging electronics industry led some large chemical firms to conduct research and development to solve these problems and to address the specific needs of the electronics industry. Among these companies were DuPont, General Electric, Dow Corning, Dow Chemical Co., Shell Chemical Co., and 3M. Following suit, during the 1960s and 1970s, many new companies emerged that were dedicated to developing electronic-grade adhesives and other polymer materials for the rapidly growing electronics industry. Among these new-start companies were Ablestik Laboratories, Amicon, Epoxylite, Furane Plastics, Epoxy Technology, AI Technology, Hysol, Loctite, and Emerson & Cuming.

Epoxies became popular for the first generation of electrically conductive adhesives introduced in the mid-to-late 1960s.<sup>[36][37]</sup> The early adhesive formulations contained organic solvents, which often became trapped in the bondline during cure and resulted in voids, especially under large chips and substrates. These early adhesives also contained large amounts of ionic impurities, notably chloride ions, which, in the case of nonconductive adhesives, resulted in reduced electrical resistivity, ion migration, and corrosion, especially in humid environments. Early epoxies were also cured with aliphatic amines, which outgassed ammonia. Yet, in spite of all this, the first generation of epoxy adhesives performed well for the small chips and devices, conventional PWAs, and low-density hybrid circuits of the time. Among the first electrically conductive die-attach adhesives was DuPont's 5504, a silver-filled, solvent-based epoxy-anhydride system.<sup>[38]</sup> Film adhe-

sives (preforms) were introduced in 1968.<sup>[39]</sup> Film adhesives, originally developed for substrate attachment, are now also used for conductive die attach, lead-on-chip (LOC) bonding, and in fabricating multilayer flex and rigid interconnect substrates. During the 1960s, both one-part and two-part room-temperature vulcanizing (RTV) silicone adhesives were introduced by General Electric and Dow Corning which met a need for higher temperature resistance and higher purity than epoxies. Some of these silicones were convenient to use because they were one-part systems that cured at room temperature on exposure to air moisture.

During this early period, polyurethanes were used where flexibility and vibration damping of large components were required. Cyanoacrylates and anaerobic acrylic ester adhesives that cured in the absence of air were formulated in the 1950s and marketed by Loctite.<sup>[40]</sup> They were studied for bonding electronic components and heat sinks to printed-wiring boards in the early 1960s. Both cyanoacrylates and anaerobic adhesives provided very rapid tacking and curing in the absence of air, but were soon abandoned for electronic applications because of their poor resistance to elevated temperature-humidity environments, especially where they had to meet military specifications. However, anaerobic adhesives found wide use in locking threaded fasteners, thread sealing, and in impregnating porous surfaces.

The next generation of adhesives (1970s) saw further improvements in purification of epoxy adhesives in which the chloride, potassium, sodium, and other ions were reduced to levels below 20 ppm. Outgassing was also reduced by changes in the hardeners used to cure the epoxies and by optimizing the cure schedules. The first specification for the qualification of adhesives was issued during this period by NASA's Marshall Space Flight Center in 1978.

In the 1980s, a third generation of high-density, high-performance IC devices and interconnect circuits having fine lines and spacings was developed and, concurrently, advances were made in high-purity (low ionic content) and non-solvent (100% solids) epoxies, polyimides, cyanate esters, and other adhesives. Interest was renewed in flip-chip devices for high-speed circuits and for high I/O devices, and underfill adhesives were introduced to fill the spaces between solder-ball connections and relieve stresses. Also, in the 1980s, high-density multichip modules were developed based on multilayer thin-film materials and processes. Thermoplastic film adhesives were used in some designs such as the overlay process developed by General Electric. Other thermoplastic films were used in constructing

flex circuits and cable. In 1987, DuPont introduced Ditac<sup>®</sup>, a thermoplastic preform for die attachment.

A fourth generation of electrically conductive adhesives based on cyanate esters and modified cyclo-olefin thermoset resins (MCOT) was introduced in the 1990s. These resins were specially formulated for low moisture absorption, high thermal stability, and low stress to be compatible with solder-reflow conditions. They were developed to prevent or reduce the so-called *popcorn* effect, a failure mode attributed to the rapid release of absorbed water in adhesives and other plastic materials on exposure to the high solder-reflow temperatures. Researchers were prolific in the 1990s in the development of new approaches to meet the high demand for miniaturized consumer electronics. The requirement for high-throughput automated assembly resulted in the wider use of snap-cure adhesives, UV and microwave rapid-curing adhesives, and silver-glass adhesives. With the greater use of flip-chip and area-array devices and new package designs, faster capillary flow and faster cure underfill adhesives were formulated. At the same time, all these developments had to be moderated by strict government regulations to reduce emissions of volatile organic compounds (VOC). A progression of improvements and advances in adhesives is summarized in Table 1.2.

## **1.4 COMPARISON OF POLYMER ADHESIVES WITH METALLURGICAL AND VITREOUS ATTACHMENT MATERIALS**

Metallurgical methods for die attachment or for die and component electrical connections consist primarily of soldering using tin-lead solder. The application of adhesive and solder paste by automated dispensing or by screen printing, placement of the components, and reflowing the solder are the main process steps for surface mounting and connecting components onto PWBs. The solder-reflow temperatures are high (220°C–240°C) and may not be compatible with other materials or components in the assembly. In addition, with the trend toward eliminating lead in solder pastes, new no-lead solders are being introduced that require even higher reflow temperatures. These high temperatures have also created a new problem for plastic-encapsulated microcircuits (PEMs) where absorbed moisture in the plastic

**Table 1.2.** Historical Developments for Adhesives Used in Electronics

<b>Decade Time-frame</b>	<b>Development</b>
1960s	<ul style="list-style-type: none"> <li>• First use of electrically conductive epoxies</li> <li>• Premixed, frozen adhesives introduced by Ablestik Laboratories, Epoxy Technology, and Amicon</li> <li>• Reduced ion content epoxies and polyimides</li> <li>• Introduction of epoxy preforms</li> <li>• First high-purity RTV silicone adhesives from G.E. and Dow Corning</li> </ul>
1970s	<ul style="list-style-type: none"> <li>• First specification to qualify die-attach adhesives (NASA MSFC-SPEC-592)</li> <li>• Low bleed-out adhesives</li> <li>• Further improvements in high-purity, low outgassing adhesives</li> </ul>
1980s	<ul style="list-style-type: none"> <li>• MIL-STD-883 Method 5011 coordinated and released</li> <li>• Thermoplastic film adhesives</li> <li>• Silver-glass die-attach adhesives introduced</li> <li>• First underfills for flip-chip devices</li> <li>• Snap-cure adhesives for high production, rapid throughput</li> <li>• Thermoplastic film adhesives for multichip modules (G.E.)</li> <li>• Introduction of anisotropic adhesives for fine-pitch assemblies</li> </ul>
1990s	<ul style="list-style-type: none"> <li>• UV/visible curing adhesives</li> <li>• Film adhesives for lead-on-chip packaging</li> <li>• High thermal conductivity die-attach adhesives</li> <li>• First generation of low-stress adhesives (paste and film)</li> <li>• Low-firing, silver-glass adhesives</li> <li>• Fast-cure, high-flow underfills</li> <li>• No-flow, fluxing underfills</li> <li>• Cyanate ester and MCOT adhesives introduced for low moisture absorption, compatible with solder reflow temperatures (popcorn resistant)</li> <li>• “Skip cure” or “on-bonder” cured adhesives</li> <li>• Variable-frequency microwave curing (Lambda Technologies)</li> </ul>
2000 to present	<ul style="list-style-type: none"> <li>• Application-specific adhesives <ul style="list-style-type: none"> <li>Chip carriers</li> <li>Chip stacking</li> <li>Optoelectronic circuits</li> <li>MEMS</li> <li>Liquid Crystal Displays</li> </ul> </li> </ul>

rapidly vaporizes producing stresses and delaminations within the module. This phenomenon is called popcorning because of the crackling sound heard during the reflow step. Since most solder pastes either contain flux or must be used together with flux, the effective cleaning and removal of flux residues has always presented a problem.

Polymer adhesives avoid most of these problems, but do not possess the high thermal or high electrical conductivities of metals or metal alloys. Adhesives also are limited in their temperature stabilities, decomposing and outgassing above a certain temperature.

Vitreous materials comprise a third type of attachment material. Glasses may be used to seal lids to packages for hermetic enclosures. Silver-glass pastes have been developed for die attachment. They have high thermal and electrical conductivities and are used extensively for single die attachment in single packages.

A comparison of the three main attachment methods was given in Table 1.1.

## 1.5 SPECIFICATIONS

As the adhesives technology matured, specifications were needed to assure the quality and properties of the incoming material and of the cured material. To this end, users and suppliers of adhesives, together with government agencies, collaborated in defining the critical requirements, the tests to be performed, and the parameters that the material had to meet to qualify and assure a reliable part. This assignment was undertaken by the Autonetics Division of Rockwell Intl. (now Boeing) under contract from NASA MSFC and, in 1974, led to the first government document for the procurement of adhesives to be used in hybrid microcircuits.<sup>[41][42]</sup> After further coordination and revisions, this initial document was formally released as a specification in 1978 and revised in 1982 as NASA MSFC-SPEC-592, "Specification For The Selection and Use of Organic Adhesives in Hybrid Microcircuits." For the first time, the critical requirements for ionic contaminants, electrical resistivity, die-shear strength, corrosivity, and outgassing were specified. Work on the development and evaluation of adhesives to meet NASA requirements continued into the mid-1980s and, as a result, several commercially available adhesives were qualified.<sup>[43][44]</sup>

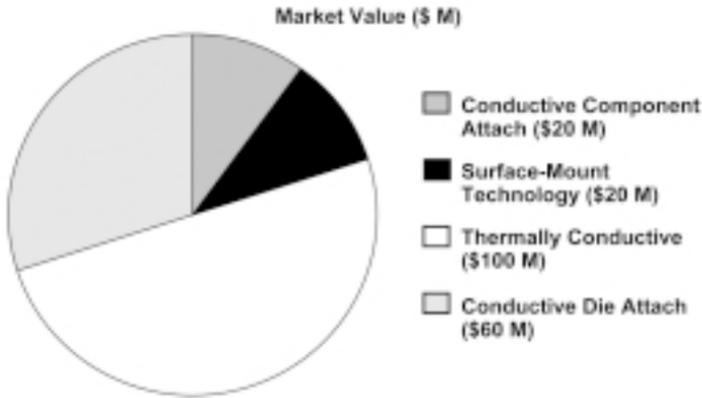
Shortly after the initial release of the NASA specification, the Army Missile Command in 1976 released a similar specification MIS 28962 and the National Security Agency (NSA) followed suit with the release, in 1978, of its own specification NSA 77-25. Ultimately, all government agencies agreed on one specification to be administered by the Air Force at Rome Air Development Center. Previous specification requirements became incorporated in MIL-STD-883 as Method 5011<sup>[44]–[46]</sup> which is still in use today for the qualification of adhesives, as well as for other polymer materials, to be used in high-reliability military and space electronics. MIL-STD-883 is now administered by the Defense Supply Center, Columbus, Ohio (DSCC).

The government-sponsored programs and the requirements and standards that were established had a pronounced effect on the development of new and improved adhesives that met the needs of the entire electronics industry and resulted in the start-up of many adhesives companies.<sup>[44]</sup>

## 1.6 THE MARKET

Epoxyes are the most widely used adhesives in electronics assembly, followed by silicones and polyimides. The use of these adhesive types, along with the more specialized types such as cyanate esters, bismaleimides, and modified cyclo-olefin thermosets, is expected to increase as the total production of electronic circuits and hardware increases. In recent years, the total value of electronic components has increased tremendously from \$59 billion in 1989 to an estimated \$215 billion in 2003. It is predicted that the cumulative growth will be 5% to 10% per year.<sup>[47]</sup> Adhesives for electronics constitute the fastest growing segment of the entire adhesives market. It is estimated that 120 million pounds of adhesives for electronic applications were shipped in 2003.<sup>[48]</sup> The market share is approximately 40%–45% for electrically conductive adhesives and 50%–60% for electrically insulative adhesives, the latter consisting primarily of thermally conductive formulations (Fig. 1.22).

In a more recent forecast,<sup>[49]</sup> the Freedonia Group expects the market for polymer adhesives used in electronics to increase at an average annual rate of 12.7% from 2003 through 2008. The total dollar value of adhesives is predicted to increase from \$259 million in 2003 to \$650 million in 2013. Adhesives for electronics comprise approximately 10% of the total market for polymeric materials used in electronics.



**Figure 1.22.** Electronic adhesives market value.<sup>[47]</sup>

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# 2 Functions and Theory of Adhesives

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Adhesives used in the assembly of electronic circuits serve four main functions:

- Mechanically attach parts such as semiconductor die, components, substrates, packages, and heat sinks.
- Electrically interconnect components on a substrate or in a package.
- Dissipate heat from components and circuits.
- Dissipate stresses.

The prime function of adhesives is to mechanically attach or bond devices, components, heat sinks, wire, connectors, and other parts onto a circuit board or an interconnect substrate. Adhesives are also used as pastes or films to attach lids in sealing cavity packages and as dielectric films in fabricating multilayer interconnect substrates. The most important consideration in obtaining a reliable adhesive bond is the ability of the adhesive to flow and wet the surfaces. For a reliable bond, strong adhesion to both surfaces and strong cohesion within the adhesive are necessary.

Besides this prime role of attachment, electrically conductive adhesives are widely used to form electrical contacts between components and the printed-wiring board or other interconnect substrate, such as thin-film or thick-film ceramic substrates or flexible cable. For this function, adhesives serve as low-cost alternates to wire, solder, and other metallurgical connections.

The third function, one that is becoming increasingly important, is to draw heat away from components. With increasing circuit densities and power generation, it is essential to avoid excessive operating temperatures to prolong device lives and avoid premature failures. High heat-generating devices are generally cooled by conduction of heat through metal heat sinks, metal tabs, metal or ceramic substrates or packages, and through liquid inert

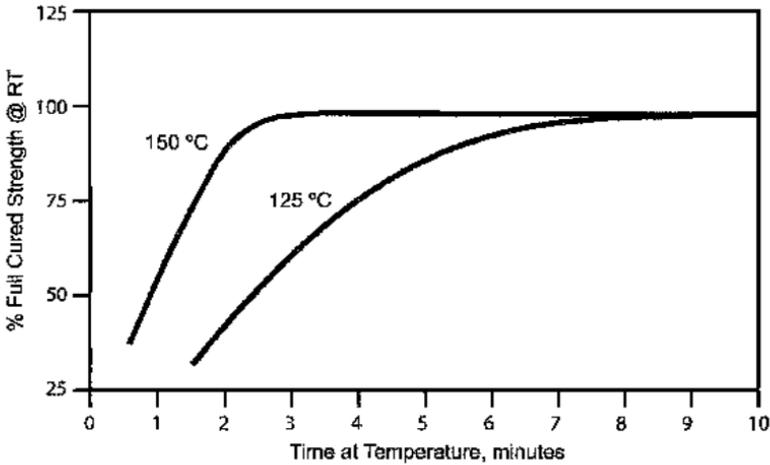
coolants. The conduction of heat to heat sinks demands that adhesives have high thermal conductivities and are applied as thinly as possible without generating voids. In their normal unfilled state, polymer adhesives are poor thermal conductors. They must be highly filled with metal or ceramic particles to increase their thermal conductivities. Heat dissipation by convection is also used to cool electronic devices and assemblies; an example of which is blowing cool air or other gas across the parts while operating.

Lastly, adhesives are used to dissipate stresses that may be generated from thermal excursions, mechanical shock, vibration, or moisture. Specially formulated adhesives are effectively used as underfills for flip-chip devices and ball-grid-array packages to compensate for mismatches of expansion coefficients among the solder, the silicon chip, and the ceramic or plastic-laminate substrate. Low-stress adhesives are also used to attach fragile devices such glass diodes and to dampen stresses due to vibration.

## 2.1 MECHANICAL ATTACHMENT

Mechanical attachment of components, devices, and other parts of an electronic assembly is the prime function of adhesives. Although adhesives are expected to bond a wide variety of materials for electronic applications, they do not need to be structural. They should, however, meet minimum tensile and shear strengths in order to withstand mechanical shock, thermal shock, thermal cycling, and vibration as specified for the intended application. For consumer and commercial products, these stresses may be minimal. For military and space systems, more severe tests defined in MIL-STD-883 and other government documents must be used.

Cohesive and adhesive strengths of adhesives develop during the curing or polymerization process and reach maximum values at some optimum time and temperature conditions, usually determined empirically by measuring shear strength or another desired property as a function of increasing cure schedules. Figure 2.1 shows how torque strength was used to establish two optimum cure schedules for a surface-mount adhesive.<sup>[1]</sup> The degree of polymerization or completeness of cure may also be measured by infrared spectroscopy from the decrease in absorption of specific groups as they are converted by crosslinking through addition or condensation polymerization. For example, the oxirane (epoxy) group of epoxy resins absorbs strongly in the 10.96  $\mu\text{m}$  frequency, but this absorption band decreases as the epoxy group is consumed during polymerization with a hardener or



**Figure 2.1.** Torque strength vs cure schedule for Loctite® Chipbonder® 3607 (strength measured on 1206 capacitors @ 22°C per IPC SM817).<sup>[1]</sup>

catalyst.<sup>[2]</sup> The change in the epoxy absorption band of diglycidylether of bisphenol A (DGEBA) resin as it reacts with a primary aliphatic amine at room temperature is shown in Fig. 2.2.

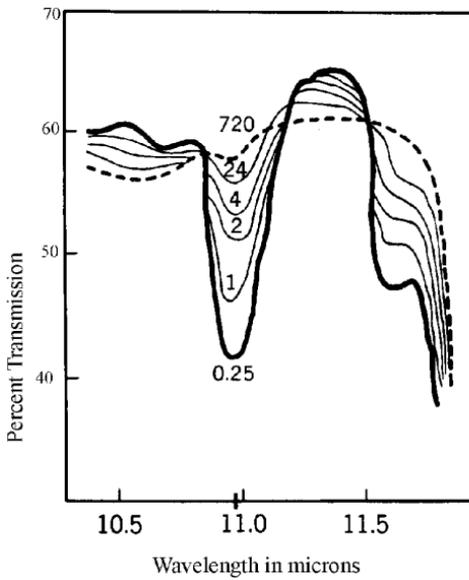
The ability of an adhesive to form a strong bond between different surfaces depends on its ability to wet the surfaces, its flow or rheology properties, and the nature of the bonding mechanism.

### 2.1.1 Wettability Theory

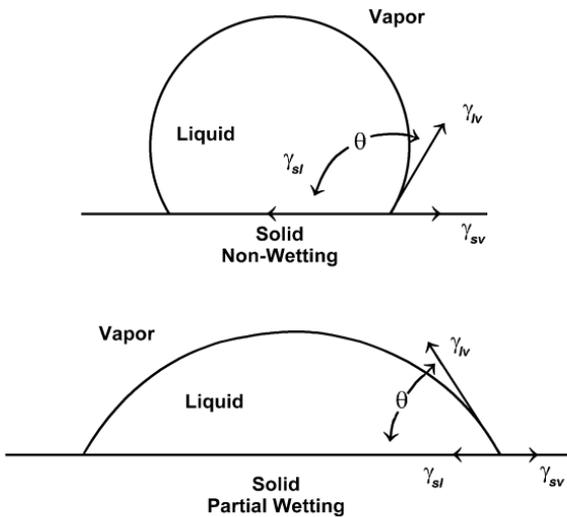
Adhesives must effectively wet and completely contact the surfaces to assure a strong bond. The ability to wet a surface, *wettability*, is related to the ease with which a liquid spreads on a solid surface and is essential in maximizing coverage and minimizing voids in the bondlines.<sup>[3]</sup> Wettability is measured by the equilibrium contact angle,  $\theta$ , which is defined by balancing surface-tension forces in Young's equation (Fig. 2.3).

$$\text{Eq. (2.1)} \quad \gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos \theta$$

where  $\gamma_{sv}$  is the surface energy at the solid-vapor interface,  $\gamma_{sl}$  is the surface energy at the solid-liquid interface, and  $\gamma_{lv}$  is the surface energy at the



**Figure 2.2.** Infrared spectra showing the degree of cure of DGEBA epoxy resin by changes in the 10.96  $\mu\text{m}$  absorption band. (Number indicates cure time in hours.)<sup>[2]</sup>



**Figure 2.3.** Wettability of adhesives and contact angle.<sup>[3]</sup>

liquid-vapor interface. Adhesive wetting is based on the concept of a work function for adhesion as derived from the first law of thermodynamics:

$$\text{Eq. (2.2)} \quad W_a = \gamma_{sv} + \gamma_{lv} - \gamma_{sl}$$

Combining Eq. (2.2) with Young's equation yields the Young-Dupree equation.

$$\text{Eq. (2.3)} \quad W_a = \gamma_{lv} (1 + \cos \theta)$$

The spreading coefficient or work function ( $W_a$ ) in Eq. (2.3) shows that good wetting ( $\theta < 90^\circ$ ) is realized when  $W_a$  is greater than zero. Good wetting also requires using a liquid having a high surface tension. As  $W_a$  decreases,  $\theta$  increases from  $90^\circ$  to  $180^\circ$  and conditions go from partial wetting to nonwetting.<sup>[4]</sup> Based on this equation, conditions of wetting versus nonwetting are as follows:<sup>[3]</sup>

$\theta = 0^\circ$ : Complete wetting; liquid spreads spontaneously;  
high surface attraction

$0^\circ < \theta < 90^\circ$ : Partial wetting

$90^\circ < \theta < 180^\circ$ : Non-wetting; liquid beads up

Some surfaces that wet well ( $\theta < 90^\circ$ ) include:<sup>[5]</sup>

- Metal oxides
- Metal plus native oxide films
- Metal plus foreign oxides (alumina, silicates)
- Metal plus adsorbed chemical films (wetting agents, surfactants)
- Hydrated silica (Si-OH surface bonds)
- Ceramics such as alumina
- Epoxy-glass laminates

Among surfaces that do not wet ( $\theta > 90^\circ$ ) are the following:<sup>[5]</sup>

- Gold
- Metals free of oxides
- Organic nonpolar polymers such as Teflon<sup>®</sup>
- Surfaces with hydrophobic contaminants such as silicones, oils, and greases

- Metals having adsorbed ions such as fluoride
- Silicon etched with hydrofluoric acid, forming Si-F surface bonds
- Strongly heated silicon, forming Si-O-Si surface bonds

These observations are consistent with the high surface energies displayed by certain metals, metal oxides, ceramics, and plastics.<sup>[6]</sup> Equations (2.2) and (2.3) also show that high surface tensions of adhesives as liquids require high surface energies of the surfaces to be bonded to produce low contact angles and good wettability. The surface tension of most epoxies is approximately 80 dynes/cm. As a general rule, if water, with a surface tension of 72 dynes/cm, wets a surface, epoxy adhesives will also wet that surface.<sup>[7][8]</sup> Wetting also occurs if the surface tension of the liquid adhesive is close to or slightly less than that of the substrate.<sup>[9]</sup>

Contact angles are modified for rough surfaces. In general, high surface roughness degrades wettability if  $\theta$  is greater than  $90^\circ$  and improves wettability if less than  $90^\circ$ . The contact angle is greater on rough surfaces compared to planar surfaces where  $\theta$  is greater than  $90^\circ$ . For example, highly roughened surfaces such as sandblasted silicon display poor wetting while mechanically polished silicon has improved uniformity and superior wetting to solder.<sup>[3]</sup> On the other hand, slightly abraded surfaces, as for thick-film gold conductors, are necessary to improve adhesion. Thus, Eq. (2.3) may be modified by introducing a “contact coefficient” that is a function of surface roughness. Another modification introduces a strain energy  $\gamma'$  function that results during the cooling down of the adhesive after heat curing.<sup>[3]</sup>

$$\text{Eq. (2.4)} \quad W_a = k[\gamma_{sv} (1 + \cos \theta - \gamma')]$$

**Factors affecting wettability.** In addition to the contact angle, surface energy, and surface tension considerations just discussed, the degree of wetting depends on the pot life and gel time of the adhesive. *Pot life* is the useful life of an adhesive after a two-part system has been mixed or after a one-part system has been removed from a container or thawed, in the case of frozen adhesives. Beyond its pot life, the adhesive increases in viscosity to an extent that it no longer flows readily and is difficult to dispense. Pot life is most often measured in terms of a viscosity increase that varies according to the product and the supplier. One supplier, for example, uses a 25% increase in viscosity as the limit.<sup>[10]</sup> Hannafin, et al., considered a 10% increase suitable for automated dispensing but a 100% viscosity increase for adhesives that are manually dispensed.<sup>[11]</sup> Material that has exceeded its pot

life may be partially gelled or partially polymerized, a condition also called *B-staged* or *B-staging*. At the gelation point, the adhesive will no longer wet the surface. As an example, the viscosity of Epoxy Technology's Epo-Tek<sup>®</sup> E3001 is stable over the first 48 hours of use, but increases significantly from less than 6,000 cps to 16,000 cps during the next 24 hours, at which point gelation has occurred.<sup>[12]</sup> Table 2.1 shows the effect of temperature on gel time for several adhesives. Adhesives are sometimes dispensed at slightly elevated temperatures to reduce their viscosity and permit better wetting, but at the expense of a reduction in pot life since elevated temperatures also accelerate polymerization and gelation.

**Excessive wetting and bleedout.** Excessive wetting may result in the separation and migration of adhesive constituents, either the resin or hardener portion, a phenomenon known as *bleedout*. Bleedout is sometimes visible as a slight discoloration of the surface around the adhesive joint or on a wire-bonding pad and may occur prior to or during cure. Bleedout is especially prevalent on surfaces that are super clean and have high surface energies. Bleedout may be considered analogous to chromatography where the substances in a multicomponent mixture absorb, wet, and migrate along the chromatography medium at different rates, resulting in separation into the individual components. Bleedout has been a problem especially with two-part epoxy adhesives where one ingredient migrates and contaminates an adjacent wire-bond pad. This contaminant interferes with the ability to form a wire bond, and if formed, results in a bond of marginal strength. The problem has been largely solved by cleaning the circuits with an oxidizing plasma prior to wire bonding. An oxygen-argon plasma effectively removes traces of organic residues.

**Table 2.1.** Effect of Temperature on Gel Time<sup>[13]</sup>

Material	Pot Life (10 gm sample)	Temperature (°C)	Gel Time (150°C)
Epibond <sup>®</sup> 7002	1–2 days	25	>2 days
		150	5 min
Epibond <sup>®</sup> 7200	1–2 days	25	>2 days
		150	5 min
Uralane <sup>®</sup> 7760	3 hrs	25	>3 hrs
		100	5 min

*Data courtesy of Vantico Corporation.*

As a better understanding of the bleedout phenomenon was gained, other techniques were used to reduce bleedout. Vacuum baking the interconnect substrate prior to attaching devices has been reported to reduce bleedout. Several theories have been proposed to explain this. One is that vacuum baking removes adsorbed moisture and other polar surface residues that have a high affinity for the equally polar resin or hardener constituents of the epoxy. This theory is reinforced by experiments that showed higher contact angles for vacuum baked than for non-vacuum baked substrates.<sup>[4]</sup> A second theory proposes that thin films of oil from the vacuum pump may backstream and deposit onto the surface. The oil film, being hydrophobic, increases the contact angle of the adhesive and reduces its flow. Auger spectroscopy has been used to identify carbon, nitrogen, oxygen, and sulfur on gold-plated surfaces after vacuum baking, confirming the presence of oily residues.<sup>[4]</sup> A more controlled method to reduce bleedout that does not rely on vacuum baking involves treating the surface with a surfactant that leaves known concentrations of hydrocarbon films. These films behave the same way as the oils backstreaming from the vacuum pump. With controlled amounts of hydrocarbon films, adhesive die-shear strengths still met the minimum requirements of MIL-STD-883.<sup>[14]</sup> Thus, there is a tradeoff and a fine line between achieving good wettability to insure high adhesive strength and reduced wettability to prevent bleedout.

Lastly, and more importantly, suppliers have reformulated their standard adhesives to reduce or prevent bleedout. For example, the widely used Ablestik Laboratories' Ablebond<sup>®</sup> 84-1 LMI (Low Mobile Ions), a silver-filled epoxy, was reformulated as a no-bleed version: Ablebond 84-1 LMI NB (No Bleed). This NB version, however, was found to have reduced wettability to capacitor terminations and, as a result, yet another version (NB1) was formulated as a compromise.<sup>[15]</sup> Adhesives that are 100% solids are more prone to bleedout than solvent-based types since they contain low-molecular-weight reactive diluents that have a greater tendency to migrate prior to complete curing. Some surface-related and material-related observations concerning bleedout mechanisms may be summarized as follows:

- Formulation ingredients that tend to bleed consist of low-molecular-weight resins, reactive diluents, and some curing agents such as imidazoles.<sup>[16]</sup>
- Extremely clean surfaces increase bleedout.
- Smooth, uniform surfaces bleed less; grainier, porous surfaces promote bleedout due to capillary action.

- Vacuum baking can reduce bleedout by removing adsorbed moisture and other polar contaminants, and it can also reduce bleedout due to pump oil backstreaming onto the surfaces.
- Solvent-based adhesives are less likely to bleed than 100%-solids adhesives.
- Adhesives on etched leadframes bleed more than on stamped leadframes; this is believed to be due to the presence of residual cutting oils on the stamped versions.
- The presence of selenium on leadframes was found to enhance bleedout.<sup>[17]</sup>
- Residues from electroplating baths also enhance bleedout.

### 2.1.2 Rheology

The rheology, or flow properties, of adhesives is important not only to achieve adequate coverage and wetting, but also to develop the process parameters necessary to dispense the adhesive (see Ch. 4). Flow properties are determined by measuring viscosity and thixotropy.

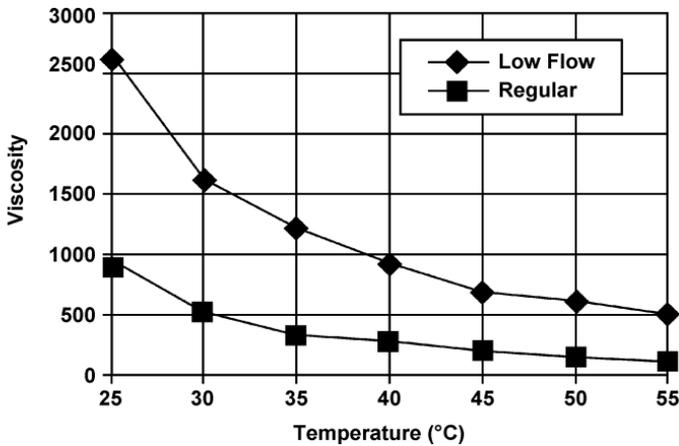
*Viscosity*,  $\eta$ , is a measure of the internal friction of a material and its resistance to flow. It is represented by the proportionality constant between shear stress and shear rate.<sup>[18]</sup>

$$\text{Eq. (2.5)} \quad \eta = \text{Shear stress} \div \text{Shear rate}$$

The viscosity of liquid adhesives decreases with increasing temperature until polymerization begins to occur, then increases. The viscosities of epoxies are reported to decrease 20% to as much as 80% for a 10°C rise in temperature above room temperature.<sup>[19]–[22]</sup> Figure 2.4 shows this viscosity reduction as a function of temperature for two anhydride-cured epoxy adhesives. For low-molecular-weight polymers, the temperature dependence of viscosity follows the Arrhenius equation:

$$\text{Eq. (2.6)} \quad \eta = Ae^{-(E/RT)}$$

where  $E$  is the activation energy for viscous flow,  $A$  is a constant,  $T$  is temperature, and  $R$  is the Boltzmann constant.

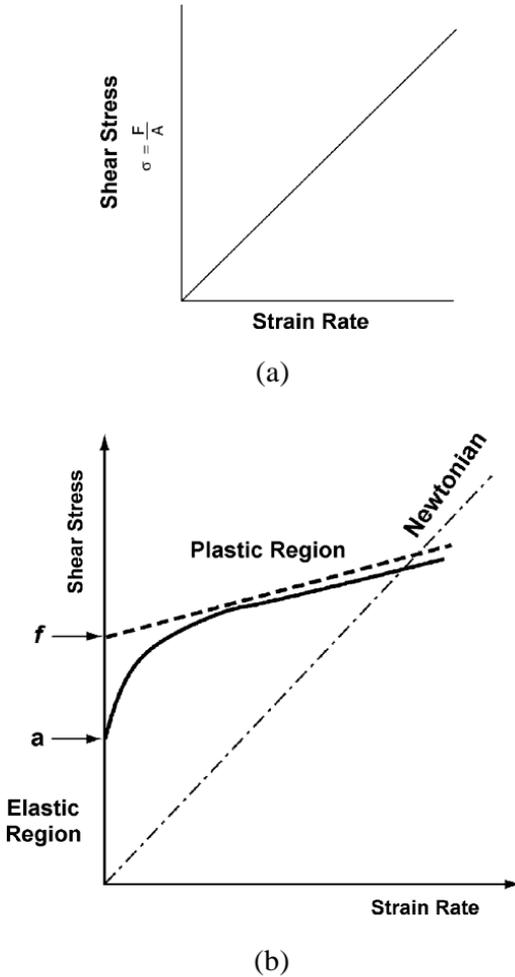


**Figure 2.4.** Viscosity (in cps) as a function of temperature for two epoxy-anhydride adhesives.

**Newtonian and non-Newtonian flow.** When the shear stress of a liquid is directly proportional to the strain rate, as in Fig. 2.5a, the liquid is said to exhibit ideal viscous flow or Newtonian behavior. Most unfilled and capillary underfill adhesives<sup>[23]</sup> are Newtonian fluids. Materials whose viscosity decreases with increasing shear rate are said to display non-Newtonian behavior or *shear thinning* (Fig. 2.5b). Non-Newtonian fluids are also referred to as pseudoplastic or thixotropic. For these materials, the shear rate increases faster than the shear stress. Most filled adhesives that can be screen printed or automatically dispensed for surface-mounting components are thixotropic and non-Newtonian.<sup>[12][18]</sup> A second deviation from Newtonian behavior is *shear thickening* in which viscosity increases with increasing shear rate. This type of non-Newtonian behavior, however, rarely occurs with polymers.<sup>[24]</sup>

*Thixotropy* occurs when clusters of filler particles break up and fluidity increases. At rest, fillers exist in clusters and their strength, size, and shape determine the static viscosity of the adhesive. The total surface area of the filler particles also contributes to static viscosity. Shear thinning occurs when the clusters, such as silver flake in silver-filled epoxies, break apart and viscosity decreases; then, as stress is removed, the clusters form again and viscosity increases.<sup>[21][25]</sup>

The thixotropic property of an adhesive may be defined by its *thixotropic index*, the ratio of viscosities measured at two shear rates, generally a



**Figure 2.5.** Viscosity behavior of adhesives: (a) Newtonian; (b) non-Newtonian.

decade apart, for example, viscosities measured at 0.5 rpm and at 5 rpm ( $1.9 \text{ sec}^{-1}$  and  $19.2 \text{ sec}^{-1}$ ).<sup>[21]</sup> Thixotropic indices are valuable in selecting the best method to dispense an adhesive. Adhesives that have an index of 2 to 5 are considered suitable for automatic dispensing. Materials with indices close to 1 are generally Newtonian types and suitable for capillary-flow underfills.

**Capillary flow.** Adhesives used to fill spaces underneath a flip-chip device or BGA package must flow readily and rapidly when dispensed at the edges of the chip in order to completely fill the gap and free space surrounding the solder bumps. To be effective, the adhesive must be drawn into the narrow

space by capillary action. The theory behind underfilling is based on capillary-flow behavior between closely spaced parallel plates (Fig. 2.6) by considering the drop in pressure ( $p$ ) across a liquid-vapor interface.<sup>[26][27]</sup>

$$\text{Eq. (2.7)} \quad \frac{\partial p}{\partial x} = \frac{-12 \mu}{h^2} \frac{\partial L}{\partial t}$$

where  $\mu$  is viscosity of the underfill material,  $h$  is the gap height, and  $L$  is the length of the die surface traveled by the underfill. The equation is solved by separating the distance ( $x$ ) and time ( $t$ ) variables, resulting in:

$$\text{Eq. (2.8)} \quad \Gamma = -\frac{2\gamma \cos \theta}{hL}$$

where  $\gamma$  is the surface tension of the liquid-vapor interface and  $\Gamma$  is a constant. Application of boundary conditions resulted in the time,  $t_f$ , to reach a distance,  $L_f$  between the parallel plates, of:

$$\text{Eq. (2.9)} \quad t_f = \frac{3 \mu L_f^2}{h \gamma \cos \theta}$$

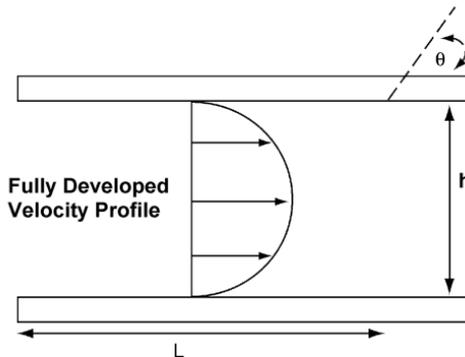
where  $\mu$  is the absolute viscosity,  $L$  is the flow distance at time  $t_f$ ,  $h$  is the gap under the part,  $\theta$  is the wetting contact angle, and  $\gamma$  is the surface tension of the underfill-to-air interface.

*Material factors affecting capillary flow.* Material, process, and physical factors all affect capillary flow. Material characteristics that affect the flow rate of underfill adhesives include viscosity, the contact angle that the adhesive makes with the surface, and ability to wet the surfaces. Viscosity and contact angle are related; increasing the viscosity increases the contact angle, thus reducing wettability and flow. The amount and nature of the filler in adhesive formulations also affect viscosity and contact angle, the higher the filler concentration, the greater the viscosity. Of three underfill adhesives from Hysol: FP4454, FP4511, and FP4527, having contact angles of 5°–10°, 18°–20°, and 10°–15°, respectively; Hysol FP4511 with the highest filler content<sup>[28]</sup> had the largest contact angle. A high filler concentration, although undesirable for capillary flow, is important in reducing the coefficient of thermal expansion (CTE) of the cured material. Thus, a

tradeoff is required between a low CTE and high capillary flow by managing the type and amount of filler. The particle sizes of fillers also affect the ability to underfill parts effectively. As a rule, the gap height should be twice the size of the filler particles. The gap should be three times the filler size when parts are to be bonded to PWBs because of the greater surface roughness of plastic-laminate boards and the fact that larger particles limit the flow through the gap.<sup>[23][29]</sup>

In practice, even for highly filled formulations, the viscosity can be lowered during the dispensing operation by heating the material or the substrate. For example, viscosity can be lowered from a typical value of 4,000 cps at 25°C to about 500 cps by increasing the temperature to 70°C–90°C.<sup>[19][30]</sup> Ablestik's underfill adhesive Ablefill<sup>®</sup> JM8806, whose viscosity is 4,000 cps at 25°C, is reduced to 200 cps at 80°C while Ablefill<sup>®</sup> JM8802B falls from 6,000–9,000 cps at room temperature to 400 cps at 80°C.<sup>[31]</sup> It is estimated that over 90% of all underfill materials are dispensed at elevated temperatures at two adjacent edges of a chip.<sup>[32]</sup> A practical limit, however, is reached when gelation or expiration of the pot life occurs at the dispensing temperature.<sup>[23][33]</sup>

Besides viscosity, the surface-wetting ability of underfills is critical to capillary flow. For capillary flow to occur, the underfill material must wet the surfaces so that the advancing contact angle is less than 90°.<sup>[34]</sup> Also, for capillary flow, the intramolecular forces of attraction among adhesive molecules must be weaker than the intermolecular attraction of the adhesive for the die, the substrate, and the solder surfaces.<sup>[35]</sup> This occurs when the surface tension of the underfill is lower than the surface energy of



**Figure 2.6.** Capillary-flow diagram showing the velocity of an advancing front of underfill material as it flows between the two surfaces. (Copyright PennWell and Advanced Packaging, 1999, reproduced with permission.)

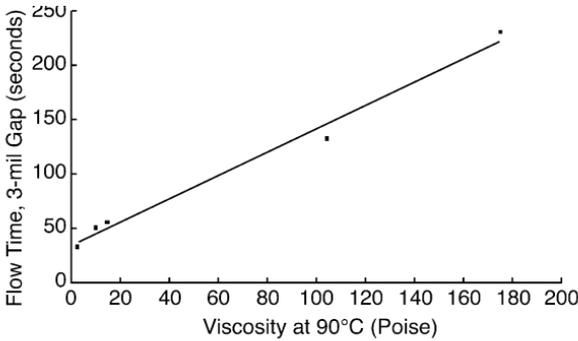
the surfaces being bonded. As a rule, suitable wetting for capillary flow results when the surface energy of the substrate is 10 dynes/cm greater than the surface tension of the underfill.<sup>[9]</sup> The surface energy of most PWBs is 35–40 dynes/cm while underfill surface tensions are about 25 dynes/cm.<sup>[33]</sup>

*Physical factors affecting capillary flow.* The gap height, size of the die, and free volume beneath the die all have a bearing on the efficiency of capillary flow, and the ability to completely underfill a device in a few seconds. Small gaps are harder to fill and require low viscosity adhesives to keep the underfill times as short as possible. To fill a 0.5-mil gap, the viscosity of the underfill should be approximately 2,000 to 4,000 cps at 25°C. As the gap increases to 1 mil, viscosities can be 6,000 to 45,000 cps and for a 3-mil gap, they may be 5,000–25,000 cps. These ranges overlap but, in practice, viscosities of underfills that differ by a factor of two exhibit about the same flow rates. This inconsistency is explained by the fact that when measuring viscosities using a Brookfield viscometer, the shear stress applied is too high to simulate capillary forces. Brookfield viscometers are better suited to determine the flow characteristics of screen printable pastes or highly filled, syringe-dispensible adhesives.<sup>[36]</sup> A more accurate test method for capillary-flow viscosity utilizes a controlled-stress rheometer\* where the shear stress is controlled to 10 dynes/cm and the temperature held at 90°C. Viscosities measured using the Haake Rheo equipment correlate well with the time required to underfill devices having different gap heights.<sup>[36]</sup> Figure 2.7 shows the flow times required to underfill a 3-mil gap with various viscosities of Hysol® FP4430.

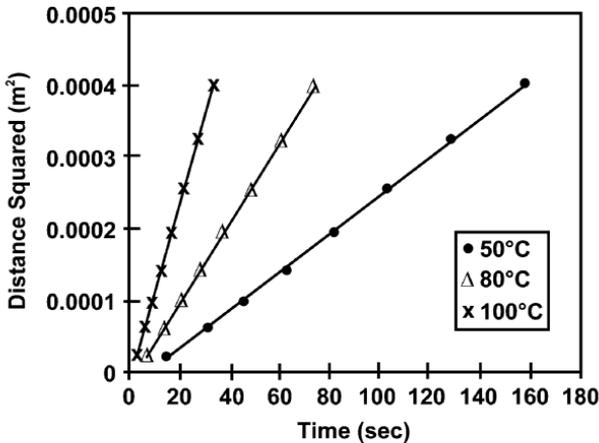
The size of the die is a further consideration in the time it takes for the underfill adhesive to traverse the distance and completely fill the gap. A plot of the square of the distance as a function of time produces a straight line as expected from Eq. (2.9)<sup>[23]</sup> (Fig. 2.8). For a given die size, increased viscosity of the underfill material also increases the time to fill the gap. For high production rates, the fill time must be as short as possible. With increasing sizes of IC chips, this has presented a challenge. For example, the die size cannot be greater than 15-mm square for a 15-second fill time using Emerson & Cuming's E-1216 underfill adhesive (6,000 cps, 20- $\mu$ m filler size). However, the die can be as large as 30-mm square if a 45 second time is acceptable.<sup>[29]</sup>

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\* For example, the Haake Rheo Stress Rheometer from Thermo Electron (Karlsruhe) GmbH.



**Figure 2.7.** Viscosity vs underfill time using controlled-stress rheometer. (Source: Loctite.)



**Figure 2.8.** Underfill time as a function of distance. (Copyright IEEE, 1988, reproduced with permission.)

The volume of underfill must be controlled to assure complete filling beneath the die and some filleting around the die. A complex combination of factors (gap height, contact angle, viscosity, wettability) affects the amount of underfill required for complete coverage. The volume of underfill ( $V$ ) is calculated based on the volume of free space under the die ( $V_c$ ), the volume of the solder bumps ( $V_b$ ), and the fillet volume ( $V_f$ ) or:  $V = V_c - V_b + V_f$ .<sup>[37]</sup>

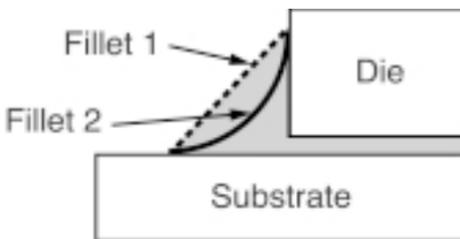
The volume of the fillet, as shown in Eq. (2.10) is a function of the die length and width and the fillet height and width, as well as a shape factor (Fig. 2.9).

$$\text{Eq. (2.10)} \quad V_f = \{[\text{Fillet height} \times \text{Fillet width} \\ \times 2 \times (\text{Die length} + \text{Die width})] \\ + \pi/3 \times (\text{Fillet width})^2 \times \text{Fillet height}\} \times \text{Shape factor}$$

The shape factor is related to the type of underfill and its wetting characteristics. Materials with large contact angles have a high shape factor close to that of Fillet 1 in Fig. 2.9; a larger reservoir remains due to reduced wetting. Allowable filleting for dispensing takes into account the tolerances of chip size and underfill gap. A large gap allows more material to flow under the device and less material remains for the fillet (shape factor Fillet 2). A small gap leaves a larger reservoir and produces a higher fillet (shape factor Fillet 1). Examples of the relationship between shape factors and contact angles are given in Table 2.2.<sup>[37]</sup>

### 2.1.3 Adhesion Mechanisms

Bonding of electronic components and parts may be metallurgical using solder, other metal alloys; or eutectics, organic using polymer adhesives; or vitreous using glass-phase adhesives. Polymer adhesive bonding may result from direct-chemical reactions, hydrogen bonding, or mechanical interlocking. In reality, bonding is quite complex and involves more than one mechanism.



**Figure 2.9.** Shape factors for underfill fillets. (Source: *Electronics Engineer*, 1998.)

**Table 2.2.** Contact Angle and Fillet Shape Factors for Underfills<sup>[37]</sup>

Contact Angle (°)	Shape Factor
1	0.1109
5	0.3202
10	0.4739
15	0.5849
20	0.6742
25	0.7505
30	0.8187
35	0.8817
40	0.9416

*Source: Electronics Engineer (1998).*

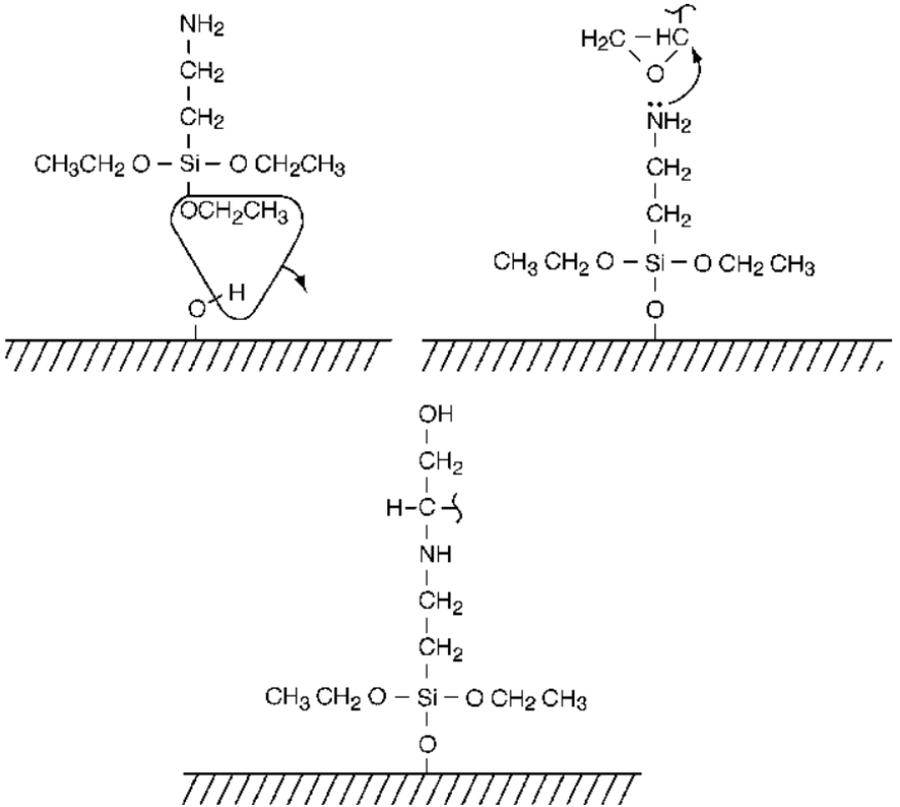
**Metallurgical bonding.** Metallurgical bonding and interconnections dominated the early electronics field. Tin-lead solder has been used for decades and is still in wide use today both for mechanical attachment and electrical connections. Examples include surface mounting of components on PWBs, soldering the leads of cable assemblies, edge connectors and transformers to PWBs, and attaching leadframes to substrates and packages. Eutectic alloying of silicon with gold was especially useful initially for bonding small transistor die and electrically connecting them. Although solder attachments have been supplanted to a large extent by polymer adhesives, they are still widely used in the large-scale production PWAs, flip-chip devices, and BGA packages. Major limitations of solder attachment that have plagued the industry from the beginning include the difficulty in thoroughly removing flux residues, most of which are corrosive; the high temperatures (220°C–240°C) required to apply and reflow the solder; and, in some cases, solder fatigue and cracking. The limitations in using eutectics for die attachment have been the high temperatures required to interdiffuse the gold with the silicon and the stresses generated when attaching large die.

**Direct bonding.** Direct-chemical bonding occurs when functional groups of a polymer react directly with functional groups of a substrate.<sup>[38][39]</sup> Strong covalent bonds can thus be formed between the functional groups of a polymer adhesive and those of a substrate such as a plastic-

laminated circuit board during the curing of the adhesive. The functional groups have to be highly reactive and high temperatures may be required for this type of mechanism to occur. For this reason, and because most other surfaces to be bonded are ceramic or metal, direct-chemical bonding is not a major type. One exception is the use of organosilane adhesion promoters, also known as silane coupling agents. Organosilanes such as aminomethyltriethoxysilane form chemical bridges between a polymer and a surface containing hydroxyl functional groups.

*Adhesion promoters.* For some surfaces, adhesion must be augmented using an adhesion promoter either as an ingredient in the adhesive formulation or separately as a primer applied to the substrate prior to dispensing the adhesive. *Adhesion promoters* are difunctional or multifunctional monomers or oligomers where one or more reactive groups chemically bond to the substrate and the other reactive groups form bonds with the adhesive, thus creating a molecular bridge. Because of this bridging mechanism, adhesion promoters are also known as coupling agents. The most widely used adhesion promoters are the aminoalkoxysilanes, such as  $\gamma$ -aminotriethoxysilane, and mercaptoalkoxy silanes. The amino or mercapto groups form chemical bonds with the polymer molecule while the alkoxy groups, after conversion to hydroxyl groups when exposed to small amounts of moisture, bond chemically to the oxide or hydroxyl groups of ceramic or metal substrates. The more chemically active sites the substrate has, preferably hydroxyl groups, the better the adhesion will be. A proposed mechanism is shown in Fig. 2.10. Adhesion promoters consist of very dilute solutions, for example, 0.1% to 1% by weight of the organosilane in a mixture of 95% methanol and 5% water. Organosilane primers are especially effective in enhancing the adhesion of polyimides to silicon, silicon oxide, and silicon nitride surfaces.<sup>[40]</sup> Organosilanes are also used to coat filler particles to enhance their adhesion to the resin matrix in formulating metal-filled epoxy or polyimide adhesives.

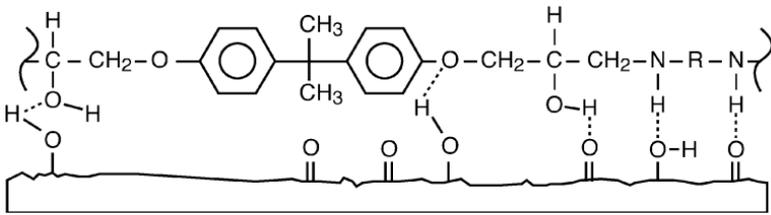
**Hydrogen bonding.** One mechanism for bonding highly polar polymers to equally polar sites on substrate surfaces involves hydrogen bonding (H-bonding). *Hydrogen bonding* occurs between the hydrogen atoms of one molecule and the highly electronegative atoms of other molecules or of a substrate.<sup>[41]</sup> H-bonding is the attractive force between atoms or groups of opposite polarities without actually forming a chemical bond. Hydrogen atoms bond strongly to highly electronegative atoms such as fluorine, oxygen, nitrogen, and sulfur. Thus, the hydrogen of hydroxyl groups, present in most epoxy, polyurethane, and polyimide resins and polymers, readily



**Figure 2.10.** Proposed mechanism for adhesion promotion using a silane.

bonds with the oxide and hydroxyl groups of metal oxides present on metal and ceramic surfaces. Hydrogen bond interactions between epoxy adhesives and epoxy-laminate or other plastic-laminate circuit boards also result in strong adhesion. Figure 2.11 shows the authors' concept of the role that H-bonding plays in the adhesion of a partially cured epoxy to an oxide surface such as a silicon oxide layer on a silicon substrate or an aluminum oxide of an alumina ceramic. The figure shows several ways in which hydrogen, oxygen, and nitrogen can participate in forming H-bonds.

**Mechanical interlocking.** Together with hydrogen bonding and, in some cases direct-chemical bonding, mechanical interlocking plays a key role in forming strong bonds. Mechanical interlocking is a mechanism whereby a low viscosity liquid or a thixotropic paste fills the porous surfaces



**Figure 2.11.** Representation of H-bonding of epoxy to an oxide surface.

of some materials or encapsulates the peaks and valleys of a rough surface. In both cases, the greater exposed surface areas compared with smooth non-porous surfaces provide greater sites for attachment. Examples include the nascent oxides that are present on the surfaces of metals such as aluminum or purposely formed oxides such as the anodizing of aluminum or the chemical oxidation of copper. Rough surfaces also enhance mechanical interlocking. Adhesives form stronger bonds to a 96% alumina substrate with a surface roughness of 15–25 microinches than to a smooth, high-purity 99+% alumina with a roughness of only 1–4 microinches.

**Vitreous bonding.** Silver-glass paste adhesives are reported to bond by a chemical reaction between the glass oxides and the oxides contained in a ceramic substrate such as alumina. A simultaneous mechanism may involve melting of the lead borosilicate glass phase and fusion with the glass phase and oxides of a ceramic substrate or with oxides of a silicon substrate. Adhesion between the silver-glass and the backside of a die is reported to occur by out-diffusion of silicon through the backside chromium-gold metallization.<sup>[42]</sup> Bonding occurs during the final temperature step in the processing of the silver glass. At the 325°C–340°C step, the glassy phase softens followed by liquifying, flowing, and sintering at temperatures of 410°C–430°C.<sup>[42]–[44]</sup> Glass die bonding is performed in an air or oxidizing ambient to avoid reducing the lead oxide of the glass to metallic lead, which then hinders the oxide bonding mechanism.<sup>[45]</sup>

## 2.2 ELECTRICAL CONNECTIONS

A second key function for adhesives is to form ohmic contacts or electrical connections between active and passive devices, connectors, leadframes, I/O leads, or other electronic parts to form a circuit. Other

applications for electrically conductive adhesives include electrostatic dissipation and electrical grounding connections.

To function as electrical conductors, epoxies and other polymer resins, because they are inherently insulators, must be filled with electrically conductive particles such as metals. The selection of electrically conductive or insulative adhesives is based largely on their conductivities or, conversely, on their volume resistivities. Electrically conductive adhesives should have low resistivities initially and retain those values on aging, moisture exposure, thermal cycling, and other operating and test conditions. The resistivities of metal-filled epoxy adhesives can range from  $10^{-3}$  to  $10^{-5}$  ohm-cm. Electrically insulative adhesives should have high volume resistivities ranging from  $10^8$  to  $10^{15}$  ohm-cm.

### 2.2.1 Conductivity and Resistivity

According to Ohm's Law, *electrical resistance* is the ratio of applied voltage to the current between two electrodes in contact with a material. Resistance is directly proportional to the length and inversely proportional to the cross-sectional area of the sample as follows:

$$\text{Eq. (2.11)} \quad R = \rho l/A \text{ and } \rho = Rwt/l$$

where

- $R$  is insulation resistance in ohms
- $l$  is length of the sample in cm
- $A$  is a cross-sectional area in  $\text{cm}^2$
- $w$  is the width of the sample in cm
- $t$  is the thickness of the sample in cm
- $\rho$  is a proportionality constant called the resistivity, in ohm-cm

It is convenient to compare and select adhesives in terms of their resistivities because these values reduce resistance measurements to a common denominator. *Volume resistivity*, which is the ohmic resistance of a cube of bulk material one centimeter per side, is frequently used to compare the electrical properties of both electrically conductive and electrically insulative adhesives.

The reciprocal of resistance is *conductance*, expressed as  $\text{ohm}^{-1}$  or mhos, and the reciprocal of resistivity is *specific conductance* or *conductivity* expressed as  $\text{ohm}^{-1}\text{-cm}^{-1}$ .

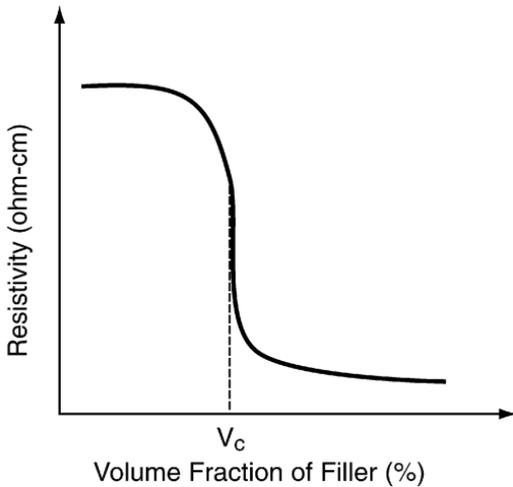
## 2.2.2 Electrical Conductivity and Fillers

Electrically conductive adhesives may be isotropic (conduction equally in all directions) or anisotropic (conduction in the  $z$ -direction only). Both types are widely used in the assembly and packaging of electronics.

**Isotropic conduction.** To obtain the lowest electrical volume resistivities (in the  $10^{-3}$  to  $10^{-5}$  ohm-cm range) and the lowest contact resistances, polymer resins must be highly filled with 70%–80% by weight (25%–30% by volume) of metal particles and must be thoroughly cured. Silver and silver alloys are the most widely used fillers but, in specific applications, other metal fillers including gold, copper, nickel, and even carbon\* are used. The resistivities of the best silver-filled epoxies used for die and chip attachment are in the  $10^{-4}$  to  $10^{-5}$  ohm-cm range. Although these values are still several orders of magnitude worse than pure silver metal, they are adequate for most circuit applications.

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\* Carbon-filled polymers are often used to dissipate static electricity or to protect from electromagnetic interference (EMI).



**Figure 2.12.** Percolation point ( $V_c$ ) for loading conductive fillers in epoxy resin.

In adding conductive filler to an insulating resin, the volume resistivity changes slowly until a critical level of filler is reached, called the percolation point. The *percolation point* occurs when the resistivity drops abruptly, then continues to drop slowly (Fig. 2.12).<sup>[25][46][47]</sup> Almost continuous linkage of metal particles occurs at the percolation point where typical filler volumes for silver flakes are 25%–30%. According to the percolation theory, there is a minimum critical volume of filler required for electrical conductivity in a polymer at which each filler particle must contact two other particles. A misconception in the use of silver flakes is that increasing the number of contacts lowers volume resistivity.<sup>[25]</sup> Actually, the converse is true because, once the percolation point has been reached, each additional contact adds resistance. Thus, increasing the particle size can increase conductivity since the total number of contacts for a fixed volume decreases.<sup>[46]</sup>

Electrical conduction in filled epoxies occurs by current flowing through and between the metal particles. Shrinkage of epoxies during cure (approximately 3%) results in a compressive stress on the silver flake particles promoting better particle-to-particle contact and improved conductivity.<sup>[48]</sup> Filler particles come in various shapes and sizes, for example, spheres, flakes, fibers, or granules. Silver is normally used as flakes along with anisometric particles added to provide a higher number of contact points.<sup>[49]</sup> The optimum particle sizes and geometries are those that require the minimum filler concentration to provide the highest conductivity.<sup>[46]</sup> In an evaluation by Jost, et al.,<sup>[50]</sup> the effect of filler size on volume resistivity was investigated. Adhesive formulations in which the fillers consisted of large flakes (6–11  $\mu\text{m}$ ) with low surface area (0.3–0.5  $\text{m}^2/\text{g}$ ) had volume resistivities two orders of magnitude lower than formulations with flakes nearly half the size (3–7  $\mu\text{m}$ ) with higher surface area of 0.6–0.9  $\text{m}^2/\text{gm}$ .

Optimum curing conditions are also important in attaining the highest conductivity. The improvements in electrical conductivity resulting from increased time and temperature cure conditions for a commercial silver-filled epoxy adhesive are found in Table 2.3.<sup>[51]</sup> This low temperature-curing adhesive is used in assemblies having temperature-sensitive components.

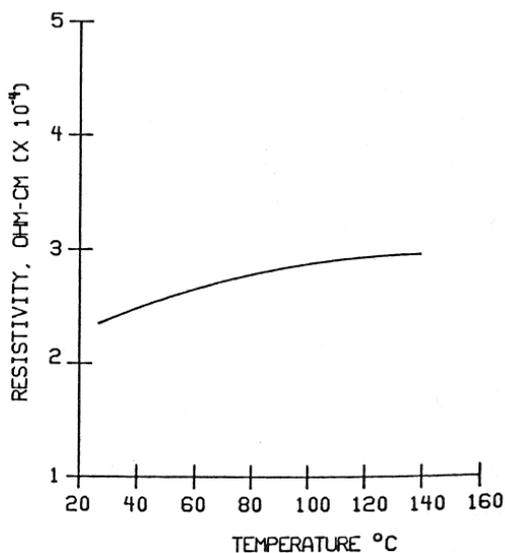
Electrical conductivities of fully cured, silver-filled epoxies are quite stable, decreasing only slightly when measured at elevated temperatures (Fig. 2.13, Table 2.4). Extended cures and aging at 150°C for 1,000 hours have even improved their conductivities.

**Anisotropic conduction.** Electrical conductivity in anisotropic adhesives occurs by a different mechanism than for isotropic adhesives. Although metal fillers are also used, they are used in much lower amounts (0.5% to

**Table 2.3.** Volume Resistivity vs Cure Conditions for a Silver-filled Epoxy Adhesive<sup>[51]</sup>

Temperature (°C)	Volume Resistivity (ohm-cm)			
	Time (hrs)			
	8	16	24	48
25	-	66	0.349	0.071
Temperature (°C)	Volume Resistivity (ohm-cm)			
	Time (hrs)			
	1	2	3	4
50	-	111	0.148	0.041
65	0.086	0.010	0.016	0.007
100	0.005	0.004	0.004	0.004
120	0.003	0.003	0.003	0.003

*Data Provided by Thermoset, Lord Chemical Products.*

**Figure 2.13.** Volume resistivity vs temperature for a silver-filled epoxy paste adhesive.

**Table 2.4.** Volume Resistivities for Silver-filled Epoxy Adhesives (ohm-cm)

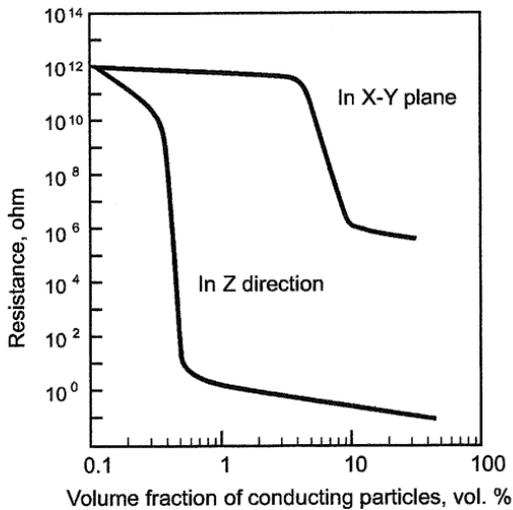
Adhesive	At 25°C	At 60°C	At 150°C	At 25°C after 1000 hours at 150°C
Ablebond® 36-2 <sup>(a)</sup>	$2.4 \times 10^{-4}$	$2.6 \times 10^{-4}$	$2.9 \times 10^{-4}$	$1.4 \times 10^{-4}$
Ablebond® 84-1-LMI <sup>(a)</sup>	$7.0 \times 10^{-5}$	$8.0 \times 10^{-5}$	$9.0 \times 10^{-5}$	$5.0 \times 10^{-5}$
Amicon C868-1 <sup>(b)</sup>	$3.4 \times 10^{-4}$	$3.8 \times 10^{-4}$	$4.8 \times 10^{-4}$	$2.1 \times 10^{-4}$
Epibond® 7002 <sup>(c)</sup>	$8.0 \times 10^{-5}$	$4.8 \times 10^{-4}$	$5.0 \times 10^{-4}$	$5.5 \times 10^{-4}$
Epo-Tek® H35-175M <sup>(d)</sup>	$2.0 \times 10^{-4}$	$2.5 \times 10^{-4}$	$2.5 \times 10^{-4}$ (at 125°C)	$2.7 \times 10^{-4}$

<sup>(a)</sup> Ablestik Laboratories, <sup>(b)</sup> Amicon Corp., <sup>(c)</sup> Furane Products Company, <sup>(d)</sup> Epoxy Technology, Inc.

5% by volume) so that the adhesive is essentially an insulator in the  $x$ - $y$  directions. On inserting the adhesive between the electrodes (for example, the metal bumps of a flip-chip device with metal pads on a flex circuit) of two parts and applying pressure and heat, the metal particles form a  $z$ -direction electrical connection between the electrodes while the surrounding material remains insulating. The shrinkage of the polymer that occurs during curing generates a compressive force on the joints that sets them in place (see Fig. 1.2). The dependence of the volume fractions of a nickel filler on the  $x$ - $y$  and  $z$  directions of an anisotropic film adhesive is shown in Fig. 2.14.

## 2.3 THERMAL DISSIPATION

Thermal dissipation is becoming more important as component densities increase and devices operate at higher speeds and consume more power. Semiconductor junction temperatures must be kept low to assure long-term reliability. This is especially critical for gallium-arsenide ICs because the thermal conductivity of gallium arsenide (GaAs) is about half that of silicon and because GaAs devices operate at higher frequencies than silicon devices. The main methods for removing heat are conduction through solids or liquids, convection by flowing cooled air or other gas over the devices, and radiation.<sup>[53]</sup> Of the three, conduction and convection are the methods most



**Figure 2.14.** Dependence of volume fractions of conductive filler on the electrical conductivity of an anisotropic adhesive.<sup>[52]</sup>

widely used for cooling electronic devices and assemblies. Adhesives play a key role in conducting heat from the devices through several interconnect substrate materials and interfaces and ultimately to a heat sink, a heat spreader, or a heat exchange unit. In high-density multichip modules, there are at least three adhesive interfaces: from die to substrate, substrate to the inside of a package base, and package case to a PWB. Because the thermal conductivities of unfilled polymer adhesives, and even of filled adhesives are low compared to metals and ceramics, they are often the limiting factor in the transfer of heat.

### 2.3.1 Thermal Conductance and Thermal Conductivity

Heat transfer by conduction is governed by Fourier's Law, which states that the flow of heat through a material is directly proportional to the cross-sectional area, the temperature difference across the material, and the time, but inversely proportional to the thickness of the material as follows:

$$\text{Eq. (2.12)} \quad Q = kA(T_2 - T_1)t/x$$

where  $Q$  is the rate of heat flow or thermal conductance  
 $A$  is the cross-sectional area  
 $T_2 - T_1$  is the temperature drop  
 $t$  is time  
 $x$  is thickness

The proportionality constant,  $k$ , is the thermal conductivity or coefficient of thermal conductivity, a value specific for each material and generally reported as W/m·K by electrical engineers or as cal/sec·cm·°C by chemists and materials engineers (cf. Appendix II for conversion factors).

Materials having the highest thermal conductivities are the metals, metal alloys, and some ceramics while plastics, polymeric materials, and glasses have the lowest thermal conductivities (Tables 2.5, 2.6, and 2.7).

The flow of heat from the junction of a semiconductor device through the device material and on through several layers of an interconnect substrate may be treated as a series of temperature drops or thermal resistances at each interface. The junction-to-case thermal resistance  $\theta_{JC}$  expressed in °C/watt is widely used in thermal analysis. The junction-to-case thermal resistance is proportional to the drop in temperature from the semiconductor junction to the case and inversely proportional to the power dissipation, thus:

$$\text{Eq. (2.13)} \quad \theta_{JC} = (T_j - T_{\text{case}})/Q_{\text{chip}}$$

where  $T_j$  is the junction temperature, °C,  $T_{\text{case}}$  is the case temperature, °C, and  $Q_{\text{chip}}$  is the power dissipated from the chip, in watts. For efficient heat flow and removal, both the temperature drop and the  $\theta_{JC}$  should be low. To achieve this, the best approaches are:

- Selecting adhesives that have high thermal conductivities.
- Using as thin a bondline as possible, since thermal conduction is inversely proportional to the bondline thickness.
- Avoiding the generation of voids in the bondline due to air or solvent entrapment.

**Table 2.5.** Thermal Conductivities of Metals and Alloys Commonly Used in Electronic Devices and Assemblies

Material	Symbol or Composition	Thermal Conductivity W/m·K
Alloy 42	58% Fe, 42% Ni	15
Aluminum 6061	Al	237
Chromium	Cr	66
Copper	Cu	401
Copper-Molybdenum	Cu (20%)-Mo	155
Copper-Tungsten	Cu (20%)-W	248
Gold	Au	318
Gold-Tin (20%)	Au-Sn (80-20)	57
Gold-Platinum	Au-Pt	130
Gold-Silicon eutectic	Au-Si	2.94
Indium	In	78
Invar	64% Fe, 36% Ni	11
Kovar <sup>®</sup> (iron-nickel-cobalt)	53% Fe, 29% Ni, 18% Co	17
Lanxide	Al-SiC	200
Lead	Pb	34
Molybdenum	Mo	130-146
Nickel	Ni	90-92
Palladium	Pd	70
Platinum	Pt	72
Silicon	Si	114-125
Silicon-Germanium	Si-Ge	114
Silver	Ag	429
Silver-Palladium	Ag-Pd	150
Tantalum	Ta	54
Tin	Sn	63
Note: Values vary depending on the test conditions and the purity of the sample. Ranges are based on values from several sources.		

(cont'd.)

**Table 2.5.** (Cont'd.)

Material	Symbol or Composition	Thermal Conductivity W/m·K
Tin-Lead solder	Sn-Pb (63/37)	53
Tin-Lead solder	Sn-Pb (37/63)	42
Tin-Lead solder	Sn-Pb (5/95)	36
Tungsten	W	160
Note: Values vary depending on the test conditions and the purity of the sample. Ranges are based on values from several sources.		

**Table 2.6.** Thermal Conductivities of Ceramic and Inorganic Materials Commonly Used in Electronic Devices and Assemblies

Material	Symbol	Thermal Conductivity W/m·K
Alumina (92%)	Al <sub>2</sub> O <sub>3</sub> (92%)	18
Alumina (96%)	Al <sub>2</sub> O <sub>3</sub> (96%)	20–35
Alumina (99%)	Al <sub>2</sub> O <sub>3</sub> (99%)	40
Aluminum nitride	AlN	170–260
Beryllia	BeO	250
Boron nitride	BN	130–260
Borosilicate glass	PbO·B <sub>2</sub> O <sub>3</sub> ·SiO <sub>2</sub>	0.8
Diamond	Crystalline	1,500–2,000
Diamond	Chemical vapor deposited (CVD)	800–1,300
Gallium arsenide	GaAs	43–50
Indium phosphide	InP	68
Quartz	Crystalline SiO <sub>2</sub>	1.4
Sapphire	Crystalline Al <sub>2</sub> O <sub>3</sub>	32–35
Silicon carbide	SiC	270
Silicon dioxide	SiO <sub>2</sub>	1.5–7
Silicon nitride	SiN	170
Note: Values vary depending on the test conditions, test method, and purity of the sample. Ranges are based on values from various sources.		

**Table 2.7.** Thermal Conductivities of Adhesives and Plastics Commonly Used in Electronic Devices and Assemblies

<b>Material</b>	<b>Filler</b>	<b>Commercial Product</b>	<b>Supplier</b>	<b>Thermal Conductivity (W/m·K)</b>
Cyanate ester adhesive	Silver	QMI 301	Loctite	1.9
Thermoplastic adhesive (paste)	Unfilled	Staystik <sup>®</sup> 383	Cookson Semiconductor Products	0.25–0.5
	Silver	Staystik <sup>®</sup> 181		3.0–3.5
	Alumina	Staystik <sup>®</sup> 783		0.5–1.0
	Aluminum nitride	Staystik <sup>®</sup> 282		1.0–1.5
Thermoplastic adhesive (film)	Unfilled	Staystik <sup>®</sup> 482	Cookson Semiconductor Products	0.25–0.5
	Silver	Staystik <sup>®</sup> 581		3.0–3.5
	Alumina	Staystik <sup>®</sup> 832		0.5–1.0
	Boron nitride	Staystik <sup>®</sup> 1172		8.0–10.0
	Aluminum nitride	Staystik <sup>®</sup> 682		1.0–1.5
Epoxy paste adhesive	Silver	Ablebond <sup>®</sup> 84-1 LMI SR4	Ablestik	2.5
	Silver (special carrier)	Abletherm <sup>®</sup> 2600BT	Ablestik	20
	Silver	ESP 8680-WL	AI Technology	8
	Silver	ME8456-ML2	AI Technology	6.5
	Silver	KO 110	Loctite	3.5

(cont'd.)

**Table 2.7.** (Cont'd.)

<b>Material</b>	<b>Filler</b>	<b>Commercial Product</b>	<b>Supplier</b>	<b>Thermal Conductivity (W/m·K)</b>
Epoxy paste adhesive	Gold	Epo-Tek <sup>®</sup> H43	Epoxy Technology	1.7–2
	Gold	Ablebond <sup>®</sup> 85-1	Ablestik s.	2.0
	Copper	Tru Bond 215	Devcon	0.98
	Diamond	ME 7156	AI Technology	11.5
	Alumina	Ablebond <sup>®</sup> 84-3 MVB	Ablestik	0.50
Low stress epoxy paste	Alumina	MEE 7655	AI Technology	1.8
	Alumina	Prima-Bond ME 7155	AI Technology	1.7
Epoxy adhesive	Silica	LCA4-BA5	Bacon Industries	0.83
	Boron nitride	Epo-Tek <sup>®</sup> 930	Epoxy Technology	4.1
Low-stress epoxy preform, thermally conductive	Aluminum nitride	ESP8450	AI Technology	3.6
Epoxy film, thermally conductive	Glass fabric	Ablefilm <sup>®</sup> 504	Ablestik	0.78
	Glass fabric	Ablefilm <sup>®</sup> 5020K	Ablestik L	0.70
Epoxy-glass laminate	Glass fabric reinforced	FR-4, G-10	Various	0.2–0.3
MCOT adhesive	Alumina	MC 723	Ablestik	1.0

(cont'd.)

**Table 2.7. (Cont'd.)**

<b>Material</b>	<b>Filler</b>	<b>Commercial Product</b>	<b>Supplier</b>	<b>Thermal Conductivity (W/m·K)</b>
Polyimide paste adhesive	Silver	Ablebond® 71-1	Ablestik Labs.	2.0
Bismaleimide paste adhesive	Boron nitride	QMI 536 HT	Loctite	0.9
Bismaleimide paste adhesive	Silver	QMI 550 EC	Loctite	3.6
Bismaleimide paste adhesive	Teflon	QMI 550	Loctite	0.2
Polyimide coating	Unfilled	2611D	DuPont	0.2
Polyimide-glass laminate	Glass fabric reinforced	Various	Various	
Polyurethane	Unknown	Flexobond 442	Bacon Industries	0.86
Silicone paste adhesive	Highly filled (unknown)	Ablebond® 12-1	Ablestik Labs.	1.25
Silicone paste adhesive	Unknown	S-6605	Dow Corning	0.85
Silver-glass paste adhesive	Silver	JMI- 5160	Ablestik Labs.	78.3
Silver-glass paste adhesive	Silver	Ablebond® 2005	Ablestik Labs.	>90
Silver-glass paste adhesive	Silver	QMI 3555R	Loctite	>80

Note: Values are those reported in suppliers' data sheets. Please contact the supplier for values to be used in specifications.

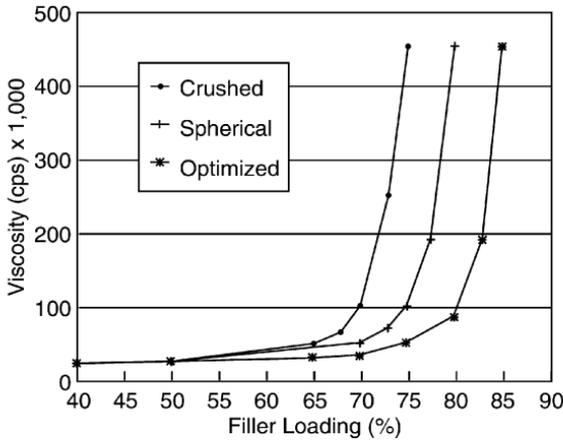
### 2.3.2 Thermal Conductivities of Adhesives

Unfilled polymer adhesives are inherently thermal insulators. Their thermal conductivities range from 0.1 to 0.3 W/m·K.<sup>[54][55]</sup> By formulating resins with metal, metal oxide, or inorganic fillers, thermal conductivities can be increased tenfold or better. Commonly used metal fillers include silver, gold, nickel, and copper. The use of metal fillers, however, also renders the adhesive electrically conductive and is not suitable where electrical insulation or isolation are required. Commonly used inorganic electrically nonconductive fillers include alumina, silica, beryllia, aluminum nitride, and cubic boron nitride. Method 5011 of MIL-STD-883 specifies 1.5 W/m·K as a minimum thermal conductivity for electrically conductive adhesives and 0.15 W/m·K for electrically insulative adhesives. Some recent epoxy formulations filled with diamond particles or with cubic boron nitride are reported to have thermal conductivities as high as 11.5 W/m·K, for example, diamond-filled epoxies.<sup>[56]</sup> Furthermore, some silver-filled epoxies are reported to have thermal conductivities as high as 7–9 W/m·K (Table 2.7).

In addition to the type of filler, thermal conductivity depends on many other factors including the amount of filler used, whether it is by weight or by volume, its form and size, the surface treatment of the filler particles, the completeness of cure, and the test conditions used for measurement. Test methods are described in MIL-STD-883, Method 1012.1 and in ASTM C518.<sup>[57][58]</sup>

### 2.3.3 Effect of Fillers on Thermal Conductivity

The conductivities of adhesives can be increased by formulating them with the maximum amount of the highest thermal filler. Thermal conductivity increases modestly, up to a filler level of approximately 70% by weight, then increases significantly, suggesting a percolation threshold similar to that for electrically conductive adhesives discussed in Sec. 2.2.2. As such, viscosity also increases rapidly at about 70% filler loading (Fig. 2.15). With filler levels above 80% by weight, the adhesive becomes so viscous that it cannot be easily dispensed. Even with such high filler loadings, the thermal conductivities of the formulations are still far below those of the filler itself (Tables 2.5–2.7). Advancements in this area will be required to meet the thermal requirements for the next generation of high-density circuits. The thermal conductivity ( $K_e$ ) of a filled adhesive may be predicted from the Lewis and Nielsen model.<sup>[60]</sup>



**Figure 2.15.** Percolation threshold of thermally conductive fillers.<sup>[59]</sup>

$$\text{Eq. (2.14)} \quad K_e = K_c \frac{1 + AB\phi_2}{1 - B\phi\phi_2}$$

where  $K_c$  is the thermal conductivity of the continuous phase (the polymer matrix) (typically 0.2 W/m·K)  
 $A$  is the shape parameter that increases with aspect ratio  
 $\phi_2$  is the volume fraction of the filler  
 $\phi_m$  is the maximum filler level while maintaining a continuous matrix phase (packing factor)  
 $\phi$  is calculated from  $\phi_2$  and the packing factor  $\phi_m$  as in Eq. (2.15)

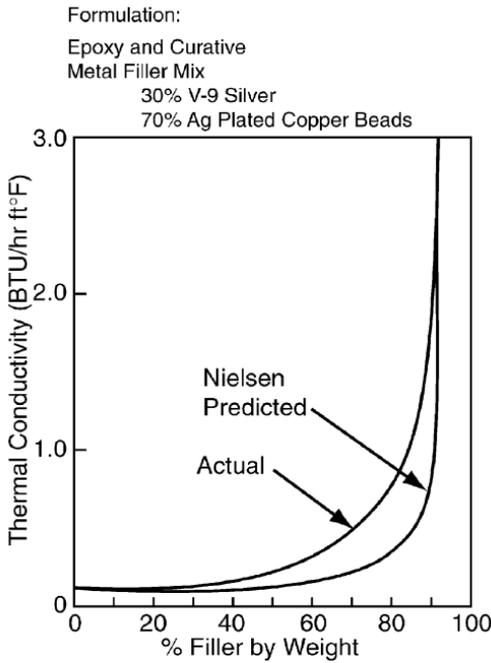
$$\text{Eq. (2.15)} \quad \phi = 1 + \left( \frac{1 - \phi_m}{\phi_m^2} \right) \phi_2$$

$B$  is calculated from the ratio of thermal conductivities of the two phases and  $A$  as in Eq. (2.16).

Eq. (2.16) 
$$B = \left\{ \frac{\left( \frac{K_f - 1}{K_c} \right)}{\left( \frac{K_f + A}{K_c} \right)} \right\}$$

where  $K_f$  is the thermal conductivity of the filler.

Graphs of the actual and predicted thermal conductivities for a silver-filled epoxy composition are shown in Fig. (2.16).



**Figure 2.16.** Predicted thermal conductivity using the Nielsen Model compared with actual data. (Copyright Adhesives Age, 1989, reproduced with permission.)

## 2.4 STRESS DISSIPATION

A function of adhesives that is becoming increasingly important is to absorb and dissipate stresses produced in electronic assemblies due to changes in environmental conditions or accelerated testing. The need for stress absorbing and dissipating adhesives has increased with advancements in microelectronics. Some advancements requiring low-stress adhesives are:

- The introduction of large-chip devices (up to 1-in square).
- An increase in the number of I/Os per device (over 500 microbumps for flip-chips).
- Use of thinned silicon or GaAs die (as low as several mils).
- Greater use of fragile components (glass diodes, fiberoptics, MEMS).

In addition, there has been greater use of flexible circuitry and foldable flex circuits requiring a corresponding degree of flexibility in the adhesives used. For these applications, solders or other metallurgical attachment materials have often failed due to cracking, delamination, electrical opens, or changes in electrical parameters. Some of these failures occur immediately after assembly while others are induced on aging, temperature cycling, vibration, thermal or mechanical shock, or exposure to moisture. A major condition for failures is a large mismatch in the CTEs of adherends bonded with high-modulus materials and subjected to large temperature extremes.

Adhesives formulated from flexible, elastomeric-type resins are now commercially available and effectively used to dissipate stresses. They are low-stress or “no-stress” adhesives that have a low-modulus of elasticity. Several guidelines that can be followed to reduce stresses are the following:

- Selecting an adhesive that has a low shrinkage during cure (<3%).
- Selecting an adhesive that after curing matches the CTEs of the adherends as closely as possible.
- Selecting an adhesive that has a low modulus of elasticity.
- Moderating the cure conditions, for example, employ a step cure instead of a rapid high-temperature shock cure.
- Selecting an adhesive whose  $T_g$  lies below or above its expected operating or testing temperature.

### 2.4.1 Thermal Expansion and Stresses

The degree of linear or volume expansion of a material with increasing temperature is an important thermomechanical parameter in predicting and assessing stresses. The coefficient of thermal expansion (CTE), the amount of expansion that a material undergoes during a temperature change, is a ratio of the change in length per °C to the length at 0°C as follows:

$$\text{Eq. (2.17)} \quad l_T = l_0 (1 + \alpha T)$$

$$\text{or:} \quad \alpha = (l_T - l_0)/l_0 T$$

where  $l_T$  is the length at temperature,  $T$ ,  $l_0$  is the length at 0°C, and  $\alpha$  is the coefficient of thermal expansion (CTE). Coefficients of thermal expansion are reported as cm/cm/°C or, more generally, as unit/unit/°C or ppm/°C. CTEs vary with temperature and are usually reported for a temperature range. The coefficients of volume expansion are generally three times those for linear expansion.

A knowledge of the CTEs of materials being bonded and of the attachment materials is extremely important in predicting and avoiding stresses due to large mismatches in expansion during temperature changes. Use of a rigid, high-modulus of elasticity material to join members that have large differences in their CTEs invariably results in warpage, cracking, and delamination. Conversely, materials having closely matched CTEs such as small silicon die (CTE = 2.6–3.0 ppm/°C) can be attached reliably to Kovar® leadframes (CTE = 5.1–5.5 ppm/°C), even with high-modulus adhesives. With the introduction and wider use of copper leadframes (CTE = 16–17 ppm/°C), only the low-modulus, low-stress adhesives can be used without delamination at the die interface or sometimes cracking of the die.

Low-stress and stress-dissipating adhesives were also found to be essential as underfills for flip-chip bonded devices, chip-scale packages, and BGA packages. Underfill adhesives are designed to protect solder-ball interconnections by minimizing the stress and strain caused by mismatches in the CTEs of the adherends, especially during temperature cycling. In effect, the underfill bonds the lower-CTE, high-modulus silicon chip to the higher-CTE, lower modulus substrate (typically a plastic-laminate circuit board or a ceramic interconnect substrate).<sup>[61]</sup> The result is that the bonded surfaces assume a “composite” CTE, constraining the substrate modulus with the high stiffness of silicon. The underfill also protects the part during

shock and vibration.<sup>[62]</sup> Ideally, one would select all materials with matched or closely matched CTEs, but this is seldom possible in practice. Thus, flexible adhesives having low moduli are used and, although they may have moderate to high CTEs, are able to absorb and dissipate stresses produced. The moduli for low-stress or no-stress adhesives range from approximately 15,000 psi to 30,000 psi at 25°C. Coefficients of thermal expansion for some non-organic materials and organic materials commonly used in electronic assemblies are given in Tables 2.8 and 2.9.

**Table 2.8.** Coefficients of Thermal Expansion for Some Non-Organic Materials Used in Electronic Assemblies

Material	CTE, ppm/°C
Alumina ceramic	5.6–6.7
Alumina, 92%	7
Alumina, 96%	7.7, 6.6
Aluminum	23.5
Aluminum nitride	3.8–4.4
Beryllia	4.7
Chromium	4.9, 6.3
Copper	16–17
Copper-tungsten (20% Cu)	6.5–8.3, 7.0
Copper-molybdenum (20% Cu)	5.8–8.3, 7.2
Diamond, single crystal	1.1
Diamond, CVD	0.4–1.5
Gallium arsenide	6.86, 5.9
Glass, borosilicate	3.24–4.5
Gold	14.1
CTE values were collected from various sources. Ranges of values or different values are due to differences in test methods, test conditions or purity of the sample.	

(cont'd.)

**Table 2.8.** (Cont'd.)

<b>Material</b>	<b>CTE, ppm/°C</b>
Indium phosphide	4.75
Invar	0.64, 1.5
Kovar <sup>®</sup>	5.1–5.5
Lanxide (Al-SiC)	6.7–7.3
Lead	29
Molybdenum	4.8
Nickel	7.8, 13.3
Palladium	11.8
Platinum	8.9
Quartz (crystalline SiO <sub>2</sub> )	0.3–0.5
Sapphire (crystalline Al <sub>2</sub> O <sub>3</sub> )	5.5
Silicon	2.6–3
Silicon carbide	2.8
Silicon-germanium	4
Silicon oxide (fused)	0.5
Silicon nitride	2.3
Silver	19.1
Tin	20
Tin-lead solder (60–40)	24.6
Tungsten	4.5
CTE values were collected from various sources. Ranges of values or different values are due to differences in test methods, test conditions or purity of the sample.	

**Table 2.9.** Coefficients of Thermal Expansion and Glass-transition Temperatures for Some Adhesives and Plastics Used in Electronic Assemblies

Adhesive Type	Product	Supplier	$T_g$ , °C	CTE, $<T_g$ , ppm/°C	CTE, $>T_g$ , ppm/°C
Hybrid chemistry paste, stress absorbing, electrically conductive, very low moisture absorption	Ablebond® 2000	Ablestik	59	65	200
Electrically conductive, polyimide adhesive for high bond strength at elevated temperatures	Ablebond® 71-1	Ablestik	240	41	-
Epoxy paste, electrically conductive, high-temperature stable	Ablebond® 84-1LMISR	Ablestik	120	40	150
Hybrid chemistry paste, highly electrically and thermally conductive	Abletherm® 2600K	Ablestik	68	36	-
Hybrid chemistry paste, highly electrically and thermally conductive	Abletherm® 2600BT	Ablestik	41	40	70
Epoxy paste, electrically insulative, high-temperature stable	Ablebond® 84-3	Ablestik	85	40	100
Electrically insulative, fast curing, modified cyclo-olefin thermoset adhesive	Ablebond® MC723	Ablestik	75	48	99

(cont'd.)

**Table 2.9. (Cont'd.)**

<b>Adhesive Type</b>	<b>Product</b>	<b>Supplier</b>	<b><math>T_g</math>, °C</b>	<b>CTE, &lt;<math>T_g</math>, ppm/°C</b>	<b>CTE, &gt;<math>T_g</math>, ppm/°C</b>
Electrically conductive epoxy paste adhesive for low-stress and in-line die attach	ME8418-DA	AI Technology	80	40	-
Thermoplastic epoxy paste, unfilled	Staystik® 182	Cookson Electronics	98	-	-
Thermoplastic epoxy pastes, filled	Staystik® 281,782,382	Cookson Electronics	98	-	-
Fast curing, electrically conductive epoxy paste adhesive	Epo-Tek® H20E	Epoxy Technology	100	31	120
Electrically conductive polyimide die-attach adhesive (screen printable)	Epo-Tek® P-1011	Epoxy Technology	180	37	-
Thermally conductive and high-purity dual $T_g$ epoxy die-attach paste	Epo-Tek® H65-175MP	Epoxy Technology	80, 150	55	165
Electrically conductive, high-purity, snap-cure epoxy die attach	Hysol® KO 110	Loctite	78	57	-
Electrically conductive, low-stress bismaleimide die-attach adhesive with ultra-fast cure	QMI 534	Loctite	-35	87	171
Highly thermally conductive, snap-cure bismaleimide paste	QMI 536HT	Loctite	4	66	177

*(cont'd.)*

**Table 2.9. (Cont'd.)**

<b>Adhesive Type</b>	<b>Product</b>	<b>Supplier</b>	<b><math>T_g</math>, °C</b>	<b>CTE, <math>&lt;T_g</math>, ppm/°C</b>	<b>CTE, <math>&gt;T_g</math>, ppm/°C</b>
Electrically conductive cyanate-ester high-throughput adhesive	QMI 301	Loctite	245	45	85
Electrically conductive paste adhesive	MD-110	Thermoset	60	56	-
Electrically conductive paste adhesive	MD-140	Thermoset	80	32	-
Epoxy film, unsupported, electrically conductive	Ablebond® 5025E	Ablestik Laboratories	90	65	150
Epoxy film, thermally conductive and high purity	Ablefilm® 5020K	Ablestik Laboratories	109	45	270
Epoxy film, thermally conductive, for gold surfaces	Ablefilm® 550	Ablestik Laboratories	102	50	300
Flexible rubber-modified epoxy film, thermally conductive	Ablefilm® 561K	Ablestik Laboratories	55	85	300
Flexible rubber-modified epoxy film, electrically conductive	Ablefilm® ECF561E	Ablestik Laboratories	47	100	380

*(cont'd.)*

**Table 2.9.** (Cont'd.)

Adhesive Type	Product	Supplier	$T_g$ , °C	CTE, $<T_g$ , ppm/°C	CTE, $>T_g$ , ppm/°C
Dielectric epoxy film, highly thermally conductive	ESP 7676-HF	AI Technology	80	40	100
Dielectric epoxy film, thermally conductive	ESP 7675-HF	AI Technology	80	40	100
Thermoplastic epoxy films, electrically and thermally conductive	Staystik® 581, 682, 882	Cookson Electronics	98	-	-
Thermoplastic epoxy film, unfilled	Staystik® 482	Cookson Electronics	98	-	-
Epoxy Polyphenylene Oxide – E glass <sup>(1,2)</sup>	Various	Various	180	12–18 (x,y) 150–170 (z)	-
Epoxy glass laminate <sup>(1,3)</sup>	FR-4, E-glass, G-10	Various	140– 200	13–18 (x,y) 55–100 (z)	-
Epoxy - Aramid, woven <sup>(1,2)</sup>	Various	Various	140– 180 <sup>(2)</sup>	6–8 (x,y) 90–150 (z)	-
Epoxy - Aramid, nonwoven <sup>(1)-(4)</sup>	Various	Various	140– 180	7–9 (x,y) 80–110 (z)	-
Polyimide- E-glass laminate <sup>(2-5)</sup>	Arlon® 33N	Arlon	>250	13–17 (x,y) 45–75 (z)	-

(cont'd.)

**Table 2.9. (Cont'd.)**

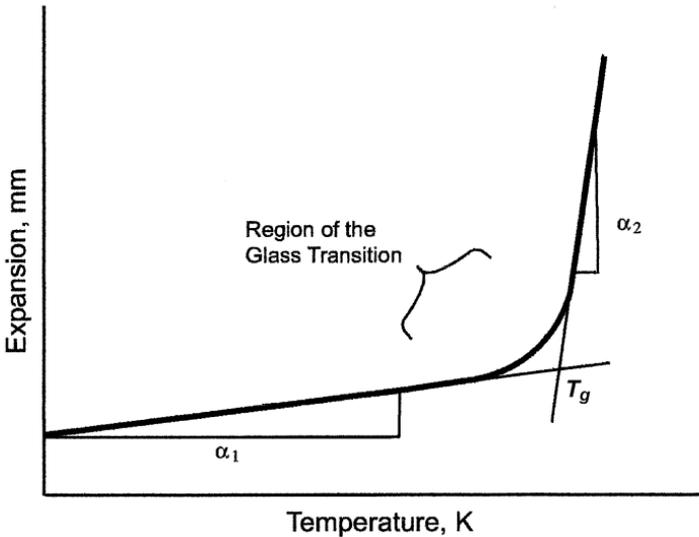
Adhesive Type	Product	Supplier	$T_g$ , °C	CTE, $<T_g$ , ppm/°C		CTE, $>T_g$ , ppm/°C
Polyimide – quartz <sup>(4)</sup>	Various	Various	>250	6–8 (x,y)	34 (z)	-
Polyimide – Aramid <sup>(2,4)</sup>	Various	Various	>250	13–15 (x,y)	4–100 (z)	-
Polyimide – Aramid <sup>(1,3)</sup>	Various	Various	>250	7–9 (x,y)	75–95 (z)	-
Polyetherimide-glass <sup>(6)</sup>	ULTEM <sup>®</sup> 2300	GE	215	23 (x,y)	-	-
Cyanate ester – E-glass <sup>(2,7)</sup>	Various	Various	>230	9–10 (x,y)	45–55 (z)	-
Cyanate ester – S-glass <sup>(1,6,7)</sup>	Various	Various	230	8–10 (x,y)	40 (z)	-
PTFE – woven glass <sup>(8)</sup>	GX	Rogers	N/A	15 (x,y)	200 (z)	-

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## 2.4.2 Glass-Transition Temperature and Stresses

In plotting the expansion of a polymeric material as a function of temperature, there is a temperature at which an abrupt or significant increase in expansion occurs. This temperature, known as the *glass-transition temperature* ( $T_g$ ), is the temperature that corresponds to the intersection of lines drawn tangent to the leading baseline and the steepest portion of the post transition curve. Figure 2.17 is a generalized thermal expansion curve showing the inflection point at which the  $T_g$  occurs.

At the  $T_g$ , a material change occurs from a solid rigid glassy state to a soft amorphous state. The polymer molecules are transformed from a somewhat ordered state to a random state of high molecular motion. The change in CTE at the  $T_g$  can be two to five times greater than its value before the  $T_g$  is reached and can induce major stresses. For this reason, adhesives suppliers should report the  $T_g$  for each adhesive and the CTEs for temperatures below and above the  $T_g$ . Generally, suppliers report two CTE values:  $\alpha_1$  from  $-55^\circ\text{C}$  to the  $T_g$  and  $\alpha_2$  from the  $T_g$  to  $155^\circ\text{C}$ .



**Figure 2.17.** Generalized thermomechanical analysis curve for epoxy adhesive.

The glass transition is a second-order transition, that is, the second derivative of the free energy function. In comparison, a first-order transition, such as the melting of a material, is the first derivative of Gibbs free energy. The equation used to determine the glass transition<sup>[63]</sup> is:

$$\text{Eq. (2.18)} \quad \alpha = \left( \frac{1}{V} \right) \left( \frac{\partial V}{\partial T} \right)_P = \left( \frac{1}{V} \right) \left( \frac{\partial}{\partial T} \right) \left[ \left( \frac{\partial G}{\partial P} \right)_T \right]_P$$

where  $\alpha$  is the expansion coefficient  
 $V$  is volume  
 $P$  is pressure  
 $T$  is temperature  
 $G$  is Gibbs free energy

The glass transition occurs where  $\alpha$  changes abruptly from a low to a high value. It is determined by monitoring either dimensional changes over a temperature range [for example, by thermomechanical analysis (TMA) or by measuring heat flow using differential-scanning calorimetry (DSC)].

### 2.4.3 Residual Stresses

*Residual stresses* are the result of shrinkage of the adhesive during curing and polymerization and during the cool-down from the curing temperature to room temperature. Residual stresses may be quantified by measuring the warp that results in a substrate from curing the adhesive on the substrate. One method is to calculate the bending stress from the radius of curvature where bending stress,  $S_b$ , is defined as:

$$\text{Eq. (2.19)} \quad S_b = \frac{Eh}{2\gamma R}$$

where  $E$  is Young's modulus,  $\gamma$  is Poisson's ratio,  $h$  is the bondline thickness, and  $R$  is the radius of curvature.<sup>[64]</sup> A high radius of curvature indicates a low stress in the bondline. The radius of curvature is calculated by measuring the amount of warp. Radii of curvature of 2,000 mm or more are possible when bonding silicon ICs to silver-plated copper leadframes with stress-absorbing epoxy adhesives.<sup>[65]</sup>

A practical test to measure the effects of residual stress is to measure the out-of-plane deformation or warpage of a substrate upon which the adhesive is cured; the greater the warpage, the greater the stress, and the lower the radius of curvature. In one example, a 300-mil-square silicon die bonded with an electrically conductive epoxy to a copper leadframe, produced 10- $\mu\text{m}$  warp after cure. Exposure to subsequent processing temperatures from wire bonding and over molding with epoxy further increased the warpage to 13  $\mu\text{m}$ . The warp further increased to 32  $\mu\text{m}$  when a larger die (500-mil square) was used.<sup>[66]</sup> The warp test has been used by formulators to develop and evaluate new low-stress adhesives.

A one-dimensional model of stress buildup in silicon devices over a temperature range is given by the following equation:<sup>[67]</sup>

$$\text{Eq. (2.20)} \quad \sigma_{\text{Si}} = \epsilon_a \times E_a = (\alpha_a - \alpha_{\text{Si}}) \times E_a \times \Delta T$$

- where  $\sigma_{\text{Si}}$  is the stress on the silicon
- $\epsilon_a$  is the strain of the adhesive
- $E_a$  is modulus of the adhesive
- $\alpha_a$  is the CTE of the adhesive
- $\alpha_{\text{Si}}$  is the CTE of silicon
- $\Delta T$  is the temperature difference

Since the coefficients of thermal expansion below the  $T_g$  for most adhesives range from 25–100 ppm/ $^{\circ}\text{C}$  and are greater than the CTEs of the device or substrate materials, stresses in bonded parts are compressive on the die and substrate and tensile on the adhesive.

Another equation for maximum stress in rectangular devices addresses differences in both coefficients of expansion and moduli as follows:<sup>[68]</sup>

$$\text{(Eq. 2.21)} \quad S_{\text{max}} = K(\alpha_{\text{sub}} - \alpha_{\text{Si}})(T_o - T) \sqrt{\frac{E_a E_{\text{sub}} L}{x}}$$

- where  $S_{\text{max}}$  is maximum stress
- $K$  is a geometric constant related to shape and filleting
- $\alpha_{\text{sub}}$  is the CTE for the substrate
- $\alpha_{\text{Si}}$  is the CTE for the silicon die
- $E_a$  is the modulus for the adhesive
- $E_{\text{sub}}$  is the modulus for the substrate

- $L$  is length of the die
- $x$  is the bondline thickness
- $T_o$  is the cure temperature
- $T$  is the application temperature

In summary, the stress (typically at the edge of the die) increases with die size, modulus of the adhesive, temperature, difference in expansion coefficients, and increasing bondline thickness.<sup>[44]</sup>

Finite-element analysis has also been applied to predict internal stress distributions and to help explain stress transfer mechanisms such as shrinkage during cure.<sup>[69]</sup>

#### 2.4.4 Effect of Curing Conditions on the Glass-Transition Temperature

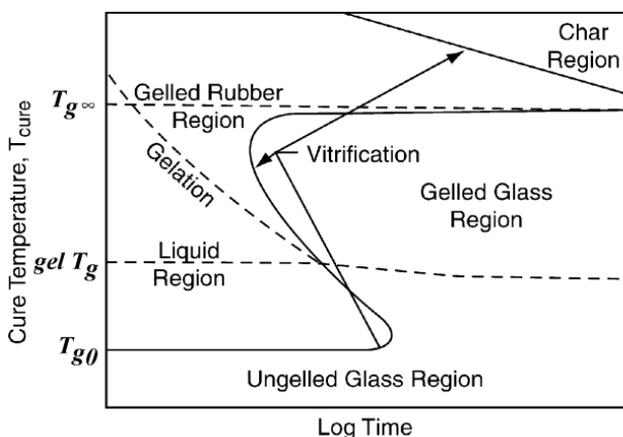
Curing a polymer resin via polymerization involves several stages. For an epoxy resin cured with a hardener, viscosity increases as crosslinking of the monomer units occur. At some time-temperature condition, gelation occurs whereupon the mass becomes semisolid and rubbery. With further crosslinking and increasing molecular weight, the gel converts to a glassy solid stage (vitrification).

Gillham<sup>[70]–[72]</sup> developed a time-temperature transformation (TTT) diagram (Fig. 2.18) to represent the curing process. The TTT diagram is a plot of the log of time on the  $x$ -axis versus the curing temperature on the  $y$ -axis. There are five distinct regions in the diagram:

- Liquid region
- Ungelled glassy region
- Gelled glassy state
- Gelled rubbery region
- Char region

The graph shows three critical temperatures:

- $T_{g\infty}$  : the maximum  $T_g$  of the fully cured material
- Gel  $T_g$  : the temperature at which gelation and vitrification occur simultaneously
- $T_{g0}$  : the  $T_g$  of the mixed reactants, corresponding to a minimum cure



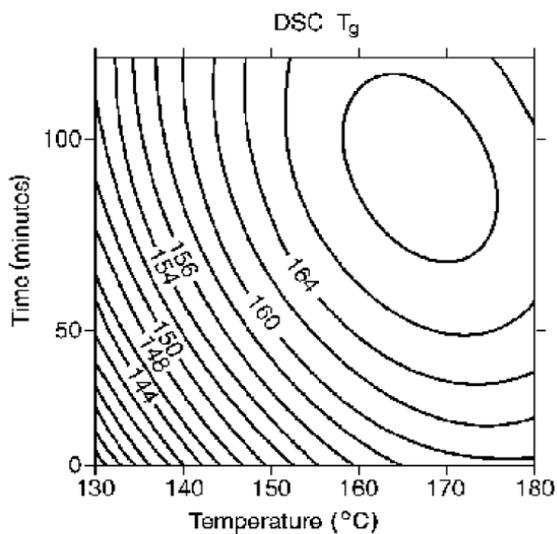
**Figure 2.18.** Time-temperature transformation diagram (TTT).<sup>[73]</sup>

In isothermal cures, at temperatures between the gel  $T_g$  and  $T_{g\infty}$ , the resin undergoes gelation followed by vitrification. Since  $T_g$  is a function of both the degree of cure and the cross-link density, it increases to a point at which all polymer reaction sites have been consumed. At that point, the  $T_g$  reaches a plateau and does not increase further with temperature until the decomposition temperature where a char region occurs (Fig. 2.18). An example of the effect of cure conditions on  $T_g$  and CTE values was shown by Konarski<sup>[74]</sup> who varied the cure cycles of an anhydride-cured epoxy from 130°C to 175°C as shown in Table 2.10. The value of  $T_g$  continued to increase while the expansion coefficient decreased with increasing cure temperature.

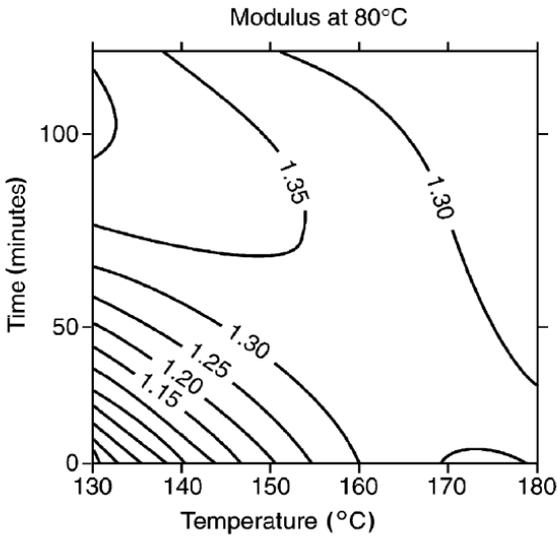
The dependence of curing temperature and time on the  $T_g$  and on the flexural properties of an experimental anhydride-cured epoxy containing 73% by weight silica filler was also demonstrated by differential-scanning calorimetry (DSC). Flexural strength and modulus were measured at 80°C according to ASTM D790.<sup>[75]</sup> Figure 2.19 shows the increase in  $T_g$  with increasing cure temperature and time. The epoxy, cured at 140°C for 50 minutes, had a  $T_g$  of 150°C. However, increasing the cure conditions to 165°C for 90 minutes raised the  $T_g$  to 185°C. The benefit of increasing the cure schedule to improve the  $T_g$  reached a maximum at about 170°C for this particular formulation. Overcuring, which results in excessive crosslinking and embrittlement, only slightly affected the  $T_g$ , but degraded both the flexural strength and modulus. Figures 2.20 and 2.21 show the effects of cure conditions on modulus and flexural strength.

**Table 2.10.** Effect of Cure Schedule on  $T_g$  and CTE for an Epoxy Adhesive<sup>[74]</sup>

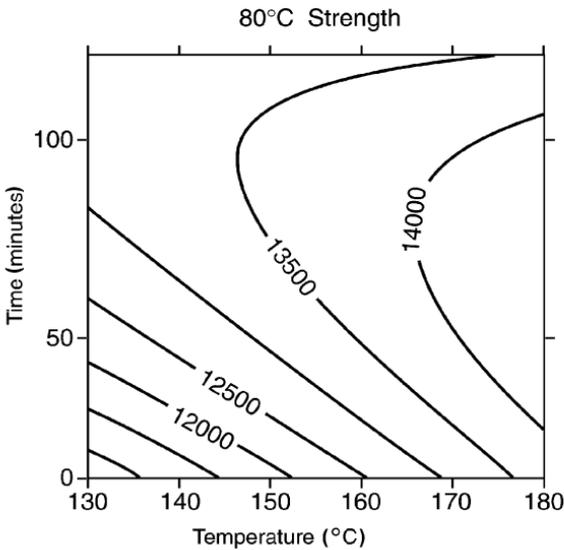
Cure Schedule (°C/hours)	$T_g$ (°C, by TMA)	CTE (25–100°C, ppm/°C)
130/2	117	22.9
146/2	127	23.8
160/2	137	26.3
175/2	146	24.3



**Figure 2.19.** Plots of  $T_g$  (°C) vs cure conditions. (Source: Dexter Hysol, now Loctite.)<sup>[75]</sup>



**Figure 2.20.** Plots of modulus (Mpsi) vs cure conditions. (Source: Dexter Hysol, now Loctite.)<sup>[75]</sup>



**Figure 2.21.** Plots of flexural strengths (psi) vs cure conditions. (Source: Dexter Hysol, now Loctite.)<sup>[75]</sup>

### 2.4.5 Effects of Gelation and Curing Conditions on Stresses

In addition to the cure temperature and time, the manner by which an adhesive is cured affects its thermomechanical properties and stresses. Stresses are greatly reduced by step curing, that is, by allowing the adhesive to gel at a temperature significantly lower than the final cure temperature. Konarski<sup>[74]</sup> found that a pre-gel prior to final cure cycles of 130°C to 175°C lowered both the CTEs and stresses compared with samples that were not pre-gelled. The pre-gel step allows the polymer chains to “anneal” prior to full cure. Step curing is often used for flip-chip underfill adhesives where stress reduction is important in preventing solder ball interconnect failures, especially for large ICs.

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# 3 Chemistry, Formulation, and Properties of Adhesives

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Adhesives are used in a wide range of electronic applications and must withstand diverse environments from benign office conditions to severe long-term military, space, and automotive environments. A design engineer must, therefore, have a basic understanding of the chemistry and properties of adhesives in order to make the right selection. Knowledge of the polymer resins, polymerization and curing mechanisms, and formulations and their bearing on the desired electrical, mechanical, and thermal properties assures the reliability of the final product.

Epoxy adhesives are the most widely used and most versatile of the polymer types. They combine numerous desirable properties including adhesive strength, thermal stability, reparability, dielectric properties, and retention of the properties under high thermomechanical stresses and environmental exposures such as humidity. Through the choice of hardeners, catalysts, fillers, and other additives and by controlling the degree and method of curing, properties can be altered and tailored for a specific application. Silicones meet the needs for very high and low temperature extremes and, because of their low moduli of elasticity and flexibility, are able to dissipate stresses and dampen vibration. Other polymers are also used for specific applications, for example:

- Polyurethane fillets for vibration damping.
- Thermoplastic films for multilayer flexible circuits.
- Polyimides, cyanate esters, and silver-glass for single-die attachment in single packages.
- Modified cyclo-olefin thermosets for low-moisture-absorbing chip attachments.

## 3.1 CHEMISTRY

The basic chemical reactions, used to synthesize monomer and polymer resins and the chemistry involved in the use of curing agents to polymerize the resins, have been extensively studied and are well documented. This section serves as a summary only of those polymers that are primarily used in adhesives formulations for electronic applications. Among these polymers are the epoxies, silicones, polyurethanes, polyimides, acrylates, cyanate esters, and cyclo-olefins. Further technical detail for these polymers may be acquired through literature searches in the transactions of the American Chemical Society (Polymer Group), Society of Plastics Engineers (SPE), and the Society for the Advancement of Materials and Process Engineers (SAMPE).

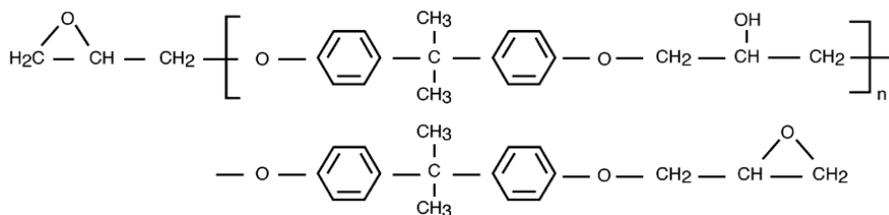
### 3.1.1 Epoxies

Epoxy adhesives are widely used in electronics assembly and packaging.<sup>[1]</sup> They are formed by polymerizing epoxy resins having one or more terminal glycidyl ether (epoxy) groups with a variety of curing agents,\* hardeners, or catalysts.

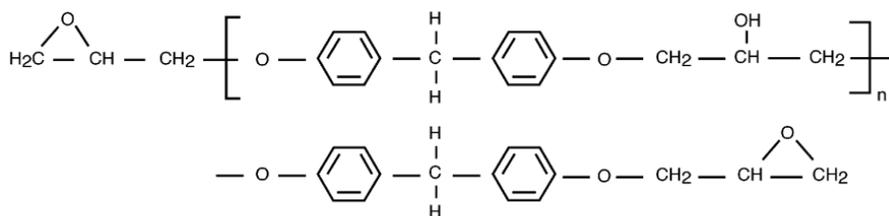
**Epoxy resins.** Most commercially available epoxy resins are based on the diglycidylethers of bisphenol-A, bisphenol-F or other phenolic compounds. A second family of epoxy resins, also used in adhesive formulations, is based on epoxidized olefin compounds such as epoxidized polybutadiene or cycloaliphatic olefins (Fig. 3.1).<sup>[2]-[4]</sup> Epoxy resins based on the diglycidylether of bisphenol-A (DGEBA) having viscosities between 8,000 and 20,000 cps are most commonly used in formulations for adhesives, coatings, laminates, and encapsulants. The DGEBA resins are formed when an excess of epichlorohydrin reacts with bisphenol-A in the presence of an alkali such as sodium hydroxide (Fig. 3.2a). The mechanism of epoxy resin synthesis involves a step-growth polymerization. Initially, the hydroxyl anion from sodium hydroxide abstracts a hydrogen atom from the bisphenol-A (Fig. 3.2b). The intermediate anion next displaces the chlorine atom from

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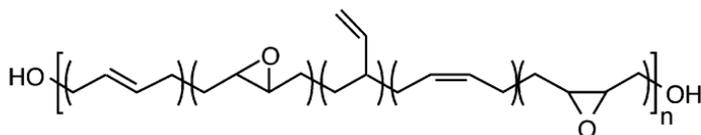
\*Curing agent is often used interchangeably with hardener and catalyst. Strictly speaking, *curing agent* is the broader term encompassing both hardeners and catalysts. A *hardener* is a curing agent that reacts with a resin and becomes part of the polymer through crosslinking while a *catalyst* is also a curing agent that initiates polymerization of the resin, but does not become part of the final polymer structure.



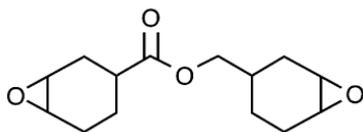
Diglycidylether of bisphenol-A epoxy resin



Diglycidylether of bisphenol-F epoxy resin



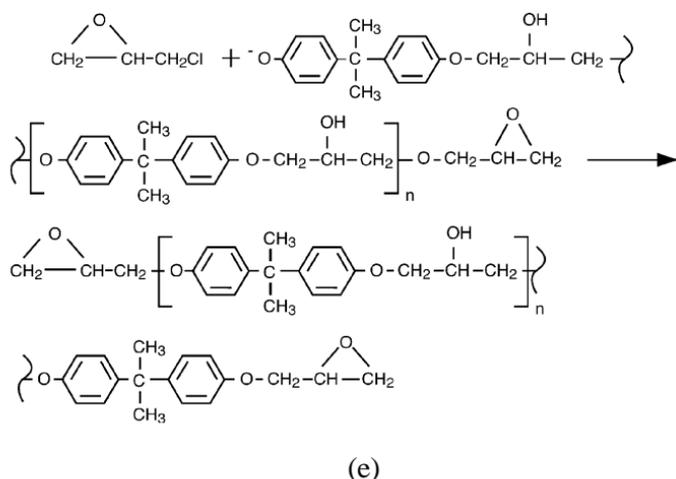
Epoxidized polybutadiene resin



Cycloaliphatic epoxy resin

**Figure 3.1.** Main epoxy resin structures.





**Figure 3.2.** (Cont'd.)

the epichlorohydrin to produce the bisphenol-A intermediate (Fig. 3.2c). The reaction may terminate there with pure DGEBA being produced or may continue to produce higher molecular weight polymers, depending on the ratio of bisphenol-A to epichlorohydrin used (Fig. 3.2d). Finally, an excess of epichlorohydrin terminates the reaction, again by a nucleophilic displacement (Fig. 3.2e). Because of the retention of sodium chloride, a by-product of the synthesis, the resin must be purified either by molecular distillation or by repeated extractions with deionized water.

The extent of reaction,  $\rho$ , is determined from the initial amount of monomeric material,  $N_o$ , and the amount remaining,  $N_t$ , after time,  $t$ , where  $N_o - N_t$  is the amount of monomer converted.

$$\text{Eq. (3.1)} \quad \rho = \frac{N_o - N_t}{N_o}$$

Since molecular weight is a function of the number of repeating monomer units,  $x_n$ , the average molecular weight,  $M_n$ , is given by:

$$\text{Eq. (3.2)} \quad M_n = M_o x_n$$

where  $M_o$  is the monomer weight. Since  $x_n = N_o/N_t$ , the degree of polymerization and the number of repeating units are related by:

$$\text{Eq. (3.3)} \quad x_n = \frac{1}{(1-\rho)}$$

Based on the generalized formula (Fig. 3.2a), pure diglycidylether of bisphenol-A has a repeating unit value of  $n = 0$ . Other epoxy resins have  $n$  values ranging from less than 1 to 18.<sup>[5]</sup> Epoxy resins having  $n$  values from 0 to 1 are typically liquids, while those with values greater than 1 are solids. The Dow Chemical Company “300 series” epoxy resins have  $n$  values less than 1; for example, the value of  $n$  for DER 331 is 0.15.<sup>[6]</sup> Examples of the main epoxy resins used in adhesive formulations are given in Table 3.1<sup>[7]</sup>

**Curing of epoxy resins.** Epoxy resins are characterized by their *epoxy-equivalent weights* (EEW), that is, the weight of resin per epoxy group. Thus, DGEBA, which has a molecular weight of 340 grams and two epoxy groups, would have an epoxy equivalent weight of 170 grams. Epoxy-equivalent weights are important in calculating the stoichiometric (theoretical) amounts of hardeners or curing agents needed to achieve optimum polymerization. With amine-curing agents, it is customary to allow one epoxy group for each active hydrogen of the amine compound. The calculated amount should then produce nearly optimum properties in the polymerized epoxy. Non-stoichiometric amounts, for example in using excess amine, tend to stop chain building and produce low-molecular weight polymers that tend to be brittle. On the other hand, too little amine results in incomplete cure.<sup>[2][8]</sup> The optimum ratios of commercially available two-part epoxy adhesives have generally been calculated and experimentally verified by the supplier so that the user needs only to follow his directions for mixing and curing.

Epoxy resins may be cured with a wide variety of curing agents, in general, any compound that has a labile hydrogen atom or hydroxyl group. These may be amines, polyamides, carboxylic acids, anhydrides, imidazoles, or amide-amines. In general, almost any compound that has a reactive hydrogen can react with the oxirane (epoxy) rings and initiate the polymerization process. Compounds that can donate electrons such as Lewis bases or accept electrons such as Lewis acids may also be used as catalysts. Examples of typical epoxy-curing agents are given in Table 3.2.<sup>[6][9][10]</sup> Advantages and disadvantages of various epoxy-curing agents are compared in Table 3.3.<sup>[11]</sup>

**Table 3.1.** Epoxy Resins Used in Adhesive Formulations<sup>[7]</sup>

<b>Epoxy Resin Type</b>	<b>Examples: Resin/ Supplier</b>	<b>Kinematic Viscosity (poise @ 25°C, unless indicated)</b>	<b>Epoxy Equivalent Weight (gm)</b>
Diglycidyl ether of bisphenol-A (very high purity)	Epon <sup>®</sup> 825/Resolution* DER 332/Dow Chemical Co.	40–60	172–178
Diglycidyl ether of bisphenol-A (standard, undiluted resin, general purpose)	Epon 828 /Resolution DER 331/Dow Chemical Co. Araldite GY 6010/Ciba Geigy Epo Tuf 37-140/Reichhold	110–150	185–192
High-purity, electronics-grade liquid bisphenol-A resin with low-chloride content	Aratronic 5001/Ciba Geigy QUATREX <sup>®</sup> 1010 epoxy resin/ Dow Chemical Co.	125–150	186–190
Diglycidyl ether of bisphenol-F	Epon 862/Resolution	25–45	166–177
Bisphenol-F based, standard, undiluted, elastomer-modified resin (carboxyl-terminated butadiene acrylonitrile)	Epon 58006 /Resolution	150,000–300,000	330–360
Epoxidized, hydroxyl-terminated polybutadiene resin	Poly bd <sup>®</sup> 605E/Sartomer	22,000 (30°C)	300
Cycloaliphatic epoxy	CYRACURE <sup>™</sup> UVR-6110/ Dow Chemical Co.	350–450	131–143
* Epon is a registered trademark of Resolution Performance Products. Epon epoxy resins were originally developed by Shell Chemical Co.			

**Table 3.2.** Typical Epoxy Curing Agents<sup>[6][9]</sup>

<b>Curing Agent</b>	<b>Application</b>	<b>Types (Suppliers)</b>	<b>Formulation and Gel Times</b>
Amines	Room temperature or low-temperature cure	Versamine® (Henkel), Ancamine® (Air Products), Aradur® (Vantico), and Epi-Cure® (Resolution)	1–15 parts per hundred resin (phr), fast gel times
Polyamides	Room temperature or low-temperature cure	Versamid® (Henkel), Ancamide® (Air Products), Aradur® (Vantico), and Epi-Cure® (Resolution)	50–70 phr, intermediate gel times
Anhydrides	Heat cure	HHPA, MHPA, and MTHPA (Lonza, Dixie Chemical, Nippon Zeon, Hitachi Chemical, Buffalo Color, and Lindau)	0.5 to 0.75 parts anhydride to 1 part epoxy, slow gel time
Lewis acids	Catalytic cure (homopolymerization)	BF <sub>3</sub> -MEA (“HT973”), BCl <sub>3</sub> -MEA (DY 9577), (Vantico, Leepoxy, and CVC Chemical)	5–12 phr, fast gel time
Imidazoles	Accelerator for anhydride systems	Curezol® (Air Products)	1–4 phr, fast gel time
Dicy	Accelerator and adhesion promoter for epoxy systems	Epi-Cure® P-104 and P-108(Resolution)	2–5 phr (P-104) and 4–6 phr (P-106), fast gel time

**Table 3.3.** Advantages and Disadvantages of Epoxy Curing Agents<sup>[1]</sup>

<b>Curing Agents</b>	<b>Advantages</b>	<b>Disadvantages</b>
Aliphatic amines	Rapid cure	Critical mix ratios
	Room-temperature cure	Strong skin irritant
	Low viscosity	High vapor pressure
	Low cost	Blushes
Often exothermic		
Polyamides	Convenience	Somewhat higher cost than amines
	Room-temperature cure	High viscosity
	Low toxicity	Low heat resistance
	Good flexibility or resilience	Low vapor pressure
	Good toughness	Tendency to outgas
Aromatic amines	Moderate heat resistance	Solids at room temperature, difficult to mix with epoxy resins
	Good chemical resistance	Long, elevated-temperature cure schedules
Lewis acid or base complexes (boron trifluoride amine complex)	Long pot life	Tendency to exotherm
	High heat resistance	Poor moisture resistance Corrosion risk
Anhydrides	High heat resistance	Long, elevated-temperature cure schedules
	Good chemical resistance	Critical mix ratios



properties. Amine-cured epoxies are characterized by moderate-to-high exotherms, fast curing at low temperatures, and short pot lives. Often the pot lives are too short to be used in production processes. Both aromatic and heterocyclic amines are also used as curing agents for epoxy resins. Aromatic and heterocyclic curing agents impart higher temperature stabilities than their aliphatic amine counterparts.

**Polyamides.** Polyamide resins are characterized by the presence of the repeating amide group along the polymer chain:  $-C(=O)-NH-$ . The polyamides are synthesized by the condensation polymerization of diamino compounds with dicarboxylic acids or esters. Naturally occurring fatty acids such as linoleic acid, or their derivatives, are often reacted with diamines to yield a series of liquid resins. Polyamides are thermoplastics used primarily as hot-melt adhesives that bond well to porous surfaces and have excellent flexibility at low temperatures.

Polyamides that contain amino or hydroxyl groups along their chains or carboxyl groups that terminate a chain can be used to cure epoxy resins, imparting their inherent flexibility.<sup>[12]</sup> The Versamides<sup>®</sup> (Henkel Corp.) are examples of polyamide curing agents.

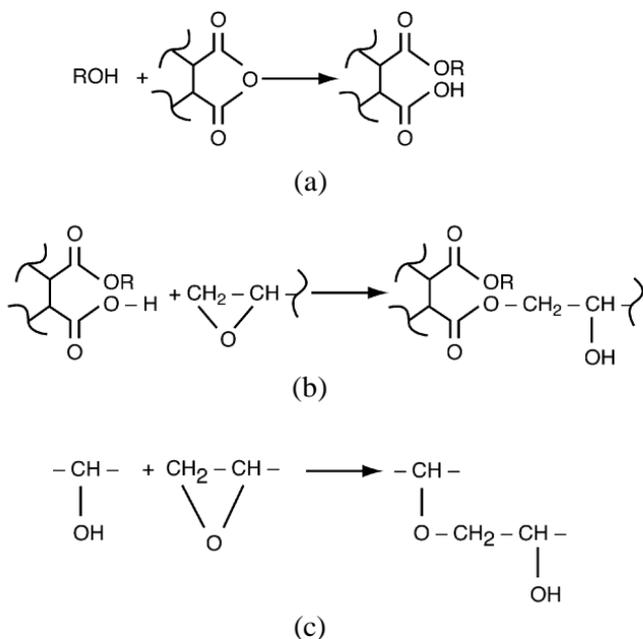
*Amide-amine-curing agents (Dicy).* The most notable and extensively used amide-amine-curing agent is Dicy, (dicyandiamide or 1-cyanoguanidine). Dicy is used as a curing agent for film epoxy adhesives and for B-staged epoxy prepregs. Unlike free amines, Dicy will not react with epoxy resins at room temperature or low temperatures. Dicy may be considered a latent curing agent since temperatures of 145°C–165°C are required to initiate polymerization. At those temperatures, Dicy decomposes releasing the very active free amines. This is a benefit in producing one-part adhesives and films that have a long pot life and shelf life.

Several problems that have been encountered during Dicy's long use in electronics should be mentioned. Because of its low solubility in the epoxy resins, Dicy is often first dissolved in organic solvents. Traces of these solvents are retained in the cured material. Because Dicy is hygroscopic, it also absorbs and retains small amounts of moisture and, if the Dicy has not been completely reacted or if an excess of Dicy was used, ammonia evolves as a decomposition product. These outgassed products have been detected in sealed packages through residual gas analysis and may or may not be serious depending on their amounts and their interactions with the electronic devices and materials. Extended vacuum baking prior to sealing has been effective in removing volatile constituents and reducing the outgassing.

*Anhydride-curing agents.* Besides amines, liquid and solid anhydrides are extensively used to cure epoxy resins. Examples of typical anhydride-curing agents are given in Table 3.2. In contrast to amines, the reaction rates of anhydrides with epoxy resins are slow, requiring temperatures of 150°C–170°C from 2–8 hours. Adding small amounts of catalysts such as a tertiary amine, however, can accelerate curing, (0.5%–3% by weight) or cobalt (II) acetylacetonate.<sup>[13]</sup> Benzyltrimethylamine, in catalytic amounts, is also widely used as an accelerator. Solid anhydrides include phthalic anhydride (PA), hexahydrophthalic anhydride (HHPA), maleic anhydride, and pyromellitic dianhydride (PMDA). Among popularly used liquid anhydrides are methyl nadic anhydride (MNA) and dodecyl succinic dianhydride. Epoxy resins cured with the solid anhydrides, especially the aromatic types such as PMDA, display high-thermal stabilities, high heat distortion temperatures, high radiation resistance, low weight loss after 500 hours at 200°C,<sup>[2]</sup> and long pot lives.<sup>[6]</sup> However, because of their low solubilities and high melting temperatures, solid anhydrides are more difficult to mix with epoxy resins than liquid anhydrides; often, elevated temperatures and solvents must be used. The liquid anhydrides are much easier to process, have lower viscosities, and are easier to blend with epoxy resins. Because all anhydrides are hygroscopic to some extent, humidity, and exposure to moisture should be controlled prior to and during cure.

Epoxy/anhydride reactions vary significantly depending on the presence of a catalyst.<sup>[14]</sup> In uncatalyzed systems, the anhydride reacts with hydroxyl groups of the epoxy resin to produce monoesters and generates a free carboxyl group (COOH) (Fig. 3.4a). The free carboxylic acid group then reacts with the epoxy group forming a second ester linkage and a free hydroxyl group (Fig. 3.4b). Lastly, the hydroxyl group can react directly with another epoxy group (Fig. 3.4c). Without a catalyst, the chemical reaction shown in Fig. 3.4c occurs to a more significant extent, even though those in Figs. 3.4a and 3.4b are the principal reactions. In the presence of a catalyst, formation of polyesters dominates (Fig. 3.4b). Maximum polymerization occurs with an anhydride/epoxy ratio of 0.85:1, although, in practice, ratios up to 1:1 are used and yield useful properties.<sup>[14]</sup>

**Catalytic-curing agents (Lewis bases and Lewis acids).** Both Lewis bases and Lewis acids in catalytic quantities (2–4 phr) cure epoxy resins rapidly without requiring heat. Lewis bases are compounds that have a free pair of electrons such as tertiary amines while Lewis acids are compounds that can accept a pair of electrons such as boron trifluoride. Lewis acids such as boron trifluoride are so reactive that, in addition to their being highly



**Figure 3.4.** Anhydride-curing mechanism for epoxies: (a) reaction of hydroxyl group (from epoxy resin) with anhydride; (b) reaction of carboxylic acid group with epoxy; (c) reaction of hydroxyl group directly with epoxy.

volatile and toxic, their pot lives are too short and exotherms too high to be useful. Although quite reactive separately, Lewis acids can form complexes with many amines neutralizing their polarities and reducing their reactivities. As complexes, Lewis acids and bases are latent catalysts that are fairly stable when mixed with epoxies until heated to a temperature at which the complexes dissociate into the reactive species. For example, the monoethylamine complex of boron trifluoride ( $\text{BF}_3\text{MEA}$ ) has negligible reactivity with epoxy resins at room temperature, but becomes reactive when heated to approximately  $80^\circ\text{C}$ . Latent catalyst complexes are easier to handle, provide longer pot lives, and are lower in toxicity and vapor pressure than their individual constituents. Triethylamine boron trifluoride, monoethylamine boron trifluoride, piperidine boron trifluoride, and aniline boron trifluoride are examples of latent-curing catalysts for epoxy resins.

Once the Lewis base or Lewis acid is released from the complex, the polymerization reactions involved are similar to those for curing an epoxy resin with a tertiary amine (Fig. 3.5).



$$\text{Eq. (3.5)} \quad \text{EEW} = \frac{w_t}{\left( \frac{w_r}{\text{EEW}_r} + \frac{w_a}{\text{EEW}_a} + \frac{w_b}{\text{EEW}_b} \right)}$$

where  $w_t$  is total weight  
 $w_r$  is weight of resin  
 $w_a$  is weight of reactive diluent  
 $w_b$  is the weight of any other additive having a reactive epoxy group.

For example, an adhesive formulation contains 20 parts by weight (pbw) of epoxy resin, 70 pbw of filler, and 10 pbw of a reactive diluent and is cured with an aromatic amine such as diamino diphenylsulfone (DADS) whose amine-equivalent weight is 62. If the resin is Epon 825 or DER<sup>®</sup>\* 332, having an epoxy equivalent of 174, the modified EEW will be:

$$\text{Eq. (3.6)} \quad \text{EEW} = \frac{20 + 70 + 10}{\left( \frac{20}{174} + \frac{10}{130} \right)} = 521.4$$

Thus, the amount of DADS required would be  $62 \times 100/521.4$  or 11.9 pbw, about 12% of the total composition.

### 3.1.2 Silicones

Silicones are a unique class of polymers due to their semi-organic molecular structure. Instead of the normal carbon-to-carbon backbone structure of most polymers, silicones have a silicon-to-oxygen structure that gives them advantages of very high thermal stabilities (up to 300°C, in some cases), flexibility at subzero temperatures (-80°C), and excellent electrical properties under both extreme conditions. Silicone adhesives, coatings, and encapsulants have been used from the inception of electronics and their

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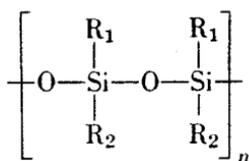
\*Epon is a registered trademark of Resolution Performance Products. Epon epoxy resins, originally developed by Shell Chemical Co., are now available from Resolution Performance Products. DER is a registered trademark of the Dow Chemical Co.

formulations have improved steadily with each new generation of micro-electronic assemblies.

The  $-\text{Si}-\text{O}-\text{Si}-\text{O}-$  backbone of silicones is referred to as siloxane. The silicon atoms may be linked to a wide variety of aliphatic or aromatic groups, as shown in Fig. 3.6 where the R groups are commonly methyl ( $-\text{CH}_3$ ), phenyl ( $\text{C}_6\text{H}_5-$ ), allyl ( $-\text{CH}_2-\text{CH}=\text{CH}_2$ ), or vinyl ( $-\text{CH}=\text{CH}_2$ ). Silicones used in electronic assembly and packaging may be either room-temperature vulcanizing (RTV) that cure by condensation polymerization or vinyl types that cure by addition polymerization initiated by a catalyst. Table 3.4 lists some formulations for each type.

**Condensation-cured silicones.** Both the heat-cured and RTV silicones are formed by condensation polymerization and are sometimes referred to as alkoxy- or acetoxy-cured systems.<sup>[18]</sup> The basic hydroxysilane starting materials are produced by the hydrolysis of mixtures of mono-, di-, and trichlorosilanes as depicted in Fig. 3.7.<sup>[19]</sup> Condensation with elimination of water produces hydroxyl-terminated alkylpolysiloxanes. These resins can be further polymerized in the presence of alkoxy-silanes such as propylorthosilicates to yield the RTV silicones (Fig. 3.8). Catalysts such as organotitanates or dibutyltindilaurate<sup>[13]</sup> may accelerate the curing process.

**Addition-cured silicones.** A second class of silicones cures by addition polymerization initiated by a catalyst. Polymerization occurs by a free-radical mechanism involving a vinyl, allyl, or other unsaturated group of a silicone monomer (Fig. 3.9). Homopolymers can be formed by polymerization of the same monomer while copolymers are formed by reactions among different monomers. The first step involves thermally decomposing the catalyst to produce active species. Addition-cured silicones are often called platinum silicones since catalysts such as platinum-divinyltetramethyl complex and platinum-divinyltetramethyl disiloxane are widely used. Addition-cured silicone adhesives are either one-part or two-part, heat-cured systems and have an advantage over RTV types in not producing by-products during curing.



**Figure 3.6.** General structure for a linear silicone polymer.

**Table 3.4.** Polymer Resins, Cross-linkers, and Catalysts Used as Raw Materials for Silicones<sup>[15]–[18]</sup>

Silicone Type	Polymer Resin (100 parts)	Cross-linker (8–12 phr)	Catalysts
One-part RTVs	Polydimethyl siloxane-silanol terminated [PS 340, 341, and 343 (United Chemical Technologies)]	Trimethoxy methyl silane [PS 9120 (United Chemical Technologies)]	Titanate catalyst (0.5 phr)
	Reactive silicone polymers-silanol terminated [Andisil OH 40, OH 75, and OH 2 (Anderson & Assoc.)]	Epoxy silane cross-linker [K10 (Anderson & Assoc.)]	Dibutyl tin dilaurate [PC-055 (United Chemical Tech.), and Andisil TL 10 (Anderson & Assoc.) zinc octanoate (PC 040) and tin octanoate [PC 050 (United Chemical Tech.)]
	Methoxy-terminated polysiloxanes	-	Amine catalysts
Two-part RTVs	Vinyl-terminated silicone polymers [Polymer VS 50, 100, 200, and 1,000 (Anderson & Assoc.)]	Polysilicon hydride cross-linkers 100, 101, 120 (Anderson & Assoc.) and 200–1210 (Anderson & Assoc.) with pendant/terminal functionalities. HMS-031, HMS-151, and HMS-301(Gelest).	Platinum-complex catalysts 500, 511, 5112 [0.05–2% Pt (Anderson & Assoc.)], and PC 074 and 075 (United Chemical Tech.)
	Polydimethyl siloxane-terminated silanol [PS 3475, (United Chemical Tech.)]		
Addition-cured silicones	Vinyl-terminated polydimethyl siloxanes DMS-V03–V22, and –V33 (Gelest)	Tri- or tetra- functional polysilicon hydride (10–15 phr)	Platinum-complex catalysts (2–50 ppm), PCO 72, 73, 74, and 75 (United Chemical Tech.)

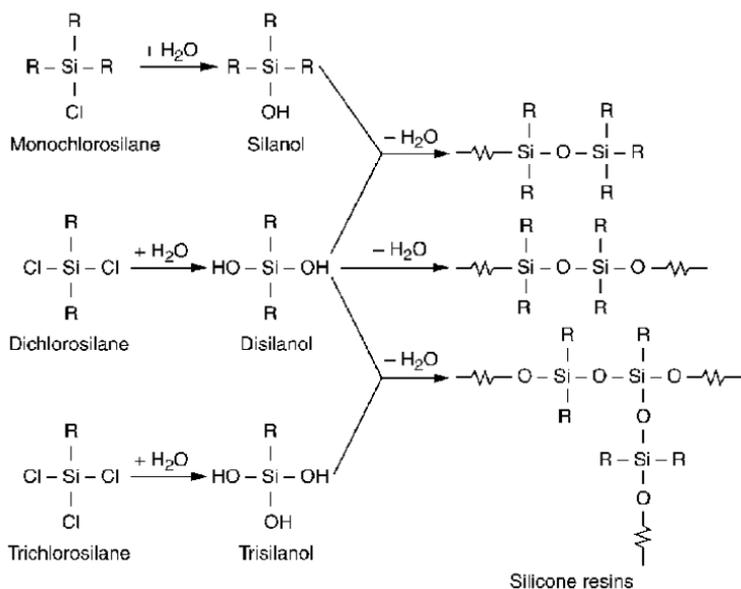


Figure 3.7. Synthesis of RTV silicone resins.<sup>[19]</sup>

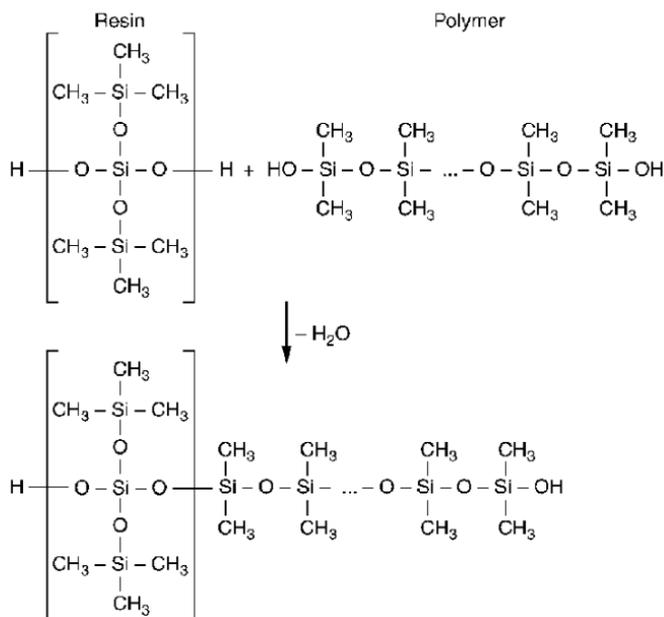
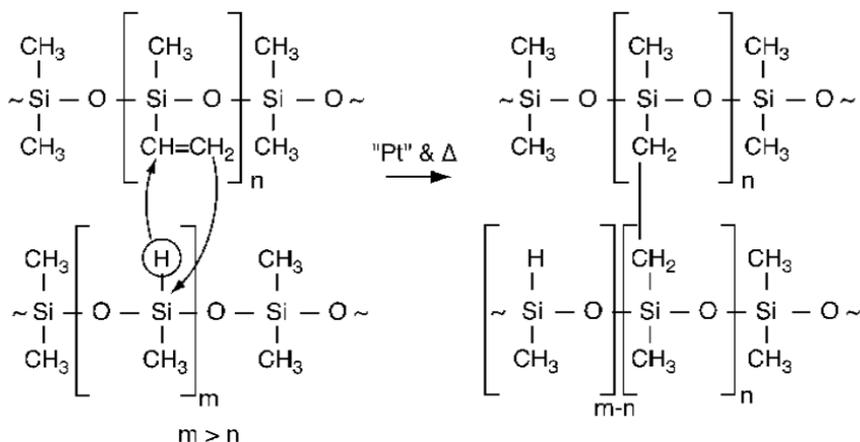


Figure 3.8. Step-growth polymerization mechanism for silicones.



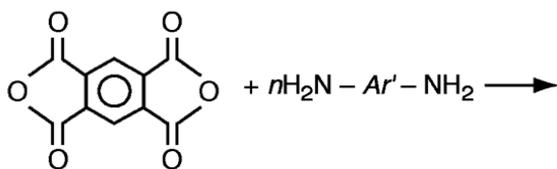
**Figure 3.9.** Addition polymerization of vinyl silicone.

**Moisture-cured silicones.** Many of the silicone adhesives used in electronics are one-part, moisture-curing types, generally cured at room temperature in a range of 30%–80% RH. Full physical and electrical properties are attained in 24–72 hours. Moisture-cured silicones consist of the normal hydroxyl-terminated silicones in which the hydroxyl groups have been blocked, rendering them inactive. On exposure to ambient moisture, the hydroxyl group is regenerated and can again enter into the polymerization reaction. Silicones may be blocked with either acetoxy or alkoxy groups, but the acetoxy types are not recommended for electronics due to the release of acetic acid during the cure with moisture. The alkoxy-blocked silicones are preferred since an alcohol is released that is generally noncorrosive. Moisture-cured silicones are used in many applications including sealing lids and housings, assembling components onto circuit boards, RF gasketing, tacking and sealing around wires, and also for chip-scale spacers and die attachment.

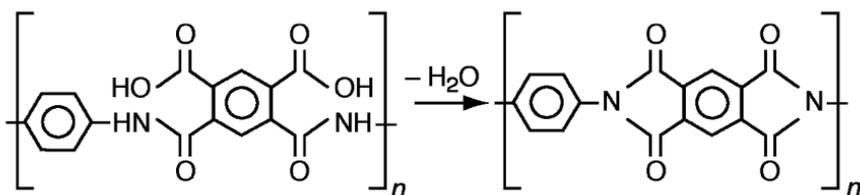
### 3.1.3 Polyimides

Polyimides are formed from polyamic acid or polyamic ester precursors by heating to temperatures as high as 400°C. Polyimide precursors are

synthesized by reacting equimolar amounts of aromatic diamines with aromatic dianhydrides forming polyamic acids or polyamic esters as in Fig. 3.10a. Widely used aromatic amines and aromatic anhydrides are shown in Table 3.5. Of these, the prepolymer from pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA) has been the most widely studied and used.<sup>[21]</sup> The precursors are available as solvent solutions (generally, N-methyl-2-pyrrolidone) that can then be formulated as adhesives, coatings, or preforms by adding fillers and other additives. Curing is not the traditional crosslinking or chain propagation using curing agents, but occurs by heating to eliminate water and close the imide rings along the chain forming the very stable polyimide structure (Fig. 3.10b). The process of ring closure is known as *imidization* and requires step curing, which, for silver-filled paste adhesives, is typically 30 minutes at 150°C, followed by 30 minutes at 275°C.<sup>[22]</sup> In some cases, however, step cures up to 400°C are necessary to achieve complete imidization, an example of which is: 15 minutes at 135°C, followed by 30 minutes at 300°C, and finally 10 minutes at 400°C. The initial temperature exposure of 135°C–150°C assures the removal of the N-methyl-2-pyrrolidone (NMP), a solvent that is present in almost all polyimide precursor formulations.



(a)



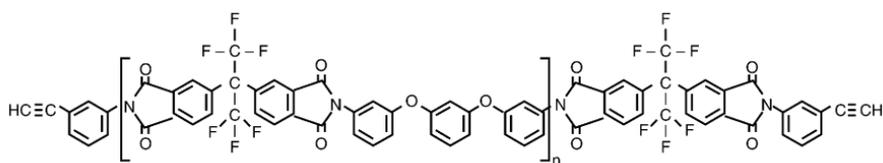
(b)

**Figure 3.10.** (a) preparation of polyimide precursors; (b) curing of polyimides by imidization.

**Table 3.5.** Typical Diamine and Dianhydride Reactants for Polyimides

Diamines	Supplier	Dianhydrides	Supplier
m-Phenylene diamine (PDA)	DuPont	Pyromellitic dianhydride (PMDA)	DuPont, Allco, Chriskev
p-Phenylene diamine (PDA)	BASF Corporation, DuPont	Benzophenone tetracarboxylic dianhydride (BTDA)	Allco, Chriskev, Daicel
4,4'-Oxydianiline (ODA)	Wakayama Seika, Deadsea Bromine	4,4'-Oxydiphthalic anhydride (ODPA)	Shanghai Research Institute (SRI), China
Methylene dianiline (MDA)	BASF Corporation, Wakayama Seika, Kogyo Co.	2,2-Bis (3,4-dicarboxy phenyl) hexafluoropropane dianhydride (6FDA)	Hoechst Celanese
4,4'-Diamino diphenyl sulfone (4,4'-DDS)	Wakayama Seika	3,3',4,4'-Biphenyl tetracarboxylic dianhydride (BPDA)	Chriskev, Mitsubishi, Ube
4,4'-Bisaminophenoxy biphenyl (BAPB)	Wakayama Seika		
4,4'-Diamino-benzanilide (DABA)	Wakayama Seika		
Aminophenoxy benzenes	Wakayama Seika		
3,3'-Diamino benzophenone (DABP)	Spectrum Bulk Chemicals		

A second type of polyimide resin is based on a prepolymer that is completely imidized, but has acetylenic end-groups (triple bonds) which can then cure by addition polymerization (Fig. 3.11). These resins do not require high curing temperatures and do not evolve water during cure as do the polyamic acid prepolymers.<sup>[23]</sup> The *bismaleimides* are yet another variation of polyimides. They are used as adhesives in surface mounting components onto printed-wiring boards and in attaching die in packages or onto interconnect substrates. Bismaleimides are known for their low moisture absorption



**Figure 3.11.** Acetylene-terminated polyimide resin structure.

and hydrophobic properties important in preventing the popcorn effect during solder reflowing (see Ch. 6 on Reliability). Examples of thermally conductive bismaleimide adhesives are boron nitride-filled QMI 536 and 536HT (Loctite®). The OxySim® 502 series (Sumitomo-Bakelite) are examples of electrically conductive bismaleimide adhesives.

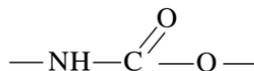
Lastly, resins are commercially available where siloxane structures have been incorporated into the polyimide chains. These *polysiloxaneimides* are noted for their flexibility and low moisture absorption. They are thermoplastics that are processed as hot-melt adhesives.<sup>[24]</sup>

Polyimide adhesives are commercially available as electrically conductive or insulative pastes used for die attachment. They are also available as thermoplastic preforms for chip-on-lead and lead-on-chip attachments.

### 3.1.4 Polyurethanes

Polyurethane adhesives are used primarily in the assembly of printed-wiring boards to attach large components such as capacitors, magnetics, heat sinks, and connectors. Their key benefits include flexibility, absorption of stresses, vibration damping, and thermal transfer. Being thermoplastic, polyurethanes are also easier to rework than epoxies.

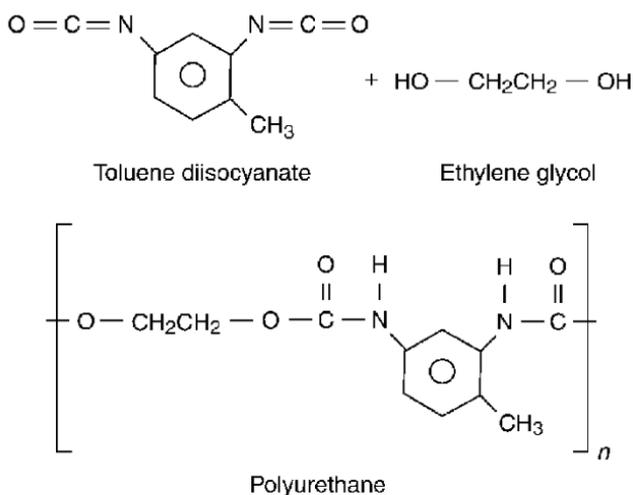
Polyurethanes are distinguished from other polymer types in containing the repeating urethane group throughout its structure:



A typical polyurethane adhesive may contain, in addition to the urethane linkages, aliphatic and aromatic hydrocarbons, esters, ethers, amides, urea, and allophanate groups. Polyurethanes are formed by the addition reaction of diisocyanates or polyisocyanates with polyols (Fig. 3.12) through a

step-growth polymerization mechanism. Polyurethanes may be either thermoplastic or thermoset, depending on the functionality of the monomers. Increasing the functional groups to three or more results in the formation of three-dimensional, highly cross-linked thermoset polymers. The most widely used diisocyanate starting materials are toluene diisocyanate (TDI) consisting of an 80:20 mixture of the 2,4- and 2,6-isomers, methylene-4,4'-di(phenylisocyanate) (MDI), and polymeric MDI (Table 3.6). Also used are 2,2',3- and 4,4',4''-triphenylmethane triisocyanate (TTI). Widely used polyols include castor oil, hydroxyl-terminated polyesters, and polyether polyols. Bayer Chemicals is a major producer of both the isocyanates and polyol starting materials for the production of polyurethane resins. Among Bayer's products are the Mondur<sup>®</sup> series of aromatic diisocyanates, the Desmodur<sup>®</sup> series of aliphatic diisocyanates and polyisocyanates, the Desmophen<sup>®</sup> series of polyester polyols, and the Multranol<sup>®</sup> series of polyetherpolyols.

An example of a polyurethane adhesive used for surface mounting components consists of Mondur M cured with castor oil or with other polyols.<sup>[25]</sup> The molecular weight and properties of polyurethanes are optimized when one equivalent weight of the isocyanate reacts with one equivalent weight of the polyol. The equivalent weights are based on the percent of hydroxide of the polyol and the percent of isocyanate of the polyisocyanate<sup>[26]</sup> as follows:



**Figure 3.12.** A basic polyurethane polymerization reaction.

**Table 3.6.** Polyisocyanate and Polyol Starting Materials for Polyurethanes<sup>[26]–[28]</sup>

Polyisocyanate*	Equivalent Weight	% NCO	Polyol*	Hydroxyl Number	Molecular Weight
Toluene diisocyanate (TDI) Ex. Mondur <sup>®</sup> TD (65/35 mixture of 2,4 & 2,6 isomers), TD 80 (80/20 mixture)	87	48	Desmophen <sup>®</sup> 1600U and 1900U (Bayer)	112, 56	-
			Polyester polyols (Dow, BASF, Huntsman, Arch Chemical, Multranol <sup>®</sup> 9195 and 9190)	28	400
Diol based on TDI (Mondur <sup>®</sup> CD)	143	29.3	Polyether polyols Desmophen <sup>®</sup> 2500, 2501	112,150	759, 1100
Triol based on TDI (Desmodur <sup>®</sup> IL)	525	7.8–8.2	Polytetramethylene ether glycol (PTMEG) 1,000, 2,000, and 3,000	6.2–38.7 (3,000), 54.7–57.5 (2,000), and 106.9–118.1 (1,000)	1,000–3,000 (PTMEG 1,000, 2,000, 3,000)
1,6 Hexamethylene diisocyanate (HDI)	84	49.7	Castor oil and castor oil polyols (OAS Chemicals, Caschem) Caspol 1842, 1962, and 5001 (Caschem)	145, 390, 290	387, 144, 193**
Biuret of HDI (Desmodur <sup>®</sup> N-75, N-100, and N-3200)	255, 191, 181	16.5, 22, 23.2	Acrylic-based polyols		
Trimer of HDI (Desmodur <sup>®</sup> N-3300 and N-3390)	195, 216	21.6, 19.4	Polyamine polyols (Multranol <sup>®</sup> 9144)	150	1,122
TDI and HDI copolymer (Desmodur <sup>®</sup> HL)	400	10–11			

\*Mondur, Desmodur, Desmophen, and Multranol are tradenames and products of Bayer Chemicals.

(cont'd.)

**Table 3.6. (Cont'd.)**

Polyisocyanate*	Equivalent Weight	% NCO	Polyol*	Hydroxyl Number	Molecular Weight
Polymeric isocyanates (Mondur <sup>®</sup> MR, MRS, MRS4, and MRS5)	130–133	31.5–32.5	Polyamine polyols (Multranol <sup>®</sup> 9144)	150	1,122
Mondur <sup>®</sup> TDS (2,4' toluene diisocyanate)	87	48			
Diphenyl methane 4,4', diisocyanate (MDI) Ex. Mondur <sup>®</sup> M, Luprinat M, Isonat 2125M	125	33.4	Polybutadiene polyols R-45 HT LO, and 45M (Sartomer)	47.1, 40.4	2,800, 2,800
Mondur <sup>®</sup> ML (4,4,' and 2,2' mixture)	125	33.4			
Hexamethylene diisocyanate (HDI), Desmodur <sup>®</sup> H	84	49.7			
Dicyclohexamethane 4,4' diisocyanate or bis (4-isocyanate cyclohexyl) methane (Hydrogenated MDI, HMDI ), Desmodur <sup>®</sup> W	132	31.8			
*Mondur, Desmodur, Desmophen, and Multranol are tradenames and products of Bayer Chemicals.					

$$\text{Eq. (3.7)} \quad \text{Equivalent weight (isocyanate)} = \frac{(42 \times 100)}{\% \text{ NCO}}$$

$$\text{Eq. (3.8)} \quad \text{Equivalent weight (polyol)} = \frac{17 \times 100}{\% \text{ hydroxide}}$$

As an example, the amounts of Desmodur N-100 required to react with 300 grams of Desmophen R-221-75 polyol can be calculated (assuming a 1:1 ratio). Desmodur N-100 has a 22% isocyanate content and Desmophen R-221-75 has a 3.3% hydroxide content. Thus, the equivalent weights are:

$$\text{Eq. (3.9)} \quad \text{Equivalent weight of N-100} = \frac{42 \times 100}{22} = 191$$

$$\text{Eq. (3.10)} \quad \text{Equivalent weight of R-221-75} = \frac{17 \times 100}{3.3} = 515$$

The number of equivalents of the polyol is 0.58, so the amount of the isocyanate required to react in a 1:1 ratio will be 111 grams.<sup>[26]</sup> The more flexible polyurethanes used in printed-wiring board applications generally employ polyols that have lower hydroxyl contents.

**Moisture-curing polyurethanes.** Urethane polymer resins that still contain unreacted isocyanate groups react with atmospheric moisture and continue curing. The reaction is a two-step process. First, water reacts with some of the free isocyanate groups producing an amine and releasing carbon dioxide as a by-product; then, the amine further reacts with the remaining isocyanate groups forming urea linkages and fully cured polyurethane ureas. Moisture-curing polyurethanes can penetrate into pores and tight spaces where moisture is usually present to form strong chemical bonds.

Moisture-curing polyurethanes can be formulated to produce a wide range of physical properties, from elastomeric and flexible to hard and rigid materials. Among some noteworthy properties are high abrasion resistance and high impact resistance.

### 3.1.5 Cyanate Esters

Cyanate-ester adhesives are formed from resins that contain cyanate groups



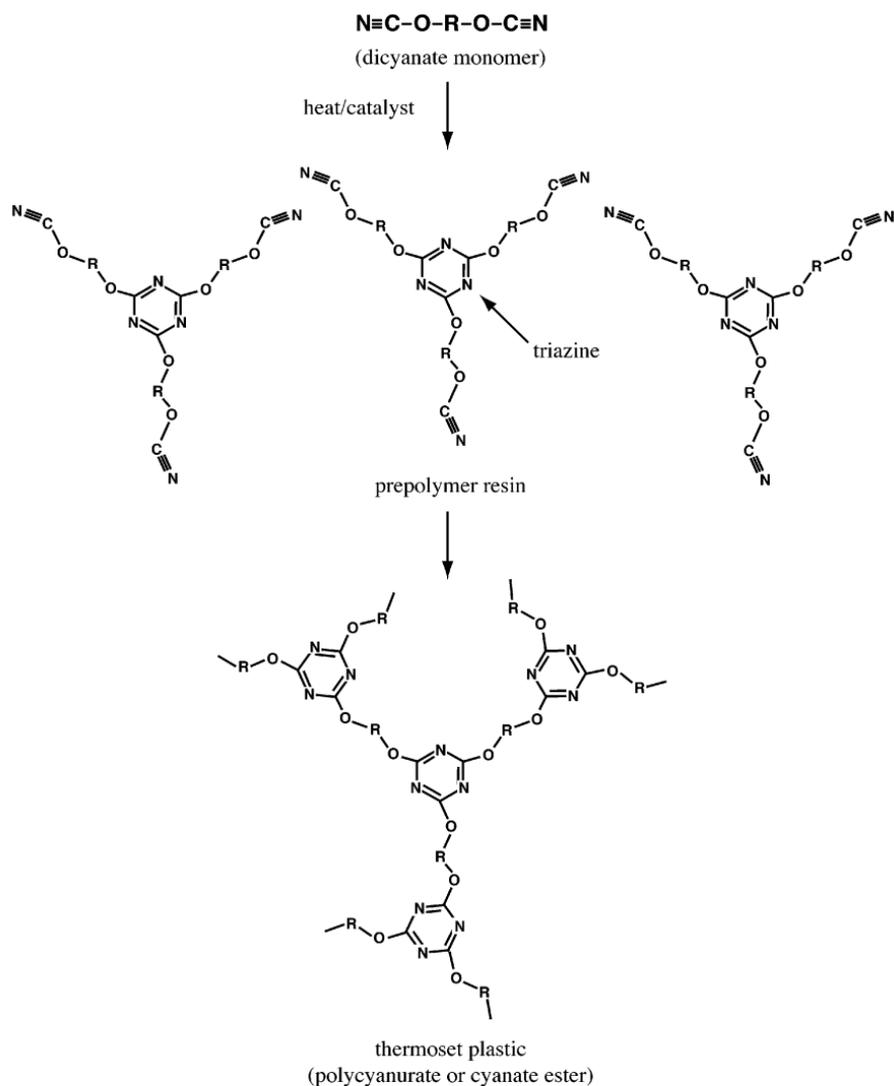
which on heating, and in the presence of a catalyst, polymerize to form highly aromatic triazine ring structures.<sup>[29]–[31]</sup> Monomers that contain two or more cyanate groups polymerize to form a highly cross-linked triazine network, a process called *cyclotrimerization* (Fig. 3.13).<sup>[32][33]</sup> Examples of some commercially available cyanate monomers include the dicyanate of bisphenol-A (Ciba Geigy's AroCy B-10<sup>®</sup>), the polycyanate of phenolformaldehyde (Allied Signal's Primaset<sup>®</sup>), the dicyanate of hexafluorobisphenol-A (Ciba Geigy's AroCy F<sup>®</sup>), and a number of other dicyanates of substituted bisphenols.<sup>[34]</sup>

Catalysts may be the soluble salts or complexes of transition metals, for example, those of tin, copper, iron, or cobalt, or compounds that have an active hydrogen atom such as mercaptans, phenols, or amines.

The triazine structures, like the imide structures of the polyimides, impart high thermal stability to the cured adhesive. Some silver-filled cyanate-ester adhesives have glass-transition temperatures as high as 245°C and can withstand temperatures of 200°C or more. However, to achieve these properties, cure temperatures of 175°C for 1–2 hours followed by a postcure above 200°C are required, making them more suitable for attaching single die in metallurgically-sealed ceramic packages than for attaching die on plastic laminates or in hybrid or multichip modules. Examples of commercially available cyanate-ester adhesives are Ablestik's Ablebond<sup>®</sup>-JM-7000 and Loctite's QMI-301.

### 3.1.6 Modified Cyclo-Olefin Thermosets (MCOT)

Modified cyclo-olefin thermoset (MCOT) resins are liquids that cure when heated at 150°C for a minimum of 30 minutes to form the general polymer structure shown in Fig. 3.14. The monomers cure by an addition polymerization and, as such, no water or other by-products are evolved. The molecular structures are essentially nonpolar which impart very low moisture absorption properties. For two formulations developed by Johnson-Matthey, water absorptions of 0.05% were recorded when exposed to 85°C/85% RH conditions for 168 hours. Only 0.1% water absorption was



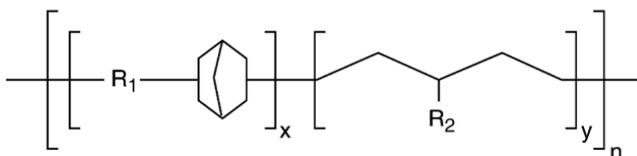
**Figure 3.13.** Cyanate-ester polymerization.

measured even after pressure cooker testing at 150°C, 85% RH, for 168 hours.<sup>[35]</sup> These low moisture absorption values make MCOT adhesives and molding compounds particularly suitable for assemblies that must subsequently be solder reflowed where the popcorn reliability problem arises (see Ch. 6). Plastic materials having water retentions of greater than 0.1% undergo rapid evaporation of the water at the 230°C–250°C solder conditions inducing stresses in the adhesive and adhesive interfaces resulting in delamination and cracking. MCOT adhesives are block copolymers.<sup>[36][37]</sup> The cyclic olefin block is a rigid segment while the linear olefin is a soft (flexible) block. In Fig. 3.14, R<sub>1</sub> and R<sub>2</sub> comprise the nonpolar and polar portions, respectively, that control the amount of moisture absorption. The optimized value for R<sub>1</sub> is 18% and for R<sub>2</sub>, 36%. A molecular weight of 3,262 is reported to provide the best combination of adhesion, moisture resistance, and viscosity properties.<sup>[38]</sup>

### 3.1.7 Acrylics and Acrylates

Acrylic adhesives were developed in the late 1960s in Germany as an outgrowth of poly(methylmethacrylate) chemistry. Because of their low cost and rapid processing, the largest market for acrylic polymers is in commercial/industrial applications such as the bonding of wood, steel, and plastics. However, some unique properties, such as their ability to be cured with UV/visible light, their transparency, and rapid low-temperature cures, are finding a niche in optoelectronics and medical applications.

**Basic acrylate chemistry.** The basic acrylic monomers or oligomers contain unsaturated double bonds (vinyl groups), and consequently cure by addition polymerization involving a free-radical reaction. Free-radical-producing compounds such as peroxides, peracetic acids, and sulfones are added to acrylic resins to initiate polymerization. Free-radical polymerization of acrylics may also be induced by exposure to UV or visible light. These UV-curing adhesives, most of which are based on acrylic or modified acrylic



**Figure 3.14.** Modified cyclo-olefin thermoset (MCOT) polymer structure.

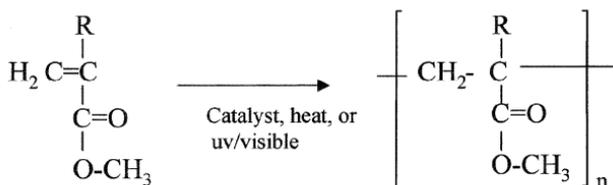
resins, are of increasing commercial importance today for the rapid bonding of electronic devices, fiber optics, and liquid crystal flat-panel displays. A key feature of acrylics is their transparency and refractive index making them useful for the bonding of optical parts.

Reactive methacrylate monomers include methylmethacrylate, diethyleneglycol dimethacrylate, and butyl methacrylate. The polymerization reaction for the basic monomer is depicted in Fig. 3.15.

**Cyanoacrylates.** Cyanoacrylates are one-part, highly polar thermoplastic polymers. The resin monomers cure in seconds when in contact with a weak base such as the moisture that is present on most surfaces. Many cyanoacrylate-adhesive formulations are commercially available, but not widely used in electronics assembly because of their poor resistance to solvents and moisture at elevated temperatures ( $>70^{\circ}\text{C}$ ). Cyanoacrylates have relatively low impact and peel strengths and may be brittle unless toughened by the addition of elastomeric resins.

### 3.1.8 Silver-Glass Adhesives

Although silver-glass adhesives are, strictly speaking, not polymer adhesives, a polymer binder is used in the paste to provide ease of dispensing, but is subsequently burned out during processing. Silver-glass adhesives contain 80%–85% by weight of silver-flake filler dispersed in a lead borate glass, a polymer binder, and an organic solvent. After automated dispensing or screen-printing onto a substrate and attaching the die, the adhesive is fired in an oven or furnace. The processing is similar to that for thick-film conductor pastes. The solvent is first evaporated at low temperatures of  $50^{\circ}\text{C}$ – $200^{\circ}\text{C}$ , followed by burning out the organic binder at  $300^{\circ}\text{C}$ ; at approximately  $340^{\circ}\text{C}$  the glass begins to soften and sintering of the silver and glass begins to occur. Completion of the sintering and bonding to the substrate occurs during the last step of 10 minutes at  $410^{\circ}\text{C}$ – $430^{\circ}\text{C}$ .<sup>[39]</sup> Of



Where R may be methyl, butyl, octyl, or other aliphatic group

**Figure 3.15.** Basic acrylic polymerization reaction.

course, at these high temperatures, silver-glass adhesives can only be used on ceramic or silicon substrates or packages.

## 3.2 FORMULATION

Besides the resin and hardener portions, adhesives are formulated with a number of additives to enhance or modify their basic properties. Fillers are extensively used to improve flow properties, reduce thermal expansion, reduce shrinkage during cure, increase thermal conductivity, or impart electrical conductivity. Reactive diluents are used to reduce viscosity and avoid the use of volatile organic solvents. Elastomeric polymers may be added to impart toughness and flexibility. Catalysts and accelerators in small amounts may also be used to initiate sluggish polymerizations. Hundreds of formulations from dozens of suppliers are available and literally tens of thousands are possible. Many of the commercially available formulations are based on the same or similar resins and hardeners, yet differ in the amount of ingredients used, the number and types of additives, and the techniques used in processing, giving rise to proprietary formulations that have unique or application-specific properties. In fact, the number and nature of the additives and the manner in which they are processed is as much an art as a science and constitutes the most proprietary aspect of a supplier's formulation.

### 3.2.1 Fillers

The most important additive in an adhesive formulation is the filler. Fillers such as metal particles are used to render adhesives both electrically and thermally conductive while electrically insulative fillers such as metal oxides are used to provide thermal conductivity alone. Regardless of whether they are electrically conductive or not, fillers provide numerous simultaneous benefits, including the following:

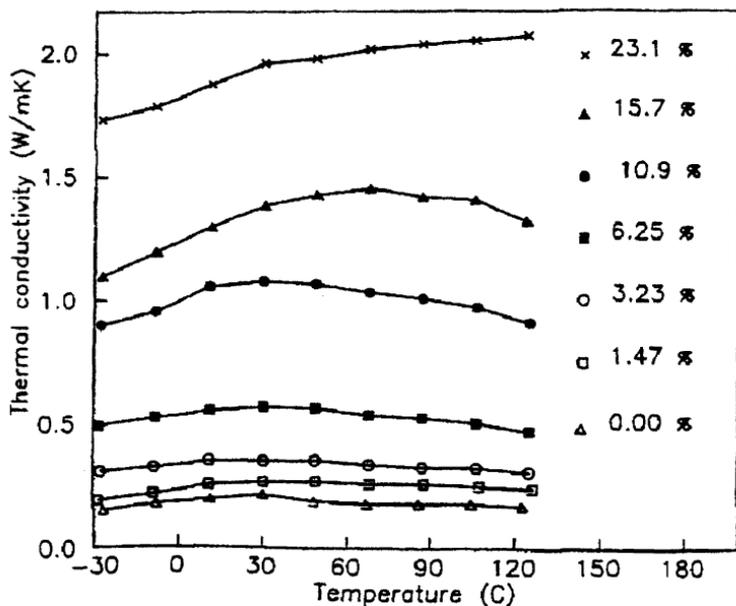
- Increased thermal and electrical conductivity
- Increased thermal stability
- Reduced CTE
- Reduced shrinkage and stresses during cure
- Improved bond strengths

- Improved flow properties
- Extended pot life

**Electrical and thermal conductivity.** To meet requirements for electrical and thermal conduction, polymer resins must be highly filled with metal particles. Silver is the most widely used filler because of its high electrical conductivity and retention of conductivity on exposure to air, heat, and humidity. Although a surface oxide is formed, silver oxide, unlike the oxides of other metals, is still electrically conductive. Copper, although also highly electrically conductive, forms an oxide that is electrically resistive so that inhibitors or plating with silver or gold must be used to stabilize its properties. Gold, nickel, and carbon are also used to a lesser extent either because of high cost, in the case of gold, or poorer electrical conductivities in the case of nickel and carbon. Gold and silver-palladium fillers are used in adhesives where silver migration may be of concern. Plated particles are widely used as fillers for anisotropic adhesives. Silver, nickel, or gold plated nonconductive core particles such as glass or plastic spheres are widely used in anisotropic film and paste formulations.

Resins can be filled to a maximum of approximately 85%–90% by weight (40%–50% by volume, depending on resin density) after which their viscosity increases to an extent that the material cannot easily be dispensed. The effect of increasing levels of silver filler and temperature on the thermal conductivity of an epoxy adhesive can be seen in Fig. 3.16.<sup>[40]</sup> To achieve high thermal conductivity and still preserve good electrical insulation properties, resins must be filled with ceramic or inorganic fillers such as alumina, silica, beryllia, aluminum nitride, boron nitride, and even diamond. Examples of some fillers used in adhesive formulations and their properties are given in Table 3.7.<sup>[41]–[47]</sup>

The processing and surface preparation of silver particles is critical to their performance as a filler. The first step in manufacturing silver flakes is to produce silver powder. Powdered silver may be produced by chemical precipitation, electrolytic precipitation, or melt atomization. Most commercially available silver powders are precipitated by reducing silver from a silver nitrate solution. Particle sizes of powdered silver range from submicron to 5  $\mu\text{m}$ .<sup>[48]</sup> Silver powders are selected based on size and morphology then milled by conventional means or, more often, in Attritor<sup>®</sup> grinding mills<sup>[50]</sup> to yield flakes of the desired size. Ball milling the powders produces a mixture of approximately 80% flat flakes, 5–10  $\mu\text{m}$  in size, and irregularly shaped particles, 1–5  $\mu\text{m}$  size.<sup>[48][51]–[53]</sup> Most silver powder feedstocks are



**Figure 3.16.** Effect of increasing amounts of silver filler and of temperature on the thermal conductivity of an epoxy adhesive. The concentrations are by volume (23% by volume corresponds to 80% by weight).<sup>[40]</sup>

**Table 3.7.** Electrical and Thermal Properties of Fillers and Filled Adhesives<sup>[41]-[47]</sup>

Material	Specific Gravity (gm/cm <sup>3</sup> )	Volume Resistivity (ohm-cm)	Thermal Conductivity (W/m·K)
Silver	10.5	$1.6 \times 10^{-6}$	429
Silver palladium	-	$2.3 \times 10^{-6}$	150
Copper	8.9	$1.8 \times 10^{-6}$	401
Gold	19.3	$2.3 \times 10^{-6}$	318
Aluminum	2.7	$2.9 \times 10^{-6}$	237
Nickel	8.9	$10 \times 10^{-6}$	91
Platinum	21.5	$21.5 \times 10^{-6}$	72

(cont'd.)

**Table 3.7.** (Cont'd.)

Material	Specific Gravity (gm/cm <sup>3</sup> )	Volume Resistivity (ohm-cm)	Thermal Conductivity (W/m·K)
Tin/Lead solder (60/40)	-	$20-30 \times 10^{-6}$	53
Tin/Lead solder (40/60)	-	$20-30 \times 10^{-6}$	42
Carbon	-	$3 \times 10^{-3}$	-
Aluminum oxide	3.45	$1 \times 10^{14}$	17–40*
Fused silica	2.2	$1 \times 10^{14}$	1.4
Aluminum nitride	3.26	$10^{14}$	170–260*
Boron nitride	2.25	$1 \times 10^{15}$	130–260*
Diamond	3.51	$1 \times 10^{13}$	800–2,000*
Unfilled epoxy adhesives	1.1	$10^{14}$ to $10^{15}$	0.2–0.3
Typical silver-filled epoxies	-	$1 \times 10^{-4}$	2.4–8
Gold-filled epoxies	5.2	$8 \times 10^{-4}$	2–3
Silver-palladium filled epoxies	2.1	$4 \times 10^{-3}$	1.3–2.0
Silver glass	-	$\leq 1.5 \times 10^{-5}$	80–90
Oxide filled epoxy adhesives	1.5–2.5	$10^{14}$ to $10^{15}$	1–2
Boron-nitride-filled epoxy adhesives	-	$10^{14}$ to $10^{15}$	3–4
Diamond-filled adhesives	-	$10^{14}$ to $10^{15}$	10–12
Silver-filled polyimide	-	$3 \times 10^{-4}$	2
Boron nitride-filled bismaleimide	1.25	$>10^{15}$	0.9
Boron nitride and silica filled modified cyclo-olefin thermoset	-	-	~1.0
Unfilled silicone	1.08	$2.9 \times 10^{13}$	0.19
Silicone rubber adhesive (thermally conductive)	2.1	$1.6 \times 10^{13}$	0.88
*Depending on purity level. Values are for comparative purposes only since values for specific compositions, processing conditions, and temperatures will vary.			

in the 0.5 to 8  $\mu\text{m}$  range and typically produce silver flakes of 1 to 10  $\mu\text{m}$ . In practice, a broad distribution of particle sizes is better than a narrow distribution in optimizing electrical conductance. Bimodal distribution also appears to enhance conduction.<sup>[54][55]</sup> Besides particle-size distributions, surface area, tap density, and percent weight loss when heated in air or in a nitrogen/hydrogen atmosphere characterize fillers. The weight loss at 110°C is a measure of the amount of water and solvents retained by the filler, while the weight loss at 538°C is a measure of the amount of lubricant used in coating the particles. Both tests are used for quality control. Table 3.8 lists some silver fillers used in epoxy formulations. The morphology of the silver flakes is influenced by numerous processing conditions including the following:

- Length of milling time
- Type and size of the milling media (for example, 3/16 in. steel balls or 6 mm glass balls)
- Rotational speed of the milling machine
- Ratio of silver-to-media
- Type of lubricant used
- Amount of solvent

Lubricants and solvents are added to the filler during milling to prevent agglomerates from forming due to cold welding of the malleable filler particles.<sup>[48]</sup> Lubricants are fatty acids or salts of fatty acids such as stearic or oleic acids in ethanol solvent.<sup>[49]</sup> The lubricant coats the silver particles during the milling process and is retained during subsequent processing because it becomes chemisorbed on the particle surfaces. Untreated particles appear as aggregates of submicron particles, typically 100  $\mu\text{m}$  in size, presumably due to the high surface tension of the untreated metal.<sup>[51]</sup> Lubricant properties necessary in processing silver filler are as follows:

- Providing lubricity to avoid agglomeration of particles.
- Allowing adequate wetting of the filler.
- Being compatible with the polymer resin and not affect its shelf life or other properties.
- Preventing degradation of the electrical or thermal conductivity of the filler or the filled cured adhesive.

The type of lubricant used may have a major effect on the volume resistivity of a cured epoxy. In one example, a conductive epoxy formulated with silver

**Table 3.8.** Silver Fillers Used in Epoxy Adhesives<sup>[56]–[59]</sup>

Product/Supplier	Description	Tap Density (gm/cm <sup>3</sup> )	Surface Area (m <sup>2</sup> /gm)	Weight Loss (%)		Particle Size Distribution (μm)		
				110°C (1 hr in air)	538°C (1/2 hr in air or H <sub>2</sub> )	90% less than	50% less than	10% less than
Silver Flake #95/Ferro, Degussa	High-purity silver flake	3.2–5.0	0.80–1.30	≤0.10	≤0.50	20.0	10.0	5.0
Silver Flake #84/ Ferro, Degussa	High-purity silver flake; low viscosity and non-ionic lubricant	4.5–5.6	0.15–0.30	≤0.10	≤0.50	20.0	10.0	5.0
Silver Flake #80/ Ferro, Degussa	High-purity silver flake; handling characteristics of flake and powder	3.2–5.0	0.40–0.70	≤0.10	≤0.50	–*	–*	–*
Silver Flake #65/ Ferro, Degussa	Fine silver flake with high-surface area	3.0–4.5	0.80–1.40	≤0.10	≤0.70	30.0	11.0	3.0
Silver Flake #40/ Ferro, Degussa	General purpose, coarse silver flake	1.7–3.4	0.40–1.00	≤0.10	≤0.80	50.0	25.0	8.0
Silver Flake #26LV/ Ferro, Degussa	Low-viscosity applications	4.0–5.8	0.80–0.30	≤0.10	≤0.80	–	–	–
Silver Flake #98/ Ferro, Degussa	High-purity silver flake	3.2–5.0	0.80–1.50	≤0.10	≤0.50	20.0	10.0	5.0

(Cont'd.)

**Table 3.8. (Cont'd.)**

Product/Supplier	Description	Tap Density (gm/cm <sup>3</sup> )	Surface Area (m <sup>2</sup> /gm)	Weight Loss (%)		Particle Size Distribution (µm)		
				110°C (1 hr in air)	538°C (1/2 hr in air or H <sub>2</sub> )	90% less than	50% less than	10% less than
Silflake 135/ Technic Inc.	Dispensable die-attach	4.7–6.2	0.30–0.55	≤0.10	≤0.70	10.4	6.8	5.5
Silflake 282/ Technic Inc.	Adhesives, inks	2.5–4.0	0.60–1.00	≤0.10	≤0.70	3.9	1.9	0.3
Silflake 499/ Technic Inc.	Dispensable die-attach	4.0–5.6	0.30–0.70	≤0.10	≤0.70	–	–	–
SF-110/HRP	Conductive adhesives	2.0–3.2	0.80–1.40	≤0.20	≤0.80	6.0–13.0	2.0–5.0	0.7–1.8
SF-160/HRP		0.5–1.5	0.75–1.5	≤0.20	≤0.80	6.0–12.0	1.5–4.0	0.6–1.5
SF-165/HRP		0.7–1.3	0.75–1.3	≤0.20	≤0.50	7.0–13.0	1.7–3.5	0.6–1.3
Chemet EA-0030/ Metalor Technologies, Advanced Materials Division	High-speed dispensing semiconductor attach	3.7–4.9	0.60–0.95	≤0.15	≤0.75	11	3	0.5
Chemet EA-0295/ Metalor Technologies, Advanced Materials Division		3.5–4.8	0.50–0.70	≤0.05	≤0.55	12	5	1

(cont'd.)

**Table 3.8. (Cont'd.)**

Product/ Supplier	Description	Tap Density (gm/cm <sup>3</sup> )	Surface Area (m <sup>2</sup> /gm)	Weight Loss (%)		Particle Size Distribution (µm)		
				110° C (1 hr in air)	538° C (1/2 hr in air or H <sub>2</sub> )	90% less than	50% less than	10% less than
Chemet SA-0201/ Metalor Technologies, Advanced Materials Division	High thixotropic die attach, fine particle, low viscosity	3.8–5.1	0.50–0.90	≤0.10	≤0.85	7	2	1
Chemet AA-9829/ Metalor Technologies, Advanced Materials Division	High purity, low- surface area, low viscosity	4.9–5.6	0.12–0.24	≤0.10	≤0.20	23.7	11.3	4.8
Chemet RA-0101/ Metalor Technologies, Advanced Materials Division	Silicone adhesives	4.0–5.0	0.10–0.30	≤0.10	≤0.30	21	9	3
Chemet AA-0909/ Metalor Technologies, Advanced Materials Division	General purpose silver flake	2.8–4.0	0.90–1.20	≤.10	≤0.30	21	9	3
*Not available.								

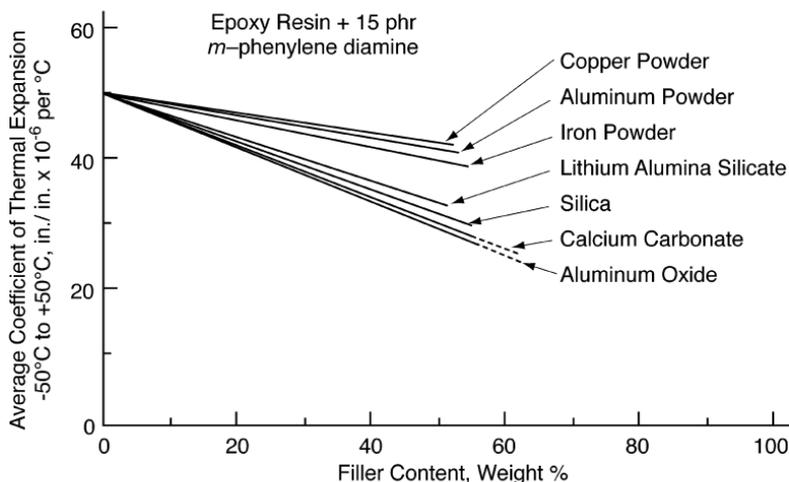
flakes using a thiol lubricant in a proprietary solvent showed consistently higher volume resistivity (4–5 orders of magnitude) than a similar composition where the silver flakes were coated with a fatty acid lubricant.<sup>[60]</sup>

**Increased thermal stability.** Weight loss is reduced by the high-temperature stabilities of the inorganic or metallic fillers compared to the resin. Thus, the more filler formulated into an adhesive, the lower the weight loss at elevated temperatures. This is due, not only to the reduced weight of resin by adding filler, but also to reduced shrinkage and increased conductivity that result from the filler.<sup>[61]</sup>

**Reduced coefficients of expansion.** Expansion coefficients are reduced by adding fillers that have a lower coefficient of thermal expansion (CTE) than the organic resin. In effect, the concentration of the higher-CTE organic phase is lowered by the presence of filler.<sup>[62]</sup> This effect is illustrated by the rule of mixtures used to predict the CTE of an adhesive ( $\alpha_{\text{adhs}}$ ) which is:

$$\text{Eq. (3.11)} \quad \alpha_{\text{adhs}} = \alpha_{\text{resin}} \times \text{vol. \%}_{\text{resin}} + \alpha_{\text{filler}} \times \text{vol. \%}_{\text{filler}}$$

By lowering the volume percent of resin and increasing the volume percent of the filler, the composite CTE is reduced. This is best illustrated in Fig. 3.17,<sup>[61]</sup> where an epoxy resin formulated with 15 phr of *m*-phenylenediamine has a CTE of 50 ppm/°C without filler. The addition of about 60% by weight of alumina, for example, lowered the CTE to about 25 ppm/°C.



**Figure 3.17.** Effect of filler content on the expansion coefficient of an epoxy resin.<sup>[61]</sup>

**Reduced shrinkage.** Fillers have a pronounced effect on reducing shrinkage during cure. Early data reported by Lee and Neville,<sup>[2]</sup> although for casting resins, are also applicable to adhesives. Unfilled epoxies may shrink 1% to 8% by volume, but adding 20% filler can reduce this shrinkage to below 1%. The 7.17% shrinkage of an unfilled DGEBA resin cured with 12 phr of diethanolamine was reduced to 4.85% when filled with 100 phr of mica. In another example, an unfilled DGEBA resin cured with a primary amine had a shrinkage of 0.91%, but was reduced to 0.67% when filled with 20% of quartz and to 0.77% when filled with 20% silica.<sup>[63]</sup>

Another measure of shrinkage is linear shrinkage. An unfilled epoxy has a linear shrinkage of  $3.5 \times 10^{-3}$  in/in that decreases to below  $2.0 \times 10^{-3}$  in/in when 60% by weight of filler is added.<sup>[61]</sup>

**Improved bond strengths.** The tensile-shear strength of an epoxy adhesive can increase from 1,000 psi (unfilled) to 3,500 psi with approximately 50 phr alumina filler.<sup>[2]</sup> The improvement in shear strength was also shown by Wiles.<sup>[64]</sup> An epoxy formulation with no filler had a shear strength of 2,760 psi at 25°C and 450 psi at 105°C. By adding 100 phr of alumina filler, these strengths increased to 3,750 psi at 25°C and to 1,650 psi at 105°C.

Another example of the effect of fillers on improving bond strength is reported for a silicone RTV-1 sealant formulated with Cabot Corporation's Cab-O-Sil® LM-130 and TS-720 materials. Cab-O-Sil fumed silicas are very effective reinforcing agents due to the very-large surface area available for polymer/filler interactions. The very low, 45 psi, tensile strength of the unfilled silicone increased to 210 psi with 14 phr of LM-130 fumed silica and to 150 psi with the same level of TS-720 fumed silica.<sup>[65]</sup>

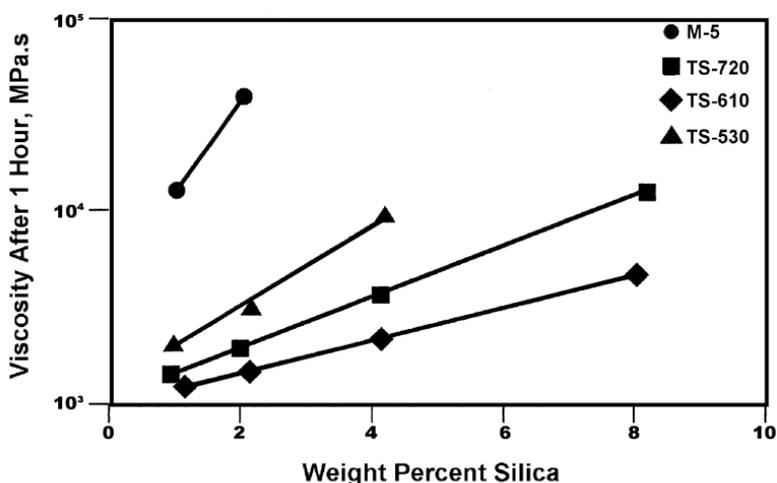
**Improved flow properties.** The flow properties of an adhesive are largely controlled by its inherent viscosity and by the alteration of its viscosity through the addition of diluents and fillers. Flow properties are important for screen-printing, automatic dispensing, and capillary flow, and can be tailored by the type of filler, amount of filler, and the particle-size distribution. Thixotropic properties are important in depositing adhesives in precise thicknesses and geometries without excessive flow-out. Thixotropic fillers prevent slumping of the adhesive until it is fully cured. This is especially important when the adhesive is applied in a vertical position such as a fillet on a component. Cab-O-Sil, a colloidal (fumed) form of silica, is often added to a formulation in concentrations of 1%–2% to provide thixotropy, rendering it easy to screen-print or dispense automatically. Cab-O-Sil enhances the formulation properties as follows:

- Improves flow control, including thixotropy.
- Minimizes or eliminates settling during storage.
- Allows extrusion control during dispensing.
- Prevents sag or slump during cure.

Surface treatments for Cab-O-Sil also influence the viscosity and thixotropic properties of an adhesive as shown in Fig. 3.18 where MS-5 is untreated Cab-O-Sil, TS-720 is treated with polydimethylsiloxane, and TS-610 and TS-530 are treated with dimethyldichlorosilanes. The silica filler treated with polydimethylsiloxane (TS-720) produces greater van der Waals forces of attraction and thus higher viscosity compared to TS-610 and TS-530.<sup>[65]</sup>

The surface area of the filler has a pronounced effect on viscosity. As the surface area of silver-flake filler increases, the frictional forces between particles increase resulting in higher viscosity. Epoxy formulations filled with constant-size silver flakes of various surfaces areas show this effect when viscosity is plotted as a function of the filler surface areas (Fig. 3.19).<sup>[49][66]</sup>

**Extended pot life.** In general, pot life is increased through formulation with fillers. Fillers lower the exotherm occurring during curing by controlling the concentration of reactants in a given mass. The exotherm heat is dissipated over the sample size, especially in the case of fillers having high thermal conductivities.<sup>[62]</sup>



**Figure 3.18.** Viscosity increase with increasing Cab-O-Sil<sup>®</sup> filler and effects of surface treatments.<sup>[65]</sup>

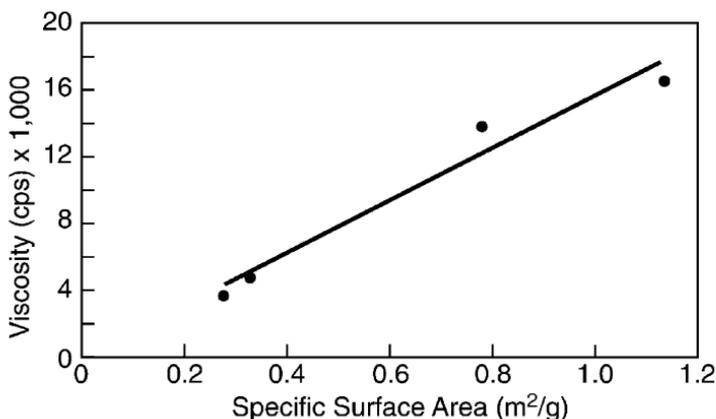
### 3.2.2 Rubber-Toughened Formulations

Adding small amounts of reactive flexibilizers to an epoxy resin can reduce the modulus of elasticity, glass-transition temperature ( $T_g$ ), and CTE of an otherwise hard and brittle material. Rubber-like materials such as a carboxyl-terminated acrylonitrile-butadiene copolymer (Fig. 3.20) are used in epoxy formulations to reduce stresses and prevent cracking. The carboxyl group reacts with the epoxy resin to produce an epoxy-terminated rubbery polymer. Small amounts of liquid rubber domains become interspersed within the epoxy matrix and mitigate crack propagation.<sup>[67]</sup> Masterbond® 10HT, an example of a rubber-toughened, stress-absorbing epoxy, was qualified by Boeing for bonding ceramic components to printed-wiring boards.<sup>[68][69]</sup>

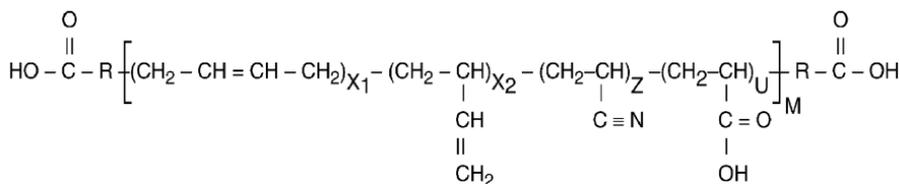
Polyamides containing amino groups are also excellent flexibilizers for epoxies since they co-react with the epoxy resin and introduce their inherent thermoplastic properties.

A second approach to reducing modulus and flexibilizing an adhesive is to add a plasticizer to the formulation. Since most plasticizers are of relatively low-molecular weight and do not co-react with the resin, there is a risk of separation, leaching, or outgassing during thermal or thermal-vacuum environments.

In general, flexibilizers improve the low-temperature bond strengths at  $-50^\circ\text{C}$  or lower by reducing stresses, but often at the expense of reducing high-temperature strengths.



**Figure 3.19.** Viscosity as a function of surface area (fixed flake size).<sup>[48][49]</sup>



**Figure 3.20.** Acrylonitrile-butadiene copolymer.

### 3.2.3 Diluents

Diluents are low-molecular-weight, low-viscosity compounds that are used to reduce the viscosity or enhance the solubility of a resin and/or hardener. Diluents may be either reactive or non-reactive, but the reactive types are more desirable since they combine chemically with the main resin during cure and are not free to outgas or leach, especially during thermal-vacuum exposure. Epoxy diluents, for example, are formulated together with epoxy resins to reduce the viscosity and still remain 100% solids. Normally, solvents would be used to reduce viscosity, but most organic solvents are now being disallowed because of their high volatile emissions. Some long-chain aliphatic reactive diluents can also improve the flexural strength of epoxy adhesives.

Examples of reactive diluents for epoxy resins include: phenyl glycidyl ether, butylglycidyl ether, allylglycidyl ether, and glycerol-based epoxy resins. Diluents should be used sparingly in amounts of 5–15 phr, enough to reduce the viscosity of the adhesive, yet not degrade the properties of the cured material.

### 3.2.4 Formulation Processes

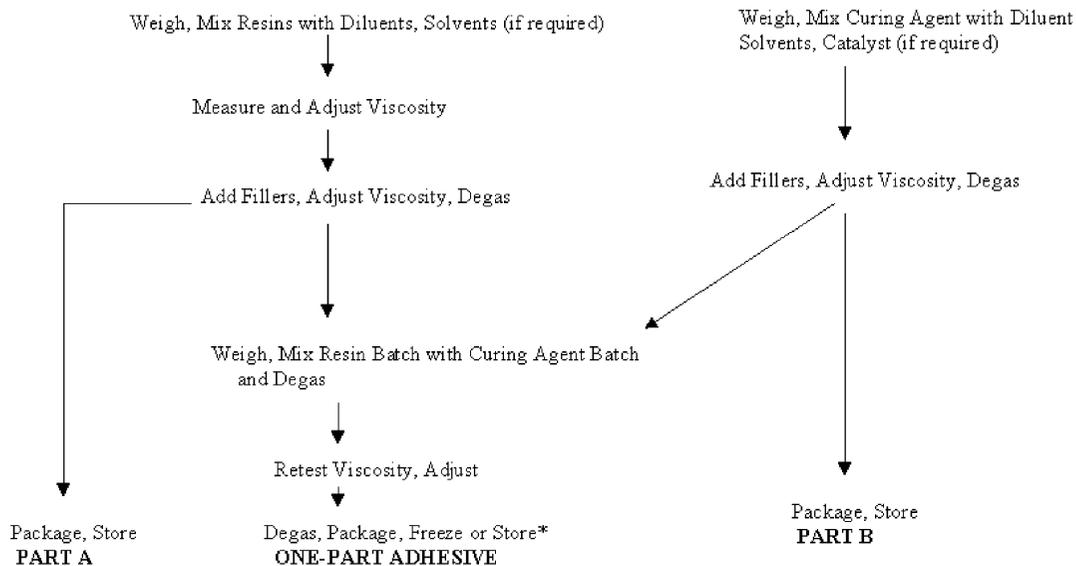
**Paste adhesives.** Paste adhesive formulations are produced by mixing the base resin with low-molecular weight diluents or solvents, if necessary, to reduce viscosity. Other prepolymer resins may be added and agitated until dissolved. Viscosity and temperature are continuously monitored and more diluents or resin added as required. Finally, one or more types of fillers are added and mixed and the viscosity of the mixture is adjusted. In incorporating the filler into the resin, best results are obtained when the filler is preheated

to drive off moisture and adsorbed gases. Thorough mixing in a three-roll mill minimizes the occlusion of air during mixing. The final mixture is usually filtered and degassed prior to being packaged as Part A of a two-part system. Frequently, the resin batch is filtered through a nylon mesh. Where the curing agent provides a long pot life or shelf life, or where the curing agent is of the latent type, it may be mixed with the Part A resin, degassed, packaged, and stored either at room temperature or at  $-40^{\circ}\text{C}$ , depending on the reactivity of the mixture. In the case of one-part frozen adhesives, the resin and hardener components are rapidly mixed, degassed, inserted in syringes, and quick frozen (Fig. 3.21).

The hardener portion (Part B) may also be mixed with fillers, diluents, solvents, and other additives. Fillers may be mixed in the resin portion alone or partly in the resin and partly in the hardener portion. Adhesion promoters such as Dow Corning A-180 silane may also be added to enhance the adhesion of the filler particles to the resin or hardener. Examples include several electrically conductive epoxy formulations that were used to evaluate their electrical stability on non-noble metal surfaces.<sup>[53]</sup> The base epoxy resin was the diglycidylether of bisphenol-F (DGEBF, equivalent wt. = 170 g). Methylhexahydrophthalic anhydride, hexahydrophthalic anhydride, and 4-methylphthalic anhydride were evaluated as curing agents with 4-methylimidazole as a catalyst. The manufacturing procedure was:

- Add curing agent to a weighed amount of epoxy resin (0.85:1 anhydride/epoxy ratio).
- Stir with heating until homogeneous.
- Cool to room temperature then add 0.5% (by weight of resin) of 2-ethyl-4-methylimidazole (Shikoku Chemical's Curezol<sup>®</sup> 2E4MZ) and mix. Curezol is a registered tradename of Air Products and Chemical Company, Inc.
- Add silver-flake filler (Ferro's 26LV) to the resin mixture at 80% by weight and blend in a three-roll mill until homogeneous.

Examples of formulations for specific applications are given in Table 3.9.



\* As frozen syringes (< -40 °C) or in room-temperature containers

**Figure 3.21.** Manufacturing steps in formulating one-part and two-part paste adhesives.

**Table 3.9.** Examples of Adhesives Formulations

Adhesive Type	General Formulation*	Examples
Surface-mount adhesives	DGEBA Resin (GY 6010, DER 331, Shell 828):40–50% Amine epoxy adduct or polyamide (Versamide <sup>®</sup> , Ancamide <sup>®</sup> , Aradur <sup>®</sup> , etc.): 20–30% Mineral filler and thixotrope: 12–25%	Amicon 125 D3, Amicon E 6752, Epo-Tek <sup>®</sup> 70E-4 Chipbonder <sup>®</sup> series (Loctite), Epi-bond <sup>®</sup> 7275 (Vantico)
	Mondur MC/castor oil and castor oil polyols (>60%), filler (<5%)	Flexobond 444 Bacon Ind.
Dispensable electrically conductive adhesive	Epoxy Resin (Bisphenol-F): 15–25% Diepoxide diluent: 1–15% Aromatic amines: 5–15% Silver flake (Ferro 26 LV, Silflake 282, etc.): 50–80%	Ablebond 84-1 series, Epo-Tek 3001, Ablebond 967-1, Epo-Tek H20 series
Dispensable electrically insulative adhesive	Epoxy Resin (Bisphenol-F): 15–25% Diepoxide diluent: 8–15% Aromatic amines: 1–5% Filler: 40–50%	Ablebond 84-3 and 84-3 LV
High- $T_g$ die-attach adhesive	High-purity Bisphenol-A (Epicon) and cycloaliphatic resins (Araldite, ERL): 15–24% Anhydride curing agents: 12–24% Catalysts: 1–2% Filler: 50–70%	Epi-bond 7002, Epi-bond 7200
Underfill adhesive (snap cure)	Epoxy resins (high purity Bisphenol-A and cycloaliphatic resins): 45–60% Resin modifier: 1–5% Curing agents (amine): 3–5% Filler (amorphous silica): 50–80%	Loctite 3563, Ablebond 7811
High performance, high- $T_g$ and fast-flow underfill	Epoxy resin: 10–30% Acid anhydride: 10–30% Silica, amorphous: 50–70%	Loctite 3564
*Excludes additives, primers, stabilizers, etc.		

*(cont'd.)*

**Table 3.9.** (Cont'd.)

Adhesive Type	General Formulation	Examples
No-flow, fluxing type underfill	Novolac and Bisphenol-F epoxy resins: 40–50% Methyl hexahydrophthalic anhydride: 20–30% Polysebacic and proprietary anhydride mixture: 7–12% Thermoplastic copolymer	Amicon E1350, 1355
No-flow underfill	Epoxy resin: 40–70% Epoxy curing agent: 15–40% Hydrogenated bisphenol-A: 7–13%	3M UF-3400
Substrate-attach preform	Nitrile-modified epoxy, glass-supported fabric, aromatic-substituted urea curing agent or aliphatic ether amine: 10–15% Dicy catalyst: 1–2% MEK solvent: <5%	Ablebond 550
Silicone RTV (low tear strength)	Part A: Silanol fluid (70%), silica powder (28%), ethyl silicate (2%) Part B: Silicone fluid (50%), silica powder (45%), DBTL catalyst (5%) (Catalyst TL10, Anders)	Dow Corning 838
Silicone RTV (high tear strength)	Part A: Silanol fluid (70%), silica powder (28%), ethyl silicate (2%) Part B: Silicone fluid (50%), silica powder (45%), DBTL catalyst (5%) (Catalyst TL10, Anders)	Dow Corning 3145, 3140
Heat cured silicone	Low and high viscosity chloroplatanic or organo platinum catalyst (1–5 ppm), vinyl resin blend (Polymer VS-50, 100, 90,000 Anders)	Dow Corning 3-6605, and 3-6265
*Excludes additives, primers, stabilizers, etc.		

**Film or preform adhesives.** Film or preform adhesives are produced by casting the premixed resin and hardener onto release liners. Single or multiple master batches of the resin mixed with the hardener are first weighed, mixed, and milled, similar to the paste adhesives. The mixture may be screened through a nylon mesh to remove gelled particles and degassed. Adhesive is applied in a two-step process. First, adhesive is coated onto a release liner and laminated to a support reinforcement such as glass fabric. Primer, such as Dow Corning Z-6040, may be applied to the fabric prior to applying the adhesive. Adhesive may also be applied to the second side of the preform or reinforcement in a “second pass” lamination. The final product is accumulated between release liners (Fig. 3.22).

**Premixed frozen adhesives.** Two-part adhesives may be mixed, deaerated, packaged in tubes or syringes and frozen. The processing of frozen adhesives is best done by the adhesives supplier who is experienced in performing these steps.<sup>[11]</sup> The user thus avoids errors that can be made by production workers in accurately weighing, mixing, and vacuum degassing the adhesive prior to use. The use of frozen adhesives also minimizes handling and reduces exposure of workers to toxic or irritant components of the adhesives, especially curing agents such as amines used with epoxies.

Frozen adhesives are transported in containers with dry ice at  $-80^{\circ}\text{C}$  and must be stored at  $-40^{\circ}\text{C}$  until ready for use, at which time only the amount needed, is thawed and dispensed. The adhesive should be thawed to room temperature in its original closed container since thawing while exposed to air causes moisture condensation and absorption. After dispensing, any unused adhesive should not be refrozen since a portion of its pot life has been expended. Adhesives that are shipped in dry ice or stored at  $-40^{\circ}\text{C}$  may contain a temperature indicator, a cube of red material that melts if the temperature exceeds  $-40^{\circ}\text{C}$ .

### 3.3 PROPERTIES

The properties of cured adhesives are a function primarily of their chemical structures, formulation ingredients, and curing conditions. To a large extent, properties such as thermal stability, moisture resistance, and electrical performance can be predicted based on the molecular structures of the basic resins and curing agents used and the type and degree of polymerization that occur. Thus, polymers that are highly aromatic or

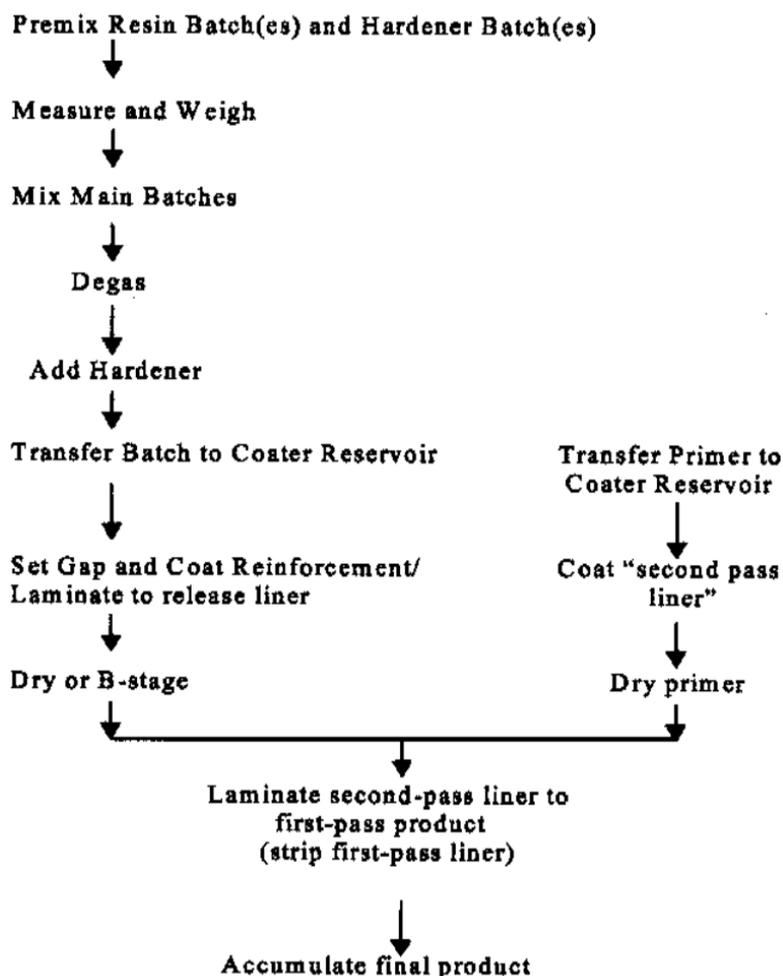


Figure 3.22. Manufacturing steps in formulating film/preform adhesives.

heterocyclic (imides and triazines) and those that are highly crosslinked are more thermally stable and radiation resistant than their aliphatic linear counterparts. In Table 3.10, the general properties of the major polymer types used in adhesive formulations are compared. These should be considered general guidelines because of the numerous possible variations in the chemical structures of any one type of polymer resin, variations in the type of curing agent that can be used, and the large number of additives that can be formulated. The properties of a specific adhesive should always be experimentally measured.

**Table 3.10.** Comparison of Adhesives for Electronic Applications

Material	Advantages	Disadvantages
Epoxies	High-temperature use. Good moisture and chemical resistance. High purity. Low outgassing.	Longer cure cycles with anhydride hardeners. Degassing required for two-component systems. Exotherms in large quantities for amine-curing agents.
Silicones	Highest purity. Stress absorbing. High and low temp. stability.	Migrate to other circuit elements. Low surface energy. Swelled by nonpolar solvents.
Polyurethanes	Good flexibility at low temperatures. Stress absorbing. Highly versatile chemistry.	Lower thermal stability and service temperature than epoxies (150°C–163°C). Average bond strength unless primer used.
Polyimides	Higher temperature stability compared to epoxies. Higher ionic purity. Reduced bleedout.	Trapped solvent can produce voids under large ICs. Multi-step curing required to volatilize solvent. High-stress materials. May absorb moisture in cured condition. Cannot be B-staged.
Silver glass	High-temperature stability. Low outgassing. Close CTE match to silicon.	High-firing temperatures. High-stress adhesive. Voiding due to solvent.
Cyanate esters	High adhesion strength. High thermal stability. High $T_g$ , low CTE.	High-moisture absorption. Popcorn susceptibility.
Modified cyclo-olefin thermoset (MCOT) technology	Low moisture absorption. Reduced popcorning. Excellent adhesion.	Marginal adhesion to some substrates.

### 3.3.1 Properties of Epoxy Adhesives

Of the many polymer types, epoxies have the best combination of properties that are desirable for electronics packaging and consequently are widely used. Among these properties are their high adhesion to almost all surfaces, good electrical insulating properties even under elevated temperature and humidity conditions, ease of curing and processing, low cost, and ease of reworking. Some limitations, which can be obviated, are their moderate-to-high absorption of water due to their highly polar structures, high amounts of chloride and other ions if not well purified, and risk of outgassing if not cured well or not vacuum baked.

**Purity.** Major improvements have been made in the amounts of chloride, potassium, and sodium ions and in the total ionic content of adhesives that are sold for electronics applications. Most electronic-grade epoxy adhesives contain only 35 to 60 ppm of chloride ion, 15–20 ppm of sodium ion, and 1–5 ppm of potassium ion. In fact, some formulations are available that have less than 5 ppm for all these ions. These low ion levels have been achieved through distillation of the resins or water extractions or by using epoxidized olefin resins instead of bisphenol-A types where there is no sodium chloride by-product to be removed. The outgassing of ammonia and low-molecular-weight amines has also been reduced or eliminated by avoiding the use of excess amine-curing agents, postcuring or curing at higher temperatures to assure complete reaction, or by using more stable amine-curing agents such as imidazoles instead of Dicy.

**Adhesion.** Adhesion of epoxies is among the highest of all polymers. As discussed in Ch. 2, this is due to the highly polar structures of epoxies and their wettability to most surfaces. Lap-shear strengths of aluminum-to-aluminum bonded specimens are typically 2,000 psi, but may run as high as 6,000 psi for some formulations and cure conditions. Die-shear strengths for electrically conductive and electrically insulative epoxy adhesives range from 5,000 psi to 7,000 psi, with snap-cured adhesives being at the lower end of the range. Integrated-circuit die, as large as 500 mils square, bonded with silver-filled epoxies are capable of surviving severe accelerated tests such as constant acceleration in the  $Y_1$  direction of 5,000 grams defined in MIL-STD-883, Method 5011.<sup>[70]</sup> Epoxy-attached components are also able to pass other MIL-STD-883 and MIL-PRF-38534<sup>[71]</sup> thermal cycling, heat aging, vibration, and mechanical shock tests. Failures have only occurred when the bonding surfaces were not well cleaned or when the adhesive was not processed according to the manufacturer's instructions.

**Thermal and thermomechanical properties.** The thermal conductivities of unfilled epoxies, as with all other unfilled polymers, are quite low, typically 0.1–0.2 W/m·K. When filled with metal or thermally conductive nonmetal fillers up to 80%–85% by weight, the thermal conductivities increase a minimum of tenfold. Some silver-filled epoxies are reported to have thermal conductivities as high as 6.5 to 8 W/m·K (AI Technology ESP 8350 and ESP 8680, respectively).

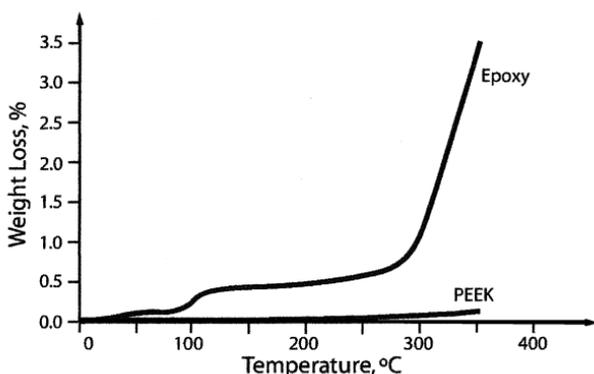
Thermal stabilities of adhesives may be measured by conducting a thermogravimetric analysis (TGA) test, that is, measuring weight loss as a function of increasing temperature at a constant rate, usually 10°C per minute. Thermal stabilities are often reported as weight loss at 300°C for comparative purposes. TGAs may also be performed at constant temperature (isothermal weight loss) as a function of time. Epoxy adhesives should actually be compared at 200°C or, at most, 250°C because, above 250°C, rapid decomposition begins to occur and also because adhesives used in electronic applications seldom require exposures above 250°C. Figure 3.23 compares the TGA curves for an epoxy film adhesive cured at 150°C for 2 hours versus a PEEK® film. In this example, the epoxy shows a weight loss of slightly over 1% at 300°C, but a sharp increase above this temperature, indicating the onset of rapid decomposition. In comparison, the PEEK film was thermally resistant above 300°C.<sup>[72]</sup> The best silver-filled epoxy adhesives show losses between 0.2% to 0.5% at 300°C.

**Thermal expansion properties.** The CTEs of most filled epoxy adhesives range from 25 to 50 ppm/°C but, as discussed in Ch. 2, increase three- to fourfold above their glass-transition temperatures.

**Electrical properties.** The initial electrical properties of fully cured, electrically insulative epoxy adhesives, regardless of the curing agent used, are excellent under normal ambient conditions. Volume resistivities range from 10<sup>12</sup> ohm-cm to above 10<sup>15</sup> ohm-cm, dielectric constants from 2.8 to 4.8, and dissipation factors from 0.003 to 0.04 when measured at 25°C and 1 MHz. Dielectric strengths range from 420 volt/mil to above 1,300 volt/mil. Although these initial electrical values are excellent, they can degrade on exposure to moisture and/or thermal aging. Both dielectric constants and dissipation factors increase with absorbed moisture (Table 3.11). Volume resistivities can drop several orders of magnitude to 10<sup>10</sup> ohm-cm or below on temperature-humidity exposure such as the widely used 85°C/85% RH test or the 10-day temperature-humidity cycle test per MIL-STD-202.<sup>[73]</sup> The high polarity of epoxy polymers that imparts such strong adhesion properties unfortunately also renders them hydrophilic, absorbing moisture

to various degrees depending on the particular epoxy and its degree of cure. If after exposure to humidity and temperature, the adhesive has not decomposed or changed chemically, drying or vacuum baking usually restores the original electrical values.

For electrically conductive metal-filled adhesives, dielectric constants and dissipation factors are not meaningful parameters, but volume resistivities and contact resistances are significant. The volume resistivities for the best silver-filled epoxies range from  $1 \times 10^{-4}$  to  $8 \times 10^{-4}$  ohm-cm.



**Figure 3.23.** Thermal stability of an epoxy compared with PEEK<sup>®</sup> film.<sup>[72]</sup>

**Table 3.11.** Electrical Properties of an Anhydride-cured Bisphenol A Epoxy\*

Property	Initial Value	Water Immersion (24 hr)
Dielectric constant		
60 Hz	4.12	4.19
1 kHz	4.07	4.15
1 MHz	3.55	3.61
Dissipation factor		
60 Hz	0.0035	0.0043
1 kHz	0.015	0.016
1MHz	0.032	0.032
Volume resistivity (ohm-cm)	$1.81 \times 10^{15}$	$2.31 \times 10^{14}$

\* Cured with methyl nadic anhydride (MNA) 16 hrs @ room temperature plus 4.5 hrs @ 150°C

### 3.3.2 Properties of Silicone Adhesives

Among the major properties of silicones, distinguishing them from other polymer types, are their wide range of operating temperatures (from  $-80^{\circ}\text{C}$  to over  $300^{\circ}\text{C}$ ), their inertness and chemical stability, and their excellent electrical insulation and dielectric properties. Other unique features include high purity, low stress, low moisture absorption, resistance to oxidation and chemicals, and inherent flame retardancy. Among the limitations of silicones are their high moisture transmission rates, low tear and tensile strengths (for some formulations), and migration of low molecular weight species to adjacent surfaces during cure.

Depending on their molecular weights and degree of cure, silicones may exist as liquids, gels, or solids; may be solvent based or solventless (100% solids); and may be either one-part or two-part systems. For adhesives applications, the one-part, 100% solids, room-temperature curing types are preferable. One-part silicones are generally the RTV and moisture-curing types. They are user-friendly requiring no weighing, mixing, or deaerating and cure on exposure to air moisture in a few hours. To assure complete cure, however, adhesive-bonded parts should cure for 24–72 hours. The cure time can be shortened by exposure to higher humidity than is present in air or by a short heat exposure. Some two-part silicones can be heat cured at  $105^{\circ}\text{C}$ – $110^{\circ}\text{C}$  in only 10–15 minutes.

**Thermal and thermomechanical properties.** Silicones, as a class, are rated among the highest temperature stable polymers. They can withstand temperatures of  $200^{\circ}\text{C}$ , almost continuously, without degradation of physical or electrical properties and have been used at temperatures as high as  $300^{\circ}\text{C}$ . Because of their high thermal stabilities, they are used as adhesives and encapsulants for electronic modules that are expected to perform in extreme temperature environments, such as near automotive engines and in deep-well sensors. Because of their low moduli of elasticity, silicones also fare well at very low temperatures. They are rated for continuous use at  $-80^{\circ}\text{C}$ , but may be used at even lower temperatures.

Associated with their low moduli and elastomeric properties is their ability to dissipate stresses and to act as stress buffers between harder, less flexible materials such as epoxies. Because of their stress-dissipating properties, soft silicones are often used to bond or encapsulate fragile components such as glass diodes, laser diodes, and electro-optical devices. However, the CTEs of elastomeric silicones are generally high (about 200

ppm/°C or higher) which, to an extent, offsets their stress-relieving properties. Other thermal properties are given in Table 3.12.

**Humidity resistance.** The behavior of silicones towards water differs considerably from that of other polymer types. Generally, a polymer that has a high water absorption will also have a high moisture-vapor permeability. Silicones are unique in that they have low moisture absorption, yet high moisture-vapor transmission rates (MVTRs). Silicones are also hydrophobic and often used as water repellants. However, even their high MVTRs are not of great concern for electronics. Because of their high purity, especially the semiconductor-grade silicones, moisture has little effect on their dielectric properties.

**Electrical properties.** The electrical properties, especially for the high-purity semiconductor-grade silicones, are excellent even at temperature extremes of -80°C and 200°C and in high humidity. Silicone adhesives are available as electrically conductive and as electrically insulative types. Typical electrical properties for moisture- and heat-cured silicone adhesives are given in Table 3.12.

**Physical properties.** Among some limitations of silicones are their poor tear resistances and low tensile strengths. Young's modulus for some highly flexible silicones range from 0.5 MPa to 20 MPa, depending on the formulation and cure. Lap-shear strengths are also relatively low compared with epoxy adhesives. They generally range from 140 psi to 875 psi depending on the formulation. The heat-cured silicones have better mechanical properties than the moisture-cured RTV types. Other physical and mechanical properties are given in Table 3.13.

### 3.3.3 Properties of Polyimide Adhesives

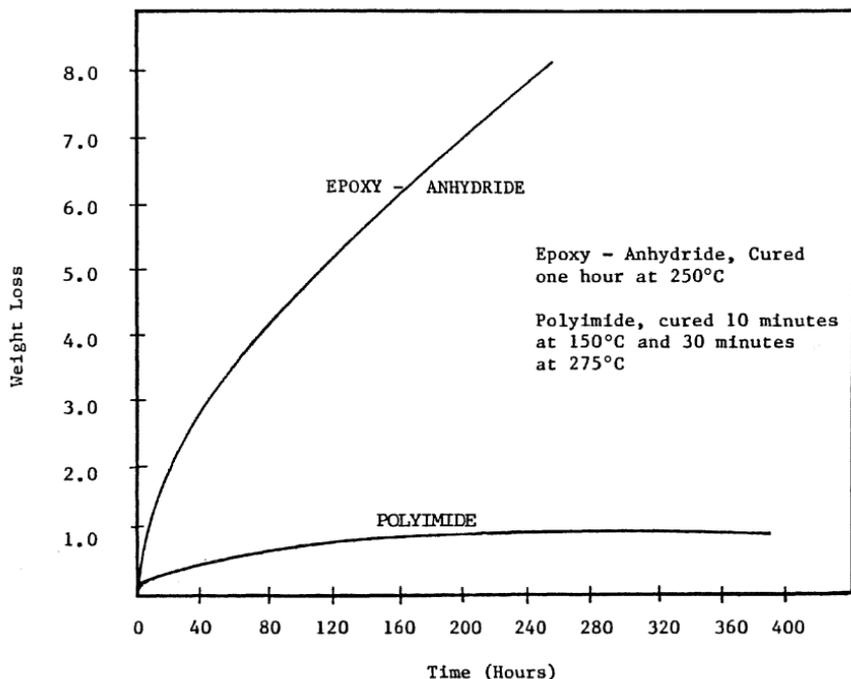
Polyimides are noted for their excellent thermal and radiation resistance properties resulting directly from their highly aromatic polymer structures (see Sec. 3.1.3). Polyimide adhesives are stable in continuous operation at 250°C and for shorter durations up to 400°C. The glass-transition temperatures, typically 180°C–240°C, are also higher than epoxies and most other polymer types. Thermal weight losses are also much lower than for some of the best epoxies. Figure 3.24 compares the weight loss at 250°C of an anhydride-cured epoxy with a polyimide as measured by thermogravimetric analysis (TGA).

**Table 3.12.** Thermal and Electrical Properties of Silicone Adhesives\*

<b>Silicone Type</b>	<b>Thermal Conductivity, W/m·K</b>	<b>CTE, ppm/°C</b>	<b>Dielectric Strength, V/mil</b>	<b>Dielectric Constant @ 100 kHz</b>	<b>Dissipation Factor @ 100 kHz</b>
One-part, moisture-cure RTV	0.18	250–380	480–510	2.38–2.83	<0.001
Two-part, room-temperature cure	0.31	285	510	3.28	<0.002
Heat cure	0.32–0.35	256–300	350–577	2.78–3.02	<0.001 to <0.0002
*Values compiled from a number of Dow Corning silicone adhesives and represent ranges for each category. Dow Corning should be contacted for specific formulations and values for specification purposes.					

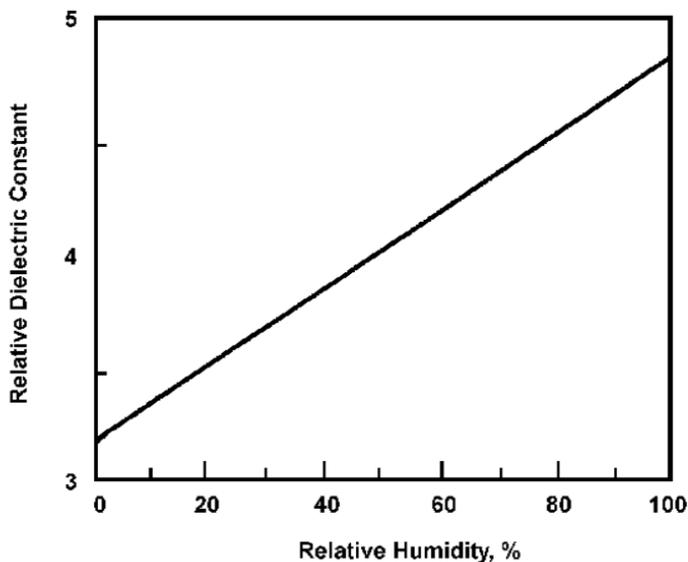
**Table 3.13.** Physical and Mechanical Properties of Silicone Adhesives\*

<b>Silicone Type</b>	<b>Tensile Strength, psi</b>	<b>Elongation, %</b>	<b>Tack-free Time @ r.t., min.</b>	<b>Unprimed Lap- shear Strength, psi</b>	<b>Unprimed Peel Strength, ppi</b>
One-part, moisture-cure RTV	170–250	185–660	4–70	140–200	30–75
Two-part, room- temperature cure	250	225	-	230	10
Heat cure	769–950	150–265	-	550–875	-
*Values compiled from a number of Dow Corning silicone adhesives and represent ranges for each category. Consult Dow Corning for specific formulations and values for specification purposes.					

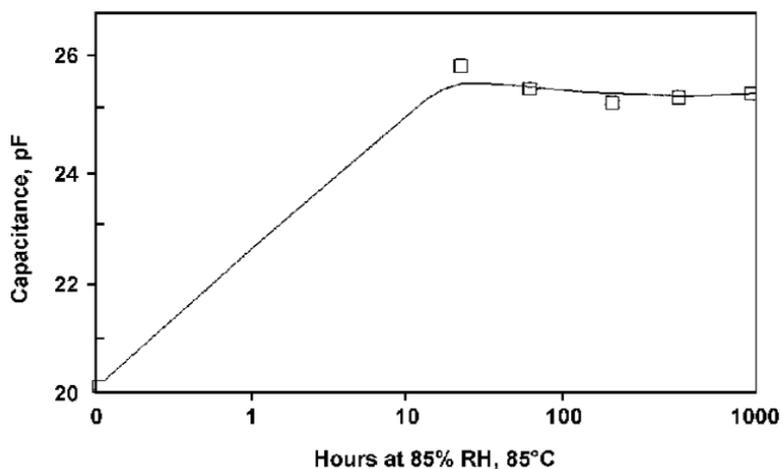


**Figure 3.24.** Weight loss of polyimide vs epoxy at 250°C in nitrogen.<sup>[74]</sup>

Along with the advantages just cited, polyimides suffer some weaknesses. They are much more difficult to process and cure than epoxies and other polymer types. The precursors must be dissolved in a highly polar, high-boiling solvent such as N-methyl-2-pyrrolidone (NMP) in order to process them as film or paste adhesives. To completely remove these solvents or traces of remaining solvent requires temperatures of 150°C–200°C. The actual curing (imidization) requires step curing to temperatures as high as 400°C although modified polyimides will cure at lower temperatures. Lastly, like epoxies, cured polyimides tend to absorb moderate to large amounts of water in humid environments. Water absorption may run as high as 2% at saturation, which degrades their electrical properties. Figure 3.25 shows a direct increase in dielectric constant as a function of exposure to increasing relative humidities. Figure 3.26 shows the increase in capacitance as a function of time exposed to 85% RH and 85°C.



**Figure 3.25.** Effect of relative humidity on the dielectric constant of polyimide.<sup>[75][76]</sup>



**Figure 3.26.** Increase in capacitance for polyimide on temperature/humidity exposure.

### 3.3.4 Properties of Polyurethane Adhesives

Polyurethanes, formulated as adhesives, are mostly two-part systems and must be mixed and deaerated prior to use. Like epoxies, they are highly polar, thus, have good adhesion to a large variety of surfaces, but their highly polar structures also result in a high affinity for moisture. On prolonged exposure to humidity-temperature environments, many of the early formulations reverted to the monomers. Reversion was caused by hydrolysis of the urethane and ester groups, breaking up the solid polymer into a sticky semisolid or fluid material. Some key properties of polyurethane adhesives are given in Table 3.14. Their advantages include the following:

- High flexibility and ability to dissipate stresses.
- Excellent adhesion to a wide variety of substrates.
- Resistance to solvents commonly used in cleaning SMT assemblies.
- Ease of reworking by melting with a hot solder iron.
- Flexibility even at cryogenic temperatures.

Some limitations are the following:

- Less thermally stable than epoxies.
- Hardening and embrittlement on exposure to ozone and UV radiation.
- Difficulty in processing due to short pot lives.
- Extra safety precautions due to handling and exposure to toxic isocyanates.

### 3.3.5 Properties of Cyanate Esters

Cyanate-ester adhesives are available as either pastes or films. They are often blended or toughened with epoxy resins or other polymers and widely used for die attachment, underfill, and encapsulants. Cure schedules are generally 165°C–175°C for 1–2 hours, but snap-cure formulations are available that cure in 10 seconds at 220°C. The thermal properties of cyanate-ester adhesives are superior to those of epoxies. They are capable of withstanding temperatures of 200°C when postcured and have glass-transition temperatures ranging from 140°C–245°C, depending on the curing temperature. Curing at 165°C–175°C for 1–1.5 hour generally results

**Table 3.14.** Properties of Some Polyurethane Adhesives

Product Name/ Supplier	Description	Viscosity (cps)	Shelf life (-40°C), Pot Life (25°C)	Cure Schedule hr @°C	Hardness (Shore A, unless indicated)	NASA Outgassing Test Results (ASTM E 595)	Lap- Shear Strength (psi)	CTE (ppm/°C)		T <sub>g</sub> (°C)	Volume Resistivity (ohm-cm)	Thermal Conductivity (W/m-K)
								α <sub>1</sub>	α <sub>2</sub>			
Uralane 7760/ Vantico	One-part thermal-transfer adhesive (CTE mismatched parts)	410,000 (RVT, Spindle #14)	3 mos/ 3 hrs	0.5 @ 100°C	70	0.471 % total mass loss (TML), 0.011 collectible volatile condensable materials (CVCM)	200	29	88	-63	2.9 × 10 <sup>14</sup>	0.69
Flexobond 442/Bacon Industries	Thermally conductive, flexible system	Paste	3 mos/ 4 hrs	2 @ 82°C	78	0.471 % TML, 0.011 CVCM	500	N/A	N/A	N/A	10 <sup>12</sup>	0.864
DIS-A- PASTE 2000-A/B/ Aptek Labs.	Soft, two-part, mineral-filled electrically insulating	115,000 (Part A), 45 (Part B)	6 mos (25°C)*/ 40 min	4 @ 100°C	83	0.15 % TML, 0.004 % CVCM	425	31	147	-60	7 × 10 <sup>14</sup>	0.744
DIS-A- PASTE 2001PMF/ Aptek Labs.	One-part, soft mineral-filled, adhesive	140,000	6 mos (25°C)*/ >2 hrs	6 @ 85°C	83	0.15 % TML, 0.004 % CVCM	425	31	147	-60	7 × 10 <sup>14</sup>	1.384
DIS-A- PASTE 2003-A/B/ Aptek Labs.	One-part, soft mineral-filled, adhesive	150,000 (A), 2,700 (B) (ASTM D-1824)	6 mos (25°C)*/ >2 hrs	6 @ 85°C	80	0.27 % TML, 0.006 % CVCM	260	31	137	-60	2 × 10 <sup>14</sup>	0.744
DIS-A- PASTE 2010-PMF/ Aptek Labs.	Electrically insulating, hybrid adhesive	Thixotropic paste	6 mos/ >2 hrs	0.75 @ 125°C	85	0.51 % TML, 0.04 % CVCM	300	50	160	<-70	8.0 × 10 <sup>15</sup>	0.80

\*Sealed containers. (Source: Compiled from suppliers' technical data sheets.)

in  $T_g$  between 140°C and 147°C, while curing or postcuring at 300°C for 30 minutes increases the  $T_g$  to 200°C–250°C.<sup>[77]</sup> Coefficients of expansion below the  $T_g$  range from 30–45 ppm/°C. The polymer derived from the basic dicyanate of bisphenol-A (Ciba Geigy's AroCy B<sup>®</sup>) is reported to have a  $T_g$  of 289°C.<sup>[34]</sup> Cyanate esters have been selected for use in many space programs because of their low outgassing in thermal-vacuum environments and their high radiation resistance.<sup>[30]</sup> Because of their unique chemistry, cyanate-ester adhesives are reported to have low moisture outgassing (less than 1,000 ppm in a sealed cavity package) and less than 1% weight loss at 300°C when measured by thermogravimetric analysis (TGA). This, coupled with their high purity and low ionic content (<20 ppm Na<sup>+</sup> or K<sup>+</sup> and <10 ppm Cl<sup>-</sup>),<sup>[77]</sup> renders cyanate esters highly desirable as die-attach and underfill adhesives for space applications.

Another property of cyanate esters important in reducing or avoiding popcorning during solder reflowing is their relatively low moisture absorptions. Moisture absorption at saturation in boiling water ranged from 0.7% to 2.5% depending on the starting cyanate monomer.

The electrical properties of cyanate esters are also quite good, even at high frequencies. Because of their low dielectric constants and dissipation factors extending into the gigahertz range, there has been considerable interest in cyanate esters for high-speed circuits. One formulation is reported to have a dielectric constant of 2.8 and a dissipation factor of 0.003 at 10 GHz.<sup>[78]</sup> Others range from 2.6 to 2.9 at 1 MHz. The bisphenol-A derivative is reported to have a dielectric constant of 2.9 at 1 MHz and 2.79 at 1 GHz. Its dissipation factor is 0.005 at 1 MHz and 0.006 at 1 GHz. The hexafluorobisphenol-A (Ciba Geigy's AroCy F<sup>®</sup>) exhibits even better electrical properties: dielectric constant of 2.66 and 2.54 at 1 MHz and 1 GHz, respectively, and DF of 0.005 at both 1MHz and 1GHz.<sup>[34]</sup> These electrical values are much better than those for epoxies and are attributed to the highly symmetrical macrostructures and absence of strong dipoles in the cured cyanate-ester polymers.

In spite of their low polarities, cyanate esters adhere well to metal conductors and maintain good adhesion up to 250°C. They are thus compatible with solder-reflow temperatures. The adhesion strengths of toughened cyanate-ester adhesives, as measured from aluminum-to-aluminum lap-shear specimens are reported to be 5,900 psi at 25°C, 2,572 psi at -67°C, and 4,000 psi at 82°C.

### 3.3.6 Properties of MCOT Adhesives

In many respects, the properties of the modified cyclo-olefin thermoset (MCOT) adhesives are similar to those of the cyanate esters. Both types were developed to solve manufacturing problems in the die attachment and encapsulation for BGA and chip-scale packages where the high moisture absorptions of other polymer types, such as epoxies and polyimides, resulted in rapid moisture expulsion popcorn effect during subsequent solder-reflow steps. MCOT adhesives when cured at 150°C for 30 minutes or less absorbed less than 0.05% water at 85°C/85 RH conditions after 168 hours and 0.1% even after HAST\* testing at 150°C, 85% RH, 168 hours.<sup>[35]</sup> Also, as with cyanate esters, MCOT adhesives are cured by addition polymerization, release no by-products, and contain very low traces of ionic impurities. Properties for two commercially available MCOT adhesives are listed in Table 3.15.

### 3.3.7 Properties of Acrylates and UV-Curing Adhesives

Acrylate adhesives differ from other polymer types in their ability to be cured rapidly by exposure to UV and/or visible light. Their main advantage over heat-curing adhesives is in bonding heat-sensitive electronic devices in 5 to 30 seconds at room temperature. Ultraviolet/visible light curing also allows time to position a device, a wire, or an optical fiber prior to cure (curing on demand). Acrylate adhesives are used for wire tacking, lens bonding, sealing, and fiber-optic circuit assembly. Adhesives as thick as 0.5 inches can be cured with UV light while depths of 1–3 inches can be cured with the visible and visible/UV types.<sup>[80]</sup> Formulations are available having a wide range of viscosities approximately 500 cps to 45,000 cps for 3M's LC 1100 and 1200 series of Light-Cure<sup>®</sup> adhesives and 120,000 to 300,000 cps for Dymax's 900<sup>®</sup> series adhesives.

The mechanical and electrical properties of acrylates are similar to those for many other polymer types. Tensile strengths range from approximately 1,300 psi to 4,500 psi and shear strengths of PCB lap samples range from 424 to 566 psi. Aluminum-to-aluminum lap-shear strengths are reported at approximately 3,000 psi.<sup>[81]</sup> Electrical volume resistivities under room ambient conditions ranged from  $1 \times 10^{14}$  ohm-cm to  $1.4 \times 10^{16}$  ohm-cm. dielectric constants from 3.15 to 3.43 at 10 MHz and dissipation factors

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\*Highly Accelerated Stress Test per JEDEC-STD-22-A110.<sup>[79]</sup>

from 0.017 to 0.024 at 10 MHz. Dielectric strengths ranged from 1,320 to 3,790 volts/mil.<sup>[80]</sup> Adhesives may range from semi-rigid to very flexible depending on the formulation.

Other properties of UV-cured adhesives of benefit to the electronics industry are that they are one-part systems, 100% solids (no solvents), and can be stored at room temperature.

**Table 3.15.** Properties of MCOT Adhesives<sup>[35]</sup>

Property	Thermally Conductive Paste	Electrically Conductive Paste
Filler type & percent	Boron nitride, 40%	Silver, 80%
Viscosity, Pa-s	10	10
Cure temperature	100–150°C	100–150°C
Cure time	<30 min	<30 min
Pot life @ 25°C	16 hrs	16 hrs
Shelf life @ -40°C	>6months	>6 months
Extractable ions	<10 ppm	<10 ppm
% weight loss (up to 300°C)	<1	<1
<b>Cured Properties</b>		
CTE (20–200°C)	85 ppm/°C	78 ppm/°C
Modulus @ 25°C	1,000 MPa	1,000 MPa
Modulus @ 200°C	150 MPa	165 MPa
Glass-transition temp.	65°C	65°C
Bulk thermal conductivity (W/m-K)	1.0	2.3
Volume resistivity (ohm-cm)	NA	$1.5 \times 10^{-4}$

### 3.3.8 Properties of Film Adhesives

Almost all film adhesives used in electronics assembly are either epoxies or polyimides on a glass fabric carrier. Film adhesives may be thermoplastic or thermosetting and generally B-staged or partially cured. They may also be electrically conductive or electrically insulative as with paste adhesives. Total film thicknesses (including the carrier) range from 3–10 mils with carrier thicknesses of 1–4 mils.<sup>[82][83]</sup> Heat curing is performed while a slight pressure is applied to the part being attached in order to equalize the flow throughout the surface and generate a small fillet at the edges.

Thermally conductive films are used to bond heat dissipating components to heat sinks. Electrically conductive silver-filled epoxy films when used to attach substrates also serve as ground planes and provide RF/EMI shielding. They are also used in the high production automated attachment of leadframes to chips and to bond chips vertically in chip stacks.

A wide variety of films and properties is available. Lap-shear aluminum-to-aluminum bond strengths range from 1,000 psi to over 3,000 psi and electrical properties are similar to those for the paste versions. Properties of film adhesives for die attachment and for substrate attachment are tabulated in Tables 3.16 and 3.17.

**Table 3.16.** Properties of Film Adhesives for Semiconductor Die Attachment

Product/ Supplier	Type	Shelf Life @ -40°C/ Pot Life @ 25°C	Cure Schedule	% Wt. Loss at 300°C	Bond Strength Al-Al lap shear (psi)	Modulus of Elasticity MPa (psi)	CTE, ppm/°C		T <sub>g</sub> °C	Volume Resistivity, ohm-cm	Thermal Conduc- tivity, W/m·K	Moisture Absorp- tion %*	Ionic Impur- ities (ppm)
							α <sub>1</sub>	α <sub>2</sub>					
Ableflex® 5204TI/ Ablestik	Polyimide	N/A/ 6 mos	1 hr @ 175°C	0.4 (150°C)	7,500	52 (7,500)	136	370	N/A	N/A	N/A	N/A	Cl <sup>-</sup> 60, Na <sup>+</sup> 8, K <sup>+</sup> 1
Ablefilm® ECF571/ Ablestik	Epoxy	1 yr/ 48 hrs	45 min @ 175°C	0.16	1,750	N/A	45	200	142	2.0 × 10 <sup>4</sup>	6.7	N/A	N/A
Ableloc® 5500/ Ablestik	Polyimide & thermoplastic polyimide carrier	18 mos (25°C)/ 26 wks	0.5–2 secs, 275°C–325°C	0.6	N/A	5,240 (760,000)	N/A	N/A	160	1.1 × 10 <sup>15</sup>	0.21	0.5	Cl <sup>-</sup> , Na <sup>+</sup> , and K <sup>+</sup> 1
ESP7676- HF/Al Tech- nology	Epoxy	1 yr (25°C)/-	N/A	N/A	N/A	6,404 (900,000)	40	100	80	>1.0 × 10 <sup>14</sup>	3.0	N/A	N/A
HM-122U/ Hitachi	Polyimide	N/A	2–3 sec. and 1–3 Kg @ 300°C–400°C	N/A	N/A	2,600 (377,000)	N/A	N/A	230	N/A	1.8	N/A	N/A
HM-122U- HR/ Hitachi	Polyimide	N/A	2–3 sec. and 1–3 Kg @ 300°C–400°C	N/A	N/A	2,800 (406,000)	N/A	N/A	230	N/A	1.8	N/A	N/A

\*After 85/85 exposure. Source: Compiled from suppliers' technical data sheets (not to be used for specification purposes) N/A: Not available.

(cont'd.)

**Table 3.16. (Cont'd.)**

Product/ Supplier	Type	Shelf Life @ -40°C/ Pot Life @ 25°C	Cure Schedule	% Wt. Loss at 300°C	Bond Strength (psi)	Modulus of Elasticity MPa (psi)	CTE ppm/°C		$T_g$ , °C	Volume Resistivity, ohm-cm	Thermal Conduc- tivity, W/m·K	Moisture Absorp- tion, %*	Ionic Impur- ities, ppm
							$\alpha_1$	$\alpha_2$					
Sumilite Adhesive (LOC) ITA-1019/ Sumitomo Bakelite	Thermoplastic polyimide	1 year 25°C	230°C -240°C, 2-10 Kg/cm <sup>2</sup> , 0.210 secs	N/A	N/A	70-100 (10,150- 14,500)	N/A	N/A	121	$4 \times 10^{16}$	N/A	0.2-1.2	Na <sup>+</sup> , K <sup>+</sup> , Cl <sup>-</sup> <5
Sumilite Adhesive (LOC) ITA-5120/ Sumitomo Bakelite	Thermoplastic polyimide	1 year 25°C	230°C -240°C, 2-10 Kg/cm <sup>2</sup> , 0.210 secs	N/A	N/A	70-100 (10,150- 14,500)	N/A	N/A	159	$4 \times 10^{16}$	N/A	0.2-1.2	Na <sup>+</sup> , K <sup>+</sup> , Cl <sup>-</sup> <5
Sumilite Adhesive (LOC) ITA-5315/ Sumitomo Bakelite	Thermoplastic polyimide	1 year 25°C	230°C -240°C, 2-10 Kg/cm <sup>2</sup> , 0.210 secs	N/A	N/A	70-100 (10,150- 14,500)	N/A	N/A	218	$4 \times 10^{16}$	N/A	0.2-1.2	Na <sup>+</sup> , K <sup>+</sup> , Cl <sup>-</sup> <5
Sumilite Adhesive (LOC) ITA-5701/ Sumitomo Bakelite	Thermoplastic polyimide	1 year 25°C	230°C -240°C, 2-10 Kg/cm <sup>2</sup> , 0.210 secs	N/A	N/A	70-100 (10,150- 14,500)	N/A	N/A	230	$4 \times 10^{16}$	N/A	0.2-1.2	Na <sup>+</sup> , K <sup>+</sup> , Cl <sup>-</sup> <5

\*After 85/85 exposure. Source: Compiled from suppliers' technical data sheets (not to be used for specification purposes) N/A: Not available.

**Table 3.17.** Properties of Film Adhesives for Substrate Attachment

Product/ Supplier	Shelf Life @ -40°C/ Pot Life @ 25°C	Cure Schedule	% Wt. Loss at 300°C	Bond Strength Al-Al lap shear, psi	Modulus of Elasticity, Mpa psi	CTE ppm/°C		T <sub>g</sub> , °C	Volume Resistivity, ohm-cm	Thermal Conduc- tivity, W/m·K	Moisture Absorp- tion, %	Ionic Impurities, ppm
						α <sub>1</sub>	α <sub>2</sub>					
Ablefilm® 550 Epoxy/ Ablestik .	12 mos/ 6 mos	30 min @ 150°C	1.1	5,700	3,820 at 25°C	95	480	105	1 × 10 <sup>14</sup>	0.2 at 121°C	2.2 at 85/85 saturation	Cl <sup>-</sup> 45, Na <sup>+</sup> 10, K <sup>+</sup> 1
Ablefilm® 566K Epoxy/ Ablestik	12 mos/ 72 hrs	120 min @ 100°C	0.26	2,200	N/A	85	300	93	1.4 × 10 <sup>13</sup>	0.80	N/A	N/A
Ablefilm® 570 Epoxy/ Ablestik .	12 mos/ 14 ds	3 hrs @ 150°C	0.27	2,800	N/A	50	350	135	6.0 × 10 <sup>14</sup>	1.73	N/A	N/A
ESP 7355/ AI Technology	12 mos/-	30 min @ 150°C	N/A	800	N/A	N/A	N/A	N/A	> 1 × 10 <sup>14</sup>	N/A	N/A	N/A
ESP 7675/ AI Technology	12 mos/-	30 min @ 150°C	N/A	N/A	N/A	N/A	N/A	N/A	> 1.0 × 10 <sup>14</sup>	N/A	N/A	N/A
ESP 8350/ AI Technology	12 mos/-	60 min @ 150°C	N/A	N/A	N/A	N/A	N/A	N/A	< 4 × 10 <sup>-4</sup>	6.50	N/A	N/A
TC8750/ AI Technology	1 yr/ 24 hrs	60 min @ 150°C	N/A	< 1000	N/A	N/A	N/A	N/A	< 5.0 × 10 <sup>-4</sup>	6.50	N/A	N/A
TK 7755/ AI Technology	1 yr/-	30 min @ 150°C	N/A	> 2,400	N/A	N/A	N/A	N/A	> 1 × 10 <sup>14</sup>	1.80	N/A	N/A
Staystik® 501 Epoxy/Cookson	N/A	3–5 min @ 300°C–375°C (0–10 psi)	N/A	>3,500	2,484 (360,000)	N/A	N/A	180–185	≤5.0 × 10 <sup>-4</sup>	3.0–3.5	N/A	N/A

Source: Compiled from suppliers' technical data sheets (not to be used for specification purposes). N/A: Not Available, ND: None Detected.

(cont'd.)

**Table 3.17. (Cont'd.)**

Product/ Supplier	Shelf Life @ -40°C/ Pot Life @ 25°C	Cure Schedule	% Wt. Loss at 300°C	Bond Strength Al-Al lap shear, psi	Modulus of Elasticity, MPa psi	CTE ppm/°C		$T_g$ , °C	Volume Resistivity, ohm-cm	Thermal Conduc- tivity, W/m·K	Moisture Absorp- tion, %	Ionic Impurities, ppm
						$\alpha_1$	$\alpha_2$					
Staystik® 611 Epoxy/Cookson	N/A	3–5 min @ 300°C–375°C (0–10 psi)	N/A	>3,000	2,484 (360,000)	N/A	N/A	180–185	$>1.0 \times 10^9$	3.0–3.5	N/A	N/A
Staystik® 872 Epoxy/Cookson	N/A	3–5 min @ 125°C–200°C (0–10 psi)	N/A	>3,000	414 (60,000)	N/A	N/A	180–185	$>1.0 \times 10^9$	0.5–1.0	N/A	N/A
Ablefilm® 561K Epoxy/Ablestik	12 mos/ 6 mos	30 min @ 165°C	0.34	3,000	4,300 (630,000)	85	300	55	$9.1 \times 10^{12}$	0.8	0.9	Na <sup>+</sup> 35, K <sup>+</sup> 9, Cl <sup>-</sup> 110
Ablefilm® 564AK HM Epoxy/Ablestik	6 mos/ 72 hrs.	120 min @ 150°C	0.16	2,700 (lap)	N/A	40	150	130	$4.5 \times 10^{13}$	0.69	N/A	Na <sup>+</sup> 10, K <sup>+</sup> ND, Cl <sup>-</sup> 10
ECF 561E Epoxy/Ablestik	12 mos/ 96 hrs	1 hr @ 150°C	0.55	2,000	N/A	100	380	47	N/A	1.60	N/A	N/A
ECF 564A Epoxy/Ablestik	12 mos/ 72 hrs	2 hrs @ 150°C	0.26	>2,200	N/A	30	–	150	$4.0 \times 10^4$	3.9	N/A	Na <sup>+</sup> 5, Cl <sup>-</sup> 20
Ablefilm® 5020K Epoxy/ Ablestik	12 mos/ 6 mos	60 min @ 150°C	0.30	3,000	N/A	45	270	109	$8.0 \times 10^{14}$	0.70	N/A	Na <sup>+</sup> 20, Cl <sup>-</sup> 60, K <sup>+</sup> 1
Ablefilm® 506 Epoxy/Ablestik	6 mos/ 24 hrs	60 min @ 150°C	N/A	1,200	N/A	45	350	3	$7.0 \times 10^{14}$	0.90	N/A	N/A

Source: Compiled from suppliers' technical data sheets (not to be used for specification purposes). N/A: Not Available, ND: None Detected.

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# 4 Adhesive Bonding Processes

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Process steps for bonding have undergone significant changes since the 1960s and 1970s. Most processes then were manual or semiautomatic, at best. Adhesives were used to attach small die in hybrid microcircuits or to attach components to sparsely populated printed-wiring boards (PWBs). Adhesives were manually dispensed from a syringe or dabbed with a probe, and components were picked up and placed with tweezers or with a vacuum pick-up tool. With the recent proliferation of electronics in consumer products, high production attachment and curing processes have been developed along with precision automated equipment for cleaning, dispensing adhesives, placing of components, and curing of the bonded parts. New high-density devices and packaging formats have also been introduced such as chip-scale packaging, flip-chip devices, ball-grid array (BGA) packages, chip-on-board (COB), and chip stacks. Challenges have had to be met in mixing different technologies in the same assembly; examples are assembling wire-bonded die alongside flip-chip attached die, large molded inductors or capacitors along with bare-chip devices, and soldered components together with components attached and connected with electrically conductive adhesives. Indeed, in the drive to reduce costs and increase circuit densities, the trend is to use a mixture of assembly technologies.

Cost has also become a driver even for the high-end military and space electronics. This is a result of the increased use of electronics in these fields, for example, in fighter planes and spacecraft. At the same time, government budgets have been reduced. Still, high reliability is required for these systems. Thus, programs are in progress to evaluate the reliability of products produced on commercial production lines for use in military and space systems. This has led to the Commercial-off-the-Shelf (COTS) program whereby industry is encouraged to purchase and apply COTS electronics to aircraft, missiles, and spacecraft, provided the contractor can

show, through testing or heritage data, that the products will be reliable for their intended use.

Added to all this, a manufacturer must now comply with a myriad of ever stringent regulations on solvent emissions, toxicity, and energy conservation. To meet OSHA, EPA, and a multitude of other federal, state, and local government requirements, changes have had to be made in cleaning solvents and processes and in adhesive materials, bonding, and curing methods. This chapter addresses the following key bonding processes:

- Cleaning
- Surface treatment
- Dispensing of adhesives
- Placement of devices or parts
- Curing
- Reworking (if necessary)

A summary of process and material requirements for each of these steps is given in Table 4.1.

**Table 4.1.** Material and Process Requirements for Bonding

Category	Process Requirements	Material Requirements
Cleaning	Batch process, high throughput	High exchange rate; low viscosity, low surface tension solvents leaving low residues; compliance with OSHA, EPA, and other regulations
Dispensing	Data-driven automated dispensing preferred. Stencil or mass pin transfer only for long production runs	High dot profile to fill component-to-board gaps; suitable viscosity for coverage; low stringing to avoid conductive pad contamination; long shelf life for production runs
Device placement	High throughput	Rheology suitable for dispensing
Curing	In-line compatible, low stress on flip-chip and large die	Rapid IR, UV, or convection oven cure, <3–4 min (in-line application preferred); Low volatile organic compounds (VOC) emissions during cure
Rework	Temperatures that do not damage components or substrates	High $T_g$ , thermally stable laminates; modest rework conditions (low $T_g$ adhesives) for specialized applications

## 4.1 CLEANING

The most important requirements in assuring good adhesion between surfaces are the cleanliness of and the chemical and physical condition of the surfaces. The adhesive chosen must be able to wet the surfaces so that a contact angle of less than  $90^\circ$  results, as discussed in Ch. 2. Unfortunately, the choice of solvent and cleaning process is often made hastily without considering the nature of the contaminants or how clean the part needs to be. Inadequate cleaning prevents or reduces adhesion and can cause corrosion or electrical deterioration over time, but extra cleaning, if not necessary, becomes costly. It is good engineering practice to analyze the types of contaminants that are likely to exist on a surface as a result of exposure to the ambient, handling, or previous processing such as plating, soldering, or etching. Analytical procedures such as infrared spectroscopy, energy-dispersive x-ray (EDX), scanning-electron microscopy (SEM), and ion analysis can be used to identify the residues. Once the contaminants are identified, the appropriate solvents and cleaning process for their removal can be selected.

Contaminants may be of three general types: particulates, highly polar (ionic) residues, and nonpolar (grease-like) residues. In many production environments, all three are present and several solvents and cleaning processes must be used to remove them. Both the choice of solvent or cleaning solution and the cleaning process are critical, and several theoretical principles may be followed in their selection. Ultimately, cleaning is more an art than a science, and the procedure chosen should be experimentally verified in each case. Qualitative and quantitative tests can be performed to determine the efficiency of a selected solvent and process.

### 4.1.1 Solvent Selection

Solvents, like contaminants, may be polar or nonpolar. As a general rule, polar solvents dissolve polar residues while nonpolar solvents dissolve nonpolar residues. Thus, ionic residues such as chlorides, salts, acids, acid fluxes, and alkalis are best dissolved and removed with polar solvents such as water, isopropyl alcohol, ethanol, or methylethyl ketone. Greases, oils, silicones, rosin flux, and low-molecular-weight monomers are best dissolved and removed with solvents such as hydrocarbons, Freons<sup>®</sup>, hydrochloro-fluorocarbons, xylene, terpenes, and naphtha. To remove both polar and

nonpolar residues, a two-step process using both types of solvents may be used or, more conveniently, an azeotrope mixture of the two solvents can be used in a one-step process. Most of the chlorofluorocarbon solvents (Freons) and their azeotropes with alcohols, methylene chloride, or ketones are being phased out due to their high ozone-depletion potentials. Solvent blends and azeotropes of hydrofluoroethers and hydrochlorofluorocarbons (HCFC) are now replacing these solvents.

**Organic solvents.** Purely organic solvents or mixtures are effective in removing rosin flux residues and other organic residues such as greases and oils. The highly polar alcohols such as isopropyl alcohol (IPA) and ethanol are also fairly effective in removing ionic and salt residues. Organic solvents have low surface tensions, good surface-wetting ability, high solvency for surface contaminants, and are easily vaporized, leaving the surfaces and electronic components dry. In fact, rinsing with fresh organic solvent is often used as the last step in aqueous cleaning to augment the removal of moisture and improve drying.

In the early days of electronics, an organic mixture found effective in removing both ionic and grease-like residues from printed-wiring assemblies was a 50/50 mixture of isopropyl alcohol and naphtha. For decades and up until recently, the chlorinated and chlorofluorocarbon (CFC) solvents were used alone or as mixtures with alcohols or ketones. DuPont's Freon TF and other Freons were among the best cleaning solvents in the electronics industry. They served the industry well because of their nonflammability, high solvency, and inertness to other circuit components. However, the phasing out of the chlorinated solvents, because of their high volatile organic compounds (VOC) and ozone-depletion properties, has created a challenge for the industry to develop replacements that are equally effective as solvents, yet meet EPA and OSHA requirements. Solvents in use today for cleaning fragile, non-hermetically sealed assemblies are the hydrofluorocarbons (HFC), hydrofluoroethers (HFE), hydrochlorofluorocarbons (HCFC), and n-propylbromide. Even among these, some, like the HCFCs, are being allowed only for a few more years, and n-propylbromide, because of its high polarity and high boiling point, may be limited in use on plastic parts. As a result, aqueous and semi-aqueous solvents are finding more uses as alternates to organic solvents. At the same time, research has produced water-soluble fluxes and "no clean" fluxes, the latter leaving only minor residues that are not considered corrosive so that final cleaning, in some cases, can be eliminated.<sup>[1][2]</sup>

Organic solvents are most effective as blends of polar and nonpolar solvents that have a constant boiling point known as *azeotropes*. Azeotropes are mixtures of two or more solvents used primarily in vapor-degreasing equipment.

HCFC, HFC, and HFE solvents are available as azeotropes with alcohols such as ethanol. Besides their effectiveness as solvents, these hydrohalocarbons are desirable because of their low toxicity, nonflammability, heat stability, and inertness to components and materials on circuit-board assemblies. Examples of azeotropes include DuPont's HFC 43-10mee (2,3-dihydrodecafluoropentane) and 3M's HFE-7100 (methylnonafluorobutyl ether) both of which are comparable or better than CFC-113.

Table 4.2 lists some commercially available organic solvents, azeotropes, and mixtures.

**Aqueous and semi-aqueous cleaners.** Aqueous and semi-aqueous cleaners are used primarily to clean printed-circuit boards prior to assembly, during application of the solder paste and adhesive (if they have been misprinted or smudged), and after assembly and solder reflowing. Highly automated multi-stage cleaning consoles are used in production where the parts are cleaned in a series of baths ending up with one or more deionized water rinses.

Water, being a highly polar solvent, is ideal for the removal of ionic and polar residues. Alone, as a co-solvent, or as an emulsion with organic nonpolar solvents, water is widely used in cleaning printed-circuit boards both prior to and after assembly. Aqueous and semi-aqueous cleaners are nonflammable and relatively inexpensive compared with organic solvents. There is also no hazardous waste or handling concerns and little or no ozone-depletion potential. Aqueous solvents may be purely aqueous (water with detergents, saponifiers, surfactants, neutralizers, or other additives) or semi-aqueous (water with an organic polar or nonpolar solvent). Examples of organic solvents used with water in semi-aqueous or co-solvent systems include alcohols, esters, and terpenes. *Co-solvents* may consist of mixtures of two solvents that are completely miscible in each other or, if not, can be rendered miscible by the addition of an emulsifier. Emulsion cleaners combine water with a hydrocarbon-based solvent. By emulsification, the hydrocarbon becomes suspended as tiny droplets in the water. The main advantages are the small amounts of organic solvent used and the reduced odor and air emissions.

**Table 4.2.** Organic Solvents and Azeotrope Cleaning Materials and Properties

Product/ Supplier	Description	Application	Properties					
			Kauri- Butanol (KB) Value	Boiling Point*, °C	Surface Tension, dynes/cm	$\Delta H_{\text{vap}}$ cal/gm	Flash Point, °C	Vapor Pressure, mm**
Lenium® ES/ Petroferm	n-propyl bromide, isopropyl alcohol, and stabilizers	Vapor degreasing, defluxing, or general precision cleaning	>150	68	25.9	58.8	None	110.8
Megasolv® NOC/ Petroferm	Propoxy propanol, methoxy and methyl ethyloxy propanol, and N-methyl pyrrolidone	Room temperature cleaning of electronic assemblies, surface- mount adhesive cleaning (misprints and stencils). Used in pressure spray, immersion, and ultrasonic applications.	N/A	180–202	Low	N/A	82	<1 (20°C)
Bioact® EC-7 Defluxer/ Petroferm	Highly-refined terpenes and nonionic surface- active agents	Flux removal from a variety of substrates	120	171–189	N/A	N/A	47	<2 (20°C)
Bioact® EC-8/ Petroferm	Aliphatic ester and non-ionic surfactants (VOC = 522 gm/l)	Immersion cleaning of inks used in PC fabrication from stencils	N/A	196–225	~25	N/A	100	0.2 (20°C)
Bioact® SC-10/ Petroferm	Alcohols, hydrocarbons, and terpenes	Screen-printing underwipe systems (cold cleaning)	>150	>152	~25	N/A	41	<2

\*Some boiling points are for concentrated solutions; \*\*at 25°C unless indicated; N/A – Not Available. (Source: Compiled from suppliers' technical data sheets.)

(cont'd.)

**Table 4.2. (Cont'd.)**

Product/ Supplier	Description	Application	Properties					
			Kauri- Butanol (KB) Value	Boiling Point*, °C	Surface Tension, dynes/cm	$\Delta H_{vap}$ cal/gm	Flash Point, °C	Vapor Pressure, mm**
Bioact <sup>®</sup> SC-23/ Petroferm	Alcohols, hydrocarbons	Non-aqueous stencil cleaning (cold cleaning)	N/A	>152	~25	N/A	58	2
Vapor Edge <sup>®</sup> 1000/ Petroferm	n-propyl bromide, isopropanol azeotrope to remove polar and nonpolar residues	Vapor-degreasing solvent	N/A	68	25.9	58.8	None	110.8
1,1,1- trichloroethane/ DuPont	C <sub>2</sub> Cl <sub>3</sub> H <sub>3</sub>	Vapor degreasing	124	74	25.6	57.5	None	28
TCE /Du Pont	Trichloroethylene (C <sub>2</sub> HCl <sub>3</sub> )	Vapor degreasing	129	87	26.4	57.8	None	57.8
CFC-113/ DuPont	Trichlorotrifluoro- ethane C <sub>2</sub> Cl <sub>3</sub> F <sub>3</sub>	Vapor degreasing	32	48	17	35	None	334
Methylene chloride/DuPont	CH <sub>2</sub> Cl <sub>2</sub>	Vapor degreasing	136	40	28.2	78.7	None	349
HCFC-141B/ DuPont	C <sub>2</sub> Cl <sub>2</sub> H <sub>3</sub> F	Vapor degreasing	56	32	19.3	52.3	None	593

\*Some boiling points are for concentrated solutions; \*\*at 25°C unless indicated; N/A – Not Available. (Source: Compiled from suppliers' technical data sheets.)

(cont'd.)

**Table 4.2. (Cont'd.)**

Product/ Supplier	Description	Application	Properties					
			Kauri- Butanol (KB) Value	Boiling Point*, °C	Surface Tension, dynes/cm	$\Delta H_{\text{vap}}$ cal/gm	Flash Point, °C	Vapor Pressure, mm**
HFC-4310/ DuPont	2,3- dihydrodecafluoro- pentane	Degreasing electronics and printed-circuit boards	14	55	14.1	31	None	226
Abzol® VG, EG, and JEG/ Albemarle	Alkyl bromide mixture	Degreasing electronics and printed-circuit boards, ionic contaminant removal	125	70–71	25.9	58.8	None	138
Vertrel® SMT/ DuPont	Vertrel XF with 1,2- dichloroethane, cyclopentane, and methanol	Vapor degreasing	N/A	37	15.5	53	None	471
Vertrel® XMS Plus/DuPont	Vertrel XF with 1,2 dichloroethane, cyclopentane, and methanol	Vapor degreasing	N/A	38	14.9	54	None	470
Zestron® FA/ Zestron	Modified alcohol	Ultrasonic, spray-under immersion, or centrifugal for low solids and rosin flux removal 40°C–45°C	N/A	162–228	28.5	N/A	73	0.17 (20°C)

\*Some boiling points are for concentrated solutions; \*\*25°C unless indicated; N/A – Not Available. (Source: Compiled from suppliers' technical data sheets.)

(cont'd.)

**Table 4.2. (Cont'd.)**

Product/ Supplier	Description	Application	Properties					
			Kauri- Butanol (KB) Value	Boiling Point*, °C	Surface Tension, dynes/cm	$\Delta H_{\text{vap}}$ cal/gm	Flash Point, °C	Vapor Pressure, mm**
Zestron® VD/ Zestron	Modified alcohol	Flux residue and SMT adhesive removal 40°–45°C (spray-in-air stencil cleaning)	N/A	170–175	27.9	N/A	62	0.76 (20°C)
Zestron® SD 301/ Zestron	Modified alcohol cleaning agent	Solder paste and SMT adhesive removal from PWBs and stencils/screens	N/A	150–170	26.1	N/A	47	1.5 (20°C)
Zestron® SD 300/ Zestron	Modified alcohol cleaner	SMT or conductive adhesive cleaning in spray-in-air cleaners at ambient	N/A	120–150	24.9	N/A	41	4.7
Ionox® HC2 and FCR/ Kyzen	Synthetic alcohol formulation with low activator (FCR) and high activator levels (HC2)	Flux cleaning including high-temperature reflow fluxes (HC2)	N/A	N/A	N/A	N/A	N/A	N/A
Micronox® MX 2301/ Kyzen	Hybrid synthetic alcohol and aprotic solvent blend	Aggressive flux removal	N/A	N/A	25–35	N/A	N/A	N/A

\*Some boiling points are for concentrated solutions; \*\*25°C unless indicated; N/A – Not Available. (Source: Compiled from suppliers' technical data sheets.)

(cont'd.)

**Table 4.2. (Cont'd.)**

Product/ Supplier	Description	Application	Properties					
			Kauri- Butanol (KB) Value	Boiling Point*, °C	Surface Tension, dynes/cm	$\Delta H_{\text{vap}}$ cal/gm	Flash Point, °C	Vapor Pressure, mm**
AK 225/ Asahi Glass Co.	Dichloropenta- fluoropropane (C <sub>3</sub> F <sub>5</sub> HCl <sub>2</sub> )	Vapor degreasing, flux removal	31	54	16.2	35	None	285
AsahiKlin AK-225 FPL/ Asahi Glass Co.	AK-225 and fluorocarbon cleaning solvents	Cleaning processes compatible with plastics	13	58	14.0	34.9	None	N/A
AsahiKlin AK-225 AES/ Asahi Glass Co.	Azeotrope with ethanol	Substitute for CFC- 113/alcohol systems	41	52	16.8	40.6	None	291
AsahiKlin AK-225 ATE/ Asahi Glass Co.	AK-225 and trans 1,2- dichloroethylene and ethanol	Demanding defluxing applications such as hybrid microcircuit cleaning and alternate to 1,1,1 trichloroethane	115	44.6	20.2	56.9	None	N/A
AsahiKlin AK-225DH/ Asahi Glass Co.	AK-225 and drying agent	Replacement for "Freon" TDF for spot-free drying after aqueous cleaning	31	54	16.3	34.6	None	N/A
*Some boiling points are for concentrated solutions; **25°C unless indicated; N/A – Not Available. (Source: Compiled from suppliers' technical data sheets.)								

(cont'd.)

**Table 4.2. (Cont'd.)**

Product/ Supplier	Description	Application	Properties					
			Kauri- Butanol (KB) Value	Boiling Point*, °C	Surface Tension, dynes/cm	$\Delta H_{\text{vap}}$ cal/gm	Flash Point, °C	Vapor Pressure, mm**
AsahiKlin AK-225T/ Asahi Glass Co.	AK-225 AES and cyclohexane	Removes rosin-blend fluxes while preventing white residue formation	63	54	17.6	47.2	None	427 (37°C)
HFE-7100/ 3M Co.	Methoxy- nonafluorobutane	Co-solvent or neat vapor degreasing	10	60	14.0	30	None	210
HFE-7200/ 3M Co.	Ethoxy nonafluorobutane	Neat, co-solvent or azeotrope in vapor-degreasing applications	10	78	13.6	30	None	109
HFE-71DE/ 3M Co.	Nonafluorobutyl ether azeotrope with trans 1,2- dichloroethylene	Immersion or vapor-degreasing applications (medium duty)	27	41	16.6	48	None	383
HFE-71IPA/ 3M Co.	Hydrofluoroether azeotrope with isopropanol	Light-duty cleaning and degreasing applications	33	40	16.4	50.0	None	381

\*Some boiling points are for concentrated solutions; \*\*25°C unless indicated; N/A – Not Available. (Source: Compiled from suppliers' technical data sheets.)

(cont'd.)

**Table 4.2. (Cont'd.)**

Product/ Supplier	Description	Application	Properties					
			Kauri- Butanol (KB) Value	Boiling Point*, °C	Surface Tension, dynes/cm	$\Delta H_{\text{vap}}$ cal/gm	Flash Point, °C	Vapor Pressure, mm**
HFE-71DA/ 3M Co.	HFE-7100 with trans 1,2- dichloroethylene and ethanol (azeotrope)	Vapor degreasing, flux removal	33	41	16.4	50	None	N/A
HFE-72DA / 3M Co.	HFE-7100, HFE- 7200, with trans 1,2- dichloroethylene and isopropanol	Medium to heavy-duty immersion and vapor- degreasing, flux removal	58	44	18	59.8	None	N/A

\*Some boiling points are for concentrated solutions; \*\*25°C unless indicated; N/A – Not Available. (Source: Compiled from suppliers' technical data sheets.)

*Thermal-phase cleaning*, also known as *microphase cleaning* (MPC<sup>®</sup>, a trademark of Zestron Corp.), is yet another variation of aqueous cleaning.<sup>[3]</sup> The thermal-phase cleaner consists of water to which is added a material such as a modified alcohol that is fully miscible at room temperature. Heating the clear solution, typically to 40°C–50°C, separates the organic alcohol as a turbid mixture of fine droplets suspended in water. The phase transition that occurs produces a mixture that exhibits the properties of both solvent and water-based cleaners, thus it is capable of dissolving both ionic and nonpolar residues. The onset of the phase change can be tailored by changing the composition of the mixture; thus, increasing the percent of alcohol increases the temperature at which phase change occurs. Thermal-phase cleaners may be used as a drop-in replacement in most equipment designed for liquid cleaning including spray and ultrasonic equipments.<sup>[4]</sup> Some reported test results comparing the efficiency of thermal-phase cleaning with conventional cleaners are given in Table 4.3.<sup>[3]</sup>

Aqueous cleaners should be used with caution when cleaning assemblies that contain highly polar polymeric materials or thin-film metallization. Plastic materials such as epoxy-glass or polyimide-glass laminates, used extensively for circuit boards, absorb moderate-to-high amounts of water which, if not subsequently baked out, degrade the adhesion strength of bonded components. Moisture retention also contributes to various corrosion and electrical failure mechanisms, including leakage currents, electrical opens and shorts, silver migration, and copper migration (conductive anodic filaments or CAF).<sup>[5]</sup>

Retention of moisture in polymer substrates or adhesives, especially in the presence of chloride or other ions, corrodes thin-film metallization such as nichrome resistors or aluminum conductors (further discussed in Ch. 6). Other limitations in using aqueous or semi-aqueous solvents include:

- Solutions must be heated to accelerate removal of contaminants.
- Solutions may have to be agitated, brushed, sprayed with pressure, or exposed to ultrasonics to improve their cleaning efficiency.
- Co-solvents are required to remove contaminants having a high organic content (oils, greases, fluxes).
- Bath lives are short and require monitoring, replenishment, and filtering.
- Expended solutions must be neutralized prior to disposal.

**Table 4.3.** Test Results for Thermal Phase vs. Conventional Cleaners\*<sup>[3]</sup>

<b>Material</b>	<b>Thermal Phase Cleaner with Saponifier</b>	<b>Neutral Thermal Phase Cleaner</b>	<b>Alcohol with Organic Saponifier</b>	<b>Inorganic Saponifier</b>	<b>Deionized Water</b>
No-clean flux (Interflux 2005M)	0.28	0.28	0.35	0.44	0.40
Water-soluble paste (Heraeus F530)	0.28	0.54	0.56	0.58	0.31
No-clean rosin-based paste (Heraeus F380)	0.29	0.33	0.28	0.49	0.28

\*In  $\mu\text{g NaCl}/\text{cm}^2$ . A value of 0.28 is baseline for an uncontaminated bare board.

Table 4.4 lists commercial cleaning solutions currently used in the electronics industry for cleaning printed-circuit boards, assemblies, ceramic printed circuits, thick-film interconnect substrates, electronic components, wiring harnesses, and stencils and screens (used in applying adhesives and solder pastes).

**Measuring solvency and cleaning ability.** An important consideration in selecting solvents or solvent-based cleaners is their solvent-cleaning abilities, which may be predicted or experimentally measured by several methods. In comparing hydrocarbon solvents for their effectiveness in dissolving residues, several tests may be used. One, the Kauri-Butanol (KB) test, is widely used to quantify solvent behavior and to rank the potencies of solvents.<sup>[6]</sup> The *Kauri-Butanol value* is the maximum amount of solvent that can be added to a stock solution of kauri (a fossil copal resin) in butanol before cloudiness occurs. Kauri resin is readily soluble in butanol, but only slightly soluble in hydrocarbon solvents. The resin-butanol solution will accept only a certain amount of the solvent before precipitation of the kauri resin occurs, as indicated by a cloudy appearance. Strong solvents such as toluene can be added in larger amounts (higher KB value) than weaker solvents such as hexane. In general, the higher the KB value, the better the solvent's cleaning ability.<sup>[7]</sup> The solvency of cleaning materials varies from neat (unmixed) solvents (KB values, approx. 10) to azeotropes (KB = 27 to 33) to co-solvents (KB > 150) (Fig. 4.1). These solvents are able to remove light flux, rosin mildly activated (RMA) flux, and "no-clean" flux, respectively. Examples of azeotrope solvents used in cleaning electronic circuits include hydrochlorofluorocarbons with ethanol (for example, Asahi AK 225AES) and hydrofluoroethers with ethanol and 1,2-dichloroethylene (for example, 3M Co. HFE-71DA). Azeotropes are very efficient solvents when used in a vapor degreasing process (see Sec. 4.1.2) and widely used for cleaning flip-chip assemblies, hybrid microcircuits, multichip modules, and other fragile assemblies.<sup>[8]</sup> Kauri-Butanol values for some solvents and cleaners are listed and compared in Table 4.5. Values for other cleaners may be found in Table 4.2.

Solvency and cleaning ability may also be evaluated as a function of density, viscosity, and surface tension. The lower the viscosity and surface tension and higher the density, the better the wettability, hence the ability to dissolve and remove residues. Surface tension is a measure of the penetrating power of a solvent; low surface tension solvents are better able to penetrate and wet tight spacings. The surface tensions of non-linear alcohols are typically low (20–22 dynes/cm) whereas that of water is high (72.8 dynes/cm).

**Table 4.4.** Aqueous and Semi-aqueous Cleaning Solutions

Product/ Supplier	Description	Application	Properties				
			Boiling Point* (°C)	Viscosity (cps, 25°C)	Surface Tension (dynes/cm)	Flash Point (°C)	Vapor Pressure** (mm)
Axarel® 32/ Petroferm	Semiaqueous defluxer; mixed aliphatic hydrocarbons, diisobutyl dibasic acid ester mixture, and Alkyloxy polyethylene oxyethanol (KB value = 64)	Removal of ionic contamination and residual rosin when used with water rinsing	N/A	2.8	N/A	96	<0.1
Axarel® 36/ Petroferm	Semiaqueous defluxer; mixed aliphatic hydrocarbons, diisobutyl dibasic acid ester mixture	Applications requiring easier water rinsing	N/A	2.8	N/A	96	<0.1
Axarel® 46/ Petroferm	Semiaqueous defluxer; mixed aliphatic hydrocarbons, diisobutyl dibasic acid ester mixture, and alkyloxy polyethylene oxyethanol	High performance solvent cleaning for batch or in-line process	N/A	2.8	N/A	96	<0.1
Axarel® 125/ Petroferm	Aqueous blend of linear alcohols	Aqueous defluxer (<25% in water) for a wide range of solder flux removal	N/A	6.0	N/A	102	<0.03 (20°C)
Axarel® 2200/ Petroferm	Isoparaffinic hydrocarbons and 1-propoxy-2-ethanol (KB value >150)	Immersion cleaning	N/A	1.9	N/A	44	5
Axarel® 2300/ Petroferm	Propylene glycol ether-based cleaning agent (KB value >150)	Solder paste and adhesive removal (20%–30% in water) from stencils and misprints	N/A	3	N/A	62	0.5 (20°C)

\*Some boiling points are for concentrated solutions; \*\*25°C unless indicated; N/A – Not Available. (Source: Compiled from suppliers' technical data sheets.)

(cont'd.)

**Table 4.4. (Cont'd.)**

Product/ Supplier	Description	Application	Properties				
			Boiling Point* (°C)	Viscosity (25°C)	Surface Tension, dynes/cm	Flash Point (°C)	Vapor Pressure** mm
Hydrex® AC/ Petroferm	Aqueous solution of ethoxylated, propoxylated secondary alcohol and polyoxypropylene-polyoxyethylene block copolymer	Stencil cleaning (43°C–49°C), with ultrasonics, 10% solution in water	N/A	1 (approx.)	N/A	None	>1 (estimated)
Hydrex® A-plus/ Petroferm	Aqueous solution of dipropylene glycol n-butyl ether and polyoxypropylene-polyoxyethylene block copolymer	Stencil cleaning (24°C–47°C), with ultrasonics, 10% solution in water	N/A	1 (approx.)	N/A	None	>1 (estimated)
Hydrex® SP/ Petroferm	Dipropylene glycol n-butyl ether and polyoxypropylene-polyoxyethylene block copolymer	Stencil misprint spray stencil clean (10% in water), 24°C–60°C or defluxing (5%–10% in water)	N/A	1 cps (in use)	N/A	105 (of concent rate)	>1 (estimated)
Hydrex® WS/ Petroferm	Methyl ethoxy, methoxy propanol in water	Stencil cleaning (24°C–60°C), with ultrasonics	N/A	1 cps (in use)	N/A	105 (of concent rate)	>1 (estimated)
Hydrex® DX/ Petroferm	Ethoxylated polyoxypropylene, sodium xylene sulfonate, and surfactant blend in water	Ultrasonic/heated (24°C–49°C), 10% in water	N/A	1 cps (in use)	N/A	105 (of concent rate)	>1 (estimated)

\*Some boiling points are for concentrated solutions; \*\* 25°C unless indicated; N/A – Not Available. (Source: Compiled from suppliers' technical data sheets.)

(cont'd.)

**Table 4.4. (Cont'd.)**

Product/ Supplier	Description	Application	Properties				
			Boiling Point* (°C)	Viscosity (25°C)	Surface Tension, dynes/cm	Flash Point (°C)	Vapor Pressure** mm
Vigon® SC/ Zestron	Neutral pH microphase cleaner (water based)	Cleaning PWAs; adhesive and solder paste removal from misprinted PCBs	98	N/A	34.6 (20°C)	None	23.8 (20°C)
Vigon® SC 200/ Zestron	Neutral pH microphase cleaner (water based)	Cleaning PWAs; adhesive and solder paste removal from misprinted PCBs	95–212	N/A	29.8 (20°C)	None	13.6 (20°C)
Vigon® SC 202/ Zestron	Microphase cleaner (water based)	Cleaning PWAs; adhesive and solder paste removal from misprinted PCBs	95–212	N/A	29.8 (20°C)	None	13.6 (20°C)
Atron® SP 200/ Zestron	Aqueous surfactant cleaner	Removal of baked-on flux (5%–20% in water)	110–174	N/A	32.0	None	N/A
Aquanox® A 4000/ Kyzen	Kyzen alcohol and mild saponifier (concentration range: 15%–30%)	Removal of no-clean fluxes in tight spacings such as µBGA (operating range: 49°C–71°C)	109–113	N/A	20–30	N/A	N/A
Aquanox® A 4402/ Kyzen	Aqueous emulsion cleaner (concentration range: 15%– 30%)	Ultrasonic stencil cleaning and mis- print adhesive and solder paste removal (operating range: 40°C–49°C)	N/A	N/A	18–28	N/A	N/A
Aquanox® A A4512/ Kyzen	Concentrated agent for aqueous cleaning	Batch or in-line spray removal of many flux residues and uncured adhesive (5%–20% concentration range, operating range: 49°C–71°C)	99–101	N/A	N/A	N/A	N/A

\*Some boiling points are for concentrated solutions; \*\*25°C unless indicated; N/A – Not Available. (Source: Compiled from suppliers' technical data sheets.)

(cont'd.)

**Table 4.4. (Cont'd.)**

Product/ Vendor	Chemistry	Application	Properties				
			Boiling Point* (°C)	Viscosity (25°C)	Surface Tension (dynes/cm)	Flash Point (°C)	Vapor Pressure** (mm)
Ionox® FCR/Kyzen	Semi-aqueous (95% alcohol and 5% water, activator, and surfactant)	Removal of difficult flux residues from electronics in dipping, immersion, centrifugal, and ultrasonic cleaning systems	178	N/A	Low	N/A	0.2
Ionox® I3330/ Kyzen	Synthetic alcohol, buffered	Batch, in-line, and ultrasonic removal of difficult soldering fluxes and assembly residues (undiluted, operating range 49°C–60°C)	177–181	N/A	22–32	N/A	N/A
Micronox® MX2301/ Kyzen	Semi-aqueous blend	Defluxing semiconductor wafer bumps in flip-chip, chip scale, and micro BGA applications	191–195	N/A	25–35	82	N/A
Lonox® L 5005/ Kyzen	10%–17% operating concentration	Removal of a broad range of paste residues, even at room temperature; compatible with organic solder protectant (OSP) coatings (operating range: 26°C–60°C)	103–107	N/A	18–28	N/A	N/A
Lonox® L 5020/ Kyzen	Saponifier (concentration range: 5%–10%)	Removal of a broad range of solder paste residues (operating range: 49°C–71°C)	114–118	N/A	N/A	N/A	N/A

\*Some boiling points are for concentrated solutions; \*\*25°C unless indicated; N/A – Not Available. (Source: Compiled from suppliers' technical data sheets.)

HFE 7100 Neat Cleaning	HFE 71DA Azeotropic Cleaning	HFE 7100/SA24 Co-solvent Cleaning
<b>Solvency (KB Value):</b>		
10	27 to 58	> 150
<b>Soils Removed:</b>		
Light Oils Halogenated Compounds Particulates Release Agents Hydraulic Fluids Light Flux	Medium Weight Oils Lubricants Low m.p. Waxes Polishing Fluids Buffing Compounds RMA Flux	Heavyweight Oils Greases Waxes No-clean Flux
<b>Parts Cleaned:</b>		
Gyroscopes Diskette Shutters	Flip Chip Assemblies Optical Components	Printed Circuit Boards Electrical Connectors

**Figure 4.1.** Relative solvency of 3M Co.'s Novec<sup>®</sup> hydrofluoroether cleaning solvents. (Copyright 2000, 3M Co., reproduced with permission.)

**Table 4.5.** Kauri-Butanol Values for Several Cleaning Solvents

Solvent	Description	KB Value
Perchloroethylene	$C_2Cl_4$	90
Trichloroethylene	$C_2HCl_3$	129
Methylene chloride	$CH_2Cl_2$	136
CFE-113	Trichlorotrifluoroethane	32
1,1,1-TCA	1,1,1- Trichloroethane	124
ABZOL <sup>®</sup> cleaner/Albemarle	Alkyl bromide mixture	125
AK-225/Asahi Glass Co.	Dichloropentafluoropropane	31
DC-OS-10/Dow Corning	Hexamethyl disiloxane	17
HFE-7100/3M Co.	Perfluorobutylmethyl ether	10
Vertrel <sup>®</sup> XF/DuPont	Decafluoropentane	9
Lenium <sup>®</sup> ES/Petroferm	n-Propylbromide with IPA	>150

Sources: Supplier data sheets and *CRC Handbook of Solubility Parameters and Other Cohesion Parameters*, 2<sup>nd</sup> Ed., (A. Barton, ed.), CRC Press (1991).

The surface tension, viscosity, and density of a solvent are related by a figure of merit called the *wetting index* (WI). The WI is proportional to the density of the solvent and inversely proportional to the viscosity and surface tension as follows:

$$\text{Eq. (4.1) } WI = (\text{density})(1,000)/(\text{viscosity})(\text{surface tension})$$

The higher the value of WI, the better the solvent will penetrate into tight spaces and remove contaminants. Representative values of wetting indices for several solvents are given in Table 4.6.<sup>[9]</sup> The effect of solvency in removing tenacious residues such as solder fluxes has been extensively studied. The removal of flux residues using a hydrofluoroether azeotrope (3M Co. HFE-71DA) versus a co-solvent (3M Co. HFE-7100 blend with Solvating Agent 24 from Petroferm) is compared in Fig. 4.2.<sup>[8]</sup> Residual ionic extracts from PWBs that were soldered using various fluxes then cleaned with the two solvents showed that the cleaning ability of the azeotrope was comparable to that of the co-solvent.

In addition to selecting an efficient solvent, manufacturers must now contend with environmental and safety regulations imposed by federal, state, and county jurisdictions. Solvents must meet volatile organic compounds (VOC) limits and, of course, there are also toxicity and flammability hazards that have to be addressed.

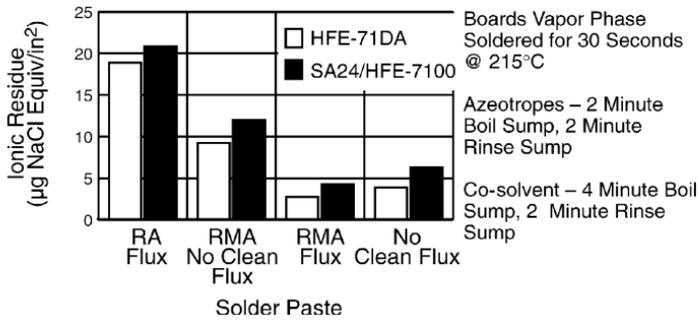
### 4.1.2 Cleaning Methods

Cleaning methods may involve solvents or cleaning solutions (wet types) or gaseous plasmas (dry types), a general comparison of which is shown in Table 4.7. Widely used wet-type cleaning processes include vapor degreasing, spraying, immersion with agitation (ultrasonic cleaning), immersion without agitation, and centrifugal cleaning.

**Vapor degreasing.** Vapor degreasing involves the vaporization of a solvent or an azeotrope and its condensation as a liquid onto the part, thus flushing the part with freshly distilled solvent. The part is cleaned with freshly distilled solvent until its temperature increases to the temperature of the vapor. Dissolved residues are carried with the condensed liquid back into the sump. Vapor degreasers have been widely used for over 40 years to clean fragile electronic assemblies. The process is benign and efficient since the vapors penetrate spaces that are inaccessible using other cleaning methods. The very low viscosity and low surface tension of vapor-phase solvents

**Table 4.6.** Comparison of Wetting Indices of Solvents<sup>[9]</sup>

<b>Solvent</b>	<b>Name/Supplier</b>	<b>Density, gm/cm<sup>3</sup></b>	<b>Surface Tension, dynes/cm</b>	<b>Viscosity, Pa.s</b>	<b>Wetting Index</b>
CFC-113	Freon <sup>®</sup> TF/DuPont	1.48	17.3	0.70	122
Isopropanol	IPA	0.79	21.7	2.4	15
Deionized water	Deionized water	0.997	72.8	1.00	14
Deionized water + surfactant	Deionized water + surfactant	0.998	29.7	1.08	31
Hydrofluorocarbon (HFC)	Vertrel <sup>®</sup> XF/DuPont	1.58	14.1	0.67	167
Hydrofluorocarbon (HFC)	Vertrel <sup>®</sup> XP/DuPont	1.53	14.2	0.68	158
Hydrochlorofluorocarbon	HCFC-141B/DuPont	1.24	19.3	0.43	149
Hydrofluoroether	HFE-7100/3M Co.	1.50	13.6	0.61	181
Hydrofluoroether	HFE-7200/3M Co.	1.43	13.6	0.61	172



**Figure 4.2.** Residual ion-extract analysis of PCBs cleaned with co-solvent HFE-7100/SA24 and with azeotrope HFE-71DA.<sup>[8]</sup> (Copyright 2000, 3M Co., reproduced with permission.)

**Table 4.7.** Comparison of Wet and Dry Cleaning Media

Cleaning Medium	Advantages	Limitations
Organic solvents	Remove adhesive and solder paste residues; have a wide-process window; can clean at room temperature; do not oxidize or corrode metals	Solvents and solvent vapors may be flammable; high cost; may be slow drying; limits on VOCs and ozone-depleting solvents (ODSs); require explosion-proof equipment
Aqueous alkaline cleaners	Relatively inexpensive; nonflammable; no ODSs or VOCs; mild odor	Do not remove adhesive residues; short bath life; narrow-process window; require an aqueous rinse and drying
Aqueous micro-phase cleaners (MPC)	Remove adhesive residues; wide-process window; nonflammable; rapid drying; long bath life	Require agitation (spray, ultrasonic, spray under immersion and overflow)
Plasma cleaning	Dry process (no solvents or chemical solutions); active oxygen plasma is an aggressive cleaner for organic residues; effective in removing adhesive bleedout	Electron-free plasma is required to avoid damage to sensitive components; cleaning surfaces with plasma prior to adhesive cure enhances bleedout

allow penetration into all areas of fine-pitch and low-standoff components. Vapor degreasing is very effective in cleaning hybrid microcircuits, multichip modules, and flip-chip assemblies. Azeotropes of both polar and nonpolar solvents are used to remove both ionic contaminants and greases and oils. Examples of some vapor-degreasing equipment and applications are listed in Table 4.8. Many vapor degreasers are equipped with a spray wand so that the parts may be sprayed with fresh liquid solvent after removal from the condensation portion of the equipment. Some of the many advantages of vapor degreasing are the following:

- No cleaning solutions to mix, maintain, or dispose.
- Solvent is reclaimed automatically within the unit; solvent waste is minimal.
- Process is simple with few variables to manage, and operator independent.
- Relatively low equipment, operation, and maintenance costs.

Some disadvantages include:

- Flammability and toxicity of some solvents require containment and safety features for the equipment.
- Many of the most efficient solvents are being disallowed by federal and local regulations because of their high VOC and ozone-depleting properties. Even some of the new replacement solvents may be phased out in the future.
- Vapor degreasers are becoming more expensive because of the added features required to prevent solvent evaporation into the air.

**Spray cleaning.** Spray-wash systems are primarily used to clean printed-wiring boards. Equipment consists of several zones including pre-wash, wash, drag-out, heated rinse, and final rinse followed by multiple drying zones.<sup>[10]</sup> Drag-out or isolation zones are designed to minimize contamination of the rinse water from the cleaning chemicals. A list of spray/wash equipment, manufacturers, and applications is given in Table 4.9.

Spraying may be conducted at relatively low pressures of 50 psi or at high pressures up to 1,000 psi. Pressures must be adjusted so that fragile assemblies such as fine wires and wire bonds are not damaged. Parts cleaned in immersion systems are usually rinsed with fresh solvent and the solvent then is recycled by filtering and/or distilling.

**Table 4.8.** Examples of Vapor Degreasers and Ultrasonic Cleaning Equipment

Supplier	Equipment Model No.	Application	Solvents/Cleaners		
			Aqueous	Semi-aqueous	Solvent
Branson	EVD-80	Vapor degreaser; cylindrical process chamber with vacuum (low emissions)	N/A	N/A	HCFCs, HFCs, HFES, NPB*, and chlorinated solvents
	LED series	Ultrasonic vapor degreaser; conductive drying/reduced emissions (high volume production)	N/A	N/A	HCFCs, HFCs, HFES, NPB*, and chlorinated solvents
	B-452R	Full-featured degreaser (high to intermediate volume production)	N/A	N/A	HCFCs, HFCs, HFES, NPB*, and chlorinated solvents
	BTC-200	Process-development tool	N/A	N/A	HCFCs, HFCs, HFES, NPB*, and chlorinated solvents
	Benchmark series	Ultrasonic cleaning (20–800 kHz)	Alkaline, acid and water dilutable cleaning solutions	Terpene, hydrocarbon alcohol-based semi-aqueous cleaning solutions	N/A

\*n-propylbromide; N/A – Not applicable.

(cont'd.)

**Table 4.8. (Cont'd.)**

Supplier	Equipment Model No.	Application	Solvents/Cleaners		
			Aqueous	Semi-aqueous	Solvent
Crest Ultrasonics	Optimum Console™	Ultrasonic cleaning (28–192 MHz), automotive, aerospace, optics, communications, and semiconductor; heavy soils, greases; cleaning to 1 µm	Water soluble chemistries (pH 2–12)	Terpene, hydrocarbon alcohol-based semi-aqueous cleaners	Engineered; combustible and flammable
Austin America	X30A	No Clean (NC), water soluble (WS) paste, flux, and adhesive aqueous cleaning, air-knife drying standard (vortex dryer for complete drying); PCB/stencil switch and water-knife option; stencils, boards	Water, aqueous mixtures (saponifier, detergent)	Nonflammable water mixture/emulsions Aquanox and Ionox (Kyzen), Hydrox and Hydrex® DX (Petroferm)	Megasolv® NOC; Axarel® 2200, 46, and 32; Ionox, isopropanol
	X30	WS paste cleaning only; stencils, boards	Water only	N/A	N/A
	X30C	NC paste, NC flux, and adhesive removal; stencils, boards	N/A	Solvent/semi-aqueous	Single solvent
	X30F	NC paste removal; stencils, boards	N/A	Same as X30A	Flammable
*n-propylbromide; N/A – Not applicable.					

**Table 4.9.** Spray/Wash Cleaning Equipment

Supplier	Equipment Model No.	Application	Solvents/Cleaners		
			Aqueous	Semi-aqueous	Solvent
Austin America	X30A	No-clean (NC), water-soluble (WS) paste, flux, and adhesive aqueous cleaning, air knife drying standard (Vortex dryer for complete drying). PCB/stencil switch and water-knife option; stencils, boards	Water, aqueous mixtures (saponifier, detergent)	Nonflammable water mixture/emulsions Aquanox and Ionox (Kyzen), Hydrox and Hydrex® DX (Petroferm)	Megasolv® NOC; Axarel® 2200, 46, and 32; Ionox, isopropyl alcohol
	X30	WS paste cleaning only; stencils, boards	Water only	N/A	N/A
	X30C	NC paste, NC flux, and adhesive removal; stencils, boards	N/A	Solvent/semi-aqueous	Unmixed solvent
Aqueous Technology	SMT 600-CL	Aqueous cleaning and water soluble (OA*) defluxing for SMT applications, -25°C to 49°C	Water only	N/A	N/A
	SMT 600-LD	Water soluble (OA), rosin (RA, RMA, and R)** flux and no-clean flux; temperatures -5°C to 77°C	PCB-wash	N/A	N/A
	Millennium	In-line aqueous cleaning system for water soluble (OA) defluxing for high throughput SMT	Water only	N/A	N/A
	AQ-201SC	Semi-automatic ultrasonic (40 kHz) stencil-cleaning system for solder paste and adhesives; removes rosin (R, RMA, and RA), water-soluble (OA), and no-clean pastes	Stencil wash, stencil wash plus, stencil wash AD SMT, stencil cleaner	N/A	N/A
*Organic acid; **Rosin activated, rosin mildly activated, and rosin, respectively; N/A – Not Applicable.					

(cont'd.)

**Table 4.9. (Cont'd.)**

Supplier	Equipment Model No.	Application	Solvents/Cleaners		
			Aqueous	Semi-aqueous	Solvent
Speedline	Aquastorm® and H 500 series	In-line spray cleaning systems, plastic and stainless steel respectively; typical applications include PCB assemblies	Water soluble, saponified, compatible with aqueous detergents and deionized water	N/A	N/A
	Aquajet®	Spray semiautomatic batch-cleaning systems; typical applications include bare boards, stencils, misprints, pallets, and PCB assemblies	Water soluble, saponified, compatible with aqueous detergents and deionized water	Compatible with most combustible semi-aqueous solvents; EC7-R typical	N/A
	Microline®	High-volume, low-pressure in-line spray cleaning system for semiconductor packages and bumped wafers	Water soluble, saponified, compatible with aqueous detergents and deionized water	Compatible with most combustible semi-aqueous solvents, EC7-R typical	N/A
Smart Sonic	Model 1500	Stencil and pallet cleaning (29-in maximum, <2 minutes) for RA, ** RMA, ** no-clean synthetic and water soluble (OA)* solder paste (ambient), solder flux residue and SMD adhesives (32°C–43°C)	SMT detergent 440-R (10%–12%, 10%, 6%–12%, and 10%)	N/A	N/A
	Model 2003	RA, RMA, no-clean synthetic and water soluble (OA) solder paste (ambient), wet SMT adhesives, and solder flux residue (38°C–43°C, ultrasonics)	2%–10% SMT detergent 440-R	N/A	N/A
	Model 6000 and 6000 LC	Fully automatic and programmable SMT stencil cleaner [for RA, RMA, no-clean and water soluble (OA), adhesives and solder paste, 72-in. max.]	SMT detergent 440-R	N/A	N/A

\*Organic acid. \*\*Rosin activated, rosin mildly activated, respectively; N/A – Not Applicable.

(cont'd.)

**Table 4.9. (Cont'd.)**

Supplier	Equipment Model No.	Application	Solvents/Cleaners		
			Aqueous	Semi-aqueous	Solvent
Stoelting	Omnijet CBW-224: In-line, spray-in-air cleaning system; all stainless steel construction	PCB, SMT, and advanced-packaging applications including BGA and flip-chip cleaning	100% water or a mixture of water and chemical (saponifier, detergents, surfactants, etc.)	Compatible with all semi-aqueous cleaners (high or no flashpoint)	N/A
	Omnijet CBW-218: In-line, spray-in-air cleaning system; all stainless steel construction	PCB, SMT, and advanced-packaging applications including BGA and flip-chip cleaning	100% water or a mixture of water and chemical (saponifier, detergents, surfactants, etc.)	Compatible with all semi-aqueous cleaners (high or no flashpoint)	N/A
	Omnijet CBW-Advanced Packaging In-Line Aqueous Cleaning System (APILACS)	High-density circuit boards and ICs on a carrier in the semiconductor industry; alternative to centrifugal cleaning	100% water or a mixture of water and chemical (saponifier, detergents, surfactants, etc.)	Compatible with all semi-aqueous cleaners (high or no flashpoint)	N/A
N/A – Not Applicable.					

**Immersion cleaning/ultrasonic cleaning.** Immersion cleaning using aqueous or semi-aqueous cleaners is usually assisted by agitating the solvent bath and heating. Agitation may be provided by ultrasonics or by pressure spraying under immersion. The removal of misprinted uncured adhesive from printed-circuit boards is more difficult than the removal of solder paste and requires the aggressive cleaning provided by ultrasonics. Ultrasonic cleaning, after electronic devices have been assembled, can be damaging to devices and, if used, the level of energy must be controlled. Ultrasonic cleaning of unsealed hybrid microcircuits and multichip modules has caused fine 1-mil-diameter wires to break and glass diodes to crack.

**Centrifugal Cleaning.** Centrifugal-cleaning systems use centrifugal force to direct streams of solvents at parts in a rotating chamber. The centrifugal force ( $f$ ) is imparted to the cleaning solvent in a cylinder of radius  $r$  that is moving at an angular velocity ( $\omega$ ).

$$\text{Eq. (4.2)} \quad f = m\omega^2 r$$

Forces generated are 60 G for a 16-inch-radius chamber, and 100 G for a 24-inch-radius chamber. Because of these high G forces, fast cycle times are realized, for example, 0.5–2 minutes for the wash cycle, 1–2 minutes for the rinse cycle, and 2–3 minutes for the dry cycle.<sup>[11]</sup> Solvents may be heated to a maximum of 82°C in the wash cycle and to 60°C for rinsing. Examples of solvents used in centrifugal cleaning are: Axarel<sup>®</sup> (Petroferm), Bioact<sup>®</sup> EC-7R (Petroferm), Bioact EC-15 (Petroferm), Ionox<sup>®</sup> FCR (Kyzen), and Zestron<sup>®</sup> FC (Zestron Corp.). Centrifugal cleaning equipment is available from Speedline Technologies and Deflex Corp. (Table 4.10).

A variation of centrifugal cleaning is Deflex's SuperFuge<sup>®</sup> system in which centrifugal shear carbon dioxide is used instead of aqueous solvents. The very low surface energy of carbon dioxide (0–5 dynes/cm) provides high solvating power and penetration beneath tight-pitch, low standoff, and densely populated flip-chip devices and packages.<sup>[12][13]</sup> Centrifugal cleaning is especially effective in cleaning low-standoff parts such as chip-scale packages (CSP), BGAs, and flip-chip devices.<sup>[14]</sup> The major benefits are:

- High efficiency.
- High penetration of solvent at cleaning temperatures where viscosity and surface tension are low.
- High penetration of low-standoff parts because of directed flow.

**Table 4.10.** Centrifugal Cleaning Equipment

Manufacturer	Model	Application	Solvents/Cleaners		
			Aqueous	Semi-aqueous	Solvent
Speedline Technologies (a Cookson Electronics Company)	MicroCel® Centrifugal Cleaning System temperature ranges: wash 25°C–82°C; rinse 25°C–60°C; dry 25°C–204°C	Electronic circuit assemblies, hybrid circuits, MCMs, bumped wafers, and advanced packages such as flip chips, BGAs, and CSPs	Aqueous (water, detergents and saponifiers), Axarel® 36, and Armakleen®	Solvent/water and emulsions (Bioact® EC-7R and EC-15), Ionox® FCR and HC (aqueous alcohols), and Zestron® FC	Chlorocarbons, chlorofluorocarbons, and alcohol-based solvents and terpenes
Deflex, Inc.	SuperFuge® liquid and SCF* CO <sub>2</sub> cleaning systems SF-1000 and SF-1200	Quartz and ceramic substrates, flip-chip bonded parts, and semiconductor devices	N/A	Micronox® MC 2301	N/A
*Super-critical fluid; N/A – Not applicable.					

- Fast cycle times.
- Compatible with fragile substrates.
- Zero solvent discharge (closed-loop system).

**Plasma cleaning.** Plasma cleaning is a dry cleaning process that avoids the use of organic solvents or water solutions. Contaminant organic residues are oxidized and volatilized by subjecting them to a gaseous plasma produced by an RF energy source in oxygen or in an oxidizing gas such as sulfur hexafluoride. Oxide contaminants may also be removed by chemical reduction using a hydrogen plasma. Whether oxidizing or reducing gases are used, in practice, they are generally admixed with argon. Plasma cleaning may also be performed entirely in an inert-gas ambient, such as argon, where the interaction with contaminants is more a physical dislodging than a chemical reaction. Plasma cleaning of electronic assemblies prior to adhesive attachment or after attachment and curing has the following benefits:

- Clean, safe, and cost-effective process.
- Avoidance of organic solvents and the consequences of toxicity and air pollution.
- Generally fast cycle times.
- Commercially available equipment.
- Improved adhesion avoiding delamination in area-array packages.
- Enhanced adhesion for die-attachment adhesives.
- Void-free underfill (plasma is effective in penetrating tight gaps in high-density arrays, increasing surface energy, minimizing voids, and increasing underfill throughput).
- Removal of bleedout that occurs during curing of some epoxy adhesives.

Some limitations are the following:

- Removal of heavy residues requires long cycle times.
- RF energy may damage some circuit components such as bare chip ICs.
- Ultraclean surfaces may promote adhesive bleedout during adhesive curing; however, bleedout is easily removed by plasma cleaning after curing.

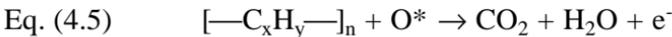
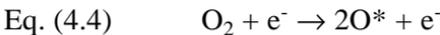
- Some discoloration of silver-filled adhesives may occur due to surface oxidation of the silver. This is considered more a cosmetic issue than a reliability problem; however, the tarnish can be removed by subsequent exposure to an argon plasma.

*Plasma-cleaning mechanisms.* Unlike solvent and aqueous-based cleaning, plasma cleaning is based on reactions with surface contaminants at the molecular or atomic level.<sup>[15]</sup> Two mechanisms are possible depending on the level of RF energy and the nature of the plasma gas.

1. An ablation mechanism similar to sand blasting whereby the surface is roughened and its area increased by the formation of peaks and valleys. This mechanism also dislodges surface particles and ionic or salt-like residues. Argon gas is usually used to form a high-energy plasma consisting of positively charged argon particles and electrons.<sup>[16]</sup>

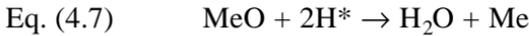


2. A chemical reaction whereby a gaseous plasma may either oxidize or reduce contaminants depending on the nature of the plasma used and the type of contaminant. To remove organic residues, such as oils, greases, silicones, and epoxies, the gas is typically a mixture of oxygen and argon. The oxygen is converted to an energized highly reactive form of monatomic oxygen that quickly oxidizes any organic residues converting them into volatile carbon dioxide and water as follows:



Typical plasma-cleaning conditions for removal of organic residues prior to wire bonding consist of 100 watts of RF power, 10–20 mTorr oxygen/argon pressure, and a 10-minute dwell time. During oxygen plasma cleaning, oxides may be formed on silver-filled conductive adhesives. These may subsequently be removed using a purely argon plasma.

To remove metal oxides or other inorganic oxide surface contaminants, a reducing gas such as a mixture of hydrogen and argon is used. In the RF plasma, hydrogen molecules dissociate into highly active hydrogen atoms that reduce the oxides to metal and water. Simultaneously, the argon plasma physically dislodges oxide and reduced oxide residues from the surface.



*Plasma-cleaning equipment.* Plasma equipment is extensively used for cleaning electronic parts and for etching surfaces to improve adhesion.<sup>[16]</sup> In its basic form, the equipment consists of a reaction chamber, a power supply, and a vacuum source. Parts are placed in the chamber and evacuated using the vacuum pump. A gas or mixture of gases is then introduced and the plasma generated by subjecting the gas to an RF frequency of 13.56 MHz and about 400 volts. Process and equipment parameters need to be well controlled since some semiconductor devices can be damaged by the electrons produced, especially if placed within the active plasma zone. However, equipment is now available that generates a down-stream plasma and has been modified so that electrons can be deflected from the part. Plasma-cleaning equipment ranges from small laboratory models having 6-inch diameter chambers to large-capacity production units. Glen Technologies' 1000P and R3A plasma cleaners are parallel-plate units that can be operated at 1,000 watts or 500 watts in both the active and electron-free plasma modes. The Glen-1000P-LMC equipment can clean multiple leadframes or devices loaded into magazines up to  $8 \times 16 \times 13$  inches. The horizontal flow of plasma gas through the magazines assures uniform cleaning. Equipment from March Instruments (a Nordson Co.) is reported to enable a user to process 500–1,000 leadframes per hour.<sup>[17]</sup> Commercially available equipment can be operated in three modes: active plasma for routine direct cleaning of surfaces, aggressive directional cleaning (reactive ion etching) for non-ESD sensitive parts, and downstream electron-free plasma for cleaning bare chip semiconductor devices and other electrically sensitive circuits.<sup>[16]</sup> The down-stream plasma is the most benign mode, capable of removing thin layers of residues 10–50 angstroms thick. Table 4.11 provides further detail for various commercially available plasma cleaners.

**Table 4.11. Plasma-Cleaning Systems<sup>[17][18]</sup>**

Manufacturer	Model	Application	Operational Parameters		
			Power (W)/ Frequency	Gases	Capacity
Glen Technologies/ Yield Engineering	Glen 1000P	Cleaning and surface modification of surfaces prior to bonding; downstream only (R3), active, RIE or electron-free (R3A, R24A, 1000P)	0–1,000/NA	All standard plasma gases (Ar, O <sub>2</sub> , H <sub>2</sub> , CF <sub>4</sub> , SF <sub>6</sub> , and any mix of above)	Four 16 × 16-in electrode sets arranged in Active, RIE or electron-free modes
	Glen R3A		0–500/NA		
	YES R3		0–500/NA		Two 12.75 × 12.75-in electrode sets arranged in downstream plasma mode
	Glen R4A		0–2,000/NA		Four 24 × 24-in electrode sets suitable for large substrates
	Glen 1000P–LMC	Cleaning of leadframes or devices contained in magazines. (active, RIE or electron-free)	0–1,000/NA		1–2 manually loaded magazines (up to 8 × 6 × 13-in)
March Instruments (a Nordson Company)	AP-1000	Contamination removal, surface activation, etch, and crosslinking	0–1,000/NA	Unlimited, typically Ar, O <sub>2</sub> , H <sub>2</sub> , N <sub>2</sub> , CF <sub>4</sub> , SF <sub>6</sub>	8 magazines, 20 leadframes/magazine (maximum)
	ITRAK		0–300/NA		1 strip/run, maximum part size: 2.75 × 9.25-in

(cont'd.)

**Table 4.11.** (Cont'd.)

Manufacturer	Model	Application	Operational Parameters		
			Power (W)/ Frequency	Gases	Capacity
March Instruments (a Nordson Company)	XTRAKM	Contamination removal, surface activation, etch, and crosslinking	0–600/NA	Unlimited, typically Ar, O <sub>2</sub> , H <sub>2</sub> , N <sub>2</sub> , CF <sub>4</sub> , SF <sub>6</sub>	1 strip/run, maximum part size: 6 × 12-in
	Multitrak				Up to 7 strips/run, maximum part size: 6 × 12-in
Plasma Etch, Inc.	Mark II	Desmear and etchback of PWBs	0–1,000 to 0–5,000/ 13.56 MHz	CF <sub>4</sub> , O <sub>2</sub>	6–24 panel loading (18 × 24-in) or custom 1¼-in shelf spacing
	Mark III	Microvia, directional etching	0–10,000 to 0–40 KW/ 40 kHz		8–32 panel loading (18 × 24-in) or custom 1¼-in shelf spacing
	BT-1	Surface activation and cleaning	0–600/13.56 MHz	O <sub>2</sub> , Ar, CF <sub>4</sub> , He, H <sub>2</sub> , N <sub>2</sub>	5 levels electrodes (20 × 20-in) 3-in shelf spacing

(cont'd.)

**Table 4.11. (Cont'd.)**

Manufacturer	Model	Application	Operational Parameters		
			Power (W)/ Frequency	Gases	Capacity
Plasma Etch, Inc.	PE-200	Surface activation and cleaning	0–300/ 13.56 MHz	Ar, O <sub>2</sub>	3 levels electrodes (13 × 13-in) 3-in shelf spacing
	TT-1 (Tunable)	Cleaning strips within magazines prior to wire bond	0–600/ 13.56 MHz		2 levels electrodes 7-in shelf spacing
	PE-2000 (Reel-to- Reel)	Continuous cleaning process	0–1,000/ 13.56 MHz	O <sub>2</sub> , Ar, CF <sub>4</sub>	Variable specs to meet customer requirements
	PE-1000	Automated in-line for cleaning bond pads		O <sub>2</sub> , Ar	Adjustable 1 level 1 to 16-in width × 51-in length

### 4.1.3 Methods for Testing and Assuring Cleanliness

Several quantitative and qualitative tests are used for qualification of a solvent/cleaning process and for in-line quality assurance. Some tests, like the water-drop spreading test, are quick and simple. In this test, a 2 to 4 microliter droplet of water is applied to a substrate, and the contact angle it makes with the surface is measured using a goniometer.<sup>[19]</sup> A contact angle of less than 40° indicates improved wetting and a relatively clean surface free of oily, nonpolar residues. In one study, 20-mm-square flip-chip devices having silicon nitride passivation had contact angles of 40° before cleaning. After cleaning in an oxygen plasma, the contact angle was reduced to 20°. This drastically reduced the flow-out time for the underfill adhesive from 60 seconds to 22 seconds, an important factor in increasing throughput of a production line.<sup>[20]</sup> In another study, after plasma cleaning copper, aluminum, and epoxy surfaces, the contact angles were reduced by 50%–74% (Table 4.12).<sup>[21]</sup> A silicon surface that is well cleaned and free of contaminants has a contact angle below 10° and results in considerable spreading of a water drop. When contaminated with hydrophobic residues, contact angles increase to 45°–90° and little or no spreading occurs. It should be noted, however, that the contact angle is useful only for determining the presence of grease-like or nonpolar residues. The presence of ions or hydrophilic residues will also give low contact angles and must be measured by other means. Colorimetric tests may also be used qualitatively to detect residues of organic materials.

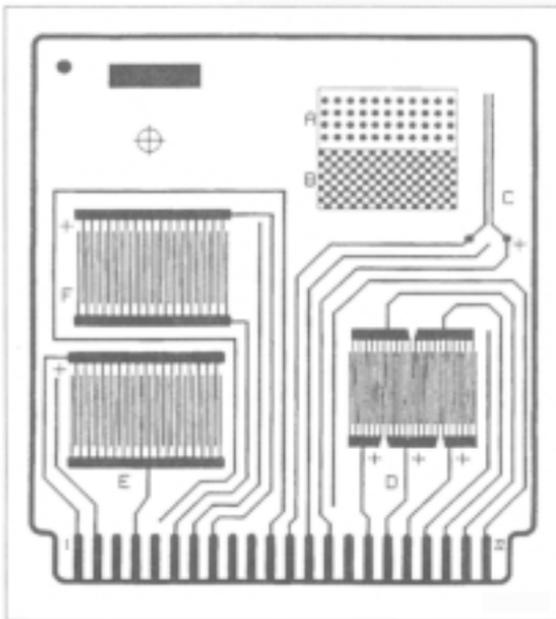
The test most widely used in the printed-circuit industry to measure the efficiency of a cleaning process is the resistivity of solvent extracts test known as ROSE. According to this test, after the assembly has been cleaned, the part is flushed with a solution of 75% isopropanol and 25% deionized water and the electrical resistivity of the extracts measured.<sup>[22]</sup> Ionic residues dissolved in the extracts reduce the resistivity of the original

**Table 4.12.** Effect of Plasma Cleaning on Contact Angles<sup>[21]</sup>

Surface	Contact Angle (°)	
	Before Plasma Cleaning	After Plasma Cleaning
Copper	88.4	31.7
Aluminum	64.5	32.0
Epoxy	85.0	22.0

solution. The resistivity is then correlated to total ionic residues removed and reported as equivalent to  $\mu\text{g}$  of  $\text{NaCl}/\text{cm}^2$ . Extraction methods may be manual, dynamic, or static. Stand-alone, modular equipment such as the Ionograph<sup>®</sup> or Omegameter<sup>®</sup> (Specialty Coating Systems, Cookson Electronics) are widely used in printed-board shops for periodic testing, but can also be integrated with the cleaning console for continuous monitoring. Although quantitative, the ROSE test measures only ionic or ionizable residues, not organic and nonpolar residues.

The level of surface cleanliness may also be evaluated by measuring the *surface-insulation resistance* (SIR) of a separate test pattern. The SIR test sample consists of an interdigitated comb pattern of conductor lines and spacings on a printed-circuit laminate representative of the actual circuit. The IPC B-25 or IPC B-24 test patterns (Fig. 4.3) are standard in the industry to evaluate the degree of cleanliness of a surface. If the test pattern is well cleaned and no ionic residues remain, the insulation resistances between conductor lines will be  $10^8$  ohms or greater and will not drop appreciably under moist ambients. If residues remain, leakage currents



**Figure 4.3.** Surface insulation resistance (SIR) test pattern (IPC B-25).

occur between conductor lines reducing the insulation resistance. The effects of ionic residues are dramatic when exposed to moisture where the ions are easily mobilized. Inadequate cleaning has been reported to cause a drop of seven orders of magnitude in SIR values in less than one-hour exposure to humidity.<sup>[23]</sup> As with ROSE, SIR is best used to evaluate the presence of ionic residues. Organic residues may remain on the surface and still give high insulation readings. Further information on SIR may be found in IPC-9201 *Surface Insulation Resistance Handbook*<sup>[24]</sup> and in IPC-TR-468, *Factors Affecting Insulation Resistance Performance of Printed Circuits*.<sup>[25]</sup> Minimum SIR values of  $10^{12}$  ohms may be required for some RF and high-speed circuits.

## 4.2 SURFACE TREATMENTS

In some cases, even the best solvent, cleaning process, and adhesive are not sufficient to produce a reliable bond. Chemically inert surfaces such as gold, other noble metals, and nonpolar plastics such as Teflon<sup>®</sup>, polyolefins, and parylene are extremely difficult to bond and require additional surface treatment besides cleaning. Roughening a gold-plated bonding pad lightly using an abrasive or scuffing the surface with an electric eraser have been found to increase the adhesive strength of epoxy adhesives. Surfaces may also be sputter etched or ion milled to remove surface contaminants and to physically etch the surface providing greater surface roughness and area for adhesives to wet and adhere.

Primers recommended by the adhesives supplier are also useful. Primers are generally not necessary for epoxies because of their high polarity and affinity for most surfaces. In fact, solvent-thinned epoxies have been used as primers to improve the adhesion of other polymer types. Primers are often required for one-part and two-part RTV silicone adhesives. Primers are low-solids, solvent-based, air-drying coatings that can be applied by spraying, brushing, dipping, or spin coating. Solvent solutions of various silanes are among the best primers.

Finally, chemical alteration of surfaces can improve adhesion. Semi-crystalline materials have low polarity and low surface tension that must be increased to enable adhesives to bond. Oxidizing processes such as corona discharge, plasma, flame treatments, or UV irradiation in the presence of air or oxygen may be used to alter normally nonpolar surfaces, rendering them

polar and increasing their wettability. Treating polymer surfaces in a plasma of reactive polar molecules results in chemically altering the surfaces rendering them more compatible with adhesives. For example, in an amine plasma such as allylamine, highly polar amine groups may be attached and chemically bonded to an otherwise non-wetting surface. Hydroxyl groups from an allyl alcohol plasma may also be grafted producing a more wettable surface for adhesives.<sup>[26][27]</sup>

Teflon and other fluorocarbon surfaces may be altered by chemical treatments using solvent solutions of sodium naphthalene complex or molten sodium. Teflon etchants, for example, Tetra-Etch<sup>®</sup>, a tradename and product of W. L. Gore Associates, are effective in improving adhesion to Teflon. Oxidation treatments for metals such as copper or aluminum also produce highly polar oxide surfaces that are more easily bondable.

### 4.3 ADHESIVE DISPENSING

Adhesive dispensing methods consist of either mass-transfer or selective dispensing. Stencil printing, screen printing, pin transfer, daub transfer, and stamping are examples of mass-transfer types. They are also referred to as tooling-related processes since hard tooling such as stencils and screens are required. In comparison, selective-dispensing methods are computer data driven, such as automated syringe or needle dispensing and jetting processes. Automated dispensing, currently used in over 80% of all production processes,<sup>[28]</sup> is a continuous process where individual adhesive dots, lines, or patterns are deposited in selected areas of an interconnect substrate using pressurized syringes or pumps. The main advantage of the data-driven processes is flexibility, accommodating a large variety of printed-circuit board types, configurations, and design changes. Selective dispensing is also the only method that can be used once components have been assembled onto a board since it does not require a flat surface as does screen or stencil printing.

Screen printing of conductive and insulative adhesives has been used for decades in the assembly of hybrid microcircuit and multichip modules. Since screen-printing processes are also used to deposit thick-film conductors, resistors, and dielectrics, the processes are fully compatible and cost effective in the production of hybrid microcircuits. Screen printing and stencil printing are both batch processes that are usually less expensive and

faster than selective dispensing for large production runs where few changeovers are expected. As an example, 1,000 dots can be stencil printed in 30 seconds compared to 1.5 minutes for a selective dispenser operating at 40,000 dots per hour.<sup>[28]</sup>

In surface mounting of components, both solder paste and adhesive need to be dispensed. The solder paste is usually screen printed or stenciled first, followed by selective dispensing of the adhesive between the solder pads. The prime function of surface-mount adhesives (SMAs) is to maintain the position of the components during subsequent reflow or wave soldering. The adhesives may be partially or fully cured prior to solder reflowing or may be cured in the same step as solder reflowing. With the trend toward mixed assembly technologies, such as solder-attached components on the same board as adhesive-attached devices, selective dispensing must be used. In such cases, the solder operations are conducted first since they require high temperatures and aggressive cleaning to remove flux residues. A summary of the advantages and limitations of the main dispensing methods is given in Table 4.13,<sup>[29][30]</sup> and a cross-reference of dispensing methods for general adhesive types is given in Table 4.14.

### 4.3.1 Screen Printing and Stencil Printing

Of the mass-transfer dispensing methods, screen printing and stencil printing are the oldest and most widely used. Screen printing has been used for over 40 years in the electronics industry to apply thick-film conductors, resistors, and dielectrics in fabricating circuits on ceramic and plastic-laminate substrates. Screen printing is also used as a batch process for depositing electrically conductive and insulative adhesives to interconnect devices on thin-film and thick-film hybrid microcircuits.

Screen printing is a simple, low-cost process for both small and large production runs. Patterns are formed on a stainless-steel mesh through a photosensitive emulsion process in which portions of the screen mesh are coated while other areas, through which the paste is to be deposited, are left open. The photolithographically formed screen patterns, however, wear out after many runs and the screens must be reprocessed or replaced. Also, separate screens are required for different circuit configurations, which presents a logistics problem in their storage, identification, and retrieval, especially where hundreds of part types are to be fabricated.

**Table 4.13.** Advantages and Limitations of Adhesive Dispensing Methods

Type	Description	Advantages	Disadvantages
Pin transfer	Surface mount, hybrid, or MCM/bed-of-nails tooling	Very fast, consistent	Difficult/expensive retooling; adhesive handling issues
Stamp transfer	Single, variable surface area tooling for adhesive pickup	Excellent in high-speed applications, Allows large areas to be bonded in a single application	Tooling intensive; adhesive handling issues
Screen, stencil printing	Surface mount, hybrid, or MCM/stencil or screen printer	Fast, multiple dot size, Dots as small as 3-mils diameter on 5-mil pitch can be printed	Stencil printing requires a new stencil per design; complex cleaning procedures for small aperture stencils; cannot be used with other components on boards
Automated dispensing	Time/pressure dispensing	Data-driven process, rates to 50,000 dph, flexible, simple operation, and easy cleanup	Higher speeds result in less consistent dots
	Auger	Data-driven process, flexible, handles wide range of adhesives, improvement over time/pressure	Sensitive to viscosity changes; some effect of speed on consistency
	Piston pump	Data-driven process, Viscosity changes do not affect flow rate; consistency at higher speeds; capable of larger dot sizes	Complex cleaning procedures; sensitive to air in fluid
Jet dispensing	SMT adhesive using a spring loaded pin or hammer to rapidly cycle adhesive through the nozzle)	10%–50% increase in dph relative to auger and piston pumps, yields higher dot profile, noncontact, less sensitive to warpage or dispense height variations, dispensing rates up to 70,000 dph, no tailing	Single dot size, complex cleanup, limited material selection
Preform/Tape bonding	Chip-on-board, hybrid or MCM, single-chip (standard and lead-on-chip)	Eliminates fluid dispensing, good thickness control	Requires die-cut preforms or manual processing

**Table 4.14.** Cross-reference of Dispensing Methods and Materials<sup>[30]</sup>

Material	Process						
	Needle	Fluid Jet	Stencil Print	Screen Print	Pin Transfer	Stamp Transfer	Film Bond
Insulative die-attach paste	XX	X	X	X	X	X	
Isotropic die-attach film							XX
Anisotropic die-attach film							XX
Isotropic paste	X		XX	X		X	
Anisotropic paste	X	X	X	XX		X	
Underfill	XX	X	X	X			
XX = Preferred. (Copyright ©1996 PennWell Corporation. Reproduced by Permission.)							

Stencils differ from screens in that the apertures are directly etched or cut into a metal sheet or foil. In both stencils and screens, the paste is squeegeed through apertures onto a substrate. Both screen printing and stencil printing can be used to deposit adhesives or solder pastes, but stencil printing produces finer dimensions and closer spacings. The key advantage of stencils over screens, especially for the laser cut and electroformed types, is the finer dimensions and smaller pitch dots that can be printed. Stencils have become essential in depositing adhesive and solder paste for small-pitch devices of less than 0.5 mm. Conductive epoxies can be printed as small as 3-mil-diameter dots on 5-mil pitch.<sup>[31]</sup> Differing from pin transfer, stencil printing can deposit small dots of various sizes and heights from a single stencil. Dots smaller than the stencil thickness can be deposited through apertures that act like tiny dispensing tips.

Stencil printing is a fast efficient process for long production runs and is widely used in surface mounting of components.<sup>[32]</sup> In surface mounting, the solder paste is generally dispensed first by stenciling, followed by needle dispensing the adhesive; however, these processes may be reversed or both the solder and adhesive can be selectively dispensed by needle.

As with most processes, numerous variables affect the final product. For solder paste deposition using stencils, Chouta and Fleck<sup>[33]</sup> identified 39 variables relating to materials, 32 variables to processes and equipment, and

10 variables to personnel and environment. Among variables critical for the successful stencil dispensing of adhesives are: stencil design, the adhesive material and its rheological properties, and the printing process.

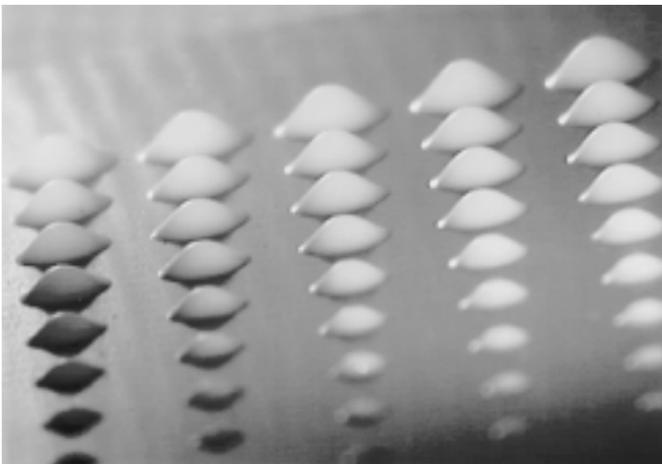
**Stencil fabrication and design.** Most stencils are fabricated from stainless steel, nickel, or copper foil 2- to 10-mils thick. Apertures are formed in the foil by one of three processes: chemical etching, laser cutting, or electroforming. Chemical etching, although the least costly of the three methods, provides the coarsest features. In chemical etching the apertures, the metal foil is coated on both sides with a photosensitive coating, exposed to UV light through a mask that has the desired aperture pattern, and developed. The part is then immersed or sprayed with a chemical etchant that removes metal only in the unprotected areas, after which the photocured coating is removed. With the trend toward finer pitch devices (less than 20-mil pitch), both laser cut and electroformed stencils must be used. Laser-cut stencils can be produced directly from Gerber data by computer numerically controlled laser cutting. Aperture dimension tolerances of  $\pm 5 \mu\text{m}$  are reported.<sup>[34]</sup> Chemically etched and laser-cut stencils are formed by subtractive processes. On the other hand, electroformed stencils are produced by an additive process in which a metal such as nickel is electroplated onto a mandrel that has a negative photoresist image of the aperture pattern. The electrodeposited nickel containing the apertures is then removed from the mandrel and used as the stencil. Because of their high precision patterns, electroformed stencils are used for ultra-fine pitch applications.

In recent years, there has been increased interest in stencils produced from plastics such as acetal and polyethylene. The prime benefit in using plastic stencils is the thicknesses that can be used (greater than 1 mm up to 8 mm). By drilling apertures of various sizes, adhesive deposits of different heights ranging from 0.2 to 2 mm were printed from a single screen thickness in one pass.<sup>[34]</sup> Figure 4.4 shows a typical range of dot heights that were produced from a 1-mm-thick plastic stencil having aperture sizes from 0.6 to 2 mm.<sup>[35]</sup> By carefully controlling the aperture size, it is possible to produce heights for every component type with a single squeegee stroke across a printed-circuit board (Fig. 4.5).

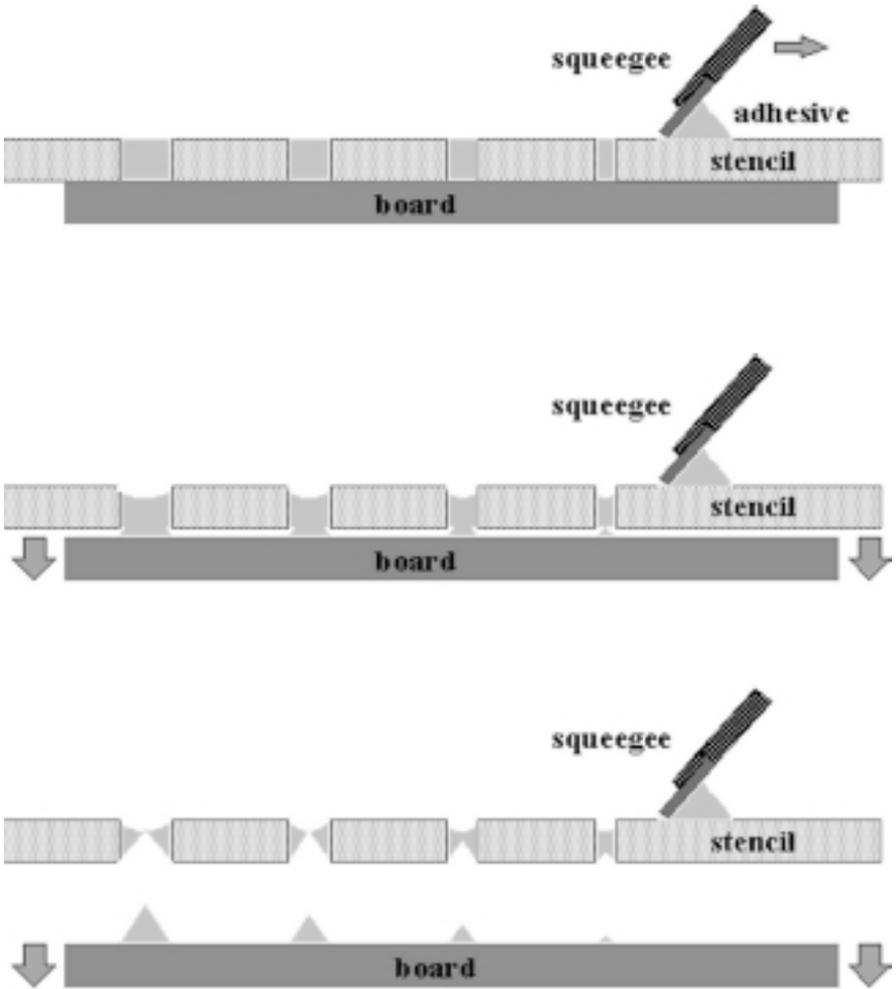
The two basic aperture shapes used to design and fabricate a stencil are dots and lines (slots). Lines or slots are used when a large volume of adhesive is required to prevent components from shifting during their placement. In determining the dot or line sizes, most design engineers use the *40% rule* according to which the size of the dot or line should be approximately 40%

of the distance between the pads.<sup>[36]</sup> Examples of dot sizes for selected discrete devices and for distances between bond pads may be found in the literature.<sup>[37]</sup> Double dot or slot designs are most widely used for two-pad devices (Fig. 4.6, top). Apertures smaller than the stencil thickness produce small dots. Circular patterns having areas roughly equal to the substrate area yield the largest dots (Fig. 4.6). An array of larger dots is recommended for high-peaked dots.

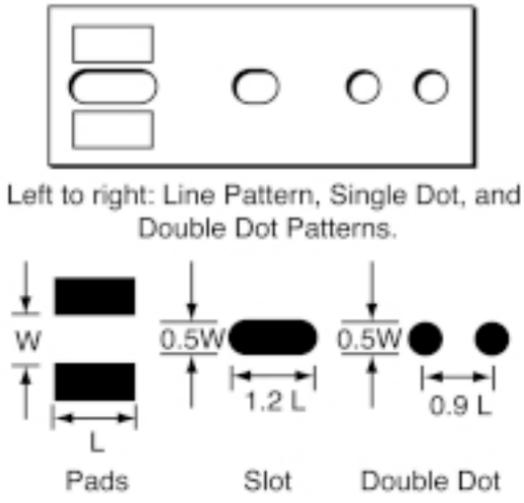
Stencil thickness should be determined by the highest dot size needed to make contact with the part. In most cases, the dot height should be 1.5 to 2 times the standoff height. Most passive components require stencils that are at least 6–8 mils thick. Large, small-outline ICs (SOICs) require stencils that are 10–12 mils thick.<sup>[32]</sup> A specific example in the use of these guidelines is given for a 12-mil (0.3 mm) thick stencil. If the stencil apertures are 0.3 mm (a 1:1 ratio of aperture width to stencil thickness), the surface tension between the adhesive and stencil will be so great that small dot diameters are formed. As the opening increases to 32 mils (0.8 mm), a 2.7:1 aspect ratio, most of the adhesive will transfer from the stencil and the dot height will be high. When the ratio of aperture diameter to stencil thickness exceeds 4:1, complete transfer occurs.<sup>[38]</sup> As a general rule, acceptable paste release is obtained when the aspect ratio of aperture width to stencil thickness is greater than 1.5. Other guidelines for stencil design are summarized in Table 4.15.



**Figure 4.4.** Typical range of adhesive dots produced using a 1-mm-thick plastic stencil (for aperture sizes ranging between 0.6 to 2.0 mm).<sup>[35]</sup> (Source: M. Whitmore, DEK Printing Machines Ltd.)



**Figure 4.5.** Schematic diagram of plastic-stencil printing process. (Source: M. Whitmore, DEK Printing Machines Ltd.)



**Figure 4.6.** Stencil patterns used to adhesively bond two-pad devices having a double dot or slot design.

**Table 4.15.** Stencil Design Guidelines<sup>[36]</sup>

<b>Typical Dot Patterns for Adhesive Printing</b>	
0.030-in round	0805 chips, SOT 23's
0.040-in round	1206's or larger, MELFs (cylindrical components, 2 dots on 0.040-in centers)
0.080-in round	SOIC's (multiple dots for each SOIC)
40% round	40% of the distance between the pads, center
<b>Typical Line Designs</b>	
0.008 in to 0.010 in	Length of line determined by the width of the component
40% line	40% of the distance between the SMT pads with the length of the line determined by the width of the component
<b>Typical Stencil Properties</b>	
Material	Stainless steel
Thickness	0.007 in to 0.012 in

**Adhesive material and rheology properties.** Adhesives used for screen or stencil printing in surface-mount applications are generally electrically insulative types whose functions are mechanical attachment and thermal dissipation. However, electrically conductive, silver-filled epoxies have been used for many years as ohmic contact adhesives to interconnect bare-chip devices in hybrid microcircuits and are beginning to be used as solder replacements for surface mounting of components on printed-circuit boards. Regardless of their conductivities, adhesives applied by screen or stencil printing should have the following properties:

- Low moisture absorption and workable viscosity over a 3–5 day period of exposure on the stencil.
- Viscosity suitable for dispensing (30,000–100,000 cps at 2.5 rpm).<sup>[39]</sup>
- Thixotropic properties (ability to flow freely through the stencil/screen apertures during printing and recover quickly after printing).
- High green strength to hold components in place during component placement and reflow soldering.
- High yield value to avoid slump and produce appropriate dot geometries.

The *yield value* (yield point) is an important parameter in dispensing adhesives. It is the minimum force required to begin the flow of adhesive from rest. The yield point is determined by extrapolating the flow or viscosity curve to the intercept on the *y*-axis or shear-stress axis.<sup>[40]</sup> In general, adhesives having high viscosities also have high yield points and produce dots having high *aspect ratios* (ratio of height to diameter). Thus, adhesives having high yield values of 200–500 Pa produce tall narrow dots while those having low yield values of 150–200 Pa produce wider, shorter dots.<sup>[32]</sup> Examples of some commercially available adhesives that can be stencil printed are given in Table 4.16.

**Stencil/screen printing process and equipment.** The printing process involves pressing the paste with a squeegee through apertures in the stencil or screen onto a substrate. The paste is applied with the squeegee at an angle of 45° or 60° in a single stroke, or often in a double stroke to assure complete filling of the apertures. Stencil printers capable of printing solder pastes can also be used to print adhesives. An important aspect of the printing equipment is the ability to form a programmable snap-off or gap

**Table 4.16.** Examples of Adhesives Used for Stencil Printing

Product/Supplier	Applications	Viscosity, Brookfield cps/rpm	Yield Value, Pa @ 23°C	Dot Profile	Process Conditions
Epo-Tek® H67-MP/ Epoxy Technology	Stencil/screen printing	300,000–400,000/1	N/A	Peaked	Screen print or automatic dispense
Epo-Tek® H70E/ Epoxy Technology	High-speed epoxy chip bonding	4,000–7,000/50	N/A	NA	Screen print, machine dispense, or stamp transfer
Chipbonder 3612/ Loctite	Metal stencil-print applications for large-component bonding	800,000/10	350–700	Peaked	12.7–50.8 mm/sec (0.5–2 in/sec)
Chipbonder® 3614/ Loctite	Metal stencil-print applications for large-component bonding	800,000/10	350–700	Peaked	12.7–50.8 mm/sec (0.5–2 in/sec)
Chipbonder® 3616/ Loctite	High speed stencil printing adhesive compatible with DEK Proflow™ dispense system	32,000/NA	300–550	Rounded	High-speed stencil printing up to 152.4 mm/sec (6 in/sec); squeegee pressure (4–6 N/cm)
Chipbonder® 3617/ Loctite	Stencil application for surface-mount devices requiring high speed and high wet strengths	32,000/NA	300–550	Rounded	60–100 mm/sec (2.4–3.9 in/sec), snap-off [1 mm (39 mils)], squeegee pressure (4–6 N/cm)
Amicon® D125 F3/ Emerson & Cuming	Large-component bonding (SOT, MELF, PLCC44, and SOIC) and excellent print definition; very low moisture absorption	550,000–650,000/10	250–300	Dome	NA
Amicon® D125 F5/ Emerson & Cuming	Large-component bonding (SOIC, PLCC); very low moisture absorption	$2.5 \times 10^6$ – $2.6 \times 10^6$ /5	600–1,000	Dome	NA

NA – Not available; MELF – Metal electrode leadframe; SOT – Small outline transistor; N/cm = Newtons per cm of squeegee length.

between the stencil and the substrate. The apertures of the stencil define the pattern for the deposited adhesive. Stencil and screen printers may be bench top for small to moderate runs, semi-automated, or automated floor models with magazine loading for production runs. Squeegee blades may consist of metal or hard plastics such as polyurethane or polyethylene. Printing speeds depend largely on the viscosity of the adhesive. In general, low-viscosity adhesives may be printed at higher speeds than high-viscosity types. Thus, some solder replacement adhesives having viscosities of 50,000–70,000 cps (at 10 rpm) can be printed at squeegee speeds of 6 inches/second. Surface-mount adhesives having high viscosities of 800,000 cps, as well as those of intermediate viscosities (75,000–250,000 cps), can be printed at 1 inch/second.

Although stencil printing is widely used for both adhesives and solder paste, and has many advantages over other dispensing processes, there are several limitations that must be addressed as follows:

- Tailing or distortion can occur during snap-off.
- Redeposition occurs on warped substrates, leading to contamination of adjacent pads.
- Tooling changes and added change-over time are required for design changes and new designs. Retooling costs are high.
- Application for very-fine pitch components is limited (sidewall influence is so great that adhesives cannot be effectively dispensed).
- Frequent cleaning of stencils is required to avoid clogging, missed dots, and misprints.
- Long exposure to air and moisture shortens the pot life and increases the viscosity of the adhesive.

### 4.3.2 Pin Transfer

Pin- and daub-transfer processes are also mass-transfer methods, but comprise less than 10% of the adhesive-dispensing processes used in production. In pin transfer, hard tooling consisting of an array of pins corresponding to the positions on the circuit board where components are to be attached is fabricated. The pin arrays are dipped into a tray containing the

uncured adhesive, then removed taking with them suspended drops of adhesive. The pins are then lowered onto the board and the adhesive transferred to the preselected areas (Fig. 4.7). The diameter of the pins and design of the pin tip are critical to ensure that the adhesive dot is not distorted. For most applications, the tip is designed as in Fig. 4.7.<sup>[41]</sup>

Pin transfer is the simplest mass-transfer process for high production runs of one or two part types, but limited where numerous types of different configurations and small quantities are to be produced. Because pin transfer uses hard tooling, each job requires new tooling and considerable time to set up and change to new tooling.<sup>[42]</sup> Other limitations of pin transfer are:<sup>[29]</sup>

- Risk of contaminating the adhesive contained in an open tray.
- Moisture absorption due to exposure of the adhesive to the ambient.
- Limited to dot printing.
- Requires flat substrates.
- Difficulty in applying adhesive to attach components smaller than 120 x 60 mils (1206 part types).
- Difficulty controlling the volume and shape of the dot.<sup>[43]</sup>

Furthermore, surface-mount adhesives (SMAs) used in pin transfer must have relatively low viscosities to facilitate pickup by the pins and transfer to the PCB. Because viscosity is so critical, the temperature of the adhesive reservoir must be controlled and preferably maintained between 25°C and 30°C.<sup>[44]</sup> Some SMAs that may be applied by pin transfer are listed in Table 4.17.



**Figure 4.7.** Pin transfer dispensing steps. (The tip of the pin is modified to prevent distorting the dot.)

**Table 4.17.** Examples of Adhesives Applied by Pin Transfer

Adhesive/Supplier	Viscosity (cps)		Thixotropic Index (1:10)
	1 rpm	10 rpm	
Amicon <sup>®</sup> D124 F1/ Emerson & Cuming	–	180,000–260,000	3.8
Amicon <sup>®</sup> D125 F4 and F4 Red/ Emerson & Cuming	550,000–750,000	130,000–190,000	2.9–5.7
Amicon <sup>®</sup> E6001/ Emerson & Cuming	600,000	180,000	3.3
Loctite 3607/ Loctite	$1 \times 10^6$ – $2 \times 10^6$	250,000–400,000	1.2–8
Loctite 3608/ Loctite	500,000– $1 \times 10^6$	100,000–250,000	2–10

### 4.3.3 Stamp Transfer

In stamp transfer, a stamping pad is dipped into a reservoir of liquid adhesive and the adhesive redeposited onto a substrate on contact. The amount of material transferred depends on its viscosity, the size and shape of the stamping tool, and the depth to which the stamp is immersed.<sup>[39][45]</sup> An advantage of stamp transfer is the ability to deposit adhesive over large areas in a single application. Pad areas as large as 500-mils square can be covered. However, like pin transfer, limitations of stamp transfer are the inability to print small areas or dots and the high tooling cost required for each application type. Some commercial adhesives that can be stamp transferred are listed in Table 4.18.

### 4.3.4 Automated Selective Dispensing (Contact Type)

Automated selective dispensing of adhesives may be contact or non-contact types. In the contact type, also known as syringe, needle, or machine dispensing, the adhesive is forced through a small orifice onto the substrate so that the dispensed dot makes contact with the substrate during dispensing. The adhesive is dispensed using a *x-y-z* positioning system. Automatic data-driven equipment is used to selectively dispense reproducible amounts of

**Table 4.18.** Examples of Adhesives Applied by Stamp Transfer<sup>[45][46]</sup>

Adhesive	Viscosity (cps)	Thixotropic Index (1:10)	Pot Life	Cure Schedule
Epo-Tek® H20S	4,710 @ 20 rpm	2.5	4 days	Snap cure (175°C, 45 sec) or fast cure (15 min, 120°C) die attach
Epo-Tek® H20S-MC	1,700 @ 100 rpm)	3.0	4 days	Snap cure (175°C, 45 sec) or fast cure (15 min, 120°C) die attach
Epo-Tek® H70E	4,000–7,000 @ 50 rpm	3.0	4 days	5 min, 150°C
Epo-Tek® P1011S	7,987 @ 20 rpm	1.8	6 mo	10–30 min. @ 70°C plus 1 hr @ 150°C, Requires prebake for large chips
Source: Epoxy Technology technical data sheets.				

adhesive with high accuracy. Large amounts of adhesive can also be dispensed onto a small area in order to assure contact with high-standoff components. Multiple small dots, 2–5 mils in diameter, can be deposited in selected areas at rates up to 50,000 dots per hour (dph), although typically speeds are approximately 15,000–20,000 dph. These speeds, seemingly high at first glance, are low compared with stencil printing where 50,000 dots or lines can be applied in 15 to 20 seconds.

The number of dots that can be dispensed per unit of time also depends on viscosity. The use of low-viscosity adhesives increases the number of dots that can be dispensed. However, there is a tradeoff between the speed at which the adhesive can be dispensed and the speed of device placement. Most automated component-placement equipment operate faster than adhesive-dispensing equipment. A comparison of the effect of viscosity on dispensing and placement times is shown in Table 4.19 for an 86-lead plastic-encapsulated leadless chip carrier (PLCC).<sup>[37]</sup>

**Table 4.19.** Effect of Adhesive Viscosity on Dispensing and Component Placement Time<sup>[37]</sup>

Parameter	Viscosity	
	Low	High
Number of dots required for one device	12	5
Dispense time per dot (msec)	120	150
Total dispense time (msec)	1,440	750
Placement time per device (msec)	2,000	2,000

Automated dispensing is now used for over 80% of all dispensed adhesives and is particularly suited to printed-circuit assemblies where some components have already been attached and, therefore, stencil or screen printing cannot be used. Another significant advantage is in bonding components smaller than  $120 \times 60$  mils. Pin transfer and stencil/screen print methods are generally not used below this size. Adhesives used for pin transfer are also difficult to control, and screens and stencils require more maintenance due to clogging and the need for frequent cleaning. Other advantages of automated dispensing include the following:

- Ideal for both short runs and production runs.
- Adhesive can be dispensed on partially assembled boards.
- Dispensers can handle a wide range of viscosities.
- No hard tooling required.
- Minimal setup and change-over times.
- Less sensitive to board warpage than stencil printing.
- High dispensing speeds up to 40,000 dph.
- Consistent dot profiles for a range of component sizes as small as the 0402 and 0603\* passive components.

Automated dispensing is used for the application of die-attachment, surface-mount, and underfill adhesives.

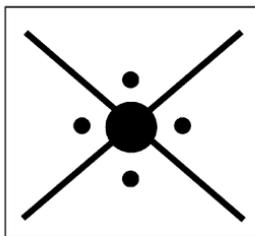
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\*0402 and 0603 are passive component part sizes. Throughout the book, part sizes are given in mils; thus 0402 is  $40 \times 20$  mils and 0603 is  $60 \times 30$  mils.

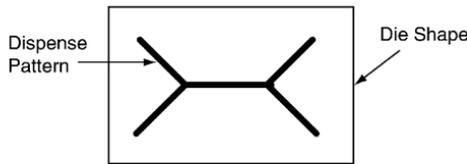
**Automated dispensing of die-attachment adhesives.** In assembling small quantities of hybrid microcircuits of many part types, manual application of the adhesive is still used, especially by smaller companies. Skilled operators are able to dispense adhesive from syringes in fairly controlled amounts that cover the bonding pad and provide enough fillet after die placement. However, for moderate-to-large runs, and even for small or prototype runs, automated dispensing provides the best method for repeatability and quality control. Automated dispensing is widely used for the assembly of integrated-circuit chips onto leadframes, for chip-scale and BGA packaging, and for bare-chip attachments to thin- or thick-film interconnect substrates. Regardless of the specific application, the dispensing patterns must be sufficient to cover the bonding pads.

The shape and size of the devices to be bonded define dispensing patterns. Patterns for square die are simpler than for rectangular die, and patterns may vary within each category as die size increases. Simple dot dispense patterns are used for small square die (less than 5 mm per side), but the volume must be estimated so that the circular area of the adhesive will spread to the edge of the die and produce a fillet.<sup>[47]</sup> Square die, larger than 20 mm per side, still require a center dot, but must also be supplemented with a cross-pattern and other dots in order for the adhesive to flow uniformly (Fig. 4.8). The lines should extend far enough so that, once the die is placed, its bonded surface will be completely covered. Typically, this involves depositing the adhesive approximately two-thirds the distance to the edge of the bonding pad.

The pattern for rectangular devices is somewhat more complex as shown in Fig. 4.9. The major line should be centered and its length should be the difference in length between the sides of the chip. The four remaining



**Figure 4.8.** Dispense pattern for a square die (>20 mm/side). (Copyright 1999, Reed Exhibition Corp., reproduced with permission.)



**Figure 4.9.** Dispense pattern for a rectangular die. (Copyright 1999, Reed Exhibition Corp., reproduced with permission.)

lines should extend approximately two-thirds the distance to the corners and make a  $45^\circ$  angle with the centerline. Another general rule is that the height of the centerline should be about 50% of the line's width.

Other machine parameters may require adjustments for die size and pattern. One parameter is the length of time spent before the dispensing pump begins to move, known as the *on-delay*. On-delay times that are too short result in thin deposits as dispensing begins. Further, the *shut-off* distance, the distance from the edge where dispensing stops, requires adjustment of machine settings. Stopping too close to the edge results in excessive filleting while too far from the edge produces incomplete coverage. The exact shut-off value depends on the filleting requirements for the bonded device.

**Automated dispensing for surface-mount adhesives.** Automated dispensing of adhesives for surface-mount technology (SMT) applications follows guidelines similar to those for die attachment. Patterns of dots and lines are deposited covering areas similar to those of the component sizes to be bonded. Surface-mount adhesives are applied primarily by automated dispensing, although stencil printing and pin or stamp transfer are also used. Regardless of the application method, surface-mount adhesives should meet the following requirements:

- Compatible rheology with the dispensing method (clog-free, no stringing) and with assembly requirements (dot profiles, green strengths).
- Short cure cycles and ability to be cured in-line or simultaneously with solder reflow.
- Preferably one-part systems.

- Long shelf life and extended working life.
- Application at speeds of 40,000 dph or greater.
- Consistent dot profiles for a range of components including very small components such as the 0402 and 0603 passive devices.

The behavior of adhesives under high-speed dispensing conditions is also critical.<sup>[48][49]</sup> The ability of a thixotropic adhesive to flow with an applied shear stress and to recover quickly after the stress is removed is critical for high-speed automatic dispensing as well as for screen or stencil printing. The rate at which the adhesive recovers its original high viscosity is as important as the shear-induced drop in viscosity. Figure 4.10 shows examples of the thixotropic loops for two adhesives. Both display excellent recovery since the return curves trace well with the original. Thus both adhesives are suitable for dispensing based on shear thinning. However, the first material (A) demonstrates quicker recovery and, therefore, is better suited for high-speed dispensing. It can be dispensed at a rate exceeding 50,000 dph, without stringing or tailing. Other material factors affecting dispensing are as follows:

- Low viscosity is required for fast dispensing.
- High green strength is necessary for dot stability.
- Cooling the adhesive may be necessary to prevent premature aging in the syringe (heating up to 70°C can occur from piston movement).

Besides premature aging, an increase in temperature during dispensing is also critical; for example, a 5°C rise above room temperature alters the quantity of material dispensed as well as the shape of dots and patterns. Increased temperatures during automated dispensing lower viscosity and increase the mass of dispensed adhesive. The increased amount of material may interfere with adjacent circuitry or with devices already assembled. A 5°C rise above room temperature also results in wider, shorter dots, creating insufficient dot height necessary for component contact. Other factors critical to dispensing are needle selection, equipment used, and pumping method.

**Needle selection.** Needle sizes must be selected to dispense the desired amount of adhesive. Dispensing too large an amount of adhesive can bridge components and lead to mechanical failures such as lifting during thermal cycling while insufficient adhesive results in low bond strengths. As a rule,

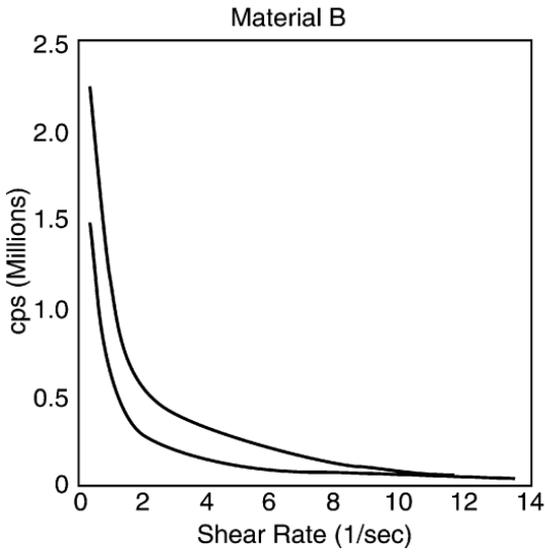
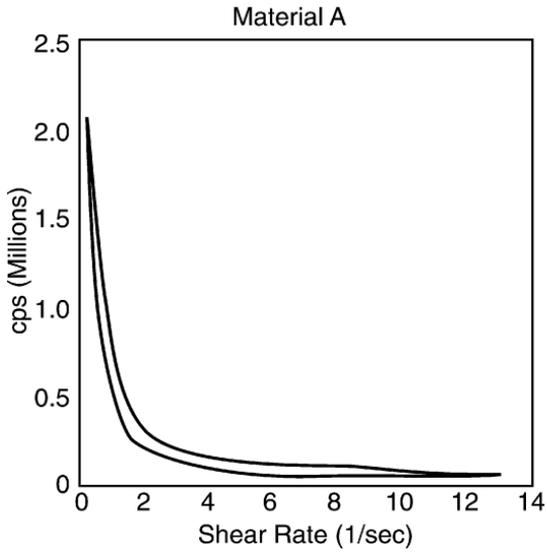


Figure 4.10. Thixotropic loops for SMT Adhesives.<sup>[37][50]</sup>

the needle's inside diameter (ID) should be at least 50% of the size of the desired dot.<sup>[48]</sup> Thus, to dispense dots 0.7–0.9 mm in diameter the needle's ID should be approximately 0.4 mm, which corresponds to a 22-gauge needle. Needle sizes are listed in Table 4.20, and a guide for selecting needle sizes for various components is provided in Table 4.21.

Composite “needle maps” have been generated for various adhesives and may be available from either the adhesives supplier or the manufacturer of the dispensing equipment. The maps are a ready reference guide in selecting the needle size and shot size for a specific adhesive and dot size. Needle maps correlate the shot size in milliseconds with the dot diameter for various needle gauges and standoffs and for various component types. An example of a needle map for a high-speed surface-mount adhesive is given in Fig. 4.11. In the figure, the needle gauges and standoffs are given at the end of each curve; thus, 21/10 indicates a 21-gauge needle with a standoff of 10 mils. For example, a 0402 part type requires a dot diameter of 10–15 mils and shot sizes of 5–50 msec. As one goes up the scale, the dot diameters become larger as do the shot sizes and thus larger diameter needles are required. Therefore, a plastic leadless chip carrier (PLCC) would require dot diameters of 40–50 mils and shot sizes above 60 msec using a 21-gauge needle.

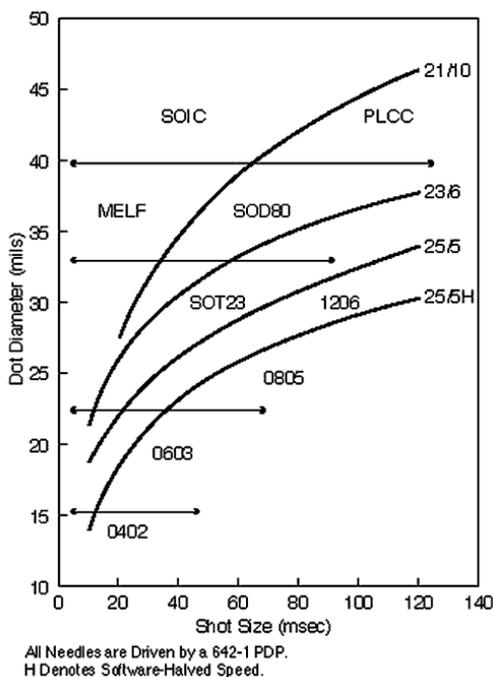
**Table 4.20.** Needle Gauge Sizes<sup>[47]</sup>

Needle Gauge	ID (mm)	OD (mm)
18	0.84	1.24
19	0.68	1.06
20	0.58	0.88
21	0.51	0.81
22	0.41	0.71
23	0.33	0.63
25	0.25	0.55
27	0.20	0.40
30	0.25	0.30
32	0.1	0.225

**Table 4.21.** Needle Selection Guide Based on Part Type

Part Type	Gauge				
	27	25	23	22	21
0402	X	X			
0603		X	X		
0805		X	X		
1206		X	X		
SOIC		X	X	X	
PLCC		X	X	X	
QFP			X	X	X

*Source: GPD Global, Application Notes, Version 1.*



**Figure 4.11.** Example of a “needle map” for Loctite® 3609 adhesive dispensed from a Cam/alot® dispenser. (Reproduced with permission of Speedline Technologies.)

**Equipment.** A wide variety and numerous suppliers of automated dispensing equipment are available as listed in Table 4.22. An important consideration in selecting an automated, contact-type dispensing system is the pump used in the system, of which there are three types: time-pressure, auger, and linear piston or positive displacement.<sup>[51]</sup>

*Time-pressure pump method.* Time-pressure, the simplest and oldest of the methods, is still in use today. According to this method, pulsating high-pressure air actuates a plunger that forces the adhesive through a syringe.<sup>[52]</sup> A needle-valve controls the amount of adhesive dispensed. Advantages of this method include lower cost and simplicity of operation compared with the auger and the linear piston types. Some disadvantages are:

- Pressure changes occur as the syringe empties due to compression of air in the syringe.
- High-speed dispensing causes heating of the adhesive which changes its viscosity, limits its pot life, and changes the volume of material dispensed. (Viscosity variations in adhesives require process adjustments during dispensing.)
- Stringing of adhesive can occur under some conditions.

*Auger pump.* A second type of pump is the auger pump. In this system, air pressure is used to feed adhesive into a reservoir that contains a feed screw or auger. As the auger turns, it shears the adhesive and forces it down the reservoir and out through the needle. Auger pumps are designed to minimize variability when dispensing adhesives at high production rates. Compared to the time-pressure pumps, the effects of changes in viscosity are reduced because the auger is mechanically feeding the needle. Some limitations of the auger pump approach are the following:

- Self heating of highly-filled, thermally-conductive adhesives at high shear rates affects the amount of material dispensed.
- Higher cost than time-pressure approach.
- Complicated cleaning process for the auger and reservoir.

**Table 4.22.** Commercially Available Adhesive Dispensing Systems

Dispensing System/ Manufacturer	Work Area Dimensions (X,Y, in)	Z-Axis Travel (in)	Dispensing Method/Speed (dph)	Applications	Examples of Compatible Adhesives
Century® C-718/ Asymtek	20 × 16 (in-line), 18 × 17 (batch)	3.5	DJ-2100 DispenseJet™ and DV-6000 rotary positive- displacement pump/20,000 (maximum)	SMT assembly	Surface-mount Adhesives: Chipbonder® 3615, Dymax 9-20367, and 9-20368, Amicon® D124F15, D125F, and Amicon® 125F DR.
Century® C-720 (Century Platform)/ Asymtek	17 × 14 (single head), 11 × 14 (dual head)	3.5	DP-3000 and DP-6000 linear and rotary pumps, and DV-7000 Heli-flow pump/20,000	Underfill	Underfill: Loctite 3563, 3565, 3567, Hysol FP4531, and Ablefill® JM8806, JM8807, and JM UF8802LM.
Millenium® M-620 (Century Platform)/ Asymtek	15 × 15	3.5	DP-3000 and DV-6000/20,000	Underfill	Underfill: Loctite 3563, 3565, 3567, Hysol FP4531, and Ablefill® JM8806, JM8807, and JM UF8802LM.
Axiom™ X-1010/ Asymtek	17 × 16 (DP- 3000), 17 × 18 (DP-7000)	3.5	DJ-2100 DispenseJet and DV-7000 Heli-flow pump/ 30,000 (maximum)	SMT assembly	SMT adhesives: Chipbonder® 3615, Dymax 9-20367, and 9-20368, Amicon® D124 F 15, Amicon® D125 F, and Amicon® 125 F DR.
Axiom™ X-1020/ Asymtek	18 × 18	3.5	DJ-3000 single action or dual action DP-3000, DV-7000, and DJ-2100 pumps/ 50,000 (maximum)	Underfill	Underfill: Loctite 3563, 3565, 3567, Hysol FP4531, and Ablefill® JM8806, JM8807, and JM UF8802LM.
Millenium® M-2010/ Asymtek	19 × 22 (DJ-2100) or 18 × 22 (DV-7000)	3.1	DJ-2100 and DV-7000 pumps/ 50,000 (maximum)	High speed SMT attachment	SMT adhesives: Chipbonder® 3615, Dymax 9-20367, and 9-20368, Amicon® D124 F 15, Amicon® D125 F, and Amicon® 125 F DR.

(cont'd.)

**Table 4.22. (Cont'd.)**

Dispensing System/ Manufacturer	Work Area Dimensions (X,Y, in)	Z-Axis Travel (in)	Dispensing Method/Speed (dph)	Applications	Examples of Compatible Adhesives
Millenium <sup>®</sup> M-2020/ Asymtek	17 × 21 (DP-3000) or 13 × 21 (dual action DP-3000 and DV-6000)	3.1	DJ-2100, DP-3000 pump or dual action DP-3000 and DV-6000/50,000 (maximum)	Underfill	Underfill: Loctite 3563, 3565, 3567, Hysol FP4531, and Ablefill <sup>®</sup> JM8806, JM8807, and JM UF8802LM.
Cam/alot <sup>®</sup> 1414/ Speedline Technologies	14 × 14	2.0	Rotary pump* standard, time/pressure available/ ≤13,000	Surface mount, semiconductor and COB mounting	SMD Adhesives: Loctite Chipbonder <sup>®</sup> 3610 (yellow), 3609, 3619, and 3621 (red), Amicon <sup>®</sup> D125 F 3 DR, and Thermoset CircuitSAF <sup>™</sup> MA-420, Heraeus PD 955PR Semiconductor and COB mounting: Ablebond <sup>®</sup> 84-1 LMI
Cam/alot <sup>®</sup> 1818/ Speedline Technologies	20 × 20 (maximum)	4.5	Rotary pump* standard, time/pressure available/ ≤16,000	Surface mount and underfill	SMD Adhesives: Loctite Chipbonder <sup>®</sup> 3610 (yellow), 3609, 3619, and 3621 (red), Amicon <sup>®</sup> D125 F 3 DR, and Thermoset CircuitSAF <sup>™</sup> MA-420, Heraeus PD 955PR ;Underfill: Loctite 3563, 3565, 3567, Hysol FP4531, and Ablefill <sup>®</sup> JM8806, JM8807, and JM UF8802LM.
*Quick-clean cartridges standard for rotary pumps.					

(cont'd.)

**Table 4.22. (Cont'd.)**

Dispensing System/ Manufacturer	Work Area Dimensions (X,Y, in)	Z-Axis Travel (in)	Dispensing Method/Speed (dph)	Applications	Examples of Compatible Adhesives
Cam/alot <sup>®</sup> 3800/ Speedline Technologies	14 × 14	2.0	Rotary pump* standard, time/pressure available/ ≤25,000	Surface mount	SMD Adhesives: Loctite Chipbonder <sup>®</sup> 3610 (yellow), 3609, 3619, and 3621 (red), Amicon <sup>®</sup> D125 F 3 DR, and CircuitSAF <sup>™</sup> MA-420, Heraeus PD 955PR.
Cam/alot <sup>®</sup> 5000/ Speedline Technologies	18 × 18	2.2	Rotary pump* standard, time/pressure available/ ≤16,000 (single head)	Surface mount	SMD Adhesives: Loctite Chipbonder <sup>®</sup> 3610 (yellow), 3609, 3619, and 3621 (red), Amicon <sup>®</sup> D125 F 3 DR, and Thermoset CircuitSAF <sup>™</sup> MA-420, PD 955PR.
Gemini <sup>™</sup> II/ Speedline Technologies	19 × 19	1.0	Rotary pump* standard, time/pressure available/ ≤45,000	High-speed SMD	SMD: Loctite Chipbonder <sup>®</sup> 3610 (yellow), 3609, 3619, and 3621 (red), Amicon <sup>®</sup> D125 F 3 DR, and Thermoset CircuitSAF <sup>™</sup> MA-420, PD 955PR.
Cam/alot <sup>®</sup> 3700/ Speedline Technologies	14 × 14	2.0	Rotary pump* standard, time/pressure available/ ≤25,000	Semiconductor, COB, die attachment	Semiconductor and COB mounting: Ablebond <sup>®</sup> 84-1 LMI.
Cam/alot <sup>®</sup> 5700/ Speedline Technologies	18 × 18	2.2	Rotary pump* standard, time/pressure available/≤25,000	Semiconductor, COB, die attachment	Semiconductor and COB mounting: Ablebond <sup>®</sup> 84-1 LMI.

\*Quick-clean cartridges standard for rotary pumps; NA – Not Applicable.

(cont'd.)

**Table 4.22. (Cont'd.)**

Dispensing System/Vendor	Work Area Dimensions (X,Y, in)	Z-Axis Travel (in)	Dispensing Method/Speed (dph)	Applications	Examples of Compatible Adhesives
XyFlex®/ Speedline Technologies	13 × 18	1.0	Rotary (auger) or multi-piston, four-head dispenser/ 140,000 (maximum)	Surface mount, semiconductor, COB, die attach	SMD adhesive: Loctite Chipbonder® 3615 (red) Semiconductor and COB mounting: Ablebond® 84-1 LMI.
XyFlexPro®/ Speedline Technologies	(7100) 13 × 10 (7200) 19 × 22	1.0	Single-head dispenser/ 30,000-120,000 (application dependent)	Semiconductor packaging or surface mount	SMD adhesive: Amicon® D125 F 3 DR and D5R, Amicon® D125 F3 and F5, Amicon® E6752, die attach.
Champion 3000/ Creative Automation	18 × 18	1.5	True Volume Pump™/ 90,000 (maximum)**	Underfill, encapsulation, Dam & Fill, conductive epoxy, SMA and solder paste	SMT Adhesives: Loctite Chipbonder® 3615 (red), Dymax 9-20365 (red) and 20366 (yellow).
Champion 3700/ Creative Automation	18 × 18	1.5	True Volume Pump™/ 90,000 (maximum)**	Underfill, encapsulation, Dam & Fill, conductive epoxy, SMA and solder paste	SMT Adhesives: Loctite Chipbonder® 3615 (red), PD 955M.
**Jet dispensing (low-viscosity adhesive), True volume positive dispensing wide range of solder paste and adhesives, TruFlow auger valve for medium viscosity adhesives, and time-pressure for low-to-medium viscosity adhesives. NA – Not Available.					

(Cont'd.)

**Table 4.22. (Cont'd.)**

Dispensing System/ Manufacturer	Work Area Dimensions (X,Y, in)	Z-Axis Travel (in)	Dispensing Method/Speed (dph)	Applications	Examples of Compatible Adhesives
Champion 8300/ Creative Automation	24 × 18	2.5	True Volume Pump™/ 90,000 (maximum)**	Underfill, encapsulation, Dam & Fill, conductive epoxy, SMA and solder paste	SMT Adhesives: Loctite 3609, 3610, 3619, and 3621; Amicon® D125 F3 DR and D5R, Amicon® D125 F3 and F5, Amicon® E6752.
MicroMax®/ GPD Global	12 × 12	2.25	True Value™ Pump/ servo-driven valve/36,000**	SMT adhesive, conductive epoxies, no-flow underfill (unheated), hybrid assembly, small-dot dispensing	SMT Adhesives: Amicon® D125F, 125FDR, Loctite Chipbonder® 3615 (red), Dymax 9-20367 (red) and 9- 20368 (yellow), Amicon® E7650, 7652, conductive epoxies: Ablebond® 84-1 LMI, no-flow underfill: Amicon® E1330 LV, 1350, and 1355.
DS-9000-SA (standalone) and 9000 IL (inline)/ GPD Global	18 × 18	1.83	NA/28,000		
DS-9100-SA (stand- alone) and 9100 IL (in-line)/ GPD Global	24 × 24	1.83	NA/28,000	SMT adhesive, conductive epoxies, no-flow underfill (unheated), hybrid assembly, small-dot dispensing	SMT Adhesives: Amicon® D125F, 125FDR Loctite Chipbonder® 3615 (red), Dymax 9-20367 (red) and 9- 20368 (yellow), Amicon® E7650, 7652, conductive epoxies: Ablebond® 84-1 LMI, no-flow underfill: Amicon® E1330 LV, 1350, and 1355.
**Jet dispensing (low-viscosity adhesive), True volume positive dispensing wide range of solder paste and adhesives, TruFlow auger valve for medium viscosity adhesives, and time-pressure for low-to-medium viscosity adhesives. NA – Not Available.					

(cont'd.)

**Table 4.22. (Cont'd.)**

Dispensing System/ Manufacturer	Work Area Dimensions (X,Y, in)	Z-Axis Travel (in)	Dispensing Method/Speed (dph)	Applications	Examples of Compatible Adhesives
Micro I (stand-alone) and II (in-line)/ GPD Global	18 × 18 (maximum)	1.83	Auger/28,000	Underfill, semiconductor die attach, and hybrid dispensing (heated) Underfill: Ablebond® 7737s, Amicon® E1252, Hysol FP4459,	Semiconductor die attach: Ablebond® 84-1 LMI SR4, Hysol KO 111, QMI 506, and QMI 505 MT, Hybrid Dispensing: Ablebond® 84-1 LMI, Ablebond® 84-3, Epo-Tek® H20-E.
MicroMax® II/ GPD Global	12 × 12	2.25	Auger/36,000		
MRSI-175 Ag/ Newport Corp.	12 × 10	—	Positive displacement, stamp dispensing (5-mil dots achievable)/18,000	Conductive epoxy dispensing, including SMT	SMT adhesives Chipbonder® 3615, Dymax 9-20367, and 9-20368, Amicon® D124 F 15, D125 F, and 125F DR.

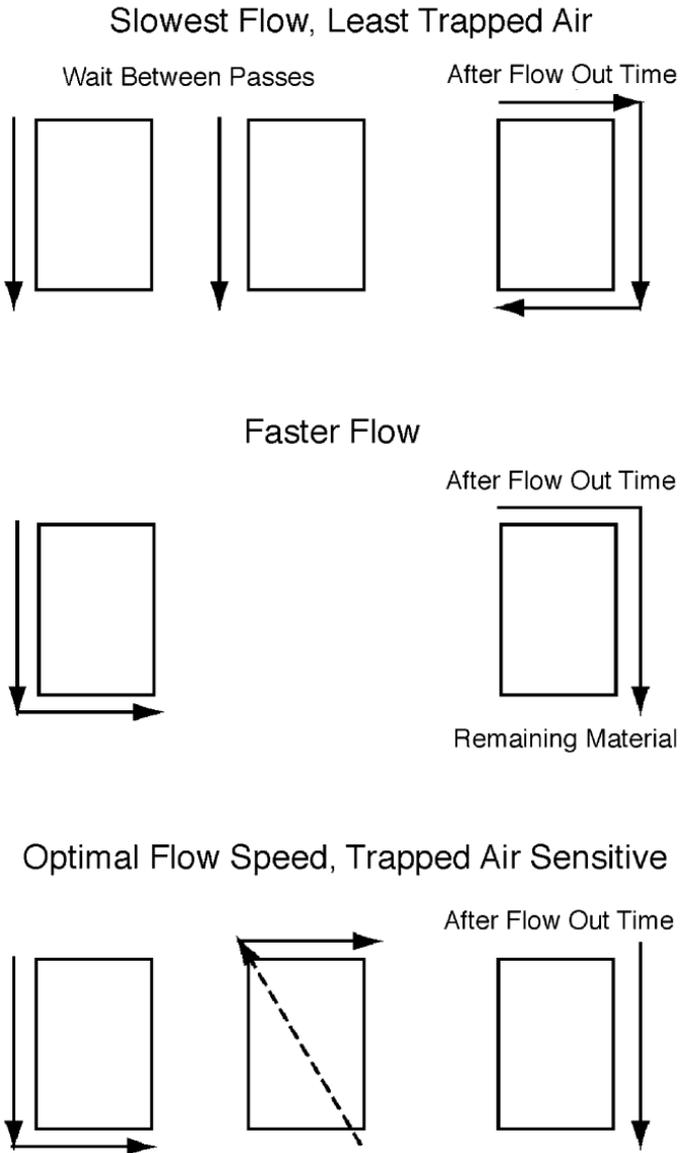
*Linear-piston pump.* The third type of pump used in dispensers, linear piston, is a true positive-displacement pump. This pump uses a piston to change the volume of a reservoir that is fed from the main syringe. The displacement of the piston produces an equivalent positive displacement of fluid through the pump. Changes in viscosity have little or no effect on the repeatability of dispensed mass. Of the three methods, the repeatability of the linear-piston type is the best ( $\pm 1\%$ , except for very small dispense volumes of less than 20 microliters).<sup>[51]</sup> Repeatability of the time-pressure method is  $\pm 10\%$  and for the auger method is  $\pm 4\%$  (short term less than 30 minutes).

**Automated dispensing of underfill adhesives.** In addition to die attachment and surface mount, automated selective dispensing is also used to apply adhesives as underfills for flip-chip devices, chip-scale packages, and ball-grid array packages. The adhesive is dispensed along one or more sides of the device and flows by capillary action beneath the devices filling in the volume around the solder balls. Some underfill materials have high flow rates and are “self filleting.” In other cases, an additional “seal” pass is required on the dispense side to create a uniform fillet around the device’s perimeter.<sup>[53]</sup> In general, the needle tip should be 1–3 mils off the substrate and offset by 1–3 mils from the edge of the device.<sup>[51]</sup>

A range of fill patterns that can be used is shown in Fig. 4.12.<sup>[54]</sup> The specific dispensing pattern used depends on the shape of the part (square or rectangular) and the size of the device.

The simple “I” dispense pattern is widely used for square devices. Multiple applications, however, may be needed followed by a fillet or seal at the other three sides using a fine gauge needle. A limitation of this approach is the time required to underfill large die. For die smaller than 3-mm square, a single pass usually suffices. Yet another option for small die is to apply a single dot at one edge.<sup>[53]</sup>

An “L” dispense pattern is also used (Fig. 4.12). After the adhesive flows out, a fillet is dispensed at the other two sides. The L pattern may be started from one corner using a single pass or from a common corner using a two-step process.<sup>[55]</sup> Die greater than 3-mm square, but less than 6-mm square, may require L-shape dispensing and 2–3 more passes after allowing sufficient time for the adhesive to flow-out beneath the device. L-shaped dispensing is also used for rectangular devices such as flip-chip ICs in which case the dispensing is started along the longer side of the device.<sup>[54]</sup> Both L- and I-shaped dispense patterns work well with small flip-chip and chip-scale package devices. Large devices, regardless of type, require the L-shape pattern.



**Figure 4.12.** Dispense patterns for capillary-flow underfill adhesives: top: “I” shaped pattern; middle: “L” shaped; bottom: modified “U.”<sup>[54]</sup>

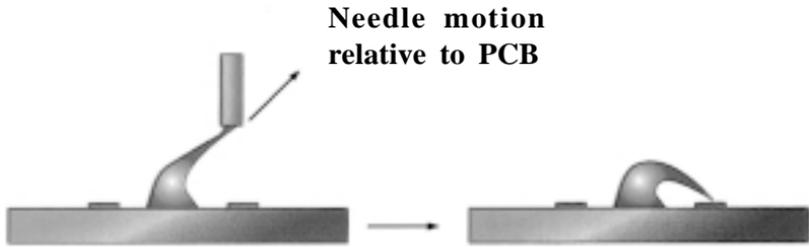
The modified U pattern is fastest to apply but, of the three methods, has the highest risk of air entrapment. The adhesive is dispensed in two strokes forming a U pattern, then is followed by a seal along the last side (Fig. 4.12).

**Material factors affecting automated dispensing.** In dispensing adhesives for underfill, as well as for die attachment and surface mount, flow properties and viscosity are paramount. Low viscosities are essential for rapid dispensing and efficient capillary flow beneath the devices. Dispense temperatures of 70°C–85°C may be used to reduce viscosities of the fluid to less than 500 cps from otherwise 20,000 cps or greater at room temperature.<sup>[56]</sup> Most adhesives experience an increase in viscosity of 25%–100% when their pot lives have been exceeded. An example of the increases in viscosity that occurred for a snap-cured epoxy used in surface mounting is given in Table 4.23. Over time, this increase in viscosity results in a decrease in the amount of material that can be dispensed. To compensate for this, one or more machine adjustments must be made such as increasing the air pressure, increasing the dwell time for dot patterns, or reducing the line speed of the dispensing head.

Several defects associated with the automated dispensing of adhesives are possible, among which are stringing, tailing, missing dots, satellite dots, and inconsistent dot heights. A common defect, known as *stringing*, occurs if, after dispensing, the adhesive does not break quickly and cleanly from the needle (Fig. 4.13). Stringing may contaminate adjacent surfaces or components. The incidence of adhesive stringing is high if the adhesive volume is too low for the needle's diameter and for the standoff height. Using a smaller-diameter needle and reducing the standoff height usually solves the

**Table 4.23.** Viscosity Changes vs Pot Life for a Surface-Mount Adhesive<sup>[57]</sup>

	at 0.5 rpm	at 5 rpm
Initial viscosity	919,143 cps	403,286 cps
After aging 3 hrs at r.t.	1,065,714 cps	533,438 cps
% change	16	32
Thixotropic index	2.3	2.0
Values are averages of seven batches of Aptek Laboratories' surface-mount epoxy adhesive: DIS-A-PASTE 2311 PMF. (Source: Aptek Labs. Inc.)		



**Figure 4.13.** Adhesive stringing during dispensing.<sup>[48]</sup> (Courtesy PennWell Corp.)

problem. A maximum standoff height of one-half the needle's ID is used; above this, stringing and inconsistent dispensing occurs. Other causes of stringing include electrostatic charge on the board, incorrect z-stroke height, board warpage, and insufficient support for the board.<sup>[48]</sup>

*Tailing* occurs when the dot size becomes less than twice the inside diameter of the needle. With a 0.4 mm ID needle, dot size should be at least 0.75 mm; with a 0.6 mm ID needle, the dot should be greater than 1 mm.<sup>[49]</sup> Tailing is also reduced by increasing the retraction speed.<sup>[47]</sup>

Missing dots result from insufficient line pressure, clogged needles, or air bubbles in the adhesive causing the adhesive to be dispensed intermittently.<sup>[58]</sup> Missing dots result in improper parts placement, incorrect orientation, and degraded bond strengths.<sup>[48]</sup>

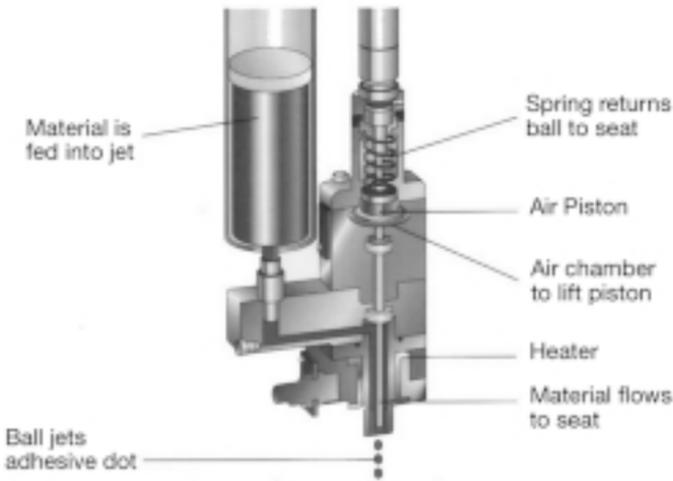
*Satellite dots* are extra, mislocated dots caused if the standoff height is too high or if the volume dispensed is too great for the needle. Satellite dots result in bond pad contamination or low-strength bonds. They can be eliminated by reducing the pressure or by switching to a needle having a larger inside diameter.<sup>[48]</sup>

Inconsistent dot heights and sizes may result from a needle standoff post that is landing on solder pads or by increases in the viscosity of the adhesive during its working life. A replacement needle with a different post usually solves the first problem. Also, increasing the dispensing pressure as viscosity increases and reducing the dispensing speed generate more reproducible dot sizes.

### 4.3.5 Jet Dispensing (Non-Contact Type)

*Jet dispensing*, also known as jetting, is a direct-dispensing process whereby the adhesive paste is forced through a fine nozzle and programmed to flow onto selected areas controlled from a computer database. It is an automated method that differs from syringe/needle dispensing in that contact with the surface is not required to produce the dots, lines, or patterns.

Jet-dispensing equipment uses a closed-loop, positive shut-off piston to dispense the adhesive. The adhesive is pressurized at the syringe to assure constant flow. Using a spring-driven ball and seat mechanism, the adhesive fills the void left when the ball retracts from the seat. When the ball returns, the force due to acceleration breaks the stream of adhesive, which is then jetted through the nozzle in precisely controlled amounts onto the printed-circuit board (Fig. 4.14). Unlike contact automated syringe dispensers, jetting requires no *z*-axis motion, the time between shots is approximately 15 milliseconds versus 90 milliseconds, and the uniformity and shape of the dots are not affected by substrate warpage or by the surface tensions of the needle and board.



**Figure 4.14.** Jet-dispensing concept, DispenseJet® DJ-2100 valve.<sup>[61]</sup> (Courtesy Asymtek.)

Jet dispensing was developed for SMT primarily to increase throughput by increasing the speed at which dots can be dispensed up to 70,000 dph. Jet dispensing also produces better quality dots and much smaller dots than are possible with syringe dispensing, thus meeting requirements for attaching very fine-pitch small devices. Droplets of adhesive in picoliter volumes can be dispensed but, if larger dots are required, they can be produced by dispensing additional shots over the first dot in rapid succession.<sup>[59]</sup> Jet dispensing has also simplified and improved the dispensing of epoxy underfill adhesives. With jet dispensing, there is no risk of a needle clipping and damaging the die or of the needle itself being damaged since there is no  $z$ -direction motion of the dispense head. Because of the absence of  $z$ -direction motion, a 20% improvement in throughput has been reported.<sup>[60]</sup>

Adhesives for jet dispensing must have relatively low viscosities of approximately 120,000 cps at 5 rpm, or 20,000–40,000 cps at 10 rpm, and fast recovery of thixotropic properties after dispensing (narrow hysteresis in viscosity loop).<sup>[62]</sup> Examples of SMT adhesives that are jet dispensible are Loctite's Chipbonder<sup>®</sup> 3621, Epoxy Technology's Epo-Tek<sup>®</sup> H70E, and Emerson & Cuming's Amicon<sup>®</sup> E-1330.<sup>[63]</sup>

In summary, the key advantages of jet dispensing are:

- High throughputs of 70,000 dph compared with less than 40,000 dph for single-head syringe dispensing. These high deposition rates are better able to match the high component placement rates.<sup>[64][65]</sup>
- Reduced cleaning operations.
- Elimination of stringing.
- Improved dot uniformity.
- Adjustable dot height and profile by stacking dots.
- Tolerance for board warpage and previously assembled components. Avoids need to compensate for height.

Some limitations include the following:

- Highly viscous materials are not suitable. Only low viscosity, highly thixotropic adhesives can be used.
- Droplets are limited to one size, however, dots can be stacked to increase their size.

### 4.3.6 Preform/Tape Attachment

Preforms, tape, or film adhesives, unlike the paste or liquid adhesives, are already in the solid state. They may be thermoplastic or thermosetting but, in both cases, may be purchased as sheets of various thicknesses and cut to size to accommodate specific device or part sizes. In using preforms, the electronics assembler avoids problems associated with the storage, handling, and dispensing of liquid adhesives. Parts such as leadframes, lids, and substrates may also be purchased with pre-attached preforms, a convenience to the user, who then avoids having to cut and handle individual preforms. Most parts can also be stored for up to one year in ambient conditions without affecting their properties.

Thermoplastic preforms provide instant bonding since they melt, bond the surfaces, and resolidify quickly on cooling. They also have the added advantage of being easily reworked. Attachment conditions vary according to the preform used, but generally consist of melting the preform at around 200°C with an applied pressure of about 10 psi. Thermosetting preforms are partially cured adhesives, primarily epoxies. By heating and applying pressure, they will also flow and wet the surfaces to be bonded, but then must be fully cured by further polymerization through continued application of heat. Flow may be induced at 60°C–100°C followed by curing at 80°C–150°C with applied pressure of 10–15 psi. Thermosetting preforms generally result in higher shear strengths than thermoplastic types and are capable of resisting higher temperatures. Die-shear strengths of 2,000–3,000 psi for thermosetting preforms are typical. Silver-filled preforms are also available and, because of their high thermal conductivities, are used to attach heat spreaders, heat sinks, and circuit substrates on PWBs or inside ceramic or metal packages. Thermal conductivities for the silver-filled preforms are typically 6 W/m·K compared with 1.5–1.6 W/m·K for the electrically insulative types. Electrically conductive preforms having conductivities of  $5 \times 10^{-3}$  to  $5 \times 10^{-4}$  ohm-cm are also used for EMI shielding.<sup>[66]</sup>

## 4.4 PLACEMENT OF DEVICES AND COMPONENTS

After the adhesive has been dispensed onto the PCBs or other interconnect substrate, bare die and other electronic components must be precisely placed. Of course, pick and place can be done manually using

vacuum pick-up tools or tweezers, but this approach is useful only for small quantities, prototypes, or for rework. The risk of human error is high and accuracy is exacerbated as more and more very fine pitch devices are used. Even placing the device in the correct location, but in the wrong orientation can result in electrical failure. Manual placement is impractical for production quantities.

Fortunately, advanced robotic equipment has been developed and is commercially available for accurate, high-speed placement of components. Entry-level automated placement machines can place 3,000–5,000 parts per hour while mid-range equipment, that can hold more feeders, can place 8,000–10,000 parts per hour. On the high-end, placement speeds of 30,000 and higher are being achieved.<sup>[67]</sup> In fact, speeds of the new equipment are so great (chipshooters can place up to 80,000 components per hour) that they often must be slowed in order for adhesive dispensing to catch up; alternatively extra adhesive dispensers must be added to the production line.

A wide variety of fully automatic machines exist. Generally, feeders, which may consist of tape-and-reel, stick, or tray, deliver the parts individually so they can be picked up and automatically inspected. Machines are equipped with vacuum nozzles to pick up the components and carry them through inspection, alignment, and placement. A list and description of commercially available component placement equipment is given in Table 4.24.

## 4.5 CURING

After dispensing the adhesive and placing the devices, the adhesive must be cured, that is, it must be advanced from a liquid or semi-solid state to a solid state for full development of its adhesive strength and dielectric properties. In the broad sense, *curing* is the processing that is involved in altering the state of the adhesive material so that it can adequately bond two surfaces. In most cases, this involves polymerization of low-molecular-weight monomers or polymers through the application of heat or other form of energy. With prepolymerized materials, such as many thermoplastics, curing simply involves evaporation of the solvent (if there is a solvent) and heating to bring the adhesive up to its melt temperature. In other cases, as with polyimides, curing involves the formation of ring structures along a prepolymerized molecular chain by heating.

**Table 4.24.** Component Placement Systems

Model/Supplier	Board Sizes (in × in)	Throughput (placements/hr)	Placement Accuracy	Part Types Placed	
TP9-UFP* and TP-11UFP/Mydata Automation	0.7 × 0.7 (minimum) to 13 × 18 (standard), 20 × 18 (optional)	6,000	0.002 mm (x) and 0.005 mm (y)	ICs, MELFs**, air-wound coils, and 0402 parts, and QFPs up to 2.2 inch square	
Models TP12-UFP and T18-UFP/ Mydata Automation		6,500			
TP9-2U/Mydata Automation		4,800			Wide range of components including SOICs
Quad IVc <sub>Mk2</sub> 115/ Quad	18 × 18	3,600	±0.06 mm (accuracy), ±0.03 mm (precision)	0402 to PLCC68	
Quad IVc <sub>Mk2</sub> 90/ Quad	18 × 22				
Quad IVc <sub>Mk2</sub> 68/ Quad	18 × 24				
Quad IVc <sub>Mk2</sub> 136/ Quad					7,000
Quad IVc <sub>Mk2</sub> 204/ Quad					9,400

**Table 4.24.** (Cont'd.)

<b>Model/Supplier</b>	<b>Board Sizes (in × in)</b>	<b>Throughput (placements/hr)</b>	<b>Placement Accuracy</b>	<b>Part Types Placed</b>
SMT 2500C/ CELMACS SMT Corp.	2 × 2 to 16 × 20	7,200	± 0.04 mm w/IC head, ± 0.1 mm w/chip head	0402 chips to 1.8 inch (45-mm) square QFP and BGA, fine pitch and non- standard shaped components
SMT 2350C/ CELMACS SMT Corp.	2 × 2 to 16 × 20 and 24–79 mils thick	Passive device chips: 6,200 ICs: 1,818	± 0.04 mm w/IC (vision) head, ± 0.1 mm w/chip (chucking) head	0402 chips to 1.8 inch (45- mm) square QFP and BGA, fine pitch and non-standard shaped components
SMT 1250C/ CELMACS SMT Corp.	2 × 2 to 16 × 20 and 24–79 mils thick	10,825	±0.1 mm	0402 chips to 1.8 inch (45- mm) square QFP
RX11/TDK	2 × 2 to 16 × 12	20,000	±0.1 mm	0402 to 1206, 0603 to 1812, and SOPs
SS-2/TDK	2 × 2 to 18 × 15	4,200	±0.1 mm (standard chip), ±0.04 mm (ICs)	0402 to 1.7-inch (44-mm) square chip components. 1206, 0603 to 1812, and SOPs
<i>(Source: Compiled from suppliers' technical data sheets.)</i>				

In a stricter sense, curing involves polymerization of monomer resins by reaction with a hardener or by initiation with catalysts and, generally, requires heat or another form of energy. Epoxy resins and other thermoset resins cure by forming a highly cross-linked structure either by condensation or an addition of polymerization (see Ch. 3). Some hardeners and catalysts for epoxy resins are so reactive that, upon mixing, curing takes place in a matter of minutes, even at room temperature. Among these fast curing agents are the primary and secondary aliphatic amines and the boron trichloride or trifluoride amine complexes. Other hardeners such as aromatic anhydrides require elevated cure temperatures for a period of time to achieve full polymerization. Heating is the most widely used method for curing adhesives and may be applied in a convection oven or by infrared lamps in a conveyor furnace. Localized heat may also be generated by microwave heating equipment. Other curing methods involve exposure to ultraviolet light or to moisture. A summary of the various curing methods with their advantages and limitations is given in Table 4.25 and a discussion of them follows.

### 4.5.1 Thermal Curing

Adhesives that are heat cured fall into three categories: conventional, fast cure, and snap-cure types. The conventional types cure in 0.5 to 2 hours at temperatures of 150°C to 175°C. These adhesives have generally been used in high-reliability applications, especially in hermetically sealed packages for multichip modules or hybrid microcircuits where subsequent outgassing can cause failures. Curing is conducted in box ovens with either circulating air or nitrogen. In the high production of consumer and commercial products, fast-curing adhesives have been developed that are compatible with automated in-line equipment. Thus, there are fast-cure systems that cure in 15 minutes or less, and the snap-cure types that cure in less than one minute at temperatures greater than 150°C. Curing is conducted following in-line component placement by moving the parts on a conveyor belt through an infrared furnace. Furthermore, surface-mount adhesives have been developed that can be partially or completely cured during the solder-reflowing step. Those that are partially cured must then receive a short postcure.

In addition to heat, some adhesives require the simultaneous application of pressure. Examples include the bonding of substrates with thermoplastic film adhesives and the bonding of flip-chip and TAB devices with anisotropic

**Table 4.25.** Comparison of Curing Methods

<b>Curing Method</b>	<b>Advantages</b>	<b>Limitations</b>
Thermal	Low cost Uses existing equipment	Long cycle times for most formulations Incomplete cure may occur with fast cure, snap cure adhesives, depending on thermal mass
Infrared	Uses existing SMT equipment in place High throughput	May require post curing
Microwave	Fast curing rates (factor of 10) over forced convection heating Reduced stress from CTE mismatched materials	Cure schedules require optimization of many parameters Specialized equipment
UV/visible	Rapid curing increases production throughput Good for heat-sensitive devices Low production costs Reduced energy requirements	Line of site process; shadow area may require a thermal post-cure Requires photosensitive formulations
Moisture	No heat or energy required Room-temperature cure Good for heat-sensitive devices	Limited to only a few polyurethane and silicone adhesives May require several days to achieve full cure May require post heat curing

adhesives. In bonding ceramic substrates to the inside of metal or ceramic packages with an epoxy film, sufficient pressure must be applied during cure so that the adhesive flows evenly, moving air and other entrapped volatiles out toward the edges and forming a fillet around the part. Often, small voids or bubbles can be seen in the fillet after curing, an indication that solvent or absorbed moisture were pushed out. This may not be serious if the number of voids within the bondline is small or nonexistent. Techniques for reducing voids include vacuum baking the surfaces prior to applying the adhesive, curing the adhesive while under vacuum and pressure, or step curing the adhesive. The degree of voiding may be quantitatively determined by scanning acoustic microscopy (SAM) or, more simply, by using glass as one of the adherends so that voids may be detected through the glass from the bottom side.

With anisotropic adhesives, pressure is necessary to squeeze the film so that electrical contacts are made between the aligned electrodes of the parts being bonded. While under pressure and while the electrodes make contact with the metal filler particles, the adhesive cures in the area surrounding the connections and fixes the positions of the  $z$ -direction connections.

**Outgassing during cure.** Solvents, low-molecular-weight additives, reactive diluents, absorbed moisture, and other constituents outgas during thermal curing. The nature of the outgassed products and their amounts vary with the adhesive formulation used and with the cure temperature. It is, of course, important that these volatiles be removed to produce sound, void-free bondlines; however, the condensation and redeposition of these volatiles (a condition called *raining*) on the interior of an oven and on other circuits being cured in the same oven presents a contamination problem. Thus, it is desirable to use adhesives that produce the least amount of outgassing during cure and that the outgassed products not be corrosive. Selecting adhesives that have the lowest weight losses during cure have been shown to produce the highest yield of good wire bonds.<sup>[68]</sup> Compounds that have been evolved from curing epoxy adhesives include methyl alcohol, carbon dioxide, acetone, methyl ethyl ketone, toluene, nitrogen heterocyclic compounds, unsaturated hydrocarbons, 2-propenol-1 (allyl alcohol), and 2-propenyl ester of formic acid.<sup>[69]</sup> Most of these are solvents used as part of a solvent-based formulation or are residual solvents that were used in the manufacture of the adhesive. Weight losses during cure can be as high as 25% (as for solvent-based adhesives such as polyimides) but, in most cases, range from 0.4% to 5% when cured according to the manufacturers' instructions.<sup>[70]</sup>

### 4.5.2 Ultraviolet/Visible Light Curing

Photosensitive adhesive formulations based on acrylates, epoxy acrylates, and polyurethane acrylics may be cured by exposure to ultraviolet or visible light. The key benefits of UV curing are the speed of curing and the avoidance of high temperatures for heat-sensitive components. UV-curing adhesives are finding increased use in high production assembly where only 5 to 20 seconds are required to cure an entire populated circuit board. The cure time depends on the formulation and on the frequency and power of the UV source. Cure times of 10–20 seconds result from using long wavelength (365 nm) from a moderate intensity source of  $50 \text{ mW/cm}^2$ . By using a higher intensity radiation source of  $150 \text{ mW/cm}^2$ , the cure time can be reduced to 5 seconds.<sup>[71]</sup> In general, optimum cures are obtained in the wavelength range of 250 to 400 nm and a radiant output of at least  $150 \text{ mW/cm}^2$ .<sup>[72]</sup>

Medium pressure mercury-vapor lamps are quite popular as a source of UV radiation. UV-curing equipment can emit light at specific frequencies matching the absorption bands of the photosensitive groups of the adhesive. The shape and intensity of the emitted radiation can be varied to flood a large area or focused for high-intensity, high-speed curing. Many companies that supply UV-curing adhesives also sell compatible curing equipment ranging from portable hand-held wands to conveyerized-belt systems.<sup>[73]</sup>

### 4.5.3 Microwave Curing

Variable-frequency microwave (VFM) curing is a fairly recent development for rapid curing of adhesives, coatings, and encapsulants.<sup>[74]</sup> VFM curing differs from conventional microwave heating in using swept frequencies instead of a fixed frequency. Variable-frequency microwave makes use of three parameters: central frequency, frequency bandwidth, and sweep rate. Through the frequency-sweeping process, problems of non-uniform temperatures and arcing associated with conventional microwave ovens are avoided. VFM curing is reported to be 2 to 10 times faster than conventional heat curing. A further advantage is the uniform distribution and precise control of microwave energy that can heat large sections uniformly. Compared with conventional heat curing, VFM curing produced similar die-attachment stresses and reduced warpage of FR-4 printed-circuit boards onto which the components were attached.<sup>[75]</sup> Since 1994, Lambda Technologies has pioneered the VFM process and has commercialized it through the development and sale of microwave equipment.

#### 4.5.4 Moisture Curing

Moisture-curing adhesives are formulated with resins that react with atmospheric moisture to form a cured polymer. Most of these resins are one-part cyanoacrylates, silicones, or polyurethanes. The key advantage, of course, is their ability to cure without the use of heat or other external form of energy. However, in many cases, several days of ambient exposure are required to achieve full properties since the rate of curing is dependent on the relative humidity and the thickness of the adhesive. If there is too much moisture on the surface, curing of polyurethanes occurs so quickly that carbon dioxide (a significant by-product) becomes entrapped resulting in voids. Conversely, in cold temperatures, below  $-9^{\circ}\text{C}$ , moisture levels are so low that the reaction curing rate is extremely slow. Moisture-cured silicones and polyurethanes are used more as sealants, filleting, and vibration-damping compounds than as true adhesives. Because of their low moduli of elasticity and low, often negative  $T_g$ , both silicones and polyurethanes are used as adhesives and sealants where stress relief is critical, especially at low temperatures. RTV moisture-cured silicones also provide both very low and very high-temperature stability.

#### 4.5.5 Degree of Cure

*Incomplete cure*, where some of the resin or hardener remains unreacted or where the monomer resin does not fully polymerize, adversely affects all the properties of the adhesive. Incomplete cures result in reduced bond strength,  $T_g$ , and electrical values and greater outgassing and moisture absorption. Incomplete curing can result from sub-optimal time-temperature curing schedule, non-stoichiometric amounts for a two-part system or inhibition of the cure due to certain contaminants. Non-curing or incomplete curing can be due to contaminants from the ambient or from the curing oven. Amines and moisture, for example, are reported to inhibit the cure of acrylic resins while organotin, other organometallic compounds, sulfur-containing compounds, and amines are reported to inhibit the polymerization of addition-cure silicones.

Overcuring, although not as serious as incomplete curing, can result in embrittlement, reduced vibration, and shock resistance. Most methods used to establish the optimum cure are based on measuring a specific physical or electrical property as a function of the time and temperature to produce an optimum value. More quantitative methods involve measuring changes in the

infrared spectrum of absorption bands of functional groups. These bands either disappear, appear, or change in intensity as a result of polymerization (see Ch. 2).

The degree of polymerization may also be measured by differential-scanning calorimetry (DSC) from heat changes that occur during cure. The degree of cure is represented by the ratio of energy at time  $t$  to the total energy.<sup>[76]</sup> Using differential-scanning calorimetry, the percent conversion of a monomer resin to the cured polymer is given by:

$$\text{Eq. (4.8)} \quad \% \text{ Conversion} = A_t/A_{\text{total}} \times 100$$

where  $A_{\text{total}}$  is the total area of the peak in the heat flow DSC curve and  $A_t$  is the area at any time  $t$ .

DSC has been used to establish optimum cure schedules for rapid curing (snap cure) adhesives and adhesives requiring longer cures. Results showed that the snap-cured adhesive was 98% cured in 3 minutes, compared with over 15 minutes for the conventional cured adhesive.<sup>[56]</sup> The cure for the latter adhesive was verified by thermomechanical analysis (TMA) by measuring the  $T_g$  as a function of cure schedules where it was shown that up to 150°C, the  $T_g$  had not yet reached a plateau after 30 minutes. At 165°C, a plateau was reached in 30 minutes, and at 170°C, the  $T_g$  peaked in 10 to 15 minutes.

Cure cycles for adhesives should not be interrupted. Step curing should be performed in the same oven without exposing the adhesive to ambient air. Moisture absorption in partially cured adhesives affects the curing process and alters properties. The effects of interrupting the cure cycle and exposing an epoxy encapsulant to air moisture were shown by Naito and Todd.<sup>[77]</sup>

## 4.6 REWORK

The decision to rework electronic devices or assemblies depends on the cost of reworking versus the value of the part. Consumer electronics, due to their low cost, are considered throwaways and seldom reworked. For some, such as plastic-encapsulated microcircuits (PEMs) that are produced in high volumes, rework is impractical because of the difficulty in removing the plastic encapsulant without destroying the components. However, for high-value assemblies, such as densely populated PWBs and MCMs, where

the final value may be as high as \$10,000 or more, the ability to rework is essential. In such cases, rework may be necessary to meet schedules when small numbers of assemblies are produced, as for example for space and many military applications.

*Rework* generally consists of removal and replacement of a failed electronic component that has been detected after initial electrical testing or testing after burn-in. The actual rework procedure is more of an art than a science. Since each component or assembly is different, considerable experience and care are required to selectively remove one device without damaging adjacent ones.

#### 4.6.1 Rework of Components and Chip Devices

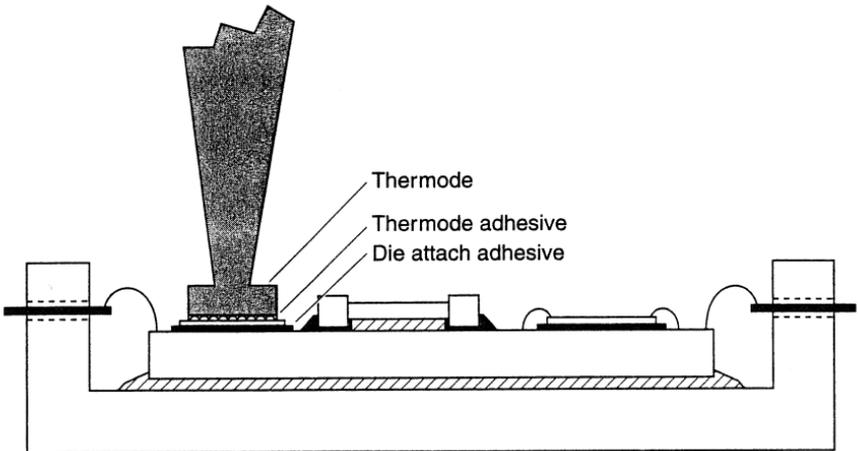
For adhesive-attached components or chip devices that are electrically connected by wire, TAB, or ribbon, the leads must first be excised. In the case of solder-connected components, the solder is heated to its melt temperature and wicked off the part.

Most electronic components are attached with epoxies. Epoxies, being thermosetting, do not melt and resolidify as do thermoplastic adhesives and solder. At sufficiently high temperatures, epoxies decompose and char and their residues are then difficult to remove. Rework procedures for thermosetting adhesives are based on selectively heating the part to a temperature slightly above the  $T_g$  of the adhesive, at which point the adhesive softens. A shear force is then applied using a wedge tool to detach the component. Where circuit components and materials are prone to thermal oxidation or decomposition, a jet of hot nitrogen gas is focused only on the part to be removed. The entire assembly or substrate is usually heated on a hot stage at moderate temperatures of 80°C to 150°C to facilitate the removal with the hot gas. Residual epoxy may be removed using a heated blade maintained at approximately 200°C or by abrading the surface. After cleaning, fresh adhesive is applied, a new device attached, and the adhesive is cured.

#### 4.6.2 Rework of High-Density Modules

With advancements in MCMs, where large chips (up to 500-mils square) are closely packed and where devices and interconnect substrates are fragile (for example, polyimide thin-film multilayer substrates used in MCM-D), new rework challenges have arisen. In these high-density circuits, spacings between the chips may be as small as 40 mils—too small

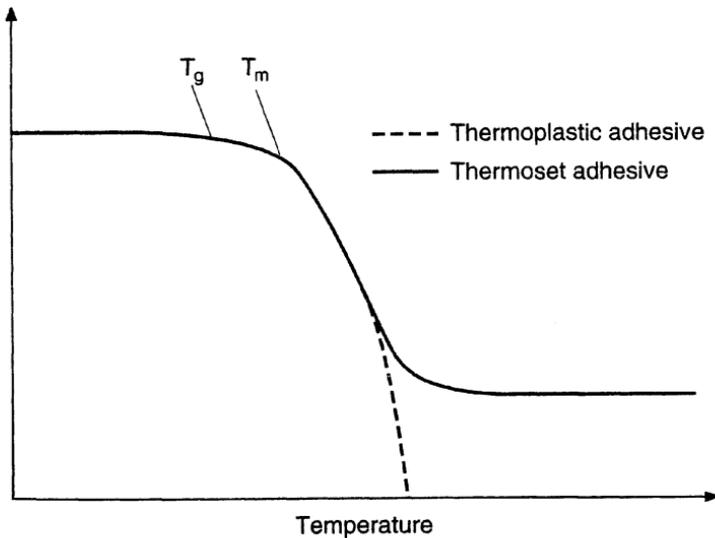
to insert a wedge tool without damaging adjacent die. Attempts to shear off the failed device also run the risk of scraping or damaging the thin-film interconnect circuitry. Furthermore, because of the large bondline areas of the chips, the force required to dislodge the chip is high.<sup>[78]</sup> Among new rework techniques developed for high-density thin-film circuits is one where a tool is bonded to the top surface of the die with an adhesive that has a higher pull strength than the adhesive originally used to attach the die to the substrate. The tool, called a *thermode*, is subsequently heated. Chips are removed by heating the thermode to 245°C for 3–5 seconds while the assembly is on a hot stage at 150°C and while a rocking motion is applied that imparts a combination of shear, tensile, and peel forces (Fig. 4.15).<sup>[79]</sup> In detaching devices bonded with Ablestik® 84-1 LMIT (electrically conductive epoxy), the thermode was attached with Ablestik 41-1. This process is a variation of the well-known Sebastian Pull Test, which uses the Sebastian Pull Tester, a nail-head tensile pull tester from Quad Group, Inc., Spokane, Washington.<sup>[80]</sup>



**Figure 4.15.** Thermode method for die removal.

### 4.6.3 Rework of Thermoplastic Adhesive-Attached Components

Components that are attached with thermoplastic adhesives are easiest to remove.<sup>[81]</sup> Parts to be removed are simply heated with a hot solder iron or by a directed stream of hot air or nitrogen to the melt temperature of the adhesive, then physically removed with tweezers or sheared off. A new part can be attached without having to completely remove adhesive residues since the resolidified adhesive residue will remelt on attaching the new component. Unlike thermosetting adhesives that soften only gradually after reaching their glass-transition temperature and that retain much of their strength, most thermoplastic adhesives melt at a specific temperature or over a narrow temperature range and lose all their strength (Fig. 4.16). Thus, they are best suited for fast-turnaround production avoiding hours of curing in controlled-atmosphere ovens.<sup>[82]</sup>



**Figure 4.16.** Relative strengths of thermoplastic and thermosetting adhesives ( $T_m$  is the melt temperature of the thermoplastic adhesive;  $T_g$  is the glass-transition temperature of the thermosetting adhesive).

#### 4.6.4 Rework of Attached Substrates or Assemblies

There are occasions when it may be desirable to salvage a populated substrate that is already attached in a sealed package; for example, if the sealed package was found to be a fine or gross leaker and the costs of the substrate and components were high. In such cases, the substrate may be detached from the package by first severing the wires that connect it to the package pins, then heating the entire module while prying the substrate loose at one edge. Some more brittle adhesives may detach from the package by carefully flexing the package. However, this procedure is risky, particularly for large-area packages, since the substrate may crack and the entire circuit be damaged. Alumina substrates, being mechanically stronger than silicon substrates, are better able to survive this procedure. Thermoplastic adhesives used to bond substrates are easier to remove and desirable, provided they have the thermal and mechanical properties to withstand vibration, thermal shock, and other application-specific requirements. Thermoplastic films such as PEEK<sup>®</sup> (polyaryletheretherketone) and ULTEM<sup>®</sup> (polyetherimide) have been investigated and reported to pass stringent MIL-STD-883, Method 5011 tests.<sup>[83]</sup>

Alternative removal methods have been reported, but none is widely used. Of these, one involves sliding a hot wire, through which current is passed, between the substrate and package. This process simultaneously softens and slices through the adhesive bondline. Another method consists of inserting a resistance heater on the underside of the substrate to generate additional localized heating at the adhesive interface.

#### 4.6.5 Rework of Underfill Flip-Chip Devices and Ball-Grid Array Packages

Reworking underfilled flip-chip devices or BGA parts also presents new challenges since both solder and adhesive are present and both must be removed. New underfill formulations have had to be developed that soften, but do not char at the temperatures required to liquefy the solder. Some equipment manufacturers have modified their flip-chip bonders to include a rework station.<sup>[84]</sup> In general, the chip undergoing rework is spot heated to melt the solder connections and simultaneously soften the underfill. Machines are equipped with bottom-side heating of the substrate to temperatures of 125°C to 175°C while the chip is heated from the top side at temperatures of 200°C and higher to melt the solder. The chip is then gripped and twisted or sheared from the substrate.

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# 5 Applications

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Polymer adhesives have found their place in numerous electronics' applications. Major uses include commercial/consumer products; computers; and military, space, automotive, medical, and wireless communications. Some adhesives may be used across several applications while others have been formulated to meet application-specific requirements. For example, reworkability is not a consideration for high-production, low-cost consumer products such as cell phones or calculators, but is important for high-value, high-density printed-wiring boards (PWBs) used in military and space electronics. Further, thermal stability at high temperatures is required for near-engine electronics in automobiles, aircraft, and for deep-well sensors, but not for office computers. The major applications for polymer adhesives are to attach and electrically insulate or to electrically connect components, devices, connectors, cables, and heat sinks to printed-circuit boards or to thin- or thick-film hybrid microcircuits. In addition, over the last several decades, new uses for adhesives have emerged for optoelectronic (OE) assemblies, microelectromechanical systems (MEMS), and flat-panel displays.

This chapter is structured into two segments: general applications, such as die attachment, surface mounting, and underfills that apply to many products, and specific applications, such as automotive, military, space, optoelectronics, and flat-panel displays.

## 5.1 GENERAL APPLICATIONS

Some adhesive materials and processes are used across many applications. For example, adhesives used to attach bare die and substrates in hybrid or multichip modules may be used for a wide variety of ground-based military

electronics, communications systems, and space systems. Adhesives are also widely used in surface-mounting components onto printed-wiring boards that serve numerous electrical functions for both low-end consumer electronics and high-reliability military and space systems. Underfill adhesives are used to provide stress relief and ruggedize the solder interconnects for almost all flip-chip and area-array devices, regardless of their function as integrated circuits.

### 5.1.1 Surface-Mount Technology

Surface-mount technology (SMT) has emerged as the major assembly process for printed-circuit boards permitting higher-density circuits than plated-through-hole single-sided or double-sided types. Surface-mount technology is now used across many applications from high-reliability space and military electronics to low-cost consumer products. Components are interconnected using solder, but are held in place with electrically insulative adhesives called *surface-mount adhesives* (SMAs) until the solder is reflowed. SMAs are also used to hold components in place for circuits that are to be wave soldered. Thus, electrically insulative SMAs play an auxiliary role in SMT solder attachment. However, electrically conductive adhesives are beginning to be investigated and used as SMAs for the primary function of replacing solder.

In the general process flow for SMT, printed-circuit boards are cleaned and dried, solder paste is stenciled or screen printed onto pad locations to which components are to be connected, adhesive is dispensed between the solder pads, and components are placed onto the wet adhesive paste. At this point, the adhesive may be fully cured, snap cured, or partially cured. In all cases, the cure should be sufficient to hold the components in place during the final solder reflow or wave soldering steps (Fig. 5.1). Adhesives may also be cured during the solder-reflow step so that solder reflowing and adhesive curing occur simultaneously, thus reducing the number of process steps (Fig. 5.2). In high production, these steps are performed using in-line modular equipment that is computer controlled (Fig. 5.3).

After the components have been placed onto the wet adhesive, the adhesive must have sufficient “green strength” (wet strength) to hold the components in place until they arrive at the solder-reflow stage. *Green strength* is the resistance to shifting of the components that can occur during the rapid acceleration and deceleration that results from moving the boards during automated assembly. Accelerations and decelerations ranging from

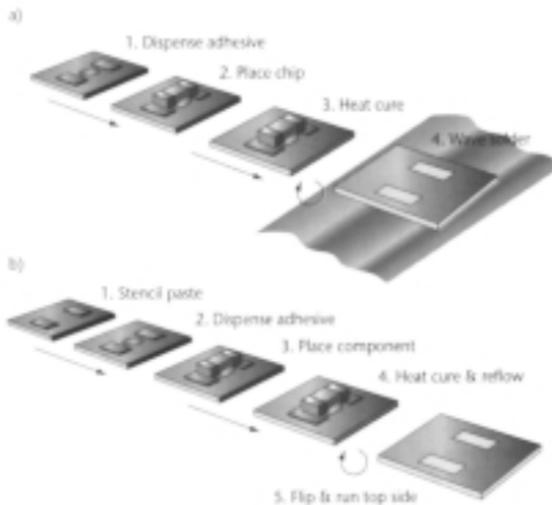
5 m/sec<sup>2</sup> to 20 m/sec<sup>2</sup> result from starts and stops in automated handling equipment.<sup>[3]</sup> Thus, high green strength is necessary to maintain component orientation prior to soldering.

Green strength may be determined by measuring the lateral force that bonded parts can withstand. In one test method (Siemens Standard SN59651),<sup>[4]</sup> a populated board is allowed to slide down an incline to a stop at the base, and the displacement of components on the board is measured (Fig. 5.4). An acceleration run of 400 mm from a height of 35 mm is made. A maximum shift of 0.15 mm (50% of the track pitch for a standard 0.3-mm pitch part) is considered acceptable.<sup>[5]</sup>

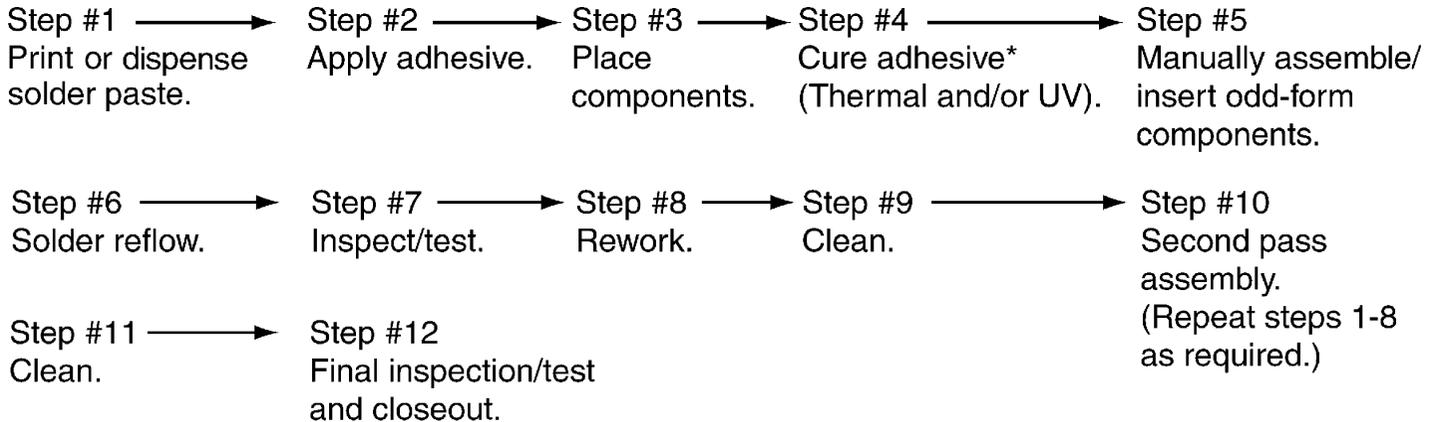
In another test, a 40-mil diameter, 10-mil thick dot is dispensed onto a test plate. A rod is lowered into the uncured adhesive and withdrawn while a load cell is used to measure the green strength in gm/cm<sup>2</sup>.<sup>[6]</sup> Green shear strengths may also be determined by mounting passive components, such as 0603\*, 0805, and 1206 onto printed-circuit boards with uncured adhesives, subjecting the boards to the full force of a high-speed, chip-shooter table motion,<sup>[6]</sup> and measuring component displacement.

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\*0603, 0805, and 1206 are designations for passive components such as capacitors and resistors based on size, thus 1206 is a component that is approximately 120 × 60 mils.

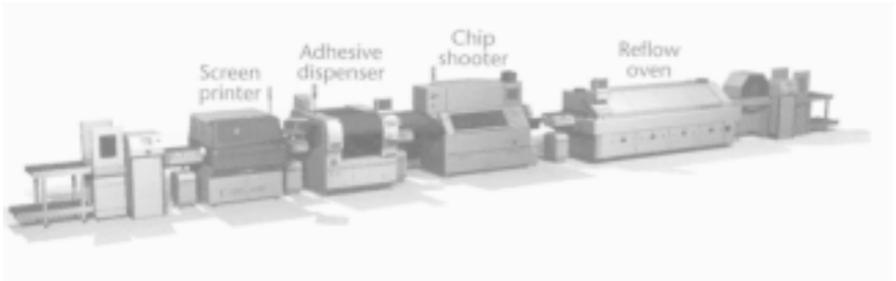


**Figure 5.1.** Representation of SMT for (a) wave soldering and (b) reflow soldering.<sup>[1]</sup>

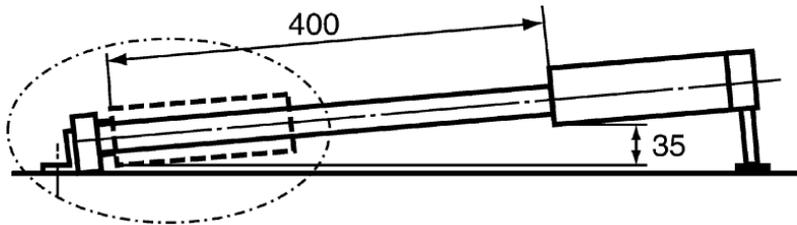


\* Optional and not required if adhesive cures in preheat zones of a reflow oven.

**Figure 5.2.** SMT process steps.



**Figure 5.3.** In-line modular SMT equipment.<sup>[2]</sup>



**Figure 5.4.** Test fixture for measuring green strength. (Source: Siemens Standard Specification SN59651).

Green strength may be affected by many variables. In general, higher viscosity adhesives display greater green strength. Other factors such as dot size and profile, number of dots, and the nature of the adherend surfaces (passivation, solder maskant) also influence the results.<sup>[7][8]</sup> Moisture absorption of the adhesive prior to cure is also critical to adhesive performance. High moisture absorption shortens pot life, reduces wettability, and affects cured properties such as the  $T_g$ . The ideal characteristics for a surface-mount adhesive may be summarized as follows.

- Excellent green (wet) strength.
- High viscosity for dispensing dots having high aspect ratios.
- High shear thinning and flow under pressure with quick recovery and limited flow after component placement (good thixotropic properties).
- Easy release from the dispensing tip with no tailing or stringing.

- Ability to retain print or dot height.
- Low moisture absorption.
- Noncorrosive.
- High strength after cure.
- Low  $T_g$  (80°C–100°C).

In surface mounting of components to plastic-laminate PWBs, curing temperatures should be chosen that do not degrade the board material, electronic components, or other parts already assembled. For epoxy-laminate PWBs, it is best to keep curing temperatures at or below 150°C for as short a time as possible, commensurate with achieving optimum properties. Curing temperatures higher than 150°C may be used on some high-grade epoxy boards, on polyimide boards, and, of course, on ceramic substrates. Lower temperatures are necessary for polyester and other low-cost consumer-grade laminates. Thus, in curing epoxy surface-mount adhesives, schedules of 120°C–150°C for approximately 1–3 minutes are used, depending on the adhesive. Table 5.1 lists some specific SMT adhesives, their recommended curing schedules, and other properties. In this table, the yield value refers to the minimum force required to start an adhesive moving. Yield values are helpful in setting the equipment parameters for screen printing or stencil printing.

After the solder has been reflowed and the adhesive has been cured, the adhesive has served its primary function of holding the components in position during solder reflow. However, since the adhesive remains permanently on the board, its cured properties must be such that it will not reduce the reliability of the assembly or cause subsequent failures.

The properties of cured surface-mount adhesives that are critical to their performance include moduli of elasticity (MOE), coefficients of thermal expansion, glass-transition temperatures, and thermal conductivities. Modulus is especially critical for large components and for adherends having dissimilar expansion coefficients. High-modulus adhesives do not readily absorb stresses during thermal cycling. Expansion coefficients for surface-mount adhesives range from 45–100 ppm/°C below the  $T_g$  and 150–190 ppm/°C above the  $T_g$ . Values of  $T_g$  range from 70°C–150°C, but some are very low and even negative, such as those for elastomeric polyurethanes and silicones. Low  $T_g$  values are better for stress relief and for rework. Generally, surface-mount adhesives should have CTEs below 50 ppm/°C, to avoid cracking of solder joints during thermal excursions.

**Table 5.1. Properties of Surface-Mount Paste Adhesives**

Product Name/ Supplier	Type	Viscosity cps <sup>1</sup>	Thixo- tropic Index <sup>2</sup>	Yield Value (N/m <sup>2</sup> , Casson)	Shelf life -40°C/ Pot Life <sup>3</sup> 25°C	Cure Schedule min @ °C	Lap- Shear Strength psi	CTE ppm/°C		T <sub>g</sub> °C	Volume Resistivity ohm-cm	Thermal Conductivity W/m-K
								α <sub>1</sub>	α <sub>2</sub>			
EpiBond® 7275/ Cookson Electronics Assembly Materials	Calcium carbonate filled epoxy resin	420,000	>6	N/A	N/A	12 @ 80°C	N/A	48	170	66	2.1 × 10 <sup>15</sup>	0.027
Amicon® E6750/ Emerson & Cuming	Polyamide-cured epoxy resin with pigments/ modifiers	185,000	4.6	2,800	3 mos (25°C)/-	3.5 @ 120°C in IR oven	2,000	N/A	N/A	65	10 <sup>14</sup>	0.25
Amicon® E6752/ Emerson & Cuming	Polyamide-cured epoxy resin with pigments/ modifiers	185,000	4.6	2,800	3 mos (25°C)/-	3.5 @ 120°C in IR oven	2,000	N/A	N/A	65	10 <sup>14</sup>	0.25
Amicon® D124F/ Emerson & Cuming	Mineral-filled epoxy adhesive	135,000– 165,000	3.2–5.0	730	3 mos (4°C)/-	3.5 @ 120°C in IR oven	>870	55–60	N/A	85	>10 <sup>14</sup>	0.30
Amicon® D124F1 Red/ Emerson & Cuming	Fluorescent epoxy adhesive	180,000– 260,000	>3.8	N/A	3 mos (4°C)/-	15 @ 100°C	>1,100	N/A	N/A	N/A	1 × 10 <sup>13</sup>	N/A
Amicon® D125 F 3/ Emerson & Cuming	Low-temperature curing epoxy adhesive	550,000– 600,000	1.8–2.7	N/A	N/A	2.5 @ 120°C in IR oven	>900	N/A	N/A	N/A	1 × 10 <sup>16</sup>	N/A
Amicon® D125 F 3 DR/ Emerson & Cuming	Low-temperature curing epoxy adhesive	N/A	N/A	210–310 (Bingham)	-/2 months (20°C)	2.5 @ 120°C in IR oven	>1,150	70–80	N/A	80–85	>10 <sup>14</sup>	0.30

<sup>1</sup>Brookfield 10 rpm unless indicated; <sup>2</sup>1:10 rpm unless indicated; <sup>3</sup>Time required to double viscosity; N/A – Not Available. Source: Compiled from suppliers' technical data sheets. Contact suppliers for specification values.

(cont'd.)

**Table 5.1. (Cont'd.)**

Product Name/ Supplier	Type	Viscosity cps <sup>1</sup>	Thixo- tropic Index <sup>2</sup>	Yield Value (N/m <sup>2</sup> , Casson)	Shelf Life -40°C/ Pot Life <sup>3</sup> , 25°C	Cure Schedule min @°C	Lap- Shear Strength psi	CTE ppm/°C		T <sub>g</sub> °C	Volume Resistivity ohm-cm	Thermal Conductivity W/m·K
								α <sub>1</sub>	α <sub>2</sub>			
Amicon® D125 F 4/ Emerson & Cuming	Low-temperature curing epoxy	130,000 to 190,000	2.9–5.4	N/A	3 months (0°C)/-	2.5 @ 120°C in IR oven	>870	N/A	N/A	N/A	N/A	N/A
Amicon® D125 F 4 Red/ Emerson & Cuming	Low-temperature curing epoxy	130,000 to 190,000	2.9–5.4	N/A	3 months (0°C)/-	2.5 @ 120°C in IR oven	>870	80–90	N/A	70–75	>10 <sup>14</sup>	0.30
Amicon® D125 F 5/ Emerson & Cuming	Low-temperature curing epoxy	2,550,000 to 2,600,000 (5 rpm)	1.9–2.2	N/A	3 months (0°C)/-	2.5 @ 120°C in IR oven	>900	55–60	N/A	70–75	>10 <sup>14</sup>	0.30
Amicon® D125 F 5 DR/ Emerson & Cuming	Low-temperature curing epoxy	2,550,000 to 2,600,000 (5 rpm)	1.9–2.1	N/A	N/A	2.5 @ 120°C in IR oven	>900	55–60	N/A	70–75	>10 <sup>14</sup>	0.30
Amicon® E6001, 6002/ Emerson & Cuming	Crystalline silica filled amine-cured epoxy	180,000	3.3	545	6 mos (0°C)/ 3 mos	2.5 @ 120°C in IR oven	>870	55	N/A	105	>10 <sup>14</sup>	0.3

<sup>1</sup>Brookfield 10 rpm unless indicated; <sup>2</sup>1:10 rpm unless indicated; <sup>3</sup>time required to double viscosity; N/A – Not Available. *Source: Compiled from suppliers' technical data sheets. Contact suppliers for specification values.*

(cont'd.)

**Table 5.1. (Cont'd.)**

Product Name/ Supplier	Type	Viscosity cps <sup>1</sup>	Thixotropic Index <sup>2</sup>	Yield Value (N/m <sup>2</sup> , Casson)	Shelf Life -40°C/ Pot Life <sup>3</sup> 25°C	Cure Schedule min @°C	Lap- Shear Strength psi	CTE ppm/°C		T <sub>g</sub> °C	Volume Resistivity ohm-cm	Thermal Conductivity W/m-K
								α <sub>1</sub>	α <sub>2</sub>			
Epo-Tek® H70E-4/ Epoxy Technology	Thermally conductive epoxy	20,000– 40,000	N/A	N/A	1 yr (25°C)/ 4 days	5 @ 150°C, 1 @ 175°C	1,150	55	185	70	1.0 × 10 <sup>14</sup>	1.44
PD955M/ Heraeus	Thermoset, solvent-free adhesive	10,000– 50,000 <sup>5</sup>	N/A	N/A	6 mos (5–12°C)/ >8 hrs	5 @ 125°C	362	N/A	N/A	N/A	>10 <sup>10</sup>	N/A
PD966M/ Heraeus	Thermoset, solvent-free	10,000– 40,000 <sup>5</sup>	N/A	N/A	6 mos (5- 12°C)/-	5 @ 125°C	362	N/A	N/A	N/A	N/A	N/A
PD955PR/ Heraeus	Thermoset, solvent-free	40,000– 90,000 <sup>5</sup>	N/A	N/A	N/A	1.5 @ 150°C	N/A	N/A	N/A	N/A	N/A	N/A
PD955PY/ Heraeus	Thermoset, solvent-free	40,000– 90,000 <sup>5</sup>	N/A	N/A	N/A	1.5 @ 150°C	N/A	N/A	N/A	N/A	N/A	N/A
Loctite 3607/ Loctite	Fast-curing epoxy	250,000– 400,000	2.2–8	N/A	N/A	2.5–3.0 @ 150°C	2,200– 4,600	70	N/A	110	2.0 × 10 <sup>15</sup>	0.4
Loctite 3609/ Loctite	High-speed dispensing epoxy	160– 2,000 <sup>4</sup>	3.3–12	400–700	N/A	1.5 @ 150°C	2,200– 4,600	45	145	73	2.0 × 10 <sup>15</sup>	0.3
Loctite 3610/ Loctite	Thixotropic epoxy	125,000– 225,000 (20 rpm)	3.3–12	400–700	N/A	1.5 @ 150°C	2,200– 4,600	45	145	73	2.0 × 10 <sup>15</sup>	0.4

<sup>1</sup>Brookfield 10 rpm unless indicated; <sup>2</sup>1:10 rpm unless indicated; <sup>3</sup>Time required to double viscosity; <sup>4</sup>Casson, 0.4–30 s<sup>-1</sup> unless indicated; <sup>5</sup>Haake Viscometer (30 s<sup>-1</sup>); N/A - not available; Source: Compiled from suppliers' technical data sheets. Contact suppliers for specification values.

(cont'd.)

**Table 5.1. (Cont'd.)**

Product Name/ Supplier	Type	Viscosity cps <sup>1</sup>	Thixo- tropic Index <sup>2</sup>	Yield Value (N/m <sup>2</sup> , Casson)	Shelf Life -40°C/ Pot Life <sup>3</sup> , 25°C	Cure Schedule min @°C	Lap- Shear Strength psi	CTE ppm/°C		T <sub>g</sub> °C	Volume Resistivity ohm-cm	Thermal Conductivity W/m·K
								α <sub>1</sub>	α <sub>2</sub>			
Loctite 3612/ Loctite	Fast-curing epoxy	800,000	3	350–700	N/A	1 @ 150°C, 1.5 @ 125°C	2,100– 2,900	52	N/A	155	1.8 × 10 <sup>15</sup>	0.3
Loctite 3614/ Loctite	Fast-curing epoxy	800,000	3	350–700	N/A	2.5–3.0 @ 150°C	2,100– 2,900	52	N/A	155	1.8 × 10 <sup>16</sup>	0.3
Loctite 3615/ Loctite	Fast-curing epoxy	2,000– 10,000 <sup>4</sup>	N/A	200–600	6 mos/ N/A	1.5 @ 150°C	2,175– 3,390	70	150	110	6.8 × 10 <sup>16</sup>	0.35
Loctite 3616/ Loctite	Fast-curing epoxy	15,000– 65,000 <sup>4</sup>	N/A	300–600	N/A	1.5 @ 150°C	1,900– 2,600	86	N/A	140	4.6 × 10 <sup>15</sup>	0.2
Loctite 3617/ Loctite	Fast-curing epoxy	15,000– 65,000 <sup>4</sup>	N/A	300–550	N/A	2.5–3 @ 150°C	2,100– 2,900	81	N/A	140	1.8 × 10 <sup>15</sup>	0.3
Loctite 3618/ Loctite	Fast-curing epoxy	2,000– 10,000 <sup>4</sup>	N/A	300–550	N/A	1.5 @ 150°C	2,200– 2,880	N/A	N/A	110	6.5 × 10 <sup>16</sup>	0.3
Loctite 3619/ Loctite	Fast-curing epoxy	20,000– 40,000 <sup>4</sup>	N/A	150–550	10 mos/ N/A	1.5 @ 150°C	3,200– 5,000	60	120	50	1.2 × 10 <sup>15</sup>	N/A
Loctite 3621/ Loctite	One-part, red, fast-curing epoxy	500– 3,000	N/A	130–380	10 mos/ 1 mo	2 @ 150°C, 3–5 @ 125°C	1,970– 3,770	100	218	110	1.3 × 10 <sup>15</sup>	0.3

<sup>1</sup> Brookfield 10 rpm unless indicated; <sup>2</sup> 1:10 rpm unless indicated; <sup>3</sup> time required to double viscosity; <sup>4</sup> Casson, 0.4–30 s<sup>-1</sup> unless indicated; <sup>5</sup> Haake Viscometer (30s<sup>-1</sup>); N/A – Not Available. Source: Compiled from suppliers' technical data.sheets. Contact suppliers for specification values.

(cont'd.)

**Table 5.1. (Cont'd.)**

Product Name/ Supplier	Type	Viscosity cps <sup>1</sup>	Thixo- tropic Index <sup>2</sup>	Yield Value (N/m <sup>2</sup> , Casson)	Shelf Life -40°C/ Pot Life <sup>3</sup> , 25°C	Cure Schedule min @°C	Lap- Shear Strength psi	CTE ppm/°C		T <sub>g</sub> °C	Volume Resistivity ohm-cm	Thermal Conductivity W/m·K
								α <sub>1</sub>	α <sub>2</sub>			
SMTA-2/ Zymet	One-part, red epoxy for syringe or pin transfer	105,000	6.5	N/A	6 mos. (-10°C)/ 1 mo	10 @ 100°C/ 1 @ 160°C	7,500	55	165	79	1 × 10 <sup>16</sup>	N/A
MA-120/ Thermoset, Lord Chem. Products	Silicone	122,500	N/A	N/A	6 mos. (5°C)/ 2 mos (25°C)	30 @ 125°C	450	N/A	N/A	-50	N/A	N/A
CircuitSAF™ MA-420/ Thermoset, Lord Chem. Products	High shear- thinning epoxy	2,100,000 (0.1 rpm)	121	N/A	9 mos (25°C)/-	1-1.5 @ 150°C	>2,000	45	140	70	9 × 10 <sup>15</sup>	0.28
Uralane 7760/ Vantico	Polyurethane with thermally conductive filler	410,000	N/A	N/A	3 mos / 3 hrs	30 @ 100°C	N/A	29	88	-63	2.9 × 10 <sup>14</sup>	0.69

<sup>1</sup>Brookfield 10 rpm unless indicated; <sup>2</sup>1:10 rpm unless indicated; <sup>3</sup>Time required to double viscosity; N/A – Not Available; Source: Compiled from suppliers' technical data sheets. Contact suppliers for specification values.

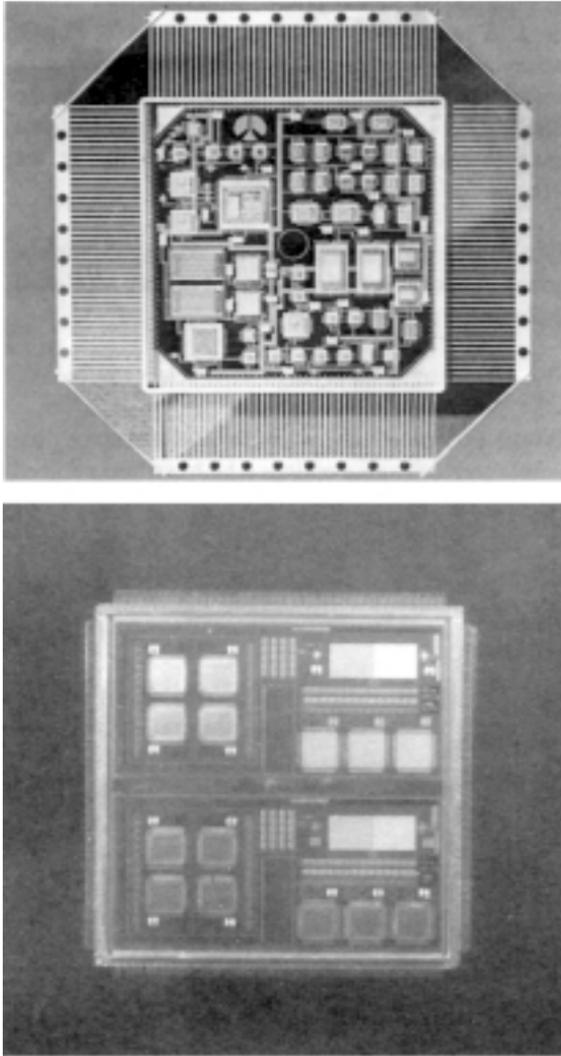
The electrical properties of SMAs are quite good. Volume resistivities are typically above  $1 \times 10^{14}$  ohm-cm at room temperature in the dry state. Although volume resistivities for epoxies usually drop to  $10^6$  ohm-cm under moist ambients, this is not considered serious for most applications, especially if the resistivities recover on drying.

### 5.1.2 Die and Substrate Attachment

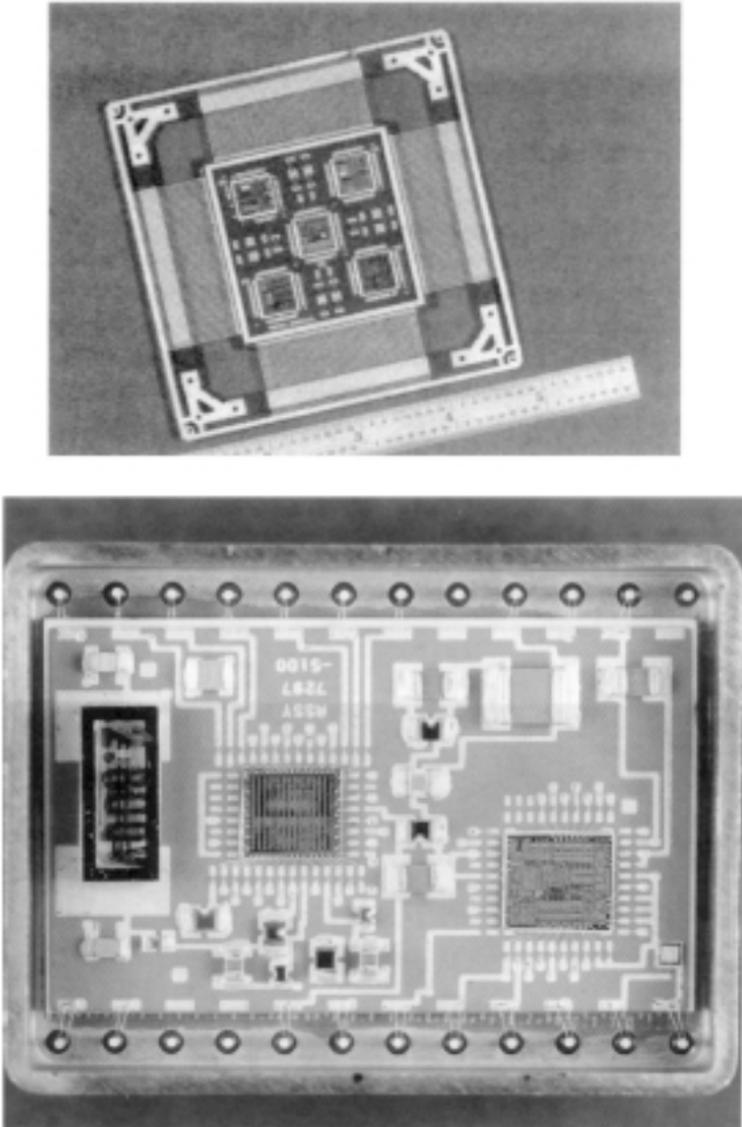
Besides their use in SMT, other major applications for adhesives are attachment of bare die in single-chip packages, in hybrid microcircuits and in multichip modules, and attachment of substrates in packages. The requirements and properties for die- and substrate-attach adhesives have already been treated in previous chapters. Thousands of part types and circuit functions have been produced by the convenient and low-cost assembly processes of attaching chip semiconductor devices and passive chip devices and interconnecting them to high-density circuit substrates. Hybrid and MCM packaging have improved military, space, and medical electronics in reducing weight and volume and increasing reliability. Some applications in which die- and substrate-attach adhesives have been used are shown in Figs. 5.5, 5.6, and 5.7. Examples and properties for some commercially available die- and substrate-attach adhesives, paste and film, are given in Table 5.2.

### 5.1.3 Underfilling

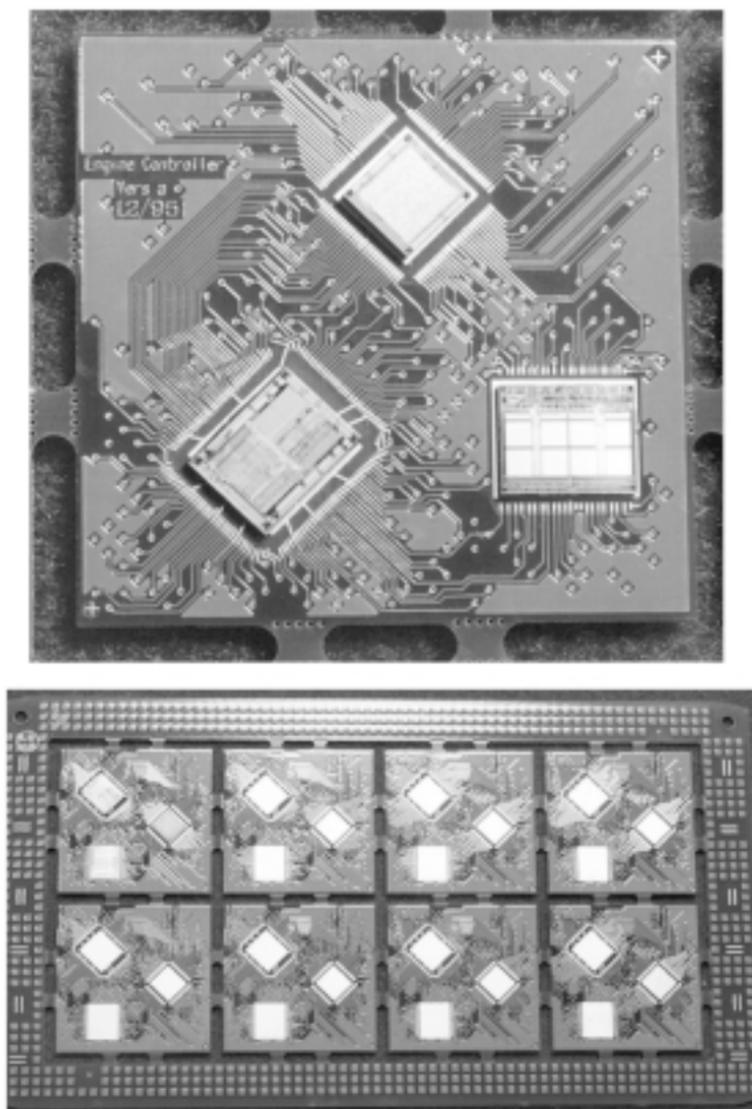
Underfilling of flip-chip devices has become a widely used process to assure that solder connections do not crack or open during thermal excursions. The use of underfill adhesives is especially necessary for attaching flip-chip devices to plastic-laminate circuit boards because of the greater CTE mismatch between solder and plastic compared with solder and ceramic boards. As a rule, to assure reliability, almost all flip-chip attached devices are now underfilled. There are three main underfilling approaches, depending on the type of adhesive used. Adhesive types include those based on capillary flow, no-flow fluxing, and preforms. Other approaches are under development to reduce the number of steps, increase throughput, reduce cost and even obviate the use of underfill entirely.



**Figure 5.5.** Examples of multichip modules (MCM-D) in which die-attach adhesives were used. Top: Aluminum/polyimide interconnect on silicon substrate in Kovar package. (Source: Rockwell Intl.) Bottom: Navy demonstrator module; aluminum/polyimide interconnect on silicon substrate in aluminum nitride package. (Source: Hughes Aircraft).<sup>[9][10]</sup>



**Figure 5.6.** Example of a ceramic multichip module (MCM-C) and a hybrid microcircuit. Top: MCM-C fabricated from high-temperature cofired ceramic. (Source: Honeywell Solid State Electronics Center.)<sup>[9]</sup> Bottom: Multilayer thick-film hybrid microcircuit. (Source: R. Wayne Johnson, Auburn Univ.)



**Figure 5.7.** Examples of laminate multichip modules (MCM-L). Top: Engine controller module. (Source: R. Wayne Johnson, Auburn Univ.) Bottom: Engine controller, array configuration. (Source: R. Wayne Johnson, Auburn Univ.)

**Table 5.2.** Properties of Some Die- and Substrate-Attach Adhesives

Product Name/ Supplier	Type	Viscosity cps*	Thixo- tropic Index**	Shelf Life (-40°C)/ Pot Life (25°C)	Cure Schedule	% Wt Loss @ 300°C (TGA)	Bond Strength psi	MOE MPa psi***	CTE ppm/°C		T <sub>g</sub> °C	Volume Resistivity ohm-cm	Thermal Conductivity W/m-K	Ionic Impurities ppm
									α <sub>1</sub>	α <sub>2</sub>				
Ablebond® 84-1 LMI SR4/ Ablestik Labs.	Silver-filled epoxy paste	8,000 (5 rpm)	5.6 (0.5/5)	1 yr/ 18 hrs	1 hr @ 175°C	0.35	6,531	3,940 (571,450)	40	150	120	1 × 10 <sup>-4</sup>	2.5	Cl <sup>-</sup> 5, Na <sup>+</sup> 3, K <sup>+</sup> 1
Ablebond® 84-3 Ablestik Labs.	Insulative epoxy paste	50,000 (5 rpm)	-	1 yr/2 weeks	1 hr @ 150°C	0.17	6,800	-	40	100	85	3.5 × 10 <sup>15</sup>	0.83	N/A
Ablebond® 71-1/ Ablestik Labs.	Silver-filled polyimide paste	14,000 (5 rpm)	2.9 (0.5/5)	1 yr/ variable	30 min @ 150°C, 30 min @ 275°C	0.35	1,348	3,400 (493,129)	41	N/A	240	1.3 × 10 <sup>-4</sup>	2.0	Na <sup>+</sup> , K <sup>+</sup> , Cl <sup>-</sup> <5
Abletherm® 2600BT/ Ablestik Labs.	Silver-filled, thermoplastic/ thermoset blend	9,300 (5 rpm)	5.6 (0.5/5)	1 yr/ 24 hrs	30 min ramp to 175°C; 60 min @ 175°C	0.5	5,400 (2 × 2 mm Si die on Ag/Cu)	4,100 (594,656)	40	70	41	2.0 × 10 <sup>-4</sup>	20	Cl <sup>-</sup> , Na <sup>+</sup> 2, K <sup>+</sup> ND
Abletherm® 5020K/ Ablestik Labs.	Insulative epoxy film	-	-	1 yr/ 6 mos	1 hr @ 150°C	0.3	>3000	N/A	45	270	109	8 × 10 <sup>14</sup>	0.7	Na <sup>+</sup> 20, Cl <sup>-</sup> 60, K <sup>+</sup> 1
Ablefilm® ECF 571/ Ablestik Labs.	Silver-filled epoxy film	-	-	1 yr/ 48 hrs	45 min @ 175°C	0.16	1,750	-	45	200	142	2.0 × 10 <sup>-4</sup>	6.7	N/A

\*10 rpm and 25°C unless indicated; \*\*10:1 unless indicated; \*\*\*Generally at 25°C; N/A – not available; ND – none detected. Source: Suppliers' technical data sheets.  
Contact suppliers for specification values.

(cont'd.)

**Table 5.2. (Cont'd.)**

Product Name/ Supplier	Type	Viscosity cps*	Thixotropic Index**	Shelf Life (-40°C)/ Pot Life (25°C)	Cure Schedule	% Wt Loss @ 300°C (TGA)	Bond Strength psi	MOE MPa psi***	CTE ppm/°C		T <sub>g</sub> °C	Volume Resistivity ohm-cm	Thermal Conductivity W/m-K	Ionic Impurities, ppm
									α <sub>1</sub>	α <sub>2</sub>				
ME 8412A/ AI Technology	Silver-filled epoxy paste	96,600 (0.5 rpm)	N/A	1 yr/-	15 min @ 150°C	N/A	>1, 600	N/A	N/A	N/A	N/A	<4.0 × 10 <sup>-4</sup>	8.0	N/A
ME 8555/ AI Technology	Silver-filled epoxy paste	94,000 (0.5 rpm)	N/A	1 yr/-	2 hrs @ 150°C	N/A	>800	N/A	N/A	N/A	N/A	<4.0 × 10 <sup>-4</sup>	8.0	N/A
ME 8418-DA/ AI Technology	Silver-filled epoxy paste	18,000 (5 rpm)	4.2 (0.5/5)	N/A	N/A	N/A	N/A	5,692 (825,556)	N/A	N/A	80	4.0 × 10 <sup>-4</sup>	3.6	Cl <sup>-</sup> 9, Na <sup>+</sup> 3, K <sup>+</sup> ND
Staystik <sup>®</sup> 211/ Cookson	Aluminum nitride thermoplastic epoxy	N/A	N/A	N/A	300°C– 375°C, 0–10 psi	N/A	>3,500	2,561 (371,442)	N/A	N/A	180– 185	>1.0 × 10 <sup>9</sup>	3.0–3.5	N/A
Staystik <sup>®</sup> 181/ Cookson	Silver-filled thermoplastic epoxy	N/A	N/A	N/A	160°C– 275°C, (0–10 psi)	N/A	>2,500	2,561 (371,442)	N/A	N/A	180– 185	≤5.0 × 10 <sup>-4</sup>	3.0–3.5	N/A
Staystik <sup>®</sup> 611/ Cookson	Insulative film adhesive	N/A	N/A	N/A	3–5 min @ 300°C– 375°C (0–10 psi)	N/A	>3,000	2,484 (360,274)	N/A	N/A	180– 185	>1 × 10 <sup>9</sup>	3.0–3.5	N/A

\*10 rpm and 25°C unless indicated; \*\*10:1 unless indicated; \*\*\*Generally at 25°C; N/A – not available; ND – none detected. Source: Suppliers' technical data sheets. Contact suppliers for specification values.

(cont'd.)

**Table 5.2. (Cont'd.)**

Product Name/ Supplier	Type	Viscosity cps*	Thixo- tropic Index**	Shelf Life (-40°C)/ Pot Life (25°C)	Cure Schedule	% Wt Loss @ 300°C (TGA)	Bond Strength psi	MOE MPa psi***	CTE ppm/°C		T <sub>g</sub> °C	Volume Resistivity ohm-cm	Thermal Conduc- tivity, W/m·K	Ionic Impur- ities, ppm
									α <sub>1</sub>	α <sub>2</sub>				
Staystik® 171/ Cookson	Silver-filled, low-stress paste	N/A	N/A	N/A	125°C– 200°C, (0–10 psi)	N/A	>1,800	427 (61,931)	N/A	N/A	25	≤ 5.0 × 10 <sup>-4</sup>	3.0–3.5	N/A
Hysol KO 110/Loctite	Silver-filled epoxy paste	7,000 (5 rpm)	4.5	9 mos/3 days	<10 min @ 165°C	NA	6,600	7,000 (1.01 × 10 <sup>6</sup> )	78	N/A	57	2 × 10 <sup>-4</sup>	3.5	Na <sup>+</sup> , K <sup>+</sup> <1, Cl <sup>-</sup> <1
Hysol QMI 301/ Loctite	Silver-filled cyanate ester paste	11,400 (5 rpm)	5.5 (0.5/5)	12 mos/ 16 hrs	10 min @ 150°C	0.2% (350°C)	5,280	7,584 (1.1 × 10 <sup>6</sup> )	45	85	245	N/A	1.9	Na <sup>+</sup> , K <sup>+</sup> ≤ 20 Cl <sup>-</sup> , <20
Hysol QMI 505-6/ Loctite	Silver-filled bismaleimide paste	12,000 (5 rpm)	4.5 (0.5/5)	12 mos/ ≥ 24 hrs	10 secs @ 200°C	0.5%	293	940 (136,336)	53	165	-30	1 × 10 <sup>-3</sup>	4.4	Na <sup>+</sup> , K <sup>+</sup> ≤ 10 Cl <sup>-</sup> , ≤ 10
Hysol QMI4030LD/ Loctite	Silver-filled themoplastic paste	32,500	11.8 (1:20)	12 mos (N/A)/ N/A	30 min @ 150°C	<0.5%	624	860 (124,732)	28	N/A	15	4 × 10 <sup>-5</sup>	15	Na <sup>+</sup> , K <sup>+</sup> ≤ 20 Cl <sup>-</sup> , ≤ 20
Hysol QMI 3555R/ Loctite	Silver-glass paste	40,000	9.5 (1:20)	12 mos (N/A)/ N/A	Profile	N/A	N/A	11,500 (1.67 × 10 <sup>6</sup> )	16	N/A	150	<1.5 × 10 <sup>-5</sup>	>80	Na <sup>+</sup> , K <sup>+</sup> ≤ 10 Cl <sup>-</sup> , F <sup>-</sup> ≤ 20

\*10 rpm and 25°C unless indicated; \*\*10:1 unless indicated; \*\*\*Generally at 25°C; N/A – not available; ND – none detected. *Source: Suppliers' technical data sheets. Contact suppliers for specification values.*

(cont'd.)

**Table 5.2. (Cont'd.)**

Product Name/ Supplier	Type	Viscosity cps*	Thixotropic Index**	Shelf Life (40°C)/ Pot Life (25°C)	Cure Schedule	% Weight Loss @ 300°C (TGA)	Bond Strength psi	MOE MPa psi***	CTE ppm/°C		T <sub>g</sub> °C	Volume Resistivity ohm-cm	Thermal Conductivity W/m·K	Ionic Impurities ppm
									α <sub>1</sub>	α <sub>2</sub>				
Epo-Tek® H20E/ Epoxy Technology	Silver-filled epoxy paste	2,200– 3,200 (100 rpm)	>3.0	1 yr/ 4 days	5 min @ 130°C and 1 min @ 180°C	0.62	>3,400	5,336 (773,922)	45	160	85	5.0 × 10 <sup>-4</sup>	2.0	N/A
JMI 7000/ Ablestik Labs.	Silver-filled cyanate ester paste	6,000– 9,000	3.0	12 mos/ 8 hrs	30 min @ 300°C	0.2 (340°C)	>2,500	10,000 (1.45 × 10 <sup>6</sup> )	33	N/A	240	2 × 10 <sup>-3</sup>	1.1 (90°C)	Na <sup>+</sup> , K <sup>+</sup> Cl <sup>-</sup> , F <sup>-</sup> ≤10
EN-4900F-1/ Hitachi	Silver-filled acrylate paste	100,000 (0.5)	5.1 (0.5/5)	N/A	60 min @ 150°C	N/A	2,124	350 (50,763)	N/A	N/A	19	4.0 × 10 <sup>-3</sup>	2.0	N/A
EN-4600B/ Hitachi	Low-stress epoxy paste	56,000 (0.5)	4.8 (0.5/5)	N/A	60 min @ 150°C	N/A	7,506	3,500 (507,633)	N/A	N/A	44	N/A	1.5	N/A
EN-4520K/ Hitachi	Silver-filled epoxy paste	113,000 (0.5)	5.8 (0.5/5)	N/A	60 min @ 180°C	N/A	1,620	4,800 (696,182)	N/A	N/A	64	N/A	10	N/A

\*10 rpm and 25°C unless indicated; \*\*10:1 unless indicated; \*\*\*Generally at 25°C; N/A – not available; Source: Suppliers' technical data sheets. Contact suppliers for specification values.

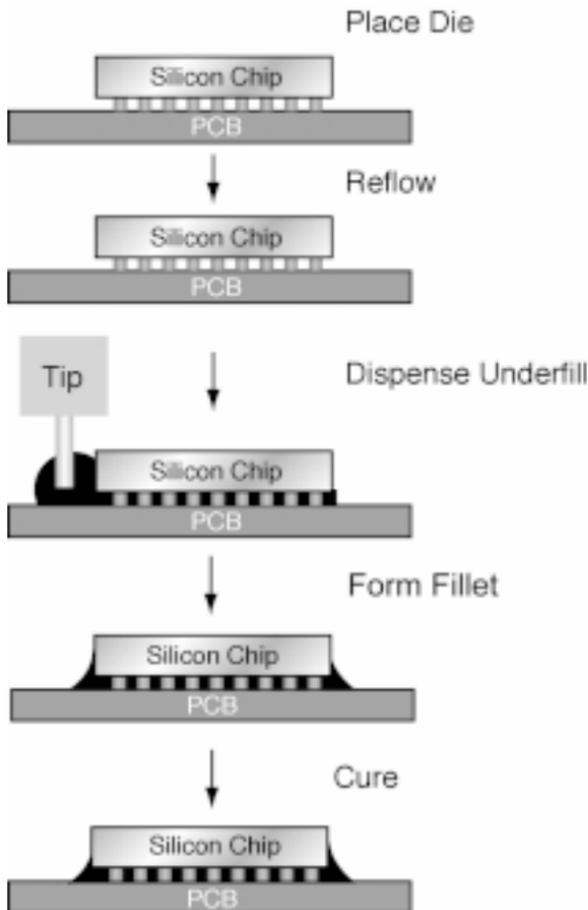
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**Table 5.2. (Cont'd.)**

Product Name/ Supplier	Type	Viscosity cps*	Thixo- tropic Index**	Shelf Life (40°C)/ Pot Life (25°C)	Cure Schedule	% Weight Loss @ 300°C (TGA)	Bond Strength psi	MOE MPa psi****	CTE ppm/°C		T <sub>g</sub> °C	Volume Resistivity ohm-cm	Thermal Conduct- ivity W/m·K	Ionic Impur- ities ppm
									α <sub>1</sub>	α <sub>2</sub>				
MD-110/ Thermoset, Lord Chem. Products	Silver-filled epoxy paste	100,000– 190,000	N/A	1 yr/ 14 days	30 min @ 130°C	N/A	5,600	N/A	56	N/A	60	8.0 × 10 <sup>-4</sup>	N/A	N/A
MD-140/ Thermoset, Lord Chem. Products	Silver-filled epoxy paste	30,000	N/A	1 yr/ 72 hrs	3-5 min@ 150°C	N/A	7,000	N/A	32	N/A	80	9.0 × 10 <sup>-5</sup>	N/A	N/A
Epibond® 7002/Vantico	Silver-filled epoxy paste	350,000	N/A	1 yr/ <48 hrs	1 hr@ 165°C	0.09	>1,720	N/A	50	140	145	2.0 × 10 <sup>-4</sup>	1.7	N/A
Epibond® 7200/Vantico	Alumina- filled epoxy paste	17,000	N/A	1 yr/ <48 hrs	1 hr@ 165°C	0.04	>3,550	N/A	30	96	145	3.9 × 10 <sup>15</sup>	0.67	N/A

\*10 rpm and 25°C unless indicated; \*\*10:1 unless indicated; \*\*\*Generally at 25°C; N/A – not available; Source: Suppliers' technical data sheets. Contact suppliers for specification values.

**Capillary-flow underfill adhesives.** It is common practice today to underfill all flip-chip devices after they have been attached and the solder has been reflowed. Capillary-flow underfilling is the method most widely used (see Ch. 4) (Fig. 5.8). Besides flip-chip devices, capillary-flow adhesives are also used for chip-scale and BGA packages, but the solder balls of these packages are often larger than for flip-chip devices, hence solder fatigue is generally less of an issue. Although advances have been made in automated dispensing (needle and jetting), and in adhesive formulations, the additional process steps and cost of underfilling are issues in high-volume production. Thus, alternate methods are continuously being investigated to reduce process steps and cost.



**Figure 5.8.** Capillary-flow underfill process steps.<sup>[11]</sup>

In the application of capillary-flow underfills, there are so many material, process, and equipment variables that empirical methods are widely used to establish the optimum processing conditions. The viscosity and flow properties of underfill adhesives are among the most important variables in rapidly filling different gap sizes and devices. A list of some commercially available underfill adhesives and their flow properties, as related to die size and gap height, is given in Table 5.3.

**No-flow underfill adhesives.** In addition to capillary-flow underfilling, a new approach to underfilling has been developed whereby the underfill material is applied before attaching the flip-chip or BGA device. Specially formulated adhesives, known as *no-flow underfills* (NFU) or *no-flow fluxing underfills* (NFFUF) do not require the tedious and time-consuming step of having to be dispensed precisely around the sides of a device and having to flow under an already solder-attached device. NFUs are basically polymer paste adhesives such as epoxies or modified epoxies that contain a fluxing ingredient that assists in making the solder connections during reflow. Whereas capillary-flow underfills are based on conventional bisphenol-A epoxies cured with amines or on cyanate esters, NFUs consist of epoxy resins cured with anhydrides and may contain carboxylic esters. Also, unlike capillary-flow underfills, some of which are highly filled (30%–60% by weight to reduce CTEs), NFUs are either unfilled or filled to less than 50% since filler particles interfere or prevent electrical contact.<sup>[12]</sup>

In processing, the NFU adhesive is squeezed out around the solder balls during placement, allowing the solder balls to directly contact the PWB bonding pads and make good electrical connections during solder reflowing (Fig. 5.9). A key advantage of NFUs is the simultaneous reflowing of the solder and curing of the adhesive, thus reducing the number of process steps. Typical reflow conditions are 220°C–230°C for 4–6 minutes. However, some NFUs cure only partially during solder reflowing and must be followed by an additional post-cure step, usually one hour at 150°C–160°C.

Once cured, the properties of NFUs are similar to those of capillary-flow underfills. One major difference is that the no-flow materials are generally unfilled and, as a result, their expansion coefficients are higher than those of their filled counterparts. However, their lower moduli more than compensate for the mismatches in expansion coefficients. NFU adhesives have shorter shelf lives than capillary-flow types because of the incorporation of the fluxing agent into the adhesive formulation. Table 5.4 is a compilation of underfills and their properties while Table 5.5 lists examples of capillary flow and no-flow underfills and their applications.

**Table 5.3.** Flow Properties of Some Underfill Adhesives

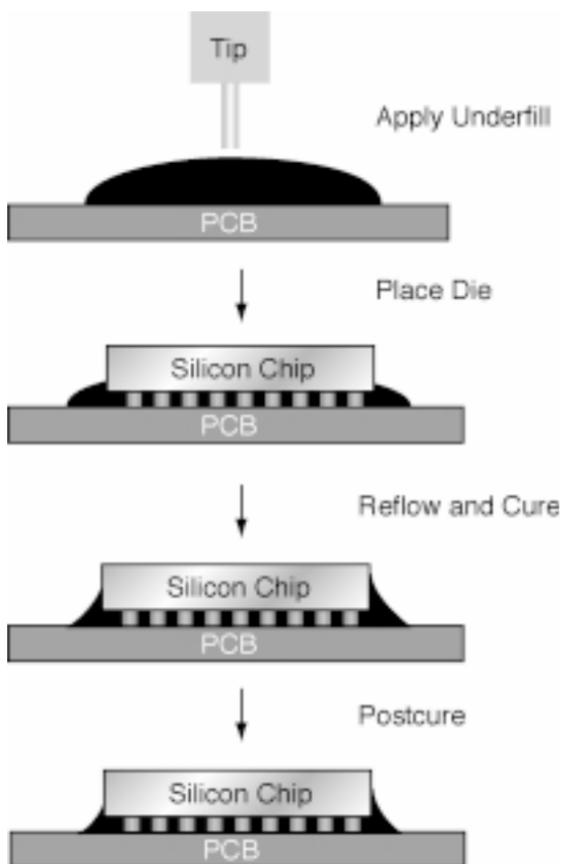
Supplier	Product	Max. Filler Size, $\mu\text{m}$	Min. Gap, mils/Max. Flow Distance (mm)	Viscosity <sup>1</sup> cps	Flow Time, sec (conditions)
Ablestik	Ablefill <sup>®</sup> JM 8806 <sup>2</sup>	25	3/38	4,000–8,000	NA
	Ablefill <sup>®</sup> UF 8802B <sup>2</sup>	10	1/38	6,000–9,000	<60 (500 mils, 1-mil gap, 95°C)
	Ablefill <sup>®</sup> UF 8807 <sup>2</sup>	50	10/NA	8,000–13,000	20 (500 mils, 13-mil gap, 100°C)
	Ablefill <sup>®</sup> JM 8801 <sup>2</sup>	NA	3/10	6,000	NA
Cookson Electronics	Staychip <sup>®</sup> 3075F	NA	0.5/25	1,500–3,000	<25 (500 mils, 2-mil gap, 100°C)
	Staychip <sup>®</sup> 3080	NA	1/25	3,300	<15 (500 mils, 1-mil gap, 100°C)
	Staychip <sup>®</sup> 3082	NA	NA	3,000	40 (750 mils, 1-mil gap, 100°C)
Loctite	FP 4544	5	1/ >50	2,600 (20 rpm)	20 (500 mils, 1-mil gap)
	FP 4531	24	3/40	10,000 (20 rpm)	30 (3-mil gap, 95°C)
	FP 4530	5	1/40	3,000 (20 rpm)	20 (3-mil gap, 95°C)
	FP 4526	27	3/40	4,700	45 (3-mil gap, 95°C)
	FP 4549	5	0.5/ >50	2,300 (20 rpm)	15 (500 mils, 3-mil gap, 95°C)
	FP 4511	10	1/30	13,000 (20 rpm)	35 (500 mils, 3-mil gap, 90°C)
	Loctite 3560	50	3/NA	5,200–16,000 (20 rpm)	NA
<sup>1</sup> 10 rpm @ 25°C unless indicated; <sup>2</sup> Former Honeywell and Johnson Matthey products; NA - Not Available. <i>Source: Suppliers' technical data sheets.</i>					

(cont'd.)

**Table 5.3.** (Cont'd.)

Supplier	Product	Max. Filler Size, $\mu\text{m}$	Min. Gap, mils/ Max. Flow Distance (mm)	Viscosity <sup>1</sup> cps	Flow Time, sec (conditions)
Loctite	Loctite 3561	40	3/15	7,500–18,000 (20 rpm)	NA
	Loctite 3563	10	1/15	5,000–12,000	<48 (500 mils, 1-mil gap, 100°C)
	Loctite 3565	10	1/15	30,000–60,000	<100 (500 mil, 1-mil gap, 100°C)
	Loctite 3567	20	1/15	6,000–16,000	<30 (500 mils, 1-mil gap, 100°C)
Emerson & Cuming	Amicon® 1172	NA	1/15	17,000 (5 rpm)	45 (394 mil, 7-mil gap, 100°C)
	Amicon® E1252	NA	1/15	20,000 (5 rpm)	9 (394 mil, 7-mil gap, 100°C)
	Amicon® E1216	NA	NA/20–25	6,000 (5 rpm)	NA
	Ablebond® 7737s	NA	1/20–25	5,000	NA
Zymet	X12131	10	2/25	15,000 (50 rpm)	NA
	X6-82-5	10	0.5/25	20,000	NA
	X6-82-5LV	10	0.5/25	3,000 (10 rpm, 65°C)	NA
	X6-82-8	10	0.5/25	3,000 (10 rpm, 65°C)	NA
	X13563	NA	0.5/38	7,250	28 (18 mm, 3-mil gap, 90°C)

<sup>1</sup>10 rpm @ 25°C unless indicated; NA – Not Available. Source: Suppliers' technical data sheets.



**Figure 5.9.** No-flow underfill process sequence.<sup>[11]</sup>

**Table 5.4.** Examples of Underfill Adhesives and Properties

Product Name/ Supplier	Description	Viscosity cps*	Shelf Life (-40°C)/ Pot Life (25°C)	Cure Schedule	Bond Strength psi	MOE MPa psi**	CTE ppm/°C		T <sub>g</sub> °C	Volume Resistivity ohm-cm	Thermal Conduc- tivity W/m·K	Moisture Absorp- tion %	Ionic Impur- ities ppm
							α <sub>1</sub>	α <sub>2</sub>					
Staychip® 3082/ Cookson	Silica-filled, epoxy- anhydride underfill	4,000	6 mos/ 32 hrs	20 min @ 165°C	10,821	4,800 (696,182)	38	141	125–136	N/A	N/A	<1	Na <sup>+</sup> <2 K <sup>+</sup> <2, Cl <sup>-</sup> <10
Staychip® 3083/ Cookson	Silica-filled, epoxy- anhydride underfill (rubber modified)	30,000	6 mos/ 18 hrs	40 min @ 165°C	7,729	6,800 (986,258)	35	133	86–88	N/A	N/A	<1	Na <sup>+</sup> <2 K <sup>+</sup> <2, Cl <sup>-</sup> <10
Staychip® 3090/ Cookson	High reliability capillary underfill	5,100	6 mos/ 12 hrs	15 min @ 165°C	N/A	3,480 (504,732)	38	130	99	N/A	N/A	N/A	N/A
Staychip® 3100/ Cookson	Silicon dioxide-filled epoxy	12,000	6 mos/ 12 hrs	60 min @ 165°C	12,118	6,200 (899,236)	35	150	114–126	N/A	N/A	1.14	Na <sup>+</sup> <1 K <sup>+</sup> <1, Cl <sup>-</sup> <1
Staychip® 3103/ Cookson	Silicon dioxide-filled epoxy	15,000	6 mos/ 12 hrs	40 min @ 165°C	10,592	5,500 (797,709)	37	136	103–106	N/A	N/A	<0.96	Na <sup>+</sup> <2 K <sup>+</sup> <2, Cl <sup>-</sup> <10

\*Brookfield @ 10 rpm and 25°C unless indicated; \*\*Generally at 25°C; N/A – Not Available. Source: Compiled from suppliers' technical data sheets. Contact suppliers for specification values.

(cont'd.)

**Table 5.4. (Cont'd.)**

Product Name/ Supplier	Description	Viscosity cps*	Shelf Life (-40°C)/ Pot Life (25°C)	Cure Schedule	Bond Strength psi	MOE MPa psi**	CTE ppm/°C		T <sub>g</sub> °C	Volume Resistivity ohm-cm	Thermal Conductivity W/m·K	Moisture Absorption %	Ionic Impurities ppm
							α <sub>1</sub>	α <sub>2</sub>					
NUF 2078E/ Cookson	Epoxy- anhydride underfill (rubber modified)	500–1,500 (N/A)	6 mos/ 24 hrs	PCB solder reflow profiles	N/A	1,800 (261,068)	65	222	130	N/A	N/A	0.855	Na <sup>+</sup> <1 K <sup>+</sup> <1, Cl <sup>-</sup> <1
FP 4549/ Loctite***	Fast-flow underfill	2,300 (20 rpm)	9 mos/ 24 hrs	30 min @ 165°C	11,000	5,600 (812,213)	45	143	140	4.1 × 10 <sup>6</sup>	0.6	1.0	Na <sup>+</sup> 2, Cl <sup>-</sup> 3
FP 4544/ Loctite	Epoxy	2,600 (20 rpm)	9 mos/ 48 hrs	30 min @ 110°C and 30 min @ 165°C	7,700	5,600 (812,213)	45	141	145	N/A	N/A	N/A	Na <sup>+</sup> <5, Cl <sup>-</sup> <10
FP 3568/ Loctite	Epoxy	30,000– 200,000 (5 sec <sup>-1</sup> )	N/A/ 30 hrs	30 min @ 150°C	1,500	733 (106,313)	40	145	70	1 × 10 <sup>14</sup>	>0.25	<2	Na <sup>+</sup> <10, Cl <sup>-</sup> <10, K <sup>+</sup> <10
FP 3595/ Loctite***	Epoxy	10,000 (20 rpm)	N/A/ N/A	5 min @ 160°C	8,900	2,053 (297,763)	24	110	116	12 × 10 <sup>15</sup>	0.6	N/A	Na <sup>+</sup> <1, Cl <sup>-</sup> <30, K <sup>+</sup> <1
FP 4527/ Loctite	Epoxy	12,000 (10 rpm)	9 mos/ 48 hrs	15 min @ 165°C (hot plate), 30 min @ 165°C (oven)	10,000	5,500 (797,709)	26	87	140	N/A	N/A	1.5	Na <sup>+</sup> 5, Cl <sup>-</sup> 5

\*Brookfield @ 10 rpm and 25°C unless indicated; \*\*Generally at 25°C; \*\*\*Now Henkel Loctite; N/A – Not Available. Source: Compiled from suppliers' technical data sheets. Contact suppliers for specification values.

(cont'd.)

**Table 5.4. (Cont'd.)**

Product Name/ Supplier	Description	Viscosity cps*	Shelf Life (-40°C)/ Pot Life (25°C)	Cure Schedule	Bond Strength psi	MOE MPa psi**	CTE ppm/°C		T <sub>g</sub> °C	Volume Resistivity ohm-cm	Thermal Conductivity W/m-K	Moisture Absorption %	Ionic Impurities ppm
							α <sub>1</sub>	α <sub>2</sub>					
Flux-fil™ 2000/ Loctite	Epoxy	N/A	6 mos/ N/A	Solder reflow profile	990	2,500 (362,595)	75	N/A	125	N/A	N/A	N/A	Na <sup>+</sup> 5, Cl <sup>-</sup> 10
Ablebond® 7737s/ Emerson & Cuming	Epoxy	5,000 (N/A)	12 mos/ 24 hrs	30 min @ 150°C	N/A	4,791 (694,877)	27	100	105	1.4 × 10 <sup>14</sup>	0.45	< 1.0	Na <sup>+</sup> <5, K <sup>+</sup> <5, Cl <sup>-</sup> <10
Amicon® 1172/ Emerson & Cuming	Epoxy	17,000 (5 rpm)	6 mos/ 2 days	6 min @ 150°C	N/A	N/A	27	N/A	135	N/A	N/A	< 1.5	Cl <sup>-</sup> <35 Na <sup>+</sup> <15 K <sup>+</sup> <10
Ablefill® UF 8807/Ablestik	Cyanate Ester	17,000 (5 rpm)	12 mos/ 8 hrs	30 min @ 165°C	N/A	10,700 (1.6 × 10 <sup>6</sup> )	21	80	135	N/A	0.6	N/A	Na <sup>+</sup> , K <sup>+</sup> , Cl <sup>-</sup> , <15
Ablefill® 8806/ Ablestik	Cyanate Ester	4,000 (5 rpm)	12 mos/ 24 hrs	90 min @ 165°C	7,000	8,700 (>1 × 10 <sup>6</sup> )	30	75	144	1 × 10 <sup>16</sup>	N/A	N/A	Na <sup>+</sup> , K <sup>+</sup> , Cl <sup>-</sup> , F <15
Ablefill® 8802-B/ Ablestik	Cyanate Ester	6,000– 9,000 (5 rpm)	12 mos/ 24 hrs	90 min @ 165°C	N/A	10,000 (>1 × 10 <sup>6</sup> )	31	84	142	N/A	N/A	N/A	Na <sup>+</sup> , K <sup>+</sup> , Cl <sup>-</sup> , F <15
Ablefill® 8801/ Ablestik	Cyanate Ester	6,000 (5 rpm)	12 mos/ 24 hrs	90 min @ 165°C	N/A	10,000 (>1 × 10 <sup>6</sup> )	25	88	146	1 × 10 <sup>16</sup>	N/A	N/A	Na <sup>+</sup> , K <sup>+</sup> <1, F, Cl <sup>-</sup> < 15
Amicon® 1330/Emerson & Cuming	Epoxy	120,000 (5 rpm)	N/A	Typical reflow cycle	N/A	N/A	90	N/A	95	N/A	N/A	<2	Cl <sup>-</sup> <20 Na <sup>+</sup> , K <sup>+</sup> <10

\*Brookfield @ 10 rpm and 25°C unless indicated; \*\*Generally at 25°C; N/A – Not Available. Source: Compiled from suppliers' technical data sheets. Contact suppliers for specification values.

(cont'd.)

**Table 5.4. (Cont'd.)**

Product Name/ Supplier	Description	Viscosity cps*	Shelf Life (-40°C)/ Pot Life (25°C)	Cure Schedule	Bond Strength psi	MOE MPa psi**	CTE ppm/°C		T <sub>g</sub> °C	Volume Resistivity ohm-cm	Thermal Conductivity W/m·K	Moisture Absorption %	Ionic Impurities ppm
							α <sub>1</sub>	α <sub>2</sub>					
Amicon® 1355/Emerson & Cuming	Epoxy	60,000 (5 rpm)	N/A	Typical reflow cycle	N/A	N/A	85	N/A	115	N/A	N/A	<2	Cl <sup>-</sup> <20 Na <sup>+</sup> , K <sup>+</sup> <10
Loctite 3560/ Loctite	Epoxy	10,000 (20 rpm)	N/A	5–20 min @ 70°C plus 3 hrs @ 150°C	N/A	N/A	27	N/A	>150	6.34 × 10 <sup>14</sup>	0.5	N/A	Na <sup>+</sup> , <20, K <sup>+</sup> <20, Cl <sup>-</sup> <20
Loctite 3561/ Loctite	Epoxy	8,500 (20 rpm)	N/A	2 hrs @ 150°C	N/A	3,960 (574,746)	<27	N/A	>150	6.0 × 10 <sup>15</sup>	N/A	N/A	Na <sup>+</sup> , <20, K <sup>+</sup> <10, Cl <sup>-</sup> <20
Loctite 3562/ Loctite	Epoxy	49,000 (10 rpm)	N/A/3 days	1 hr @ 165°C	N/A	N/A	<25	N/A	>150	8.1 × 10 <sup>15</sup>	N/A	N/A	Na <sup>+</sup> , K <sup>+</sup> <15, Cl <sup>-</sup> <20
Loctite 3563/ Loctite	Epoxy	8,000 (20 rpm)	-/24 hours	5 min @ 165°C	N/A	2,846 (413,062)	35	110	130	1.0 × 10 <sup>15</sup>	0.38	<0.5	N/A
Loctite 3564/ Loctite	Epoxy	3,000 (5 rpm)	3 mos/-	20 min @ 150°C	1,700	3,202 (464,412)	35	177	125	1.9 × 10 <sup>16</sup>	0.3	<1	Na <sup>+</sup> , K <sup>+</sup> <1, Cl <sup>-</sup> <10
Loctite 3565/ Loctite	Epoxy	45,000 (20 rpm)		30 min @ 150°C	2,000	3447 (500,000)	25	80	155	1.9 × 10 <sup>15</sup>	0.48	<0.25	Na <sup>+</sup> , K <sup>+</sup> <1, Cl <sup>-</sup> <10
Loctite 3566/ Loctite	Epoxy	4,500	3 mos/-	5 min @ 165°C	2,000	2068 (300,000)	50	120	135	1–10 <sup>15</sup>	0.25	0.65	Na <sup>+</sup> , K <sup>+</sup> <1 Cl <sup>-</sup> <25

\*Brookfield @ 10 rpm and 25°C unless indicated; \*\*Generally at 25°C; N/A – Not Available. *Source: Compiled from suppliers' technical data sheets. Contact suppliers for specification values.*

(cont'd.)

**Table 5.4. (Cont'd.)**

Product Name/ Supplier	Description	Viscosity cps*	Shelf Life (-40°C)/ Pot Life (25°C)	Cure Schedule	Bond Strength psi	MOE Mpa psi**	CTE, ppm/°C		T <sub>g</sub> °C	Volume Resistivity ohm-cm	Thermal Conduc- tivity W/m·K	Moisture Absorp- tion %	Ionic Impur- ities ppm
							α <sub>1</sub>	α <sub>2</sub>					
Loctite 3567/ Loctite	Epoxy	11,000 (10 rpm) (68°C)	3 mos/-	5 min @ 165°C	1,566	1,117 (162,000)	65	190	94	N/A	N/A	N/A	Na <sup>+</sup> , K <sup>+</sup> <10 Cl <sup>-</sup> <200
UF-3400/ 3M Co.	Epoxy	1.9 × 10 <sup>6</sup> (1 sec <sup>-1</sup> )	4- 6 mos (2-4°C)/ 8 hrs @ 50°C	Temp. plateau 135-165°C, ramp to reflow temp.	9,509	2,200 (319,084)	55	157	>150	>5.0 × 10 <sup>12</sup>	0.23	3.8	N/A
X6-82-5/ Zymet	Epoxy	<3,000 (68°C)	N/A	15 min @ 150°C 5 min @ 165°C	N/A	4,000 (580,152)	31	N/A	120	N/A	N/A	N/A	Na <sup>+</sup> K <sup>+</sup> <5 Cl <sup>-</sup> <20
X12131/ Zymet	Epoxy	15,000 (50 rpm)	N/A	15 min @ 150°C 5 min @ 165°C	N/A	N/A	42	N/A	120	1 × 10 <sup>14</sup>	N/A	N/A	Na <sup>+</sup> <5 K <sup>+</sup> <5 Cl <sup>-</sup> <20
FC-1150-1/ Zymet	Epoxy	11,000 (1 rpm)	6 mos/ 2 days	15 min @ 150°C 5 min @ 165°C	N/A	4,000 (580,152)	31	N/A	120	1 × 10 <sup>14</sup>	N/A	N/A	Na <sup>+</sup> , K <sup>+</sup> <5 Cl <sup>-</sup> <20
Film Fill FF7673/ AI Technology	Quartz-filled epoxy	N/A	N/A	30 min @ 150°C, plus 3-5 psi	2,000	N/A	26	N/A	170	>10 <sup>14</sup>	0.71	N/A	N/A
Film Fill FF7675/ AI Technology	Alumina-filled epoxy	N/A	N/A	30 min @ 150°C, plus 3-5 psi	2,000	N/A	28	N/A	170	>10 <sup>14</sup>	1.4	N/A	N/A

\*Brookfield @ 10 rpm and 25°C, unless indicated; \*\*Generally at 25°C; N/A – Not Available. Source: Compiled from suppliers' technical data sheets. Contact suppliers for specification values.

**Table 5.5.** Examples of Capillary-flow and No-flow Underfill Adhesives and Applications

<b>Adhesive/ Supplier</b>	<b>Type</b>	<b>Gap Size, mil</b>	<b>Substrate or Surface Type</b>	<b>Dispensing</b>	<b>Application</b>
Ablefill® JM8806/ Ablestik	Moisture-resistant cyanate ester (silica filled)	3	Ceramic substrates	Dispense (22–25 gauge needle), capillary underfill	Flip-chip
Ablefill® UF880H/ Ablestik	Moisture resistant cyanate ester (silica filled)	1	Ceramic substrates	N/A	Fine pitch and small gap flip-chip
Ablefill® UF 8802B/ Ablestik	Moisture-resistant cyanate ester (silica filled, no pigment)	1	Ceramics, silicon	Dispense (22–25 gauge needle), capillary underfill	Flip-chip requiring improved thermal-cycling performance; absence of pigmentation eliminates frequency interference.
Ablefill® UF 8807/ Ablestik	Moisture-resistant cyanate ester (silica filled)	10	Plastic, ceramic, and PWB laminates	Dispense, capillary underfill	CSP or BGA packages and high- density interconnect substrates
Ablefill® UF 8822/ Ablestik	Moisture-resistant cyanate ester (silica filled)	N/A	Plastic, ceramic, FR-4, polyimide, and Rigid BT	Dispense (22–25 gauge needle), capillary underfill	Underfill for lead-free interconnects; die sizes over 10-mm square (self filleting)
Ablefill® UF 8826/ Ablestik	Moisture-resistant cyanate ester (silica filled)	N/A	Plastic, ceramic, FR-4, polyimide, and Rigid BT	Dispense (22–25 gauge needle), capillary underfill	Underfill for lead-free interconnects; die sizes over 20-mm square (self filleting)

N/A – Not Available. *Source: Compiled from suppliers' technical data sheets.*

(cont'd.)

**Table 5.5. (Cont'd.)**

<b>Adhesive/ Supplier</b>	<b>Type</b>	<b>Gap Size, mil</b>	<b>Substrate or Surface Type</b>	<b>Dispensing</b>	<b>Application</b>
Ablefill® UF8806LP/ Ablestik	Moisture-resistant cyanate ester (silica filled)	1- 3	Plastic, ceramic, FR-4, polyimide, and Rigid BT	Dispense (22–25 gauge needle), capillary underfill	Alpha-emission sensitive, fine- pitch applications
Ablebond® 7737/ Emerson & Cuming	High-purity, low- modulus underfill	1	Laminates and ceramic substrates	Dispense, (21-gauge or larger) capillary underfill	Flip-chip assemblies requiring low-stress materials for improved thermal cycling. Self filleting except for very large die.
Staychip® 3100/ Cookson	High- $T_g$ , aromatic- amine cured epoxy (silica filled)	<1	Ceramic, laminates	Dispense, capillary underfill	Flip-chip in package or flip-chip on board
Staychip® 3103/ Cookson	Moderate $T_g$ , aromatic-amine- cured epoxy (silica filled)	<1	Ceramic, laminates	Dispense, capillary underfill	Flip-chip in package or flip-chip on board (low-stress)
Staychip® 3105/ Cookson	Low $T_g$ , aromatic- amine cured epoxy	<1	Silicon, ceramic, laminates	Dispense, capillary underfill	Flip-chip in package or flip-chip on board (low-stress, large die)
Staychip® 2078E/ Cookson	Epoxy anhydride, fluxing underfill	N/A	Ceramics, laminates	Automatic dispense or stencil	Area array on PWBs using solder- reflow cycle for underfill curing
Staychip® 3090/ Cookson	Amine-cured epoxy underfill	N/A	Ceramics, laminates	Dispense, capillary underfill	Flip-chip in package or flip-chip on board
Loctite 3560/ Loctite	Flowable epoxy	3	Silicon, ceramics, laminates	Dispense, capillary underfill	Flip-chip underfill in chip carriers and chip-on-board laminates
N/A – Not Available. <i>Source: Compiled from suppliers' technical data sheets.</i>					

(cont'd.)

**Table 5.5. (Cont'd.)**

<b>Adhesive/ Supplier</b>	<b>Type</b>	<b>Gap Size, mil</b>	<b>Substrate or Surface Type</b>	<b>Dispensing</b>	<b>Application</b>
Loctite 3561/ Loctite	High-purity liquid epoxy	1	Ceramics, laminates	Automated dispensing	Bare chip protection in chip on board, MCMs, BGAs, and pin-grid arrays.
Loctite 3562/ Loctite	High-purity epoxy	3	Ceramics, laminate	Dispense, capillary underfill	Flip-chip underfill
Loctite 3563/ Loctite	Rapid-cure, fast-flow, capillary epoxy underfill	1	Ceramics	Dispense, capillary underfill	Flip-chip underfill in bare-chip protection (memory cards, chip carriers, hybrids and MCMs)
Loctite 3564/ Loctite	Fast flowing, liquid epoxy underfill	1	Silicon, ceramics, laminates	Dispense, capillary underfill	Flip-chip underfill in bare-chip protection (memory cards, chip carriers, hybrids and MCMs)
Loctite 3566/ Loctite	Rapid curing, fast flowing epoxy underfill	0.5	Silicon, ceramics, laminates	Dispense, capillary underfill	Unfilled material required for bare chip protection (advanced packaging).
Loctite 3567/ Loctite	Epoxy liquid underfill, mineral filled	1	Silicon, ceramics, laminates	Dispense, capillary underfill	Flip-chip (polyamide passivation), BGA and CSP
Loctite 3568/ Loctite	Epoxy liquid underfill, mineral filled	1	Silicon nitride, ceramics, and laminates	Dispense, capillary underfill	Flip-chip (polyamide passivation), BGA, $\mu$ BGA, and CSP
N/A – Not Available. <i>Source: Compiled from suppliers' technical data sheets.</i>					

(cont'd.)

**Table 5.5. (Cont'd.)**

<b>Adhesive/ Supplier</b>	<b>Type</b>	<b>Gap Size, mil</b>	<b>Substrate or Surface Type</b>	<b>Dispensing</b>	<b>Application</b>
Loctite 3593/ Loctite	Snap-cure underfill	1	Ceramics, laminates	Dispense, capillary underfill	Chip-scale packages requiring improved thermal cycling and mechanical-shock protection.
Loctite 3594/ Loctite	Fluxing (no-flow) underfill	NA	Device passivations, OSP* – copper, copper-nickel- gold	Automated pattern dispense	Flip-chip-on-board using SMT reflow profiles. Suitable for high- frequency applications ( $\epsilon \sim 2.9$ at 100 kHz).
FP4526/ Loctite	Fast-flow, epoxy underfill	3	Ceramic, solder masks and polyimide	Automated, 22-gauge needle	Flip-chip-on-board
FP4530/ Loctite	Snap cure, fast-flow underfill	1	N/A	Automated	Flip-chip underfill
FP4531/ Loctite	Fast-flow underfill	1	N/A	Automated dispensing (21-gauge needle)	Flip-chip applications requiring snap cure.
FP6100/ Loctite	Unfilled, flexible- epoxy underfill	1	Laminates	N/A	Low-modulus, low-stress underfill for CSP and BGA applications requiring reworkability

\*Organic solderability preservative; N/A – Not Available; NA – Not Applicable. *Source: Compiled from suppliers' technical data sheets.*

(cont'd.)

**Table 5.5. (Cont'd.)**

Adhesive/ Supplier	Type	Gap Size, mil	Substrate or Surface Type	Dispensing	Application
FluxFill 2000/ Loctite	No-flow, fluxing underfill (volcano reflow)	Not applicable	CSP (ceramic), FCOB (silicon with passivation) and OSP*- copper, copper- nickel-gold, and PWBs	Dispense, 18-gauge needle @ 10 psi	Fluxing CSP or flip-chip on board (volcano cycle)
FluxFill 2200/ Loctite	No-flow, fluxing underfill (solder reflow)	Not applicable	CSP (ceramic), FCOB (silicon with passivation), OSP and copper- nickel-gold and PWBs	Dispense, 18-gauge needle @ 10 psi	Fluxing CSP or flip-chip on board (solder-reflow cycle)
Amicon® E 1216/ Emerson & Cuming	Snap-cure, non- anhydride chemistry, capillary-flow underfill	>5 mil	Ceramic, plastic, laminate	Automated dispensing (21-gauge needle)	Flip-Chip, CSP, and BGA
Amicon® E 1172/ Emerson & Cuming	Fast-flow, non- anhydride capillary- flow underfill	>1 mil	Laminates	Automated dispensing (21-gauge needle)	CSP, BGA, and Flip-chip on board

\*Organic solderability perservative; N/A – Not Available. *Source: Compiled from suppliers' technical data sheets.*

(cont'd.)

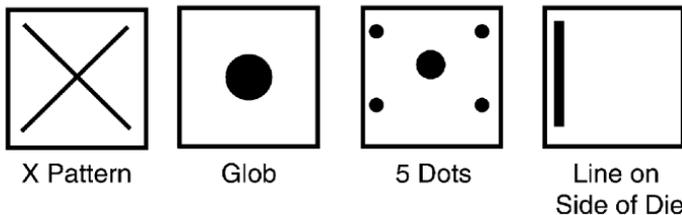
**Table 5.5. (Cont'd.)**

<b>Adhesive/ Supplier</b>	<b>Type</b>	<b>Gap Size, mil</b>	<b>Substrate or Surface Type</b>	<b>Dispensing</b>	<b>Application</b>
Amicon® E1330LV/ Emerson & Cuming	Unfilled, no-flow fluxing underfill (reworkable)	Not applicable	Nickel-gold and OSP* finishes	Syringe, jet dispense, or stencil print	Flip-chip, CSP, BGA; modest post-reflow cure (offline) required. Reworkable, 300 second reflow cycles; 225°C peak, Variable frequency microwave curable.
UF-3400/ 3M Co.	No-flow, unfilled epoxy resin	-	Flip-chip/BGA or CSP assembly and CSP bonding to PWBs (tin/lead eutectic solder bumped devices)	Automated dispensing (22- gauge needle)	CSP assembly and FCOB and CSP bonding to laminates.
*Organic solderability perservative; N/A – Not Available. <i>Source: Compiled from suppliers' technical data sheets.</i>					

Katze<sup>[13]</sup> evaluated four dispense patterns as shown in Fig. 5.10. The X and the five-dot patterns were most susceptible to air entrapment. The single-dot and single-line patterns gave the best coverage. Initial coverage beneath the die was approximately 50%, but flow-out completed the coverage.<sup>[14]</sup> Prebaking the printed-circuit board to remove moisture and limiting the exposure time of the adhesive to ambient moisture are recommended to reduce voids.<sup>[15]</sup>

**Preforms.** A third approach to underfilling involves applying an insulative thermoplastic preform (film) prior to attaching the device. Under pressure and heat, the preform softens and flows around the solder bumps, then solidifies quickly on cooling. The devices may then be solder reflowed to make the connections or the preform may be formulated to flow and encapsulate the solder during solder reflow. Table 5.6 lists some commercially available preforms used as underfills. Anisotropic film adhesives have also been used as underfill preforms, in which case *z*-direction conductive paths are formed beneath the solder bumps at the same time that rest of the insulating film flows and cures around the bumps. Anisotropic paste adhesives can be similarly used (Fig. 5.11).

**Alternate underfill approaches.** Alternate approaches that eliminate the capillary-flow underfill process currently used by electronics assemblers, involve pushing the problem back to the wafer stage. One process, *wafer-level underfill* (WLU) (Fig. 5.12), consists of applying the underfill material to a bumped wafer and then B-staging the underfill. The wafer is then diced and the die are positioned on corresponding connection pads on an interconnect substrate and solder reflowed. During reflow, solder connections are made simultaneously with the flowing, filleting, and curing of the adhesive.



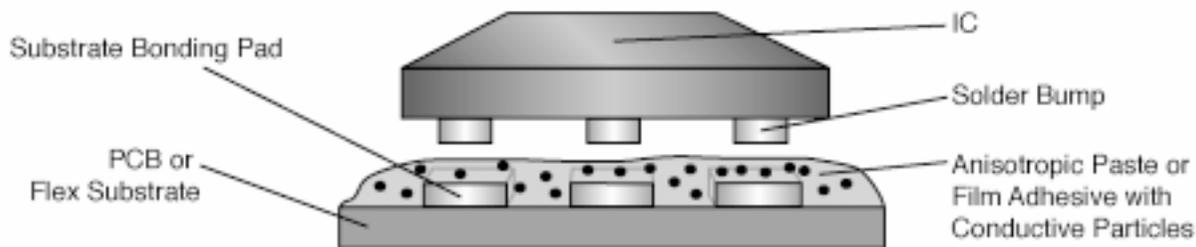
**Figure 5.10.** Dispense patterns for no-flow fluxing underfill.

**Table 5.6.** Examples of Underfill Preform Adhesives

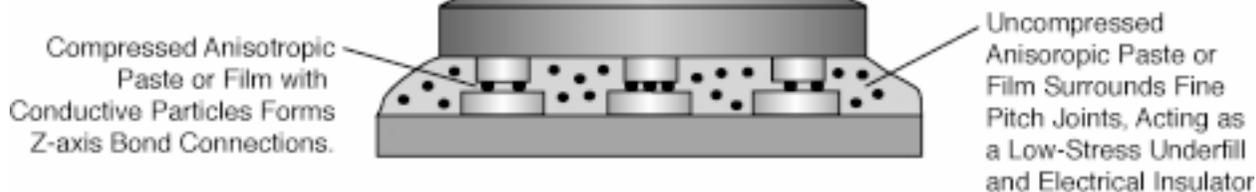
<b>Adhesive/Supplier</b>	<b>Type</b>	<b>Bonding Conditions</b>	<b>Application</b>
Film Fill FF7673/ AI Technology	Epoxy insulative film, quartz-filled, 0.7 W/m-K thermal conductivity	150°C, 10 psi, 1 sec	Flip-chip to ceramic or laminate substrates
Film Fill FF7675/ AI Technology	Epoxy insulative film, alumina-filled, 1.4 W/m-K thermal conductivity	150°C, 10 psi, 1 sec	Flip-chip to ceramic or laminate substrates
UF-511/ Hitachi	Insulative film	180°C, 145 psi, 20 sec	Flip-chip to substrate, CTE mismatched substrates
UF-526/ Hitachi	Insulative film	180°C, 145 psi, 20 sec	Flip-chip to substrate, CTE mismatched substrates
FC-212B/ Hitachi	Anisotropic film	180°C, 145 psi, 20 sec	Flip-chip underfill and electrical connections

*Source: Compiled from suppliers' technical data sheets.*

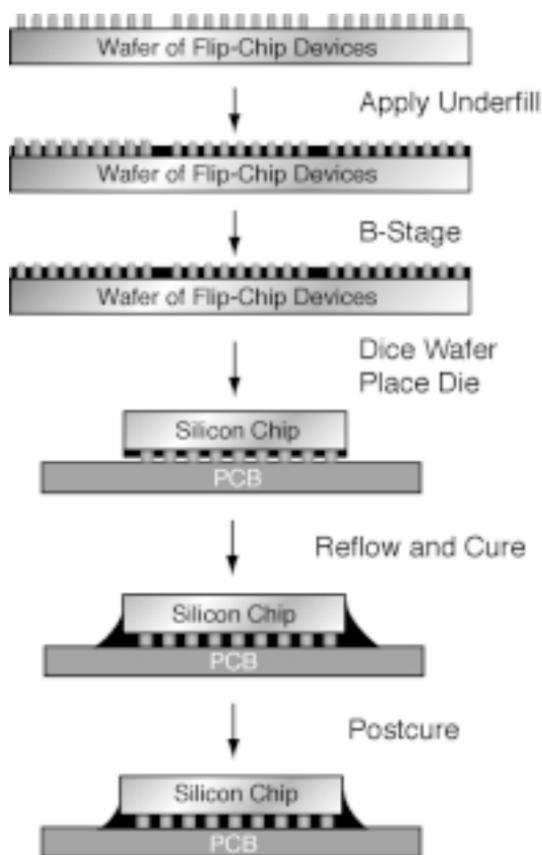
**Before Cure . . .**



**After Cure . . .**  
(Heat and Low Pressure)



**Figure 5.11.** Anisotropic film or paste underfill.



**Figure 5.12.** Process steps for underfill pre-applied at wafer stage.<sup>[11]</sup>

In a similar process, known as *polymer-film interconnect* (PFI), an insulative thermoplastic film is laminated over the devices at the wafer stage, and vias are opened over the bonding pads using a laser. At that point, either the normal solder bumps can be formed or a silver-filled conductive adhesive can be stencil printed into the vias to form polymer bumps. After printing, the epoxy is B-staged and the flip-chip devices are diced. In assembly, the devices are heated to a temperature that completes the cure of the B-staged bumps and simultaneously reflows the thermoplastic underfill material.<sup>[16][17]</sup>

Recently, Loctite has been investigating applying a coating around the solder balls of devices also at the wafer stage. The process, called *pre-applied underfill*, consists of stenciling a modified epoxy coating/adhesive to 50%–80% of the height of the bumps, heating to remove the solvent, and B-staging. The flip-chip devices are then singulated and ready for fluxing, attachment, and solder reflowing.<sup>[18]</sup>

A unique process, developed by K&S Flip Chip Division (Kulicke and Soffa), consists of forming a polymer collar around each solder bump at the wafer stage. The mini-collars reinforce and dissipate stresses from each solder bump. The collars are produced by a batch photolithographic process and are reported to increase the life-cycle performance of the solder connections up to 50% after temperature cycling.<sup>[19][20]</sup> Most of the problems associated with both capillary-flow and pre-applied underfills that are used with tin-lead solder connections have been resolved, and the materials and processes are fairly mature. However, with the trend towards replacing lead-alloy solders, a new set of underfill adhesives issues has arisen. Non-lead solders generally require reflow temperatures that are 10°C–30°C higher than tin-lead solders and generate flux residues that are different. New underfill materials are needed that will survive these higher temperatures and be compatible with the flux residues. Pre-applied material should not gel or cure before the solder joints are formed.<sup>[11]</sup>

### 5.1.4 Conductive Adhesives as Solder Replacements

Electrically conductive adhesives, primarily silver-filled epoxies, are finding uses as replacements for solder in surface-mounting components on printed-circuit boards and in flip-chip attachments. There are several driving forces for this application, a major one being the trend to eliminate lead and tin-lead solders because they may be health hazards. Also associated with the use of solder, is the need to eliminate ozone-depleting solvents presently used to clean and remove flux residues. Electrically conductive “polymer

solders”, as alternatives to tin-lead and other metal alloy solders, provide environmentally friendly materials and processes along with other benefits, such as the lower processing temperatures (often required in assembling heat-sensitive components), and finer pitch and tolerances for high-density interconnections. Cure temperatures of 120°C–150°C can be used for most adhesives while reflow temperatures of 220°C–240°C are required for solders. However, many adhesives have been formulated to cure during a typical solder-reflow cycle, thus are compatible with existing SMT production lines.

Two issues that must be addressed in substituting adhesives for solder are their compatibility with the variety of component-termination materials and PWB surfaces. Adhesion and electrical-contact resistance can vary widely depending on the nature of these surfaces. Terminations may consist of tin, tin-lead, nickel, silver-palladium, and gold. Board surfaces may consist of tin-lead solder, plated gold, or *organic-solderability preservative* (OSP) copper. OSP consists of a thin organic film that reacts selectively with the copper surface preventing it from oxidizing and guaranteeing solderability for many months. OSP provides a conductive surface that is compatible with fluxes and solder. The compatibilities of several solder-replacement adhesives with various metallizations, surface finishes, and printing resolutions are given in Table 5.7.

Solder-replacement materials may be applied by stencil printing, screen printing, or automatic dispensing and can produce fine-pitch bonding pads for flip-chip devices. Emerson & Cuming’s CE-3100 and Ablestik Ablebond® 8175A, for example, applied by stencil printing can produce 20-mil pitch pads, while Emerson & Cuming’s CE-3103 and 3502 adhesives may be used to process 12-mil-pitch conductor pads. Many commercially available solder-replacement adhesives are also suitable for ultra-fine-pitch applications (<12 mils) and are compatible with a variety of surfaces including antioxidant-free copper, OSP-copper, and tin-lead soldered surfaces. The contact resistance of polymer bumps to aluminum bonding pads is higher than for solder bumps so that a more compatible metallization such as gold needs to be formed over the aluminum through barrier and adhesion layers such as titanium/tungsten and copper. The contact resistance of a silver-filled epoxy is reported to be approximately 25 micro-ohms compared with 10 micro-ohms for tin-lead solder.<sup>[16]</sup> The properties of some adhesives reported to be useful as solder replacements are given in Table 5.8.

**Table 5.7.** Compatibility of Various Solder Replacement Adhesives with Surfaces and Printing Resolutions

Solder Replacement/ Supplier	Compatibility with Surface Finish				Printing Resolution	
	Sn/Pb	OSP* Coated Copper	Sn	Au	20-mil pitch	12-mil pitch
CE 3100/ Emerson & Cuming	X	X			X	
CE 3103/ Emerson & Cuming	X	X	X			X
CE 3502/ Emerson & Cuming		X				X
XCE 3104XL/ Emerson & Cuming		X			X (Au-Ni)	X
Ablebond® 84-1 LMI/ Ablestik		X	X		X	
Ablebond® 8175A/ Ablestik		X			X	
QMI 4030SR/ Loctite	X				N/A	N/A
Epo-Tek® E 2116/ Epoxy Technology		X		X		X
Epo-Tek® E 2116-4/ Epoxy Technology		X				X
Epo-Tek® E 2116-5/ Epoxy Technology	X	X				X

\*Organic Solderability Preservative; N/A – Not Available.

**Table 5.8. Properties of Adhesives Used as Solder Replacements**

Product Name/ Supplier	Type	Viscosity cps*	Shelf Life (-40°C)/ Pot Life (25°C)	Cure Schedule	% Weight Loss @ 300°C by TGA	Bond Strength psi	Modulus of Elasticity MPa psi**	CTE ppm/°C		T <sub>g</sub> °C	Volume Resistivity ohm-cm	Thermal Conduc- tivity W/m-K	Ionic Impurities ppm
								α <sub>1</sub>	α <sub>2</sub>				
Polysolder LT/ Cookson Semiconductor Products	Silver- filled epoxy	150,000 (1 rpm)	-/8 hrs	10 min @ 140°C	N/A	>2,500	N/A	54	N/A	90	≤ 5.0 × 10 <sup>-4</sup>	3.5	N/A
Polysolder L/ Cookson Semiconductor Products	Silver- filled epoxy	250,000– 350,000 (1 rpm)	-/8–10 hrs	10 min @ 150°C	N/A	>6,700	N/A	57	N/A	90	1.4 × 10 <sup>-3</sup>	3.5	N/A
Polysolder SE3001/ Cookson Semiconductor Products	Silver- filled epoxy	150,000– 220,000 (1 rpm)	-/8–12 hrs	15 min @ 130°C	N/A	>2,300	N/A	54	N/A	90	≤ 1 × 10 <sup>-4</sup>	4 -5	N/A
ME 8452-HF- IR/AI Technology	Silver- filled epoxy	N/A	12 mos/-	15 min @ 150°C	N/A	1,500	N/A	N/A	N/A	N/A	<1 × 10 <sup>-4</sup>	8.0	N/A
QMI 4030SR/ Loctite	Silver- filled thermo- plastic	42,500 (10 rpm)	12mos (25°C)/-	15 min @ 150°C	N/A	624	1,100 (159,542)	30	N/A	30	1.6 × 10 <sup>-4</sup>	5.0	Na <sup>+</sup> , K <sup>+</sup> ≤ 20 Cl <sup>-</sup> , F ≤ 20
CE 3100/ Emerson & Cuming	Silver- filled epoxy	30,000– 75,000	12 mos/-	3 min @ 150°C or 6 min @ 130°C	N/A	>1 × 10 <sup>6</sup>	6,300 (913,739)	51	148	99	3 × 10 <sup>-4</sup>	N/A	Cl <sup>-</sup> < 79 Na <sup>+</sup> < 1 K <sup>+</sup> ND

\*Brookfield @ 5 rpm and 25°C, unless indicated; \*\*Generally at 25°C; N/A – Not Available; ND – None Detected. Source: Compiled from various suppliers' data sheets. Contact suppliers for specification values.

(cont'd.)

**Table 5.8. (Cont'd.)**

Product Name/ Supplier	Type	Viscosity cps*	Shelf Life (-40°C)/ Pot Life (25°C)	Cure Schedule	% Weight Loss @ 300°C by TGA	Bond Strength psi	Modulus of Elasticity MPa psi**	CTE ppm/°C		T <sub>g</sub> °C	Volume Resistivity ohm-cm	Thermal Conduc- tivity - W/m·K	Ionic Impurities ppm
								α <sub>1</sub>	α <sub>2</sub>				
CE 3103/ Emerson & Cuming	Silver- filled epoxy	45,000	12 mos/-	3 min @ 150°C or 6 min @ 130°C	N/A	N/A	7,100 (1.03 × 10 <sup>6</sup> )	43	144	104	3 × 10 <sup>-4</sup>	N/A	Cl <sup>-</sup> < 30 Na <sup>+</sup> < 10 K <sup>+</sup> < 5
Ablebond® 84-1 LM/ Ablestik	Silver- filled epoxy	28,000	12 mos/ 10 days	1 hr @ 150°C or 2 hrs @ 125°C	0.19	6,500	N/A	55	150	103	2 × 10 <sup>-4</sup>	2.40	Cl <sup>-</sup> < 20 Na <sup>+</sup> < 20 K <sup>+</sup> < 10
Ablebond® 8175A/ Ablestik	Silver- filled epoxy, fast curing	70,000	12 mos/-	3 min @ 150°C or 6 min @ 130°C	0.43	5,500	N/A	65	250	80	3 × 10 <sup>-4</sup>	4.0	Cl <sup>-</sup> < 50 Na <sup>+</sup> < 10 K <sup>+</sup> < 5
Ablebond® 8175/ Ablestik	Silver- filled epoxy	55,000	12 mos/-	1 hr @ 130°C	0.30	1,650	N/A	55	200	90	3 × 10 <sup>-4</sup>	3.2	N/A
CE 3502/ Emerson & Cuming	Silver- filled epoxy	310,000– 350,000	12 mos/-	5 min @ 120°C	N/A	N/A	>4 (>580)	55	N/A	80	2 × 10 <sup>-4</sup>	3.0	Cl <sup>-</sup> < 20 Na <sup>+</sup> < 10 K <sup>+</sup> < 10 NH <sub>4</sub> <sup>+</sup> < 50
Epo-Tek® E2116/Epoxy Technology	Silver- filled epoxy	80,000 (1 rpm)	12 mos/ <24 hrs	15–30 min @ 150°C	0.48	3,400	N/A	42	140	100	1–5 × 10 <sup>-4</sup>	2.0	Cl <sup>-</sup> < 20 Na <sup>+</sup> < 15 K <sup>+</sup> < 5 NH <sub>4</sub> <sup>+</sup> < 25

\*Brookfield @ 5 rpm and 25°C unless indicated; \*\*Generally at 25°C; N/A – Not Available; ND – None Detected. *Source: compiled from various suppliers' data sheets. Contact suppliers for specification values.*

(cont'd.)

**Table 5.8. (Cont'd.)**

Product Name/ Supplier	Type	Viscosity cps*	Shelf Life (-40°C)/ Pot Life (25°C)	Cure Schedule	% Weight Loss @ 300°C by TGA	Bond Strength psi	Modulus of Elasticity MPa psi**	CTE ppm/°C		T <sub>g</sub> °C	Volume Resistivity ohm-cm	Thermal Conductivity W/m-K	Ionic Impurities ppm
								α <sub>1</sub>	α <sub>2</sub>				
Epo-Tek® E2116-4/ Epoxy Technology	Silver- filled epoxy	22,000	12 mos/ <24 hrs	15–30 min @ 150°C	0.75	3,400	4,826 (700,000)	28	100	115	1–5 × 10 <sup>-4</sup>	2.0	Cl <sup>-</sup> 20 Na <sup>+</sup> 12 K <sup>+</sup> 5 NH <sub>4</sub> <sup>+</sup> 20
Epo-Tek® E2116-5/ Epoxy Technology	Silver- filled epoxy	120,000 (2.5 rpm)	12 mos/ <24 hrs	15–30 min @ 150°C	0.75	3,400	4,826 (700,000)	28	100	115	1–5 × 10 <sup>-4</sup>	2.0	N/A
Loctite 3880/ Loctite	Silver- filled epoxy	75,000– 200,000	6 mos. (5°C)/ 7 days	10 min @ 125°C, 3 min @ 175°C	N/A	>1,000 (Al/Al lap shear)	N/A	45	N/A	40	8 × 10 <sup>-4</sup>	N/A	N/A
ESS 8450/ AI Technology	Silver- filled epoxy	N/A	N/A	5 min @ 150°C, 5–10 psi	N/A	>2,000	120 (17,404)	N/A	N/A	-60	<4 × 10 <sup>-4</sup>	5.7	N/A
ESS 8459/ AI Technology	Silver- filled epoxy	N/A	N/A	5 min @ 150°C, 5–10 psi	N/A	>2,000	120 (17,404)	N/A	N/A	-60	<5 × 10 <sup>-3</sup>	5.7	N/A

\*Brookfield @ 5 rpm and 25°C unless indicated; \*\*Generally at 25°C; N/A – Not Available; ND – None Detected. Source: Compiled from various suppliers' data sheets. Contact suppliers for specification values.

## 5.2 SPECIFIC APPLICATIONS

For many applications, adhesives are formulated and tailored around specific products and environments. Among these are the ground communication and control equipment for the military that must withstand a wide spectrum of harsh terrestrial climates in addition to high levels of shock and vibration. Spacecraft electronics will be subjected to high vacuum, low temperatures, and particle bombardment from both radioactive and physical particles. Other specific applications include memory modules, automotive, flat-panel displays, optoelectronics, MEMS, and EMI shielding.

Adhesives are also tailored to meet specific requirements of the packaging or assembly technology used (Table 5.9). Thus, the requirements for single-chip packaging in hermetically sealed ceramic packages such as CERDIPs will be somewhat different from those of plastic dual-in-line packages (PDIPs) and plastic-encapsulated microcircuits (PEMs).

### 5.2.1 Military Applications

Adhesives are used extensively in military electronics. Communication systems, sensors, and navigation systems used in army, navy, and marine corps equipment rely heavily on printed-wiring boards and assemblies because of their ruggedness and ability to survive shock and vibration, temperature cycling, and aggressive handling. Adhesives are also used to reinforce and protect other parts of an assembly, for example, to provide vibration damping, to seal enclosures from moisture, and to protect signals from electromagnetic interference.

Military electronics may be ground-based or airborne but, in either case, must be capable of withstanding the harsh extremes of terrestrial environments. Ground-based electronics must also be resistant to fungus and other microorganisms, salt spray (if close to an ocean), and high humidity. Moisture remains one of the major causes of electronic failures.

Thus, components that are surface mounted with adhesives must maintain their strength and electrical properties during and after these combined environments and after repeated stresses. To assure reliability, numerous accelerated tests have been developed and incorporated in military and industry specifications. Among specifications governing the mechanical, electrical, and qualification requirements for electronic components, modules, subsystems, and systems, most of which could not be met without using qualified and reliable adhesives, are: MIL-STD-883,<sup>[21]</sup> MIL-STD-810,<sup>[22]</sup> MIL-STD-202,<sup>[23]</sup> and MIL-PRF-38534.<sup>[24]</sup>

**Table 5.9.** Adhesives Requirements for Various Packaging Technologies

<b>Packaging Technology</b>	<b>Typical Adhesive Requirements</b>	<b>Examples of Adhesives</b>
Hermetic CERDIP, CBGA, CSP	High-adhesion strength, low-moisture absorption, stability of packages to processing temp. >350°C (if silver-glass adhesives are used)	Silver-glass die attach, silver-filled cyanate ester, polyimide
Molded plastic, smaller die sizes (PDIP, QFP)	High strength, low-temperature processing (<250°C), moisture resistance	Silver-filled epoxy, modified cyanate-ester and thermoplastic/thermoset blends
VLSIC in TQFP/thin outline plastic	Low modulus of elasticity (MOE), low-moisture absorption	Epoxy, cyanate-ester blends
PBGA, thermally enhanced BGA	Low MOE, low stress, high thermal dissipation	Epoxy blends, cyanate-ester blends, modified cyclo-olefin thermoset (MCOT), silicone materials, highly filled thermally conductive adhesives
CSP	Ultralow MOE, stress and moisture resistance, good mechanical integrity	Epoxy blends, cyanate-ester blends, modified cyclo-olefin thermoset (MCOT), silicone materials
Hybrid microcircuits and MCMs	MIL-STD-883, Method 5011-compliant, low outgassing, high-purity, reworkability	Silver-filled or insulative epoxies, thermoset or thermoplastic pastes or films
Chip-on-board	Low MOE, reworkability	Epoxy pastes
Flip-chip bonding	Screen or stencil printable or z-axis (anisotropic conductive), or isotropic conductive bumps,	Anisotropic and isotropic conductive pastes or films, underfill epoxies or modified epoxies

## 5.2.2 Space Applications

Besides the mechanical and electrical requirements that adhesives must meet for terrestrial applications, a separate set of requirements apply to space applications. The space environment, depending on the orbit, consists of high vacuum ( $10^{-8}$  Torr or lower); extremes of temperature; proton, electron, and ionizing radiation; atomic oxygen; and debris and micrometeoroids. Adhesives and polymeric materials are a major concern in both unmanned and manned spacecraft. If directly exposed to the space environment, adhesives and other polymeric materials outgas and volatile products can condense and contaminate adjacent electronic, optical, or precision instrument parts. Even 100 angstroms of condensed organic material can affect the reflectance or absorbance properties of optical parts. In manned spacecraft, some outgassing products as low as parts per billion can be toxic to astronauts.

To assure safety and reliability, NASA and other government agencies require all polymeric materials to be qualified and, as a minimum, to pass outgassing tests defined in ASTM-E-595.<sup>[25]</sup> This specification defines two tests: the *total mass loss* (TML) and the *collected volatile condensable materials* (CVCM). The TML is the weight of material lost after exposure for 24 hours at 125°C in a vacuum of less than  $5 \times 10^{-5}$  Torr and is specified as 1% or less. The CVCM is the amount of volatiles that condense on a collector plate maintained at 25°C during the same conditions and is required to be 0.1% or less. Through many years of testing, an extensive databank of materials that pass these requirements is available.<sup>[26][27]</sup> In some cases, an adhesive that fails when cured at one schedule will pass under other cure conditions. Outgassing data for some die- and substrate-attachment adhesives are given in Table 5.10.

In direct exposure to the natural space environment, total radiation flux can also degrade the physical and electrical properties of the adhesive. Long-term radiation exposure embrittles some adhesives through continued crosslinking or causes polymer degradation with outgassing. The radiation resistance of polymeric materials varies depending primarily on their molecular structures. Aromatic and heterocyclic polymers and highly cross-linked polymers are more tolerant to high radiation doses than are aliphatic polymers. Thus epoxies cured with aromatic amines fare better than epoxies cured with aliphatic amines. Polyimides and phenyl silicones, because of their aromatic structures, are also highly resistant to total radiation doses up to  $10^8$  rads. Where radiation data are not available, testing to the total ionizing dose expected should be performed according to MIL-STD-883, Method

**Table 5.10.** NASA Outgassing Data for Some Die- and Substrate-attach Adhesives<sup>[26]</sup>

Material Information		NASA Outgassing Results (%)		
Adhesive/Supplier	Cure Schedule	TML	CVCM	WVR
Ablebond <sup>®</sup> 36-2 (silver-filled epoxy)/ Ablestik	30 min @ 150°C	0.30	0.00	—
Ablebond <sup>®</sup> 71-1 (silver-filled polyimide)/ Ablestik	30 min @ 150°C and 30 min @ 275°C	0.17 0.25	0.01 0.00	0.14 0.17
Ablebond <sup>®</sup> 84-1 LMI (silver-filled epoxy)/ Ablestik	1 hr @ 150°C	0.12	0.00	0.04
	2 hrs @ 125°C	0.12	0.01	0.09
Ablebond <sup>®</sup> 84-3 (electrically insulative epoxy)/ Ablestik	1 hr @ 150°C	0.23	0.00	0.16
Ablefilm <sup>®</sup> 5020K (epoxy film)/ Ablestik	1 hr @ 150°C	0.24	0.02	0.18
Ablefilm <sup>®</sup> 5025E/ Ablestik	1 hr @ 150°C or 2 hrs @ 125°C	0.30 0.32	0.06 0.08	0.08
Ablefilm <sup>®</sup> 561K/ Ablestik	2 hrs @ 125°C	0.42	0.13	0.09
Ablefilm <sup>®</sup> ECF 550/ Ablestik	30 min @ 150°C	0.49	0.10	0.18
Epibond <sup>®</sup> 7275/ Vantico	30 min @ 80° C	1.82	0.08	0.26
Epo-Tek <sup>®</sup> H20E (silver-filled epoxy)/ Epoxy Technology	1 hr @ 150°C	0.62	0.01	0.09
Epo-Tek <sup>®</sup> H35-175MP/ Epoxy Technology	1.5 hr @ 150°C	0.30	0.02	0.18
Epo-Tek <sup>®</sup> H70 E-4/ Epoxy Technology	6 hrs @ 05°C	1.2	0.01	0.23
ME 7156/ Epoxy Technology	1.25 hrs @ 175°C	0.5	0.15	0.1
<i>Source: Outgassing Data for Selecting Spacecraft Materials, NASA Publication 1124.</i>				

1019.5.<sup>[28]</sup> Fortunately, through metal shielding, encapsulation, or hermetic sealing of electronic assemblies, radiation exposures can be largely mitigated.

Another space-specific issue is the embrittlement or stiffening of an otherwise flexible adhesive at the low temperature extremes of space. Of the many polymer types, silicones best maintain their flexibility and physical properties at operating temperatures as low as  $-80^{\circ}\text{C}$ , or even lower for some formulations, thus are widely used in satellites and space vehicles.

Materials that are directly exposed to the space environment must also withstand or be protected from atomic oxygen. Atomic oxygen is prevalent in the low earth orbit (LEO), approximately 100 to 350 miles from Earth. At this distance, molecular oxygen reacts with ultraviolet light to produce monoatomic oxygen which is extremely chemically reactive and erosive. Most adhesives used in spacecraft, however, are sandwiched between two adherends, thus not directly exposed.

### 5.2.3 Automotive Applications

Adhesives are used extensively in the manufacture of automobiles both for structural and non-structural assemblies, and the requirements they must meet are among the most severe in industry. Electronic assemblies situated under the hood or near the engine must withstand continuous temperatures of  $125^{\circ}\text{C}$  to  $150^{\circ}\text{C}$ , thousands of temperature cycles, vibration, and mechanical shock. In addition, when not operating, they must be capable of withstanding severe global climates and climatic changes ranging from tropical high humidity, high temperatures to frigid subzero temperatures. While the surrounding ambient may be as high as  $150^{\circ}\text{C}$ , semiconductor device junctions must be kept cool. To this end, die-attachment and underfill adhesives must have the highest thermal conductivity possible in order to transfer heat from the devices. Low CTE, stress-absorbing adhesives are definitely required as underfills for flip-chip and BGA packages because of the added problem of solder ball deterioration expected under extended high-temperature and thermal excursions. Coupled with all this is the requirement for very low cost.

Among the better adhesives that meet automobile engine conditions are the aromatic anhydride-cured epoxies, polyimides, silicones, and silver-glass. A proposed qualification test requirement that adhesive-bonded assemblies survive 2,000 thermal cycles with 1% or less of failures has been difficult to meet.<sup>[29]</sup>

## 5.2.4 Medical Applications

Many types of medical electronic devices, both internal to the body and external, rely on adhesives for their assembly. The requirements for devices in medical applications differ from, and are more severe than, those for other applications, especially where the devices will be implanted or come into contact with the body. The standards and regulations for the medical industry are far different from other industries, often requiring approval from the Food and Drug Administration (FDA). Medical electronic devices include pacemakers, defibrillators, drug-releasing pumps, hearing aids, and diagnostic equipment for measuring, monitoring, and recording body functions such as heartbeat and brain waves. Major requirements for medical devices are the following:

- Miniaturization.
- Reliability (reliability is essential for implantable electronics, but also for external devices where accuracy is critical in diagnosing a patient's condition).
- Biocompatibility and non-toxicity.
- Resistance to sterilization (parts should be able to be sterilized, often more than once, without degrading electrical or physical performance).

**Miniaturization.** Miniaturization, low weight, and low volume are as important in medical electronics as in space electronics and other applications. The small size and weight are benefits of hybrid microcircuits; they have been used for a long time in pacemakers and defibrillators. The attachment and packaging of bare-chip devices with conductive and insulative adhesives has provided major reductions in weight and space over printed-wiring board technologies. The hermetic sealing by welding has also assured protection of the electronics from moisture and other body fluids, as well as protecting the body from outgassing or other contaminants from the electronic modules. Miniaturization is necessary for the new generation of hearing aids. Some designs consist of a thinned silicon IC embedded and connected to a flexible polyimide circuit that is then folded to reduce volume.

**Reliability.** The performance of the electronic devices implanted in the body is extremely important. Malfunctioning can result in death. For hybrid microcircuits and multichip modules, the qualification tests and accelerated tests required of military and space applications also apply, although some shock and vibration tests are not realistic for humans. In addition, the Food and Drug Administration (FDA) becomes involved in testing and reviewing

data for toxicity, compatibility with body fluids, and failure modes and mechanisms. Some of the early pacemakers failed after being implanted and had to be removed and replaced. Failures occurred due to corrosion within hermetically sealed hybrid circuits due to moisture outgassed from adhesives and other polymer materials and to contaminants that were not completely removed during cleaning.

For externally used diagnostic electronics, reliability may also be a life-or-death situation if instruments do not provide accurate information.

**Toxicity and biocompatibility.** Adhesives used in medical devices that are implanted or in contact with the body must be tested and shown to be non-toxic, biologically inert, and compatible with blood and body fluids. Compatibility with blood and other body fluids is especially critical. Surfaces in contact with blood must not serve as sites for coagulation and clotting of blood. Generally, qualification testing is performed to ISO-10993<sup>[30]</sup> or to U. S. Pharmacopoeia (USP) Class VI. The two standards specify slightly different tests.<sup>[31]</sup> The USP Class VI standard specifies acute systemic (over the tissue), intracutaneous (under the skin), and muscle implantation tests. The ISO-10993 standard is a set of 12 documents that is more universal and more extensive than the USP standard. It specifies:

- Intracutaneous injection tests to evaluate irritation potential.
- Acute systemic injection to evaluate for toxic effects.
- Cytotoxicity tests to evaluate the effect on monolayer cells.
- Blood compatibility.

Some adhesives suppliers already have test data showing compliance of their adhesives to ISO-10993 and will provide a certificate of compliance for their products. However, passing the ISO or USP Class VI tests should be considered a starter in proving that an adhesive has a low level of toxicity; it does not guarantee FDA approval. The FDA often requires more extensive testing.

**Sterilization.** All devices implanted in the body or that come into contact with body fluids or blood must be sterilized and be resistant to the sterilization conditions. Adhesive-bonded parts are not used in direct contact with the body fluids. They are generally part of an electronic module that is hermetically sealed or otherwise encapsulated or shielded. However, the sterilization conditions for the module must not degrade the internal adhesive-attached components. Some adhesives such as cyanoacrylates and UV-cured acrylics degrade at the elevated temperatures and high humidity

encountered in dry heat and autoclave sterilization. Thus, adhesives, even though not directly exposed, should be tested and qualified based on their resistance to the sterilization process that will be used. The main sterilization procedures are gaseous ethylene oxide, autoclave, dry heat, and gamma radiation.

**Gaseous ethylene oxide (EtO).** Exposure to ethylene oxide, admixed with a carrier gas such as carbon dioxide or a chlorofluorocarbon, is the most widely used sterilization process because it has the least damaging effect on materials and devices and is low cost. EtO sterilization is a room-temperature process that affects only the external surfaces of a module.

**Autoclave.** Autoclave sterilization consists of exposing the parts to steam in a pressurized vessel. Temperatures of 121°C to 132°C at pressures up to 2 atmospheres are reached with saturated moisture. Under these conditions, some polymer materials hydrolyze and revert to monomers with loss of adhesive strength. Materials most susceptible to reversion include some polyurethanes, acrylics, and silicones. Epoxies are most resistant.

**Dry heat.** In dry-heat sterilization, the parts are exposed for 2–3 hours at 165°C–170°C. Dry-heat exposure is the least effective sterilization method and most likely to degrade materials and electronic devices. Although adhesives may have been cured at 165°C prior to hermetic packaging, the additional temperature exposure within the sealed package can result in further outgassing of moisture and corrosive volatiles causing electrical failures. Outgassing is worse if the adhesive had been cured at a temperature below 165°C.

**Gamma Radiation.** Exposure to gamma radiation or to other high-energy radiation source (beta, electron beam) is an effective sterilization process but requires expensive equipment and strict safety controls. Gamma rays are highly penetrating even affecting materials and devices within an enclosure. Some electronic components, especially bare semiconductor devices, may be temporarily or permanently damaged.

## 5.2.5 Chip-Scale Packages (CSP)

Bare die such as integrated circuits may be assembled in plastic or ceramic carriers whose dimensions are slightly larger than the chip. These are called *chip-scale packages* (CSP) and are defined as packages that are no larger than 1.5 times the area of the die or no more than 1.2 times the width or length of the die.<sup>[32][33]</sup> If the carrier is a BGA type, an alternate definition is that the solder-ball pitch be less than 1 mm.<sup>[34]</sup> The pitch of interconnects varies by I/O count. Parts having fewer than 100 I/Os have pitches of 1 mm

decreasing to 0.5 mm as the number of I/Os increases to 500.<sup>[35]</sup> Chip-scale packages have many advantages over bare-chip attachment especially in their ease of handling, electrical testing, and automated soldering or epoxy attachment. They also have advantages over QFP and PGA packages in the higher levels of silicon density that are obtained. While the silicon density (ratio of silicon-to-package area) of a QFP is 10% to 60%,<sup>[36]</sup> that for a single chip in a CSP may be as high as 60% to 100%.<sup>[37]</sup> CSPs may be bumped for flip-chip connections or may be wire bonded. Adhesives are used to attach the chip to the carrier and the carriers to an interconnect substrate. In the past decade, there has been a proliferation of designs and configurations for CSPs, and they have become the preferred method of packaging ICs having up to 500 I/Os. Table 5.11 lists some examples of commercially available chip-scale packages, suppliers, and applications.

### 5.2.6 Memory Modules and Vertical-Stack Packaging

In the quest to produce ever-higher density memory modules, various stacked 3-D packaging configurations have been developed and are being used. Historically, focal-plane arrays with on-board processing and solid-state data recorders for military and commercial satellites have driven the development of 3-D high-density memory modules. For example, the data storage unit of the Hubble space telescope consists of 3-D stacked memory chips. More recently, the driver for 3-D stacking has been cell phone handsets where increased functions are being integrated in smaller units. For these consumer products, separately packaged Static Random Access Memory (SRAM) or flash memory chips are no longer sufficient to support the growing demand for new features such as voice, video, and data without substantially increasing the size and weight of the product.<sup>[38]</sup> Vertical-stack packaging designs may be of four types as illustrated in Fig. 5.13.

**Chip stacking.** Bare ICs are stacked and interconnected to achieve the densest level of integration. The chips are held together by thin layers of adhesive. Interconnects are made by vapor depositing and photodelineating thin-film metallization along the sides, by applying electrically conductive epoxy adhesive, and by using TAB leads or by wire bonding.

**Package stacking.** IC chips are first inserted into packages, then the packages are stacked and interconnected using either the package leads or extensions from the board. Package stacking is a better solution for some applications because the packaged die can be burned in and electrically tested prior to stacking, assuring known good devices.

**Table 5.11.** Examples of Chip-Scale Packages, Suppliers, and Applications

<b>Leadframe-Based CSP</b>			
<b>Construction</b>	<b>Advantages</b>	<b>Examples (Supplier)</b>	<b>Applications</b>
Copper leadframe, low-loop wire bonds or flip-chip interconnect, over-molded	50% size reduction compared to thin-shrink small-outline package (TSSOP) inductance (MicroLeadFrame®) and very low inductance flip-chip MicroLeadFrame	MicroLeadFrame® (wire bond) and flip-chip MicroLeadFrame® (fcMLF) (Amkor)	Portable electronics (cell phones and personal data assistants) (PDAs), MicroLeadFrame® and high-performance applications in the 5–40 GHz range
Standard bumped chip carrier (BCC) and electrically/thermally enhanced (BCC+) center-exposed-pad technology, over-molded	Structure without interposer for low standoff height	BCC* (Fujitsu)	Flash memory, portable electronics
Copper C194 (taped and gold flash), wire bonded	Near CSP format, excellent electrical and thermal characteristics	MicroLeadFrame (MLF) and Quad Flat-Pack No-Lead (QFN) (Orient Semiconductor Electronics USA)	Microwave, RF, and hand-held portable communications
Exposed die-attach pad	50% reduction in inductance/capacitance compared to leaded parts.	MLP (MicroLeadFrame Package) (Carsem)	PDAs, Global-Positioning Systems (GPS), RF product for Bluetooth™
*NA – Not Available.			

(cont'd.)

**Table 5.11. (Cont'd.)**

<b>Rigid Interposer CSP</b>			
<b>Construction</b>	<b>Advantages</b>	<b>Examples (Supplier)</b>	<b>Applications</b>
Rigid laminate substrate (with or without soldermask), wire bonds, over-molded	Small outline, low profile (1.0 mm), enhanced electrical performance over 2.4 GHz, JEDEC moisture sensitivity level (MSL) 3	Plastic thin fine pitch quad flat no lead package (P-TFQFN), plastic thin shrink small outline no lead package (P-TSSON), and fine-pitch BGA, FBGA (National)	Portable applications, flash memory
Stacked chips on rigid substrate	Chip scale packaging efficiency integrating multiple functionality and high silicon density	Thin profile fine pitch BGA (TFBGA), low profile fine pitch BGA (LFBGA) (Orient Semiconductor Electronics USA)	Portable electronics requiring flash memory, SRAMs, DRAMs, and controller chips
	Combines Flash and SRAM die, high silicon density (2-layer stack)	M <sup>2</sup> CSP (ChipPAC)	Memory (Flash/SRAM), Embedded (logic/flash and logic DRAM), PDAs, pagers, hard disks
Thin-core laminate, low-loop wire bond, and standard over-mold	Thinnest available package (0.5 mm mounted height), and JEDEC MSL 1	Extremely thin CSP™, <i>erCSP™</i> (Amkor)	EEPROM devices, PCMCIA card applications, and minidisk drives
	Low inductance for high speed application, small footprint (near chip size)	Chip Array® Package (Amkor)	Memory PLDs and ASIC devices, PCs, GPS, PDAs, and wireless applications
NA – Not Available.			

(cont'd.)

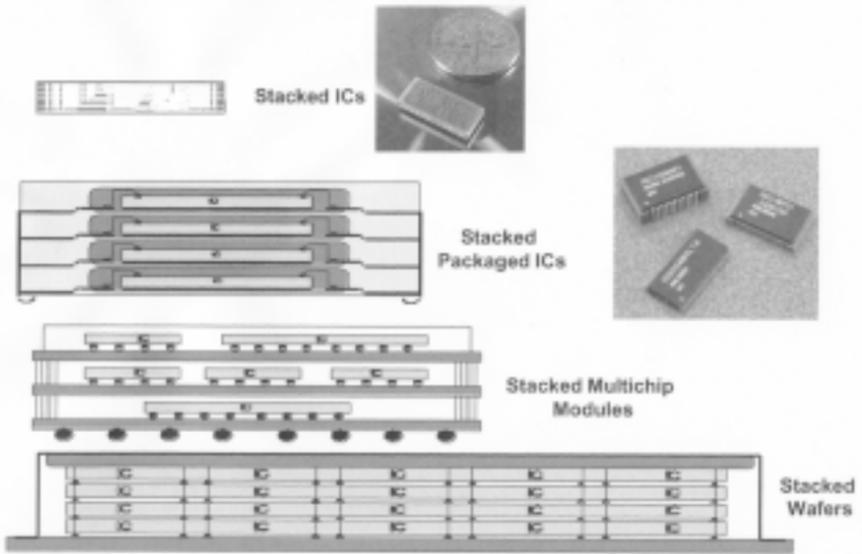
**Table 5.11. (Cont'd.)**

<b>Flexible Interposer CSP</b>			
<b>Construction</b>	<b>Advantages</b>	<b>Examples (Supplier)</b>	<b>Applications</b>
Compliant layer and redistribution layer (rigid)	No underfill required, JEDEC MSL 1	$\mu$ BGA (Tessera)	Flash memory, SRAM, and DSP for portable electronics, high-reliability automotive, military, and medical applications
Polyimide film interconnect and Nubin (elastomer), over-molded	Excellent electrical performance and JEDEC MSL 1	$\mu$ BGA (ChipPAC)	SRAM, DRAM, and flash memory and low to medium I/O applications
Flex substrate, die up and wire bonded configuration, over-molded	Near CSP packaging efficiency	<i>flex</i> BGA (Amkor)	Portable electronics (cell, pagers) and digital cameras and PCs/disk drives
Upilex tape, wire bonded, over-mold	Near chip-scale package	Economic Chip Scale Package-Tape, (EconoCSP-T, ChipPAC)	DSPs, ASICs, flash memory, SRAMs, and PC chipsets
Polyimide tape, die and wire bond, over-mold	Near CSP	FBGA-T (ChipPAC)	DSPs, memory products, ASICs, and SRAMs, cell phones, and pagers
NA – Not Available.			

(cont'd.)

**Table 5.11. (Cont'd.)**

<b>Wafer-level CSP</b>			
<b>Construction</b>	<b>Advantages</b>	<b>Examples (Supplier)</b>	<b>Applications</b>
Glass-silicon sandwich structure; solder bumped	Reduced light loss	ShellOP (Shellcase)	CCD cameras, digital photography, finger-print sensors
Repassivation and deposition of solder bumps	Eliminates need for underfill, standard SMT processes, smallest footprint per I/O with space savings on PWB	<i>MicroSMD</i> , standard and thin versions (National Semiconductor)	N/A
Thin-film redistribution process using wafer-level passivation and cyclotene dielectric	High-performance wafer-level CSP, JEDEC MSL 1	<i>UltraCSP™</i> (Flip Chip Technology, Amkor and K&S Flip Chip Division of Kulicke & Soffa)*	EEPROM, Flash memory, DRAM, and standard electronic devices, PDAs, laptop PCs, disk drives, GPS, and MP3 players
Compliant layer between silicon and rigid redistribution substrate	Controlled impedance, low inductance and resistance, no underfill required	Wave (Tessera)	Large die size and small I/O applications (memory base band, ASIC)
Polyimide layer for redistribution traces, over-molded	30% reduction in board area, 65% thinner profile.	Super CSP (Fujitsu)	Flash memory and ASIC
*Technology licensed to Amkor; NA – Not Available.			



**Figure 5.13.** Vertical-stack packaging designs. (Source: Volcan Ozguz, Irvine Sensors.)

**Multichip stacking.** Several IC chips are assembled using MCM techniques and the layers are stacked similarly to package stacking. Layer-to-layer interconnects are produced using an interposer such as fuzz button layers that differentiate this approach from the package-stacking approach.

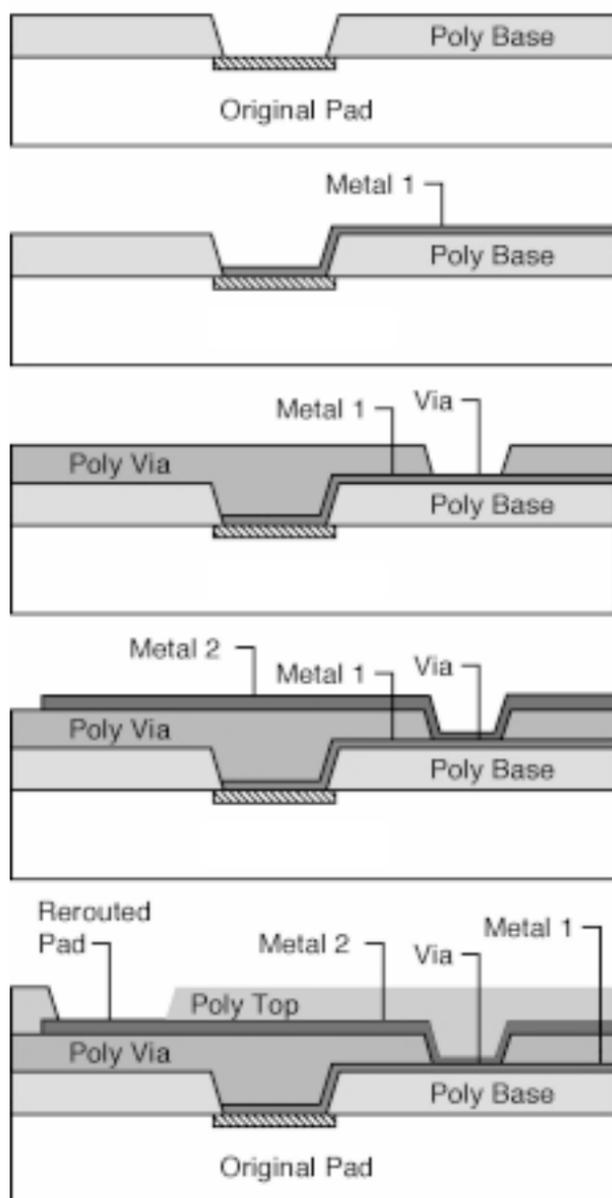
**Wafer stacking.** In this approach, entire wafers or segments of wafers containing ICs are stacked. Interconnections are formed from vias in the silicon.

In vertically stacking memory chips or other IC chips, the chips are first thinned to several mils (4 mils or less), then adhesive bonded, and electrically interconnected directly from chip-to-chip, either from the edges or through vias in the silicon. In these approaches, both electrically conductive and electrically insulative adhesives are used. Thermally conductive preform adhesives or thin thermoplastic films are used to bond and isolate the chips within the stack and to dissipate heat. Several processes are available to vertically stack and interconnect chips of the same size and function such as SRAM, flash, and DRAM memory chips. Other processes have been developed to vertically stack chips of different sizes and functions, or to horizontally interconnect different chips in one layer, then vertically stack the layers.<sup>[39][40]</sup>

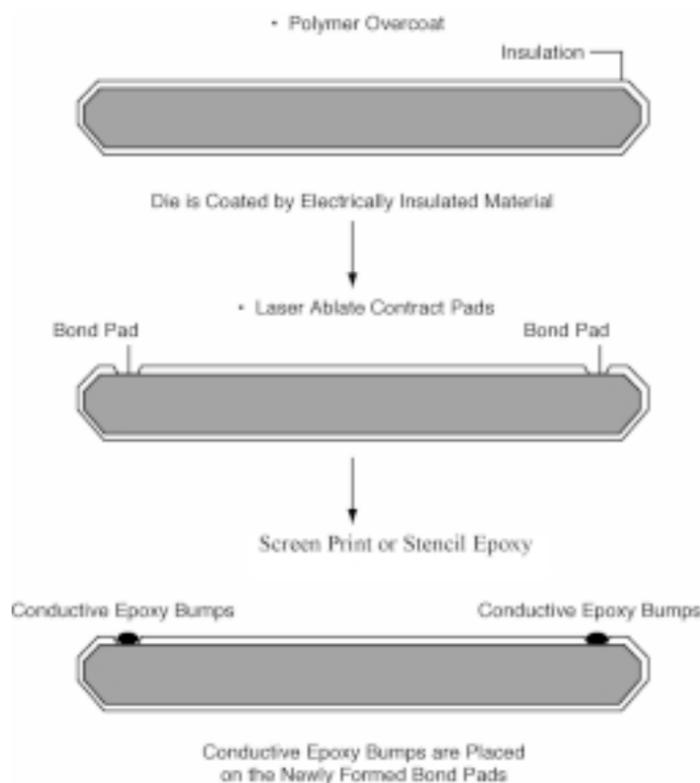
In most cases, the vertical-stacking process begins at the wafer stage where the normal bond pads are first redistributed toward the edges of the die by several photolithographic process steps shown in Figs. 5.14 and 5.15 and described as follows.

- Apply and cure a dielectric coating such as polyimide over the entire top surface of the fabricated memory wafer.
- Etch vias in the dielectric directly over the original bond pads using a photoresist process. Vias may be chemically etched, plasma etched, or laser ablated.
- Vapor deposit a thin layer of metal, such as gold, over the entire surface, covering all the dielectric and filling in the vias. The original aluminum bonding pads are usually transitioned to gold by first metallizing with barrier and adhesion metals such as titanium, tungsten, nickel, and copper.
- Through another photoresist process, delineate the metalization to form conductor traces that extend to the new redistributed bonding pads.
- Coat the entire surface again with polyimide dielectric and etch vias over the new pads.
- Fill the vias by screen printing or stencil printing sufficient silver-filled epoxy to form bumps or leave the vias open for wire bonding.

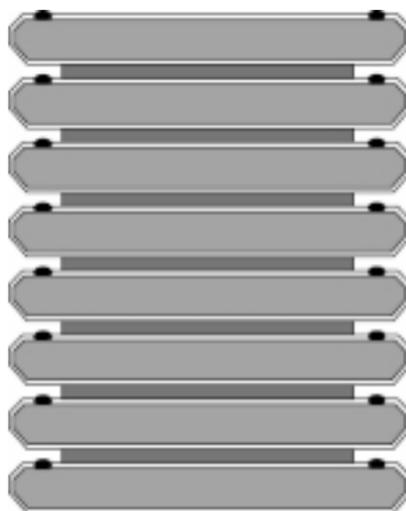
Once the epoxy bumps have been formed, the wafer is thinned from the backside, the devices are singulated, and their edges beveled at  $45^\circ$  to expose gold pads at the periphery of die. The chips are then stacked and bonded with thermally conductive, electrically insulative epoxy (Fig. 5.16). Paste adhesives are cost effective and can be dispensed with existing epoxy dispensing equipment. However, with increasing miniaturization, paste adhesives present problems in the control of voids, fillet coverage, bondline thickness, bleedout, and die tilting. Film adhesives have advantages over paste adhesives in all these areas and are being used to a greater extent in new designs. After stacking, the assemblies may be interconnected from the perimeter pads using fine wire or interconnected on the vertical edges by thin-film metallization or by applying electrically conductive epoxy stripes (Fig. 5.17).



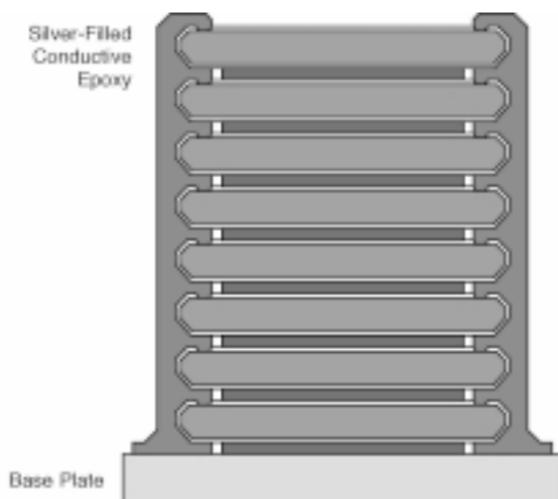
**Figure 5.14.** Redirection of bond pads at wafer stage.<sup>[39]</sup>



**Figure 5.15.** Conductive epoxy bumps on redistributed bonding pads.<sup>[39]</sup>



**Figure 5.16.** Chip stack built up using thermally conductive preform between die layers.<sup>[39]</sup>

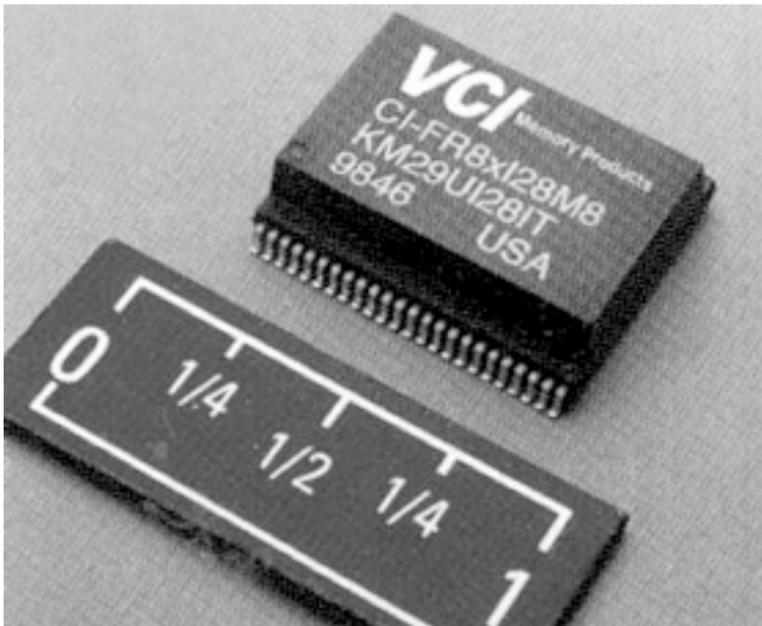


**Figure 5.17.** Interconnection of die from sides using conductive epoxy.<sup>[39]</sup>

The assembled stacks are then attached to a leadframe or substrate again with conductive epoxy or wire bonds, and encapsulated with epoxy. Alternately, they may be packaged in thin, small-outline packages (TSOP) or BGA packages. If multiple die are used on each layer, as many as 64 die may be incorporated in one stacked module.<sup>[41]</sup>

By vertical stacking, eight 256-Mbit memory chips can be stacked and interconnected at their edges resulting in a 2-Gbit flash Synchronous Dynamic Random Access Memory (SDRAM) module. Storage densities of more than 2.0 gigabytes per cubic inch using 16 Mbit DRAMs are reported.<sup>[41]</sup> Vertical stacking has resulted in numerous benefits, among which are reduced power consumption of 15%–20%, reduced capacitance, elimination of package parasitics, and, of course, smaller volume and higher density.<sup>[42]</sup> A 3-D memory stack is shown in Fig. 5.18.

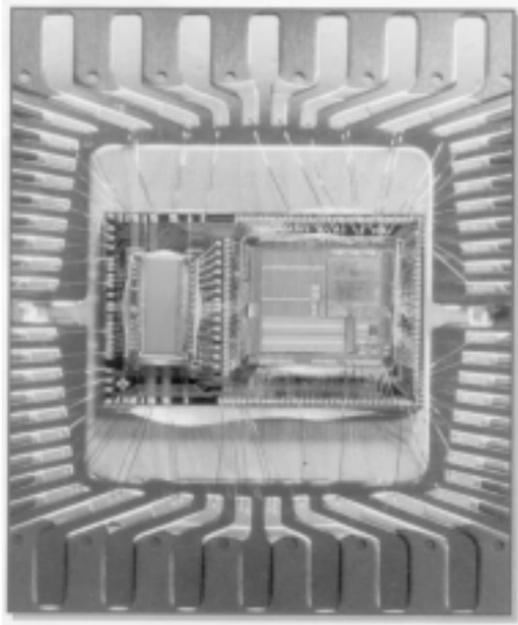
Other stacking approaches that do not require edge electrical connections are under development. In one approach, vias were formed in the silicon from the top surface to the bottom surface much like through-holes in PWBs. These vias are formed at the wafer stage and metallized so that direct connections can be made from chip-to-chip.<sup>[43]</sup>



**Figure 5.18.** 3-D memory stack. (Source: Vertical Circuits, Inc.)

## 5.2.7 System-in-Package (SIP)

At a higher level of integration, stacked IC chips of various functions may be combined with passive devices (capacitors, resistors) and connected as a functional block known as *system-in-package* (SIP). The SIP packaging approach provides a small form factor for multiple electronic functions important in mobile phones and other telecommunication products. The vertically stacked chips are interconnected either by wire bonding or by flip-chip attachment onto a BGA substrate, then epoxy molded to form a module that can be treated as a discrete standard component in board-level manufacturing. In maintaining a low-profile package, the die must be thinned before stacking. Thus, a 5-chip stacked package can be produced having a height of only 1.4 mm. An example of a SIP that uses chip stacking is shown in Fig. 5.19. Carsem, Inc., offers a line of SIPs (Table 5.12).<sup>[44]</sup> As with memory stacks, both conductive and nonconductive paste and film adhesives may be used in processing SIPs.



**Figure 5.19.** Stacked system-in-package. (Source: Strand Interconnect AB.)

**Table 5.12.** System-in-Package Products<sup>[44]</sup>

Package Size, mm	I/Os	Substrate	Number of Passive Devices	Number of ICs	Number of Flip Chip
4.9 × 3.2	8	BT-epoxy	2	3	-
11 × 9	24	BT-epoxy	1	1	1
10 × 10	32	BT-epoxy	-	8	-
10 × 14	34	Ceramic	49	1	1
11.4 × 10.2	36	FR4	1	1	1
11.5 × 75	56	BT-epoxy	13	3	-
11 × 11	133	BT-epoxy	3	6	2
14 × 14	219	BT-epoxy	16	6	1
<i>Source: Carsem, Inc.</i>					

## 5.2.8 Flat-Panel Displays\*

Polymer adhesives are essential in the manufacture of flat-panel displays. Adhesives are used in fabricating the display panels, in laminating the polarizers and optical films, and in assembling the driver electronics. In particular, adhesives have played a critical role in the development of liquid-crystal displays (LCD). The durability, reliability, and functionality of state-of-the-art LCDs have been made possible by advancements in both film and paste adhesives.

**Liquid crystal display fabrication.** In liquid crystal displays, the liquid crystals are sandwiched between two glass plates, one of whose backside has been processed with thin-film conductor electrodes [usually indium tin oxide (ITO)] that can energize and orient the crystals. The two glass panels are bonded and sealed at the edges using one of a number of adhesives. This is a critical process since the adhesive must selectively bond only the edges, must not penetrate and contaminate the liquid crystals, must cure at a low temperature so as not to degrade the liquid crystals, and must provide sufficient adhesion to seal and prevent air and moisture from penetrating. Low-viscosity adhesives that will penetrate by capillary flow are required. Among adhesives that have been used are silicones, acrylics, and epoxies.

\* This section was written in part by Lawrence Tannas of Tannas Electronic Displays, Inc., Orange, CA.

**Lamination of polarizers and optical films on glass.** Every square inch of LCDs, both top and bottom, must be covered with a laminated polarizer and additional polymer films having unique optical birefringent properties. Polarizer films are needed to control the passage of light through the liquid-crystal (LC) cell. Polarizers and analyzers separate the image created by the electrically altered orientation of the birefringent LC film between the glass plates. The optical films are called “compensating films” and are used to enhance the viewing angle range with birefringent optical compensation in three axes. The polarizer film is pre-cut with adhesive layer, compensator layer, and second adhesive layer for lamination to the LCD glass. This laminant stack uses a carrier film for placement and protection. The film is packaged in large rolls for automatic application to the LCD using custom lamination machinery. After application, the display is placed in an autoclave to cure the adhesive at typically two atmospheres pressure and 60°C. The cured adhesive layers must have unique optical and mechanical properties to be used in an LCD. The index of refraction of the polymer film must closely match that of the glass to assure minimal scattering and absorption. The most difficult properties to achieve are mechanical because the adhesive must maintain its bond strength for dissimilar materials over a wide temperature range from -40°C to +80°C, and preferably wider for industrial and aerospace applications. The polymer films must also be removable for repair of the LCD if the polarizer film becomes scratched or damaged.

**Lamination of glass filters.** For high-performance aerospace LCDs, a glass filter is laminated to the front and back of the LCD polarizers. The glass filter has a transparent EMI film and an anti-reflective coating on the front filter, and a transparent heater and anti-reflective coating on the back filter. Epoxies, silicones, and other adhesives, both thermal and UV-light curing, have been used to laminate the filter on either side of the polarizer. The potential problems with adhesives are the formation of voids, delamination, optical effects, and strain-inducing LCD cell gap changes. There is no known repair or recovery procedure for the filters and LCD. At best, the yield is 80% and, when failures occur, the entire LCD with filters is lost. Further, the lamination must have the performance of the polarizer adhesive and must survive temperature excursions from -55°C to +90°C. Lastly, the completed package must protect the polarizers from high humidity in both operating and storage conditions.

**Electronics assembly.** Rapid advances have been and are still being made in the development of large flat-panel displays (FPD), especially LCDs. Generally, the electronics that drive the display have been assembled and packaged separately, then mechanically and electrically connected to the glass display portion with a flexible cable. The flex connector is mechanically and electrically bonded to the row-and-column ITO electrodes of the glass panel. The separate assembly and packaging of the electronics adds to the volume and weight of the final product and increases its cost. Thus, the focus in recent years has been to integrate the electronics with the panel by forming or assembling the driver electronics directly onto the panel, reducing the overall thickness and assembly costs. The ultimate integration would be to extend the thin-film processes used to fabricate the active matrix circuits on the glass, that is, to fabricate the integrated circuits on the available area at the periphery of the glass. This is a major step that has not yet been accomplished. As an intermediate approach, electronic components and bare chips are being attached and connected on the edges of the top side of the glass display. However, the normally used solder attachment of devices or connectors to the LCD runs the risk of degrading the liquid crystals due to the high solder temperatures involved. Furthermore, the fine-pitch connections required for chip devices work poorly for solder due to solder bridging and smearing. Thus, polymer adhesives, because of their low temperature and rapid cures, have found a specific niche in the assembly of flat-panel displays.

Several approaches using electrically conductive adhesives instead of solder have been explored and are proving successful. Anisotropic adhesives (See. Ch. 1), for example, have been used to connect flex circuits and cables from the separate driver circuits to the panel, avoiding the use of solder connections. More importantly, integrated-circuit chips can be bonded directly to the ITO conductor traces on the panel, a technology called chip-on-glass (COG). IC chips can be flip-chip bonded, then underfilled with a stress-free underfill adhesive, if necessary. For protection, the chips may then be encapsulated with epoxy (glob topped).

Alternately, flip-chip devices or TAB devices may be connected using an anisotropic film adhesive which, with moderate heat and pressure, forms electrical connections between the bumps or leads of the device and the conductor pads on the panel. In using an anisotropic film adhesive, the film is first attached to the glass at 80°C–100°C under pressure of 50–100 N/cm<sup>2</sup> (based on bump area) for 3–5 seconds. The protective

layer is then removed from the film, components are placed and aligned, and the connections are made by bonding at 170°C–180°C under pressure of 200–400 N/cm<sup>2</sup> for 20–30 seconds.<sup>[45]</sup> Anisotropic adhesives are used to connect (using the TAB process) large-scale integration (LSI) chip-carrying polyimide film with traces to traces on the glass edge of LCDs. The traces are at densities of over 200-line pair per inch. The adhesive must survive temperatures from -40°C to +80°C and be repairable. The resolution of the LCD is limited by the achievable line-pair density. If the lines are too closely spaced, the conductivity between the lines becomes too high. The LCD industry has been the prime motivator for improving anisotropic-conductive adhesives with very low line-pair pitch.

UV-curing adhesives are also finding an application in flat-panel electronics. Because the panel is glass and transparent to UV light, devices can be attached with a UV-curing adhesive on the topside and, after accurate positioning, exposed to UV light from the backside of the panel and cured in a few seconds.

Thermoplastic “hot melt” adhesives have also found use in flat-panel displays (FPDs) because of their rapid bonding and ease of reworking.

### **5.2.9 Electromagnetic Interference (EMI) Shielding and Grounding**

Electrically conductive adhesives play a key role in shielding electronic circuits, modules, and subsystems from electromagnetic interference (EMI) and in grounding. EMI shielding generally involves surrounding or enclosing the part with an electrically conductive wire mesh, a metallic coating, or a metallized foil that is attached with pressure-sensitive adhesive tape. Conductive adhesives and sealants are also used to ground chasses and electronic boxes. Adhesives are used to fill in gaps and electrically bridge lids to chassis, to bond conductive gaskets in place, to attach conductive grounding pads, and to attach connector EMI gaskets. EMI shielding is important for the successful operation across all major electronics applications including military, space, and consumer communication systems, computers, servers, and medical instruments. With the proliferation of wireless electronic devices, EMI shielding becomes even more essential. Even though PWAs and other electronic modules can be designed to minimize or avoid EMI, it becomes increasingly difficult as frequencies increase beyond 800 MHz and into the high GHz regions where most wireless devices operate.

Both conductive paste adhesives and pressure-sensitive tapes are widely used for EMI protection. Two-part epoxies or one-part silicones filled with silver or silver-plated copper particles are widely used as paste adhesives while acrylic conductive and nonconductive adhesives on aluminum or copper foil are used as pressure-sensitive tapes. EMI shielding tapes are suitable for temperatures ranging from -40°C to 121°C and are available in thicknesses from 1.5 mil to 5 mil.<sup>[46]</sup> Shielding effectiveness is measured as attenuation in dB at several frequencies, for example, from 1 MHz to 20 GHz. Values for several ARclad<sup>®</sup> shielding tapes are given in Table 5.13.

The electromagnetic shielding effectiveness of a nickel-graphite filled silicone gasket with and without an EMI adhesive, measured over a wide frequency range, is shown in Fig. 5.20.<sup>[47]</sup> Test methods and requirements for the control of EMI may be found in MIL-STD-461.<sup>[48]</sup>

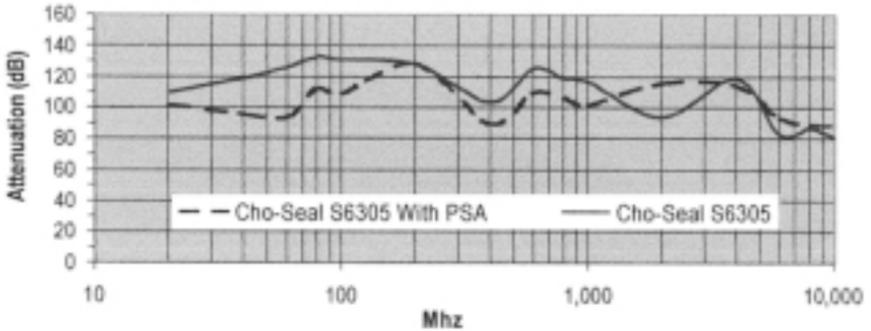
### 5.2.10 Optoelectronics

Adhesives, especially those that cure on exposure to UV/visible light, are used in a myriad of optoelectronic (OE) applications among which are active and passive optical fiber alignment and coupling, charge-coupled device (CCD) attachment, lens bonding, fiber tacking, fiber strain relief, laser assembly, and light-emitting diode (LED) attachment. Adhesives are contributing to reducing the cost of assembling and packaging optoelectronics by facilitating the alignment and coupling of optical fibers with laser diodes, lenses, and other optical parts.

**Table 5.13.** Shielding Effectiveness of EMI Tapes

Attenuation at Frequency (in dB)				
	1 MHz	500 MHz	1 GHz	18 GHz
ARclad <sup>®</sup> 5795 (5-mil Al foil/acrylic adhesive)	55	71	85	49
ARclad <sup>®</sup> 6738 (3.5-mil Al foil/acrylic adhesive on Cu carrier)	93	65	82	52
Flexshield <sup>®</sup> 8269 (4-mil Cu foil/acrylic adhesive on Ni/Cu/polyester carrier)	102	90	90	80

*Source: Technical data sheets, Adhesives Research, Inc.*



**Figure 5.20.** Electromagnetic shielding effectiveness of Cho-Seal S6305 gasket with and without CL-130 pressure sensitive adhesive. (Source: Chomerics, Div. of Parker Hannifin Corp.)

Precision alignment and attachment of optical fibers to couple them with lenses, transmitter and receiver components, and laser diodes is still largely a manual, labor-intensive process. Optical fibers must be aligned to insure that the optimum amount of light is transmitted between the fiber on the outside and the laser, photodiode, or other optical component on the inside of a package. Alignment may be active or passive.<sup>[49]</sup> In active alignment, the device is powered while a precision stage adjusts its position until maximum coupling is measured. The positioned components must then quickly and permanently be fixed in place, for example by adhesive bonding, soldering, or welding. Passive alignment relies on selecting materials and processes that have precise tolerances and known controllable dimensional changes after assembly.

Once in place and bonded, the bonding material must not change dimensionally, otherwise loss of coupling power occurs. Although metallurgical attachments (solder or laser welding) are used and are dimensionally stable, they require high temperatures or special, expensive equipment.<sup>[50]</sup>

Ultraviolet-light-curing adhesives that can reduce costs and be more easily manipulated than solder or other metallurgical attachment methods are being widely explored as alternates. The greatest benefit in using UV-curing polymer adhesives is that the adhesive will not cure until exposed to a UV source, thus curing is “on demand” allowing sufficient time for alignment and measurements. However, as with all polymeric materials, thermal expansion, shrinkage during cure, and continued dimensional changes occur during aging, thermal exposures, and humidity absorption. In spite of

this, good results have been obtained with some UV-curing adhesives. In the assembly of  $1 \times 8$  collimator array with a  $1 \times 8$  lens array, Zhou et al.,<sup>[51]</sup> measured coupling losses as a function of adhesive thickness and displacement after curing. The coupling loss for three UV-curing adhesives evaluated was less than 1.5 dB for all channels, and the variation among all eight channels was less than 0.5 dB. A list of some commercially available UV-curing adhesives and their properties is given in Table 5.14. In active alignment processes, cyanoacrylate adhesives have been used for rapid tacking, but have had to be reinforced by laser welding because of the poor adhesive properties of cyanoacrylates in high humidity and temperature environments. Thermosetting adhesives such as epoxies provide excellent bond strengths, but require elevated temperatures and extended times to cure. The use of rapid setting UV-cured adhesives followed by a short heat cure holds promise of meeting all requirements.

Passive alignment of fibers holds more potential for reducing costs than active alignment, but requires greater attention in selecting and processing materials so that they maintain tight dimensional tolerances and result in repeatable high efficiency signal propagation. Since adhesives and polymer materials in general, have high CTEs as well as CTEs and  $T_g$  that vary with degree of cure and small changes in composition, the choice and control of the adhesive is critical.

One study of a fiber pigtailed module illustrates the extensive use of adhesives in its assembly.<sup>[52]</sup> Optical fibers were assembled and coupled to laser diodes on both precision-machined silicon and injection-molded plastic substrates. V-grooves were formed in the substrates to contain and position the fibers. A second cavity was formed in-line with the V-groove to contain the laser-diode chip. Electrically conductive, electrically insulative, and thermally conductive adhesives and both heat-cured and UV-cured adhesives were all used at various stages in the assembly and alignment. First, the laser-diode chip was attached to the substrate with Epoxy Technology's Epo-Tek<sup>®</sup> H20E, a silver-filled epoxy, which also provided an ohmic contact between the n-portion of the diode and a conductor at the base of the cavity. The p-contact was made by bonding with a 1-mil-diameter gold wire. The wire-bonded contact was reinforced with a small drop of the conductive adhesive. The adhesive bondline thickness, combined with a 100  $\mu\text{m}$  copper shim, provided the exact vertical alignment for the diode chip. The substrate was next mounted onto an L-shaped metal submount with a thermally conductive adhesive (Epoxy Technology's Epo-Tek 353ND T).

**Table 5.14.** Examples of UV-curing Adhesives

Adhesive/Chemistry	Supplier	Cure Depth (inch)	Bond Strength* (psi)/substrate	Cure Conditions	Cure Time or Belt Speed	Application
Dymax <sup>®</sup> OP-60/ urethane acrylate	Dymax	<0.125	4,000/N/A	UV (50–150 mW/cm <sup>2</sup> at 300–500 nm)	60 sec (tack-free)	Optical bonding where precision alignment and no movement after placement is required
Dymax <sup>®</sup> Light Weld 931/ urethane acrylate		0.5	2,053/N/A	UV light	5 sec	Coil termination and wire tacking
Dymax <sup>®</sup> 911/ urethane acrylate		0.12	3,000/N/A	UV light or heat	<10 sec	Strain relief and wire/parts tacking (PCBs) where resistance to wave-solder profiles is required
Dymax <sup>®</sup> 9-20265/ modified acrylate		N/A	3,000/ steel-steel	UV light	<5 sec	High-speed surface-mount adhesives
Dymax <sup>®</sup> 991/ modified urethane		0.10	2,500/N/A	UV light, heat or activator	<5 sec	Thermal-transfer adhesives for heat sinking
Dymax <sup>®</sup> Multicure <sup>®</sup> 995 and 996/ modified urethane		N/A	3,000 (995) and 4,000 (996)/N/A	UV light or heat	<3 min @ 150°C or 10–20 secs of low-intensity 365 nm UV exposure	High throughput SMT bonding for large components requiring high green strength; 996 is used for high dot profile (TI = 5) and 995 is used for maximum throughput (TI = 3.5); compatible with screen and pin transfer

\*Tensile strength, unless indicated; N/A – Not available. (Source: Compiled from suppliers' technical data sheets.)

(cont'd.)

**Table 5.14. (Cont'd.)**

Adhesive/Chemistry	Supplier	Cure Depth (inch)	Bond Strength* (psi)/substrate	Cure Conditions	Cure Time or Belt Speed	Application
Ablelux <sup>®</sup> A4025/ N/A	Ablestik	N/A	N/A	UV (>50 mW/cm <sup>2</sup> @ 365 nm) or visible (>100 mW/cm <sup>2</sup> @ 470 nm)	N/A	Optical, fiberoptic, and optoelectronic devices
Ablelux <sup>®</sup> A4061T/ N/A			2,600 (die shear)/ glass/stainless)		5 sec (tack-free)	
Ablelux <sup>®</sup> A4086/ N/A		0.5 (unfilled) 0.25 (filled)	970/glass/glass		N/A	Optical, fiberoptic, and optoelectronic assembly
Lite-Lok 463/ urethane acrylate	Bondmaster	0.004	380/steel	UV (315–400 nm, 200 mw/cm <sup>2</sup> )	N/A	Tough and flexible adhesive for applications requiring thermal cycling
Loctite 3525/ modified acrylic	Loctite	0.08–0.50	1,480/steel/ glass	50 mW/cm <sup>2</sup> , 365 nm	10–15 sec	General purpose bonding of a wide range of substrates
Loctite 3526/ modified acrylic		0.5 (maximum)	2,720/steel/ steel	30–50 mW/cm <sup>2</sup> , 365 nm	≤5 sec	General purpose bonding of a wide range of substrates
Loctite 3338/ epoxy		N/A	9,015/N/A	50–100 mW/cm <sup>2</sup> , 365 nm	≤5 sec	Bonding and tacking applications in low-outgassing applications
Hysol <sup>®</sup> UV 702		0.24	100/ glass/ stainless	10–20 secs (6 mW/cm <sup>2</sup> @ 365 nm)	N/A	Bonding of lenses, prisms, v-grooves and other optical components with small gaps (<25 μm)
TRA-COAT 611	TRA- CON	0.005	2,800/ N/A	300 W/in UV	5–10 fpm	Bonding fibers or other photonics
TRA-COAT WCC2B		0.200	2,500/ N/A	200 W/in UV	5–10 fpm	Fiberoptic, glass, and general-purpose bonding

\*Tensile strength, unless indicated; N/A – Not available. (Source: Compiled from suppliers' technical data sheets.)

(cont'd.)

**Table 5.14. (Cont'd.)**

Adhesive/Chemistry	Supplier	Cure Depth (inch)	Bond Strength* (psi)/ substrate	Cure Conditions	Cure Time or Belt Speed	Application
ELC 4480	Electro-Lite	N/A	3,000/ N/A	10 mW/cm <sup>2</sup> (365 nm)	2–30 sec	Fiberoptic joining, structural bonding, coil terminating
ELC 4195		0.003	N/A	200 W/in, 10 mW/cm <sup>2</sup> (365 nm)	10 sec (depending on thickness)	Surface-mount adhesive
LiteFast™ A-1000/ polyurethane	Micro-Lite Technology	N/A	1,200/ N/A	300 W/in, 350–400 nm	2 sec	Medical bonding applications
UVIBOND® 7100/ Urethane	Aptek Labs.	N/A	N/A	1.30 Joules/cm <sup>2</sup> UV radiation	5 fpm	General electrical/electronic applications (low ionic impurities)
UVIBOND® 7101/ Urethane	Aptek Labs.	N/A	N/A	2.20 Joules/cm <sup>2</sup> UV radiation	10 fpm	General electrical/electronic applications (Low ionic impurities, flexible adhesive)
UVISTAKE® 7205LM-PMF/ Urethane	Aptek Labs.	N/A	N/A	7.5 Joules/cm <sup>2</sup> UV radiation	1 fpm	General electrical/electronic staking applications (low outgassing)
LC-1210/acrylate	3M Co.	~ 0.4	3,180/ N/A	400–500 nm (visible) 250–380 nm (UV)	5 sec, 400–500 nm (visible), 0.28 sec (single pass), 25 fpm 3.336 W/cm <sup>2</sup> (D line)	UV-visible deep-section curing through UV-opaque substrates, semi-rigid bond

\*Tensile strength, unless indicated; N/A – Not available. (Source: Compiled from suppliers' technical data sheets.)

(cont'd.)

**Table 5.14.** (Cont'd.)

Adhesive/Chemistry	Supplier	Cure Depth (inch)	Bond Strength* (psi)/ substrate	Cure Conditions	Cure Time or Belt Speed	Application
LC-1211/acrylate	3M Co.	~ 0.4	1,420/ N/A	400–500 nm (visible), 250–380 nm (UV)	5 sec, 400–500 nm (visible), 0.28 sec (single pass), 25 fpm 3.336 W/cm <sup>2</sup> (D line)	UV-visible deep-section curing through UV-opaque substrates, flexible bond
LC-1212/acrylate		~ 0.4	4,500/ N/A	400–500 nm (visible), 250–380 nm (UV)	10 sec, 400–500 nm (visible), 0.28 sec (single pass), 25 fpm 3.336 W/cm <sup>2</sup> (D line)	UV-visible deep-section curing through UV-opaque substrates, semi-rigid bond
LC-1213/acrylate		~ 0.4	1,930/ N/A	400–500 nm (visible), 250–380 nm (UV)	10 sec, 400–500 nm (visible), 0.28 sec (single pass), 25 fpm 3.336 W/cm <sup>2</sup> (D line)	UV-visible deep-section curing through UV-opaque substrates, flexible bond
LC-1214/acrylate		~ 0.4	1,320/ N/A	400–500 nm (visible), 250–380 nm (UV)	5 sec, 400–500 nm (visible), 0.28 sec (single pass), 25 fpm 3.336 W/cm <sup>2</sup> (D line)	UV-visible deep-section curing through UV-opaque substrates, very flexible bond

\* Tensile strength, unless indicated; N/A – Not available. (Source: Compiled from suppliers' technical data sheets.)

The fiber was aligned with the laser by inserting it in the groove and positioning it to within 30  $\mu\text{m}$  of the laser. The fiber is supported by the sharp edges of the groove such that it does not touch the bottom of the groove. After positioning to obtain the maximum coupling efficiency, the fiber was bonded in place using several drops of a UV-curing adhesive (Loctite 3525) which cured in 10 seconds on exposure to a UV light source. In dispensing the adhesive, spreading was controlled so it did not completely fill the groove. The assembled module is shown in (Fig. 5.21).

### 5.2.11 Smart Cards

Electrically conductive adhesives are being used to interconnect flip-chip devices in smart cards resulting in thinner and smaller structures. Flip-chip silicon devices that have been thinned to several mils may be connected to a substrate with silver-filled paste epoxy or with anisotropic film adhesive instead of solder, then embedded and laminated to form a card that is less than 40-mils thick. Requirements for adhesives used in smart cards, in many respects, are more severe than those for other commercial applications. Besides having to withstand high humidity and temperature extremes, smart cards must take the continued abuse of human handling, repeated bending, exposure to human sweat and salt residues, and exposure to ultraviolet radiation from sunlight.



**Figure 5.21.** Fiber pigtailed module using precision-machined substrate for laser-to-fiber passive alignment.<sup>[52]</sup>

In one study,<sup>[53]</sup> a series of smart cards was fabricated in which the microchip was attached and laminated with three anisotropic-conductive adhesives and one silver-filled paste adhesive. The anisotropic films were hot-melt types all filled with rigid silver-coated glass particles, but differed in the polymer matrix. Polymer matrices included thermoset nitrile rubber/phenolic resin, thermoplastic polyester, and thermoplastic polyetherimide. The paste adhesive was a silver-filled, one-part, 100% solids, modified acrylic that was used with an insulative thermoset nitrile/phenolic film. A series of accelerated tests was used as shown in Fig. 5.22. Tests included functional testing before and after subjecting parts to torsion, bending (up to 1,000 cycles), temperature cycling, thermal shock, tropical conditions, low and high temperatures, chemicals, and UV irradiation. In addition, scanning-acoustic microscopy (SAM) was used to study the adhesion between the

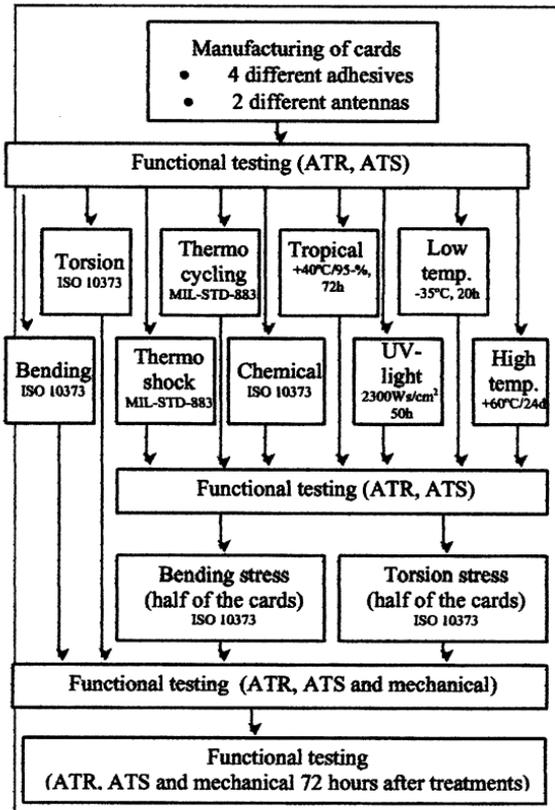


Figure 5.22. Accelerated reliability tests for smart cards. (Source: VTT Electronics.)

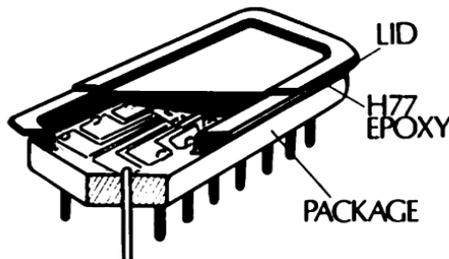
chip and antenna structure after the environmental tests. Functional tests were Answer to Reset (ATR) and Answer to Select (ATS). In general, parts assembled with the thermoset polymer binder passed all mechanical and functional tests while the parts that employed the thermoplastic anisotropic adhesives displayed many failures.

The reliability of these cards has been reported to be quite good. VTT Electronics reported extended bend cycles up to 17,500 at which point the card plastic fractured, but electrical interconnects were still sound.

### 5.2.12 Lid Sealing

Adhesives can be used to attach and seal lids to a variety of ceramic or metal packages in lieu of seam welding, soldering, or glass attachment (Fig. 5.23). As with other applications, the main advantage of using polymer adhesives is low cost. In lid sealing with adhesives, there are the added advantages of ease of delidding for rework, avoidance of metal-particle contamination from solder or welding processes, low-processing temperatures ( $<165^{\circ}\text{C}$  for curing), and low-cost equipment. Both paste and preform insulative adhesives, typically epoxies, modified epoxies or silicones, have been used. B-staged epoxy preforms and thermoplastic films are convenient since the preform can be cut to size, tacked onto the lid, then stored at low temperature until ready for use. With preforms, there is also better thickness control than for paste adhesives.

Sealing with adhesives does not provide the long-term hermetic properties associated with seam welding. Some adhesives suppliers report passing a  $1 \times 10^{-8}$  cc/sec helium leak-rate after 100 hours exposure to 90% RH and  $32^{\circ}\text{C}$ .<sup>[54]</sup> Others<sup>[55]</sup> demonstrated reliable use of epoxy-sealed



**Figure 5.23.** Cross-section of cavity package with epoxy-attached lid. (Source: *Epoxy Technology*.)

hybrid microcircuits for radio and communication systems used in commercial aircraft. Packages were 1 x 1 inch, ceramic flat packs with ceramic lids. The environment was that of the cabin aircraft which was rather benign. Hybrid microcircuits sealed with Ablefilm<sup>®</sup> 507 initially passed both the fine leak test ( $<5 \times 10^{-7}$  atm-cc/sec) and the gross leak test according to MIL-STD-883, Method 1014, Condition C. Actual field data demonstrated reliable performance for aircraft cabin environments. Although analysis of packages recovered from aircraft after three years of service showed the presence of moisture, some in amounts greater than the maximum 5,000 ppm specified in military specifications, no failures could be attributed to the presence of moisture. The internal condition of the circuit showed no corrosion even on the thin film, closely spaced aluminum conductors. It was concluded that the circuits were very clean and that moisture alone in the absence of ionic contaminants did not affect the reliability of the modules. However, a moisture requirement is still considered important since the cleanliness of circuits produced by different suppliers or by the same supplier for different batches cannot be guaranteed.

For military, high-reliability, and ground-based applications, where humidities up to 100% and temperature extremes from sub-zero to 50°C are encountered, there would be considerable risk in using adhesive-sealed packages. Sealed microcircuits must pass a series of mechanical and environmental tests for both qualification and acceptance prior to moisture analysis. In a study performed for NASA, MSFC,<sup>[56]</sup> the permeation of moisture through epoxy-sealed packages was measured by enclosing calibrated moisture sensors in the epoxy-sealed packages and subjecting them to 98% RH and 60°C. Although the moisture content remained low (less than 1,000 ppm for the first five days), an abrupt and linear increase occurred at the end of the fifth day, and it continued to increase (Fig. 5.24). The latent period of 4–5 days may be explained as the time that was necessary for moisture to saturate the epoxy adhesive, traverse the width of the bond, and be released at the other end into the package.

### 5.2.13 Power Circuits and Power Devices

In power circuits or power devices, heat must be removed by convection by blowing air across the part, by conduction through several solid materials and interfaces to a heat sink or heat exchanger, or by a combination of conduction and convection. If heat transfer depends solely on conduction, the adhesive used for attachment is often the limiting factor providing the

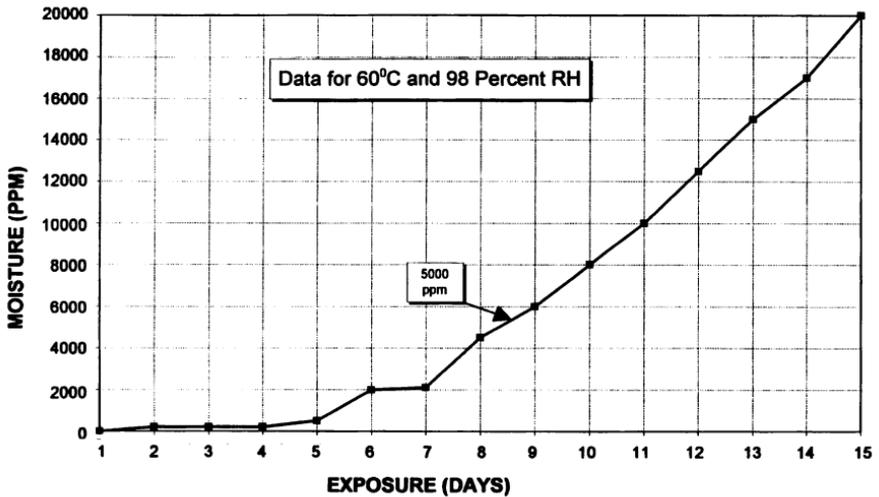


Figure 5.24. Moisture permeation through epoxy-sealed ceramic package.<sup>[56]</sup>

high thermal impedance compared to solder, metals, or ceramic interfaces. Generally, heat must flow through several materials and interfaces, each of which contributes its own thermal resistance. A simple thermal analysis can be performed based on a knowledge of the thermal conductivities of each of the materials, their thicknesses, and contact areas. The total thermal resistance is calculated by adding the individual resistances in a manner similar to conducting an electrical circuit analysis. Thus, if a power device dissipates  $5 \text{ W/cm}^2$  and the difference between the device junction temperature and the backside temperature of a package must be kept at less than  $20^\circ\text{C}$ , the total impedance must not exceed  $4^\circ\text{C/watt}$ . In a typical case where a silicon IC is attached to an alumina ceramic substrate that, in turn, is attached to the inside of a metal or ceramic package, the two epoxy interfaces can easily contribute  $2.5^\circ\text{C/watt}$  to the total resistance. However, some silver-filled epoxies are reported to have high thermal conductivities, thus contributing  $0.6^\circ\text{C}$  to  $1^\circ\text{C/watt}$ .<sup>[57]</sup> Actual measurements may differ considerably from calculated values because of reported thermal conductivities that differ from the actual, differences in the thicknesses of bondlines, voids in the adhesive, and incomplete mating of surfaces. Further in the

analysis, the effects of lateral flow of heat and interactions of heat flow among adjacent components are often neglected.

In practice, several techniques can be used to maximize the dissipation of heat. Of course, solder and other metallurgical attachments provide the lowest thermal resistance but, where adhesives must be used, those having the highest thermal conductivities should be selected. Some silver-filled adhesives, formulated with unique suspensions of silver, resin, and carrier fluid are reported to have thermal conductivities of  $20 \text{ W/m}\cdot\text{K}$ <sup>[58]</sup> approaching those of ceramics and some metals. An adhesive having a high silver loading is produced once the carrier fluid has been removed, and the adhesive is fully cured.

To assure optimum conductance, the adhesive must be applied as thinly and uniformly as possible. To control the thicknesses bondlines, thermally conductive paste adhesives have been formulated with collapsible spacers. The spacers are reported to control bondline thickness to 1.2 mils. These adhesives were developed for stacked die packages, but may also be used to attach ICs and other devices to substrates in plastic BGAs, CSPs, and array packages based on flexible tape or plastic laminates.<sup>[59]</sup> Bondline thicknesses and uniformity may also be achieved by using film or preform tape adhesives and controlling the applied pressure and heat during cure.

Lastly, a technique that has been used for many years involves first eutectic or solder attaching high-power devices to small heat spreaders such as *moly tabs* (gold-plated molybdenum tabs that are the same size or slightly larger than the die). Thermally conductive adhesive is then used to attached the die-tab parts to a ceramic or laminate interconnect substrate.

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# 6 Reliability

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The reliability of an adhesive and its impact on the performance of an electronic assembly should be considered in the initial selection of the adhesive and the design of the system. The function that the adhesive must perform for a specific application, the environment it is expected to encounter, and its duration are all important. Various approaches may be used to predict and assure reliability. Key among these approaches is a basic understanding of possible failure modes and mechanisms. Most failure modes attributed to adhesives are now well understood and documented so that they can be avoided in the initial selection and qualification of the adhesive and in its processing.

Secondly, accelerated tests can be used to qualify adhesives for specific applications, and the data from them can sometimes be extrapolated to long-term, real-time performance. Accelerated tests are also valuable as screen tests and as acceptance tests and are specified in material-procurement documents or in hardware acceptance specifications. Adherence to material and process specifications and their quality-control provisions is an essential element in assuring reliability. Life prediction through modeling is yet another approach, but it is outside the scope of this chapter.

Lastly, there are extensive databanks of real-time performance for adhesives that have been used in numerous applications, various environments, and for extended periods of time—the so-called heritage data.

## 6.1 FAILURE MODES AND MECHANISMS

The major failure modes of adhesives include loss of adhesion, high thermal impedance, loss of electrical contact, and corrosion. To a lesser extent, failures may occur because of metal migration causing high leakage currents and even electrical shorting. Sloughing of particles from the

adhesive during vibration is also known to damage wire bonds, fine wire, and thin-film metallization in sealed packages, causing opens or shorts, depending on the type of particle.

### 6.1.1 Loss of Adhesion (Delamination)

Loss of adhesion or loss of mechanical strength may result from cohesive failure within the adhesive or adhesive failure at the bondline interfaces, such as between the adhesive and the substrate or the adhesive and the device. Adhesion failures result in delamination or separation of ICs, substrates, packaged devices, heat sinks, or other attached parts. It is important that the mechanical strength of adhesives be maintained over the operational lifetimes of the bonded parts and at elevated temperatures or other environmental conditions.

Reliability requirements may be classified as short term or long term. Thus, delamination may occur shortly after curing due to contaminated surfaces, improper ratios of adhesive-curing agents, or inadequate cure or later during environmental stress testing. Short-term requirements include maintaining mechanical strength under conditions encountered during the assembly, processing, and testing of electronic modules. Long-term reliability requires maintaining adhesion strength after repeated thermal cycling, elevated-temperature exposure, or temperature-humidity exposure. Mechanical reliability for die or substrate attachment over time may be determined by comparing die-shear strength or lap-shear strength before and after aging or after exposure to actual- or accelerated-stress conditions.

Delamination may be complete or partial. Complete delamination results in gross separation of the device, substrate, or other adherend. Partial debonding can result in device or substrate cracking with complete detachment occurring in time. Numerous factors and mechanisms contribute to delamination, some of which are:

- Selection of an adhesive, whose adhesive or cohesive strength is initially marginal or poor. In the case of two-part systems, poor strength may be due to using non-stoichiometric ratios of resin to hardener.
- Insufficient cure time or temperature, leaving unreacted resin or hardener or excessive cure conditions resulting in embrittlement.

- Insufficient cleaning leaving surface contaminants that reduce wetting (resin bleedout or volatile outgassing that redeposits on surfaces).
- Insufficient or nonuniform adhesive coverage (generally, a minimum thickness of 2 mils is required). Nonuniform or insufficient pressure in applying film adhesives.
- Stresses due to large mismatches in the CTEs of the adherends or residual stresses due to shrinkage during cure.
- Adhesives having too high or too low a modulus for the size of the device.
- Voids in the bondline due to entrapped air, moisture, solvents, or low-molecular-weight volatile compounds.
- High amounts of absorbed moisture in the die-attach or underfill adhesive.

Of these failure mechanisms, the major ones associated with delamination include contaminated surfaces, inadequate adhesive coverage, stresses, voids, and moisture absorption. Many of these mechanisms are also responsible for other failure modes besides delamination.

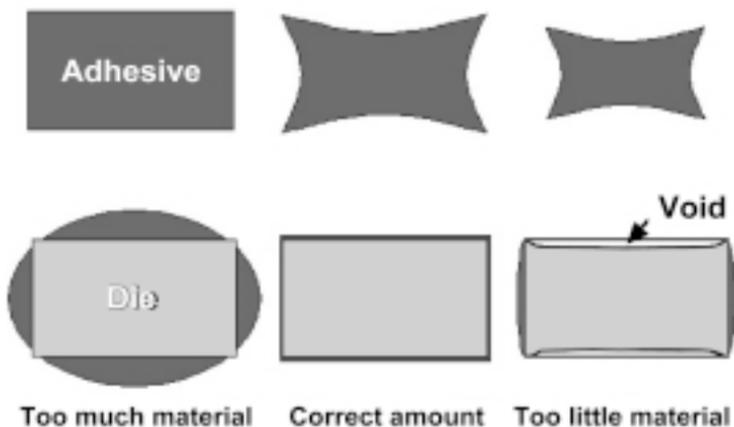
**Contaminated surfaces and poor wettability.** A major cause of delamination is poor wettability of liquid or paste adhesives, or insufficient contact and surface wetting for film adhesives because of low or nonuniform pressure applied during cure. In either case, inadequate cleaning is a prime cause of partial or complete separation of the adhesive from the device, the substrate, or both. Besides the normal contaminants from processing or handling that may remain because of inadequate cleaning, contaminants may be introduced during cure. Contaminants may consist of solvents, epoxy diluents, silicone fragments, or other low-molecular-weight compounds that volatilize and deposit onto die-bonding pads, leadframe fingers, top of the die, or bottom of the die pad in single-chip packaging or onto substrates in multichip packaging. In the case of leadframe attachment, redeposited volatile materials reduce adhesion of the subsequently applied molding compound, effectively acting as a release agent. Reduced adhesion occurs because residues as thin as 70 to 500 angstroms are enough to “coat” the highly polar and reactive surface groups such as free hydroxyl or oxide groups that normally form strong bonds with the adhesive. Depositions on

the bottom of leadframes can occur when parts are stacked in magazines and cured in an oven. In comparison, parts cured on a hotplate showed excellent resistance to delamination.<sup>[1]</sup> Volatile diluents from epoxy adhesives may also deposit on the walls of curing ovens and then redeposit onto other parts being cured in the same oven.

**Adhesive coverage.** Poor adhesion and delamination can also result from dispensing insufficient adhesive to cover the entire bondline (Fig. 6.1). Generally, a minimum thickness of 2 mils is required. A visible fillet around two or more sides of an attached die or substrate provides assurance that sufficient adhesive has been used and has spread and covered the bondline. In fact, the appearance and extent of fillet is an inspection criterion for the acceptance of high-reliability circuits as defined in MIL-STD-883, Method 2010 for monolithic ICs and Method 2017 for hybrid microcircuits. According to these methods, at least 75% of the fillet should be visible along each side of the device. Applying a uniform thickness is also important. Nonuniform thicknesses result in tilted devices with the potential for cracking and separation.

**Stresses.** Besides inadequate cleaning, the second most common cause of delamination is stress buildup in adhesive joints due to residual stresses generated during thermal curing and cooling or to those resulting from large mismatches in the CTEs of the adherends. It should be noted, however, that although adhesives can contribute to stresses and failures,

The role of improper dispensing of material in producing voids



**Figure 6.1.** Accept/reject criteria for adhesive coverage. (Courtesy CALCE Electronic Products and Systems Center, Univ. of Maryland.)

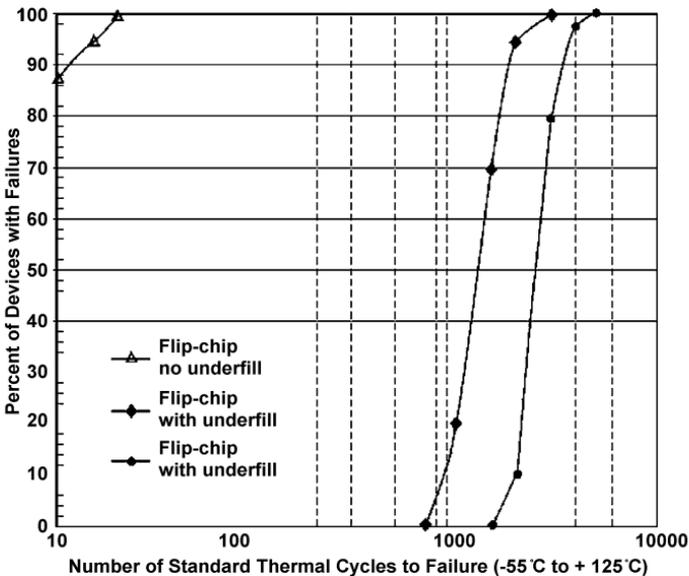
they may also absorb, dissipate, and reduce stresses. An example is their wide and indispensable use as underfills for flip-chip devices. Figure 6.2 compares the reliability of flip-chip devices with and without underfill adhesives showing the dramatic advantage of the underfills in dissipating stresses generated during temperature cycling.<sup>[2]</sup>

**Residual stress.** Residual stresses may be measured from the radius of curvature of the warpage that occurs on a substrate when the adhesive is cured on that substrate. The bending stress,  $S_b$ , is inversely proportional to the radius of curvature,  $R$ , and directly proportional to the modulus,  $E$ , and the thickness,  $h$ , of the adhesive according to:

$$\text{Eq. (6.1)} \quad S_b = Eh/2\gamma R$$

where  $\gamma$  is Poisson's ratio.

High-modulus adhesives are likely to have high bending stresses, high deflections, and low radii of curvature. As examples, a typical silver-filled epoxy with a deflection of  $3 \mu\text{m}$  had a low radius of curvature of  $1,070 \text{ mm}$ <sup>[3]</sup> and a cyanate-ester adhesive reported to have a high modulus of  $10,000 \text{ MPa}$  had a radius of curvature of  $5,000 \text{ mm}$ .<sup>[4]</sup>



**Figure 6.2.** Reliability of flip-chip devices with and without underfill.

Low-modulus adhesives, on the other hand, have low deflections, low bending stresses, and high radii of curvature. For example, silicones and other elastomeric adhesives have low deflections of approximately  $0.01 \mu\text{m}$  and radii of curvature of over 125,000 mm.

Stress build-up in bonded devices may also be characterized over a temperature range as a function of the coefficients of expansion of the adhesive and of the substrate according to the following one-dimensional model.<sup>[5]</sup>

$$\text{Eq. (6.2)} \quad \sigma_{\text{Si}} = \epsilon_a \times E_a = (\alpha_a - \alpha_{\text{Si}}) \times E_a \times \Delta T$$

where:  $\sigma_{\text{Si}}$  = stress on the silicon  
 $\epsilon_a$  = strain of the adhesive  
 $E_a$  = modulus of the adhesive  
 $\alpha_a$  = CTE of the adhesive  
 $\alpha_{\text{Si}}$  = the CTE of silicon  
 $\Delta T$  = temperature difference

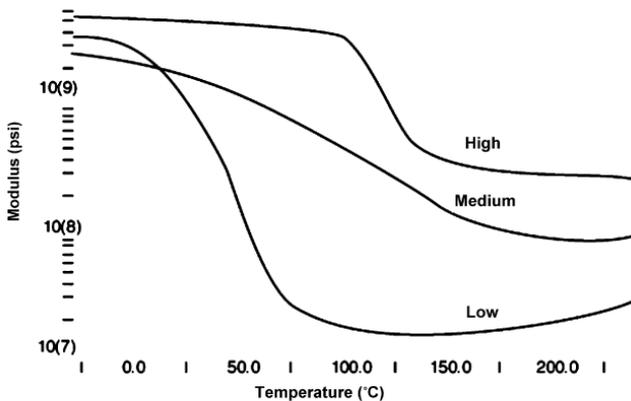
Yet, a third equation defines maximum stress for rectangular devices taking into account the size of the device, bondline thickness, and cure and exposure temperatures in addition to modulus and CTEs.<sup>[6]</sup>

$$\text{Eq. (6.3)} \quad S_{\text{max}} = K(\alpha_{\text{sub}} - \alpha_{\text{Si}})(T_o - T) \sqrt{\frac{E_a E_{\text{sub}} L}{x}}$$

where:  $S_{\text{max}}$  = maximum stress  
 $K$  = geometric constant related to shape and filleting  
 $\alpha_{\text{sub}}$  = CTE for the substrate  
 $\alpha_{\text{Si}}$  = CTE for the silicon die  
 $E_a$  = modulus for the adhesive  
 $E_{\text{sub}}$  = modulus for the substrate  
 $L$  = length of the die  
 $x$  = bondline thickness  
 $T_o$  = cure temperature  
 $T$  = application (exposure) temperature

Based on these equations, stresses that can result in failures are a function of many parameters including modulus of elasticity, expansion coefficients of the adhesive and adherends, glass-transition temperature, cure temperature, operating or exposure temperatures, and bondline thickness.

**Modulus of elasticity.** The modulus of elasticity, also known as tensile elastic modulus or Young's modulus, is the stress required to produce unit strain. The modulus is measured by pulling a sample of the cured material in a tensile-testing machine while measuring the change in length by attaching an extensometer to the sample. The *stress* (force per unit area) divided by the *strain* (change in length normalized by the initial length) is the *elastic modulus*. In flexural modulus, a bending stress instead of a tensile stress is applied, the deflection produced is recorded and the modulus calculated from the ratio of stress to strain. The method applies only to materials within the elastic region, that is, where applied forces do not irreversibly stretch the material. Thus, modulus is a measure of the rigidity or flexibility of adhesives—an important parameter in selecting the type of adhesive to use in various semiconductor packages. Moduli can range from less than 30,000 psi to greater than 1 million psi at 25°C. In all cases, the moduli decrease with increasing temperature. Those that decrease the most are classified as low-modulus types (Fig. 6.3). Adhesives having the lowest moduli at both room temperature and at elevated temperature generate the lowest stresses and are especially useful in preventing delamination and cracking in thin plastic packages such as thin quad-flat packages (TQFP).



**Figure 6.3.** High, low, and intermediate modulus curves as a function of temperature. (Courtesy Ablestik, a National Starch and Chemical Co.)

Stresses in adhesive-attached die become critical as the size of the die increases and as dissimilar adherends are used. Silicon die, smaller than 100-mil square, attached with high-modulus adhesives to leadframes or other substrates have been quite reliable even when large differences in the CTEs of the adherends exist. However, for large devices (greater than 300-mil square) low-modulus adhesives are necessary to absorb or dissipate stresses.<sup>[7]</sup>

In one study, adhesives having various moduli ranging from high to low were evaluated for bonding ferrite cores and magnetic devices to low-temperature, cofired-ceramic (LTCC) substrates. Two adhesives having high moduli of  $1.3 \times 10^6$  psi at 25°C (35,000–40,000 psi at 125°C) displayed the highest stresses at 25°C and produced cracks in the substrates. An intermediate-modulus adhesive had a lower stress while the lowest-modulus adhesive (19,000 psi) displayed the lowest stress and produced no failures (Table 6.1).<sup>[8][9]</sup>

Low-modulus adhesives produce low bending stresses and have higher radii of curvature than intermediate- or high-modulus adhesives. The radius of curvature of parts bonded with low-modulus adhesives increases with the size of the die. Post-cure–temperature exposures such as those subsequently encountered during wire bonding or molding also increase the radius of curvature indicating stress relaxation in the adhesive by an annealing mechanism.<sup>[10]</sup>

**CTE mismatches.** Large mismatches between the expansion coefficients of the adhesive and the two adherends have been the primary cause of numerous failures resulting in high stresses and cracking or delamination. Unfortunately, the CTEs of most polymeric materials are much higher than those of the ceramic substrates or silicon devices that are used. Further contributing to stresses is the often abrupt increase in the CTEs of adhesives and other polymers that occurs at and above the  $T_g$ . Since the thermal expansion coefficients of adhesives below the  $T_g$  may range from 25–100 ppm/°C (that is, greater than the CTEs of the device or substrate materials) stresses in bonded parts are compressive on the die and substrate and tensile in the adhesive.

Where the adherends have closely matched CTEs as for silicon die (CTE = approx. 3 ppm/°C) attached to Kovar<sup>®</sup> leadframes (CTE = approx. 5 ppm/°C), a high-modulus adhesive could be used. As Kovar leadframes were replaced by copper leadframes (CTE = 16–17 ppm/°C), low-modulus, stress-free adhesives were required to compensate for the large mismatches in CTEs. Large CTE mismatches also occur when silicon devices are directly attached to epoxy printed-circuit boards as for COBs or CSPs.

**Table 6.1.** Effect of Modulus, Expansion Coefficient, and Temperature on Adhesive Stress<sup>[8][9]</sup>

Property	Adhesive A (High Modulus)			Adhesive B (High Modulus)			Adhesive C (Intermediate Modulus)			Adhesive D (Low Modulus)		
	-55°	25°	125°	-55°	25°	125°	-55°	25°	125°	-55°	25°	125°
Temperature (°C)	-55°	25°	125°	-55°	25°	125°	-55°	25°	125°	-55°	25°	125°
$\Delta T$ (150 - $T_{use}$ )	205	125	25	205	125	25	205	125	25	205	125	25
CTE ( $\alpha_1$ or $\alpha_2$ )	40.3	40.3	119.9	25.9	36.1	117.0	37.8	37.8	116.1	33.2	167.4	159.3
Modulus (psi)	$1.61 \times 10^6$	$1.31 \times 10^6$	35,000	$1.73 \times 10^6$	$1.29 \times 10^6$	40,000	621,000	432,000	15,000	$2.59 \times 10^6$	19,000	12,000
Stress* (psi)	10,000	4,962	96	5,639	4,209	107	3,539	1,501	40	12,318	373	45
% Reduction from adhesive A value	–	–	–	43.6	15.2	11.5 (increase)	64.6	69.8	58.3	23.2 (increase)	92.5	53.1
Lowest possible cure stress (psi) (25°C only)	–	3,030 (125°C cure)	–	–	0 (25°C cure)	–	–	1,201 (125°C cure)	–	–	373 (150°C)	–
<p>*Stress = <math>(\alpha_{adhs} - \alpha_{sub}) \times 10^{-6} \times (T_{cure} - T_{use}) \times \text{modulus}</math> (-55°, +25°, +125°C), where <math>\alpha_{sub} = 10</math> ppm/°C for ferrite cores and <math>\alpha_{adhs}</math> (above or below <math>T_g</math>, respectively). (Copyright ©1999 IMAPS — International Microelectronics and Packaging Society, and 2001 by Elsevier Press. Reproduced by permission.)</p>												

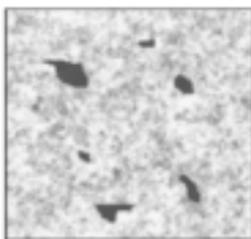
**Voids and moisture absorption.** Two other related factors that can cause delamination are voids and moisture absorption. Voids can be generated during the attachment process and may result from dewetting, the entrapment of air, or the volatilization of absorbed gases during curing. Voids may also be produced during cool-down from heat curing if shrinkage occurs with separation from the substrate. The distribution and size of voids across the bond layer determine the effects they might have on device performance (Fig. 6.4). Generally, small random voids have a minor effect on both mechanical strength and thermal conductance. Large, contiguous voids are detrimental to both mechanical strength and thermal performance.

Acoustic microscopy is a widely used method for analyzing the integrity of adhesive bondlines. Acoustic microscopy is based on the fact that each material has an acoustic impedance designated as:

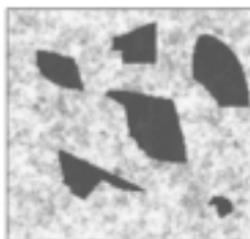
$$Z = \sqrt{K\rho}$$

where  $K$  is the bulk modulus and  $\rho$  is the density.<sup>[11]</sup> Acoustic reflection at interfaces is based on the following:

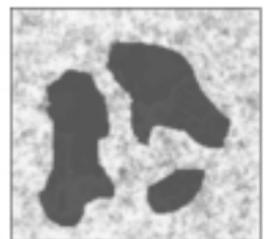
- Ultrasound propagating from a high acoustic impedance material to a lower impedance material that produces a negative reflection.
- Ultrasound propagating from a material of low acoustic impedance on top of a high impedance material, thus generating a positive reflection.



Small, random



Large, random



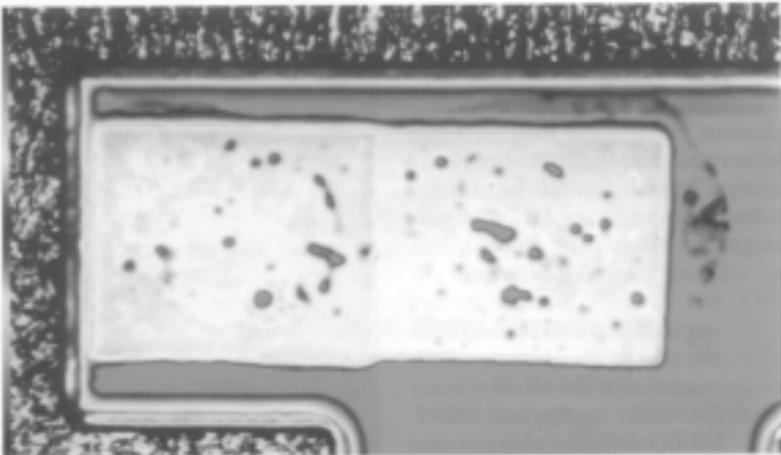
Large, contiguous

**Figure 6.4.** Types of die-attach voids. (Courtesy CALCE Electronic Products and Systems Center, Univ. of Maryland.)

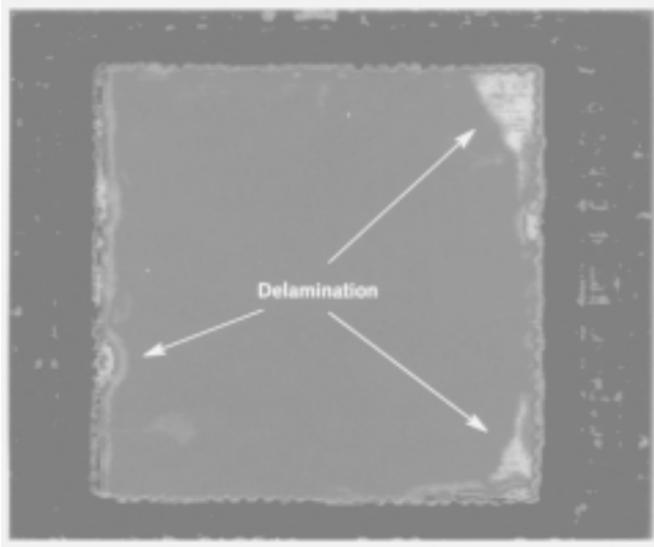
When voids are present in a bondline or when delamination occurs, the air that fills the voids has an acoustic impedance of  $0 \text{ kg/m}^2 \text{ sec}$  and a large amplitude and total negative reflectance occurs. Most polymeric materials have acoustic impedances of  $2.0$  to  $4.5 \times 10^6 \text{ kg/m}^2 \text{ sec}$  compared to copper ( $42 \times 10^6 \text{ kg/m}^2 \text{ sec}$ ) and silicon ( $20 \times 10^6 \text{ kg/m}^2 \text{ sec}$ ). Examples of acoustic micrographs showing voids and delamination in an adhesive bondline are pictured in Figs. 6.5 and 6.6.

Moisture is absorbed by adhesives and other plastic materials to various degrees and can accumulate in voids within the bondline during assembly, testing, and operation. The absorption of moisture in adhesives as well as in other polymeric materials, such as molding compounds, has been proven to cause failures when parts are subsequently solder reflowed and exposed to the high solder melt temperatures of  $200^\circ\text{C}$  and above. The rapid evaporation and expulsion of the moisture results in stresses that cause cracking and delamination, a phenomenon referred to as popcorning.

The absorption of moisture in underfill adhesives induces a tensile hydrothermal stress on the solder-ball connections causing electrical opens in the connections and cracking in the adhesive. These tensile stresses offset the compressive stresses that underfill adhesives provide in improving the reliability of flip-chip and ball-grid-array devices.



**Figure 6.5.** Acoustic micrograph of voids. (Source: *Using acoustic micro-imaging to inspect multichip modules*, Sonoscan Brochure.)



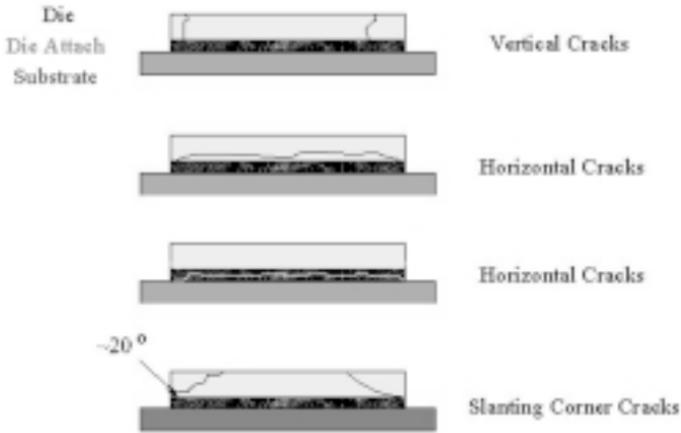
**Figure 6.6.** Acoustic micrograph of delamination. (Source: *Using acoustic micro-imaging to inspect multichip modules*, Sonoscan Brochure.)

### 6.1.2 Die Fracture

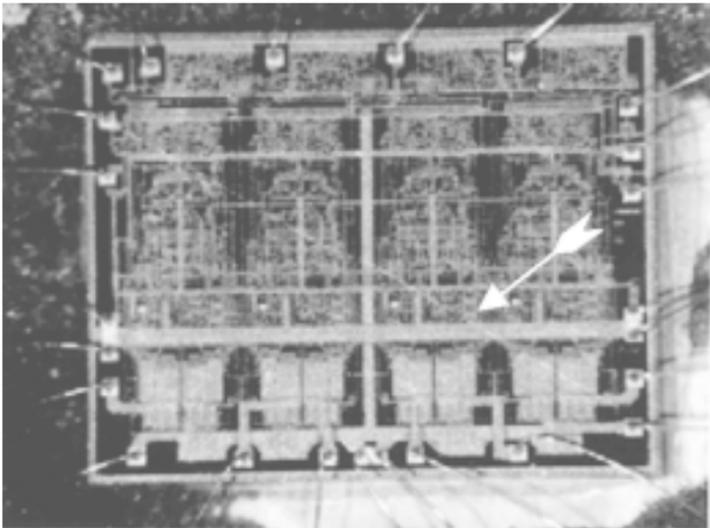
Besides delamination, actual cracking of silicon die is a failure mode that can occur from excessive adhesive stresses, voids, and moisture absorption. Residual stresses in adhesive-attached single-chip devices become critical as the size of the device increases and dissimilar die and leadframe materials are used. Several types of fractures that can occur within the die or within the adhesive are shown in Fig. 6.7. A hairline crack in an IC chip that resulted from adhesive stress is shown in Fig. 6.8.

### 6.1.3 High Thermal Impedance

Overheating of devices resulting in electrical malfunctioning or reduction in the life expectancy of the device and circuit can be the direct result of poor conductivity and high thermal impedance of the adhesive. Thermal conductivity of adhesives becomes critical as devices are operated at higher speeds, consume more power, and dissipate more heat. Semiconductor junction temperatures must remain within normal limits, particularly for



**Figure 6.7.** Types of fractures in die and die-attach adhesives. (Courtesy CALCE Electronic Products and Systems Center, Univ. of Maryland.)



**Figure 6.8.** Fracture in silicon IC device resulting from adhesive stress. (Courtesy CALCE Electronic Products and Systems Center, Univ. of Maryland.)

gallium-arsenide devices that operate at high frequencies and whose thermal conductivity is much lower than that of silicon devices (approximately 60% lower). In such cases, high thermal conductivity materials throughout the conduction path from the junction of a semiconductor device through the die-attach adhesive to the package case are required to maintain the junction-to-case temperature ( $\theta_{JC}$ ).<sup>[12]</sup> The flow of heat through materials is directly proportional to the cross-sectional area, the temperature difference across the material, and the time, but inversely proportional to the thickness (see Ch. 2). Some mechanisms for increased thermal impedance attributed to adhesives are as follows:

- Poor initial thermal conductivity of the adhesive chosen.
- Voids in the adhesive bondline generated during curing from entrapment of solvents, air, or moisture.
- Air pockets and delaminated areas due to poor wetting.
- Applying too thick an adhesive layer or a nonuniform thickness.

**Poor initial thermal conductivity.** *Thermal conductivity* is defined as the proportionality constant between the rate of heat flow and the cross-sectional area of known thickness and temperature drop. *Thermal impedance* is the temperature drop, from junction to case, divided by the power dissipated by the device and is reported in °C/watt. Among the important steps in assuring adhesive reliability is the selection of an adhesive having the highest thermal conductivity. If electrical insulation is not a factor, the silver-filled epoxies are among the best thermal conductors. The thermal conductivities of silver-filled epoxies range from 0.5 W/m·K to 8 W/m·K. However, some silver-filled epoxies formulated with unique solvent blends are reported to have values as high as 20 W/m·K. The highest values (>40 W/m·K) are found with silver-glass adhesives.

Thermal-transfer adhesives that are electrically insulating also exhibit wide ranges of thermal conductivities, depending on the filler type and amount. The thermal conductivities of epoxies filled with boron nitride or diamond are approximately 4 W/m·K and 12 W/m·K, respectively, while those of the more common aluminum-oxide-filled adhesives range from 1–2 W/m·K.

Thermal conductivity requirements are specified in both military and industry specifications generally as 1.5 W/m·K or greater for electrically conductive adhesives and 0.15 W/m·K or greater for electrically insulative adhesives.

The selection of highly conductive adhesives is a necessary factor, but not the only one in minimizing thermal impedance. Applying as thin a bondline as possible and avoiding the introduction or creation of voids are also essential in reducing thermal impedance.

**Bondline thickness.** The control of bondline thickness is essential for high-power devices. A thin bondline is required since thickness is directly proportional to the junction-to-case thermal resistance,  $\theta_{JC}$  (see Ch. 2). Specially formulated solvent-based hybrid adhesives can produce uniform bondline thicknesses of one mil or less.<sup>[13]</sup> Small hard spacers, acting as shims, added to paste adhesive formulations, have also been used to control thickness.<sup>[14][15]</sup> The use of preforms instead of paste adhesives also assures reproducible thicknesses provided uniform pressure and temperature are applied during curing.

**Voids and outgassing.** Besides contributing to delamination, voids and outgassing in adhesive bondlines lower thermal conductance due to entrapped air. Voids may be introduced during the application of the adhesive because of poor wetting or improper dispensing conditions. Other sources of voids include volatilization of moisture or solvents. Entrapment of moisture, solvents, or low-molecular-weight polymer additives during curing also reduces thermal conductance. Steps that are often used to prevent voids include use of low-moisture-absorption adhesives, degassing adhesives prior to cure, prebaking the components to remove adsorbed moisture, and step curing at low temperatures to allow air and volatiles to escape before full cure.

#### 6.1.4 Loss of Electrical Contact

Silver-filled epoxies and other electrically conductive adhesives are widely used to electrically connect chip devices or packaged components to interconnect substrates or printed-circuit boards. Chip capacitors, resistors, transistors, diodes, and magnetic components may be attached with silver-filled epoxies whose volume resistivities range from  $1 \times 10^{-4}$  to  $3 \times 10^{-4}$  ohm-cm or with gold-filled epoxies whose volume resistivities are approximately  $8 \times 10^{-4}$  ohm-cm. Conductive adhesives are also finding use as replacements for solder balls in flip-chip devices. In all cases, to achieve reliable connections, initially low-contact resistances or volume resistivities must remain low on aging and on exposure to operational stress conditions, such as humidity, temperature, vibration, shock, and power.

Increases in electrical resistance or complete loss of electrical contact (electrical opens) can result from several failure mechanisms, such as:

- Loss of backside electrical contact on transistors and other semiconductor devices due to redistribution of filler at the interface or to oxidation/corrosion of the metallization.
- Separation of the adhesive and electrical opens due to one or more of the factors already discussed for delamination, such as poor wettability, shrinkage stresses, and large CTE mismatches.
- Electrical instability of silver-filled epoxies on non-noble metal surfaces when used as replacements for solder.
- Instability of silver-filled epoxies on aluminum surfaces due to oxidation and corrosion processes.

**Loss of backside electrical contact on semiconductor devices.** A reliability concern with semiconductor devices, such as chip transistors in which one of the connections is made through the backside metallization by attaching with either eutectic alloy or conductive epoxy, is the loss of backside ohmic contact. Loss of ohmic contact may be due either to mechanical/physical or chemical mechanisms.<sup>[16]</sup> Mechanical failures occur from partial or complete delamination of the adhesive interface. The smooth surface of the die metallization contributes to the problem whereas roughening the surface improves results. Loss of contact is evident from increases in resistance during initial electrical testing, but may better be detected after temperature cycling or mechanical shock screen tests, for example with hybrid microcircuits, before the product is shipped.

Failures may be related to the adhesive formulation as well as the contact metallization. The first generation of 100%-solids conductive epoxies contained 70% by weight of silver flake, and the final cured adhesive contained 21% silver by volume. Settling or disproportioning of the filler during cure in these early adhesives resulted in a resin-rich layer at the die metallization interface and a high contact resistance. Subsequent adhesives were formulated with the same amount of filler by weight but with a higher volume (34% after cure). The risk of conductivity loss due to filler redistribution for these formulations was thus minimized.<sup>[17]</sup> Increases in the “effective filler loading” is also possible from the shrinkage that occurs when some solvents in the formulation evaporate. The shrinkage prevents separation effects at the interfaces resulting in more stable interconnect resis-

tances. However, as previously discussed, that excessive shrinkage during cure produces high stresses.

Compared with mechanical and physical mechanisms, chemical mechanisms are slow and may not be detectable until well after the product has been in use, at which point the failures may be catastrophic. One chemical mechanism involves the formation of an oxide layer at the die-epoxy interface. A poorly alloyed gold-backed surface has been identified as one cause of degraded interfacial resistance. Although this is one cause, adhesives formulations also may play a role, for example, adhesives having excess (unreacted) curing agent absorb large amounts of water, thereby accelerating the oxidation process. Adhesives having less than the stoichiometric amount of curing agents may improve performance. Adhesives having a high chloride-ion content (greater than 200 ppm) are also known to cause corrosion and increase the contact resistance, especially when used to attach die having less than 125  $\mu\text{m}$  of gold thickness.

**Stability of solder replacements on non-noble metal surfaces.** A new area of concern for electrical stability arises because of the increasing use of conductive adhesives as replacements for solder. Some conductive adhesives show unstable electrical-contact resistance when used on non-noble metal surfaces such as copper or tin-lead solder. Although stable on gold, palladium, platinum, and silver surfaces, the same adhesives were found to be unstable on tin, tin-lead, copper, and nickel surfaces.<sup>[18][19]</sup> The unstable resistance and increase in resistance in temperature-humidity exposures have been attributed to the growth of an oxide layer separating the filler particles from the substrate at the interface, a mechanism similar to that for the loss of backside contact in die-attach materials.

The unstable behavior of some solder-replacement adhesives has been attributed to galvanic corrosion. Similar to most corrosion mechanisms, condensed or absorbed moisture on the surface and dissimilar metals are required to form a galvanic cell. The silver filler acts as a cathode while the substrate metallization acts as an anode and is oxidized. In the case of tin-lead solder surfaces, the solder, which has a lower electrochemical potential (0.13 V) than silver (0.79 V), becomes the anode at which corrosion and oxidation occur. A smaller potential difference between a copper surface and silver accounts for some improvement in contact resistance over the solder-silver couple.

The reliability of several silver-filled epoxies as solder replacements has been studied and reported by several investigators.<sup>[20][21]</sup> In one study,<sup>[22]</sup> adhesives formulated with an epoxy resin (Epon 862<sup>®</sup>) and cured with

several anhydrides were evaluated for their electrical stabilities on non-noble metal surfaces and extended exposure to 85/85 conditions (Table 6.2). The anhydride-curing agents evaluated were hexahydrophthalic anhydride (HHPA), methyl hexahydrophthalic anhydride (MHHPA), and 4-methylphthalic anhydride (MPA). In all cases, resistance changes were negative up to 300–600 hours after which they became less negative and finally positive after 1,000–1,500 hours exposure. The initial decreases in contact resistances were attributed to further leaching out of the lubricant from the silver-flake filler or to fillers penetrating the initial oxide layer present on the non-noble metal surface during postcuring of the adhesive. Results were promising based on the acceptance criterion set by the National Center of Manufacturing Science (NCMS) that contact-resistance change should be less than 20% after 500 hours aging at 85/85 conditions.<sup>[23]</sup>

Although some results are promising, the extent of resistance change and direction depend largely on the formulation used and should be evaluated for each application, especially on non-noble metal surfaces.

To minimize the corrosion reactions, oxygen scavengers and corrosion inhibitors may be used as additives in solder-replacement adhesives. The percent changes in contact resistances for cured formulations without scavengers or inhibitors were found to be two to three times greater than those containing scavengers.<sup>[19]</sup> Contact resistances after 500 hours of 85/85 testing were significantly reduced for those adhesives containing oxygen scavengers and less than 10% and 20% for those with and without the inhibitors, respectively.

**Stability of epoxies on aluminum surfaces.** Erratic and high resistance changes have also been reported when silver-filled epoxies are used to attach devices to thin-film–aluminum metallization and exposed to temperature-humidity environments.<sup>[24]</sup> In practice, however, aluminum-bonding pads and aluminum conductors on the top surface of an interconnect substrate are protected with barrier coatings of titanium-tungsten or chromium followed by plated gold as the top bonding surface.

### 6.1.5 Corrosion

Corrosion of conductor metallizations, devices, wire, wire bonds and other connections, and platings occur by direct or indirect-chemical reactions. The metals most susceptible to chemical attack are the non-noble metals among which are thin-film aluminum used for conductors or bonding pads, thin-film nichrome used for precision resistors, tin-lead solders used for

**Table 6.2.** Behavior of Solder Replacement Adhesives on Non-noble Metal Surfaces<sup>[22]</sup>

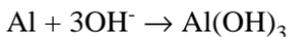
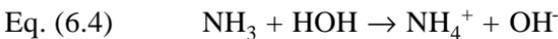
Adhesive No.	Curing Agent	$T_g$ (°C)	Moisture Absorption (% , 350 hrs of 85/85)	Percent Resistance Change (85°C/85% RH Exposure) (Relative to Initial Reading)								
				100 hrs			300 hrs			500 hrs		
				Sn	Sn/Pb	Cu	Sn	Sn/Pb	Cu	Sn	Sn/Pb	Cu
1	HHPA <sup>1</sup>	114.76	0.9	-30	-15	-50	-80	-40	-70	-90	-40	-75
2	MHHPA <sup>2</sup>	97.89	1.1	-40	-10	-70	-60	-30	-75	-70	-20	-90
3	MPA <sup>3</sup>	136.93	1.0	0	-30	-50	-35	-60	-55	-40	-60	-60
Adhesive No.	Curing Agent	$T_g$ (°C)	Moisture Absorption (% , 350 hrs of 85/85)	Percent Resistance Change (85°C/85% RH Exposure) (Relative to Initial Reading)								
				1,000 hrs			1,500 hrs*					
				Sn	Sn/Pb	Cu	Sn	Sn/Pb	Cu			
1	HHPA <sup>1</sup>	114.76	0.9	-90	-40	-70	-70	-10	-70			
2	MHHPA <sup>2</sup>	97.89	1.1	-45	+50	-75	0	+100	-80			
3	MPA <sup>3</sup>	136.93	1.0	-40	-35	-50	0	+10	-55			

<sup>1</sup>Minimum at 400 hours exposure; <sup>2</sup>Minimum at 300 hours exposure; <sup>3</sup>Minimum at 600 hours exposure; \*Exception for Adhesive #1 (1,400 hours). (Table compiled from Lu and Wong.<sup>[22]</sup>)

surface-mounting components, and copper used for conductor traces on PWBs or as heat sinks. All these metals are susceptible to chemical attack and corrosion, ultimately leading to high-resistance paths, electrical opens, or high-leakage currents. Corrosion may result from constituents from the curing agent, catalyst, or resin portion of an adhesive that has not been fully cured or has been used in excess of the optimum ratios. These constituents may be reactive enough to directly react with the metal or may do so after decomposing or first reacting with moisture. Other constituents may outgas and, in the presence of moisture, produce highly acidic or alkaline solutions that attack the metals.

**Corrosion from curing agents.** In two-part systems, the curing agents and catalysts are generally much more corrosive than the basic resin. Early epoxy-adhesive formulations used boron trihalide complexes such as boron trifluoride ethanolamine to achieve rapid room-temperature cures. Unreacted trihalides dissociated forming hydrogen chloride or hydrogen fluoride that, in the presence of small amounts of moisture, generated hydrochloric or hydrofluoric acids, both highly corrosive to aluminum.<sup>[17]</sup>

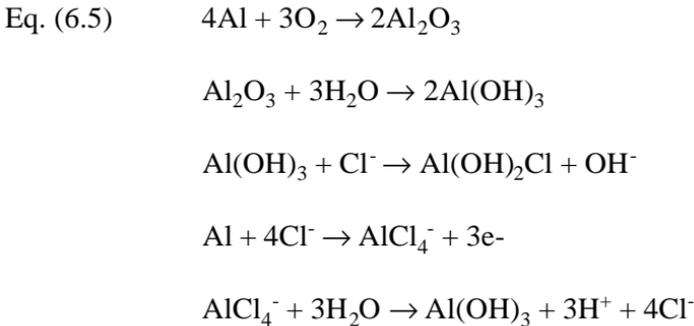
Unreacted excess amines, such as dicyandiamide (Dicy), were also a cause of corrosion in some early epoxy formulations. Dicy decomposes producing ammonia and other reactive amine compounds. The primary and secondary amines, being quite alkaline, react rapidly with aluminum. Analysis of sealed hybrid microcircuits that used dicy-cured epoxies showed quantities of ammonia as high as 30,000 to 100,000 ppm<sub>v</sub> and extensive corrosion in the presence of moisture.<sup>[17]</sup> Other investigators corroborated the presence of ammonia and low-molecular-weight amino compounds. Ammonia and amines were generated from a Dicy-cured epoxy (Ablefilm<sup>®</sup> 550) substrate-attachment film adhesive after postcure aging 24–300 hours at 125°C.<sup>[25]</sup> Ammonia, in the presence of moisture, forms a highly alkaline ammonium hydroxide solution that reacts with and converts aluminum to aluminum hydroxide as follows:



Corrosion due to alkaline condensates may be controlled by selecting curing agents that do not generate ammonia and by vacuum baking assembled circuits at 125°C to 150°C for 16–96 hours to remove moisture prior to sealing.<sup>[26]</sup> A related failure mechanism involving alkaline solutions is that of

“vanishing” nichrome thin-film resistors. Nichrome resistors were found to disappear in the presence of moderate-to-high amounts of moisture and alkaline or ionic contaminants, especially during the cold cycle of temperature-cycle testing where the moisture condenses as a liquid. Residual-gas analysis showed that no failures occurred if the moisture content was less than 1,000 ppm<sub>v</sub>. However, moisture ranging from 7,000–10,000 ppm<sub>v</sub> having dewpoints close to room temperature produced failures during the cold cycle. In quantities above 17,000 ppm<sub>v</sub>, liquid water and contaminants exist at room temperature and failures may occur early in testing.<sup>[16][27]</sup>

**Ionic impurities.** Ionic contaminants from adhesives or from other sources have been a serious problem, not only in contributing to corrosion, but also in causing electrical-parameter changes in semiconductor devices and high leakage currents across closely spaced conductors. Chloride ions are particularly detrimental since they act as catalysts and are continuously regenerated while etching away aluminum and other metals. Increasing the chloride-ion content in adhesives from 10 ppm to over 200 ppm was reported to reduce the time to failure by a factor of 4.<sup>[28]</sup> The mechanism for chloride-ion etching of aluminum is shown in Eq. 6.5<sup>[29]</sup>



High levels of chloride ions, above 600 ppm, and sodium ion levels above 100 ppm were reported for the early “first generation” epoxy adhesives.<sup>[30]</sup> The epoxy resin itself is a source of both chloride and sodium ions if not properly purified. Most epoxy resins are synthesized from epichlorohydrin and bisphenol-A in the presence of sodium hydroxide and produce sodium chloride as a byproduct (see Ch. 3). Continuous extraction of the ions with deionized water or distillation of the resin are two methods used to purify the resin.

Besides corrosion, the presence and mobility of ions, together with moisture, contribute to the phenomenon of metal migration resulting in high-

leakage currents between conductor lines and eventual electrical shorting. Ions and other contaminants, together with moisture, form an electrolytic medium and generate an electrochemical cell between two metal conductors. A small applied bias of several volts causes oxidation of the positively charged metal electrode (anodic conductor), migration of the positively charged metal ions towards the cathode, reduction back to pure metal at the cathode, and a metal buildup that eventually bridges the gap, known as *dendritic growth*.<sup>[31]–[33]</sup> Although most non-noble metal conductors are prone to metal migration, silver has been the prime cause of most circuit failures.

Perkins and Licari<sup>[34]</sup> showed the importance of moisture in initiating and accelerating silver migration from silver-filled epoxy adhesives. Test specimens consisted of pairs of thick-film gold pads separated by a 10-mil gap and formed on ceramic substrates. One pad of each pair was overcoated and cured with a silver-filled epoxy adhesive. Tests were run on samples that were cooled to just below the room-temperature dew point at which point condensation of moisture from the air occurred. Other samples were cooled using dry ice so that moisture condensed as frost. With 2 volts/mil applied, water droplets condensed and coalesced. Dendritic growth of silver occurred when continuous water paths formed across the gap. Current increased from initially low microamps to high milliamps until shorting occurred in less than one hour. On the other hand, the frost-covered samples showed no silver migration and low microamp current for over 5 hours, but rapid migration as soon as the frost was melted.

**Outgassing and moisture.** Outgassing from adhesives that are used in hermetically sealed circuits, especially the outgassing of moisture, has been and still is a major cause of circuit failures and a reliability concern. The amount of moisture released depends on the adhesive used, its cure schedule, the extent of vacuum baking prior to sealing, and the temperature and exposure conditions after sealing. Even with optimum-curing and vacuum-baking conditions, if the temperature of the sealed units during thermal cycling or burn-in exceeds the cure or vacuum-bake temperatures, an extra surge of outgassing occurs. If exposed to very high temperature, major decomposition of the adhesive occurs as indicated by large amounts of moisture, carbon dioxide, and hydrocarbons. Semiconductor device failures due to moisture are not as prevalent now as during the 1970s and 1980s when the silicon oxide or silicon nitride passivation layers on semiconductor devices were porous and not yet fully perfected. Yet today, even with improvements in high-reliable devices, the presence of moisture and

ionic contaminants leads to corrosion of thin-film metallizations and wire bonds. Generally, moisture alone without contaminants is not damaging to electronics but, because it is difficult to determine how clean a circuit is and because ions can be generated after cleaning, it has been found necessary to place a limit on the amount of moisture allowable. Over the years, the limits for moisture that started out at 3,000 ppm<sub>v</sub> for space applications (Class K) and 5,000 ppm<sub>v</sub> for military applications (Class H) were, for a period of time, tightened to 1,000 ppm<sub>v</sub> and 3,000 ppm<sub>v</sub>, respectively. Today, the moisture limit for both classes and for all sealed electronic devices used in military, aircraft, space, and other high-reliability applications has been established at no greater than 5,000 ppm<sub>v</sub>, measured after a series of screen tests including thermal cycling according to MIL-PRF-38534.

Residual-gas analysis (RGA), a mass-spectrometric method, is the most accurate method for measuring moisture and other low-molecular-weight volatile compounds released from polymeric materials. Interpretation of RGA data has at times proven difficult since small differences in the processing of samples intended to be identical resulted in major differences in the results and analyses of the same circuits by different laboratories. Most of these differences have been resolved by using laboratories that are certified by government agencies, such as Defense Supply Center at Columbus (DSCC), using their own standards.

Analysis of RGA results provides a good indication of the sources and mechanisms for the generation of the outgassed materials. Table 6.3 shows RGA data of sealed packages containing various die-attachment materials and processing conditions.<sup>[35]</sup>

In Table 6.3, *Case 1* shows an analysis of dry nitrogen used as an inert ambient during sealing. The analysis showed almost 100% nitrogen, no detectable oxygen, and insignificant amounts of moisture and carbon dioxide. The small amount of argon in the absence of oxygen could not be explained.

Control packages in which the die was attached with eutectic alloy (no adhesive) and sealed in air indicated the approximate composition of air (*Case 2*), but, in a second analysis, the high carbon dioxide and moisture content were attributed to an organic contaminant on a new lot of ceramic lids. In *Case 3*, the die was again attached with eutectic alloy, but was overcoated with polyimide. Analysis indicates extensive outgassing from the polyimide (apparently not completely cured) but also the possibility of a package leak due to the presence and amounts of oxygen and argon. The ambient analyses for *Cases 4* and *5* are quite good.

**Table 6.3.** Examples of Residual Gas Analysis (RGA) Data

Case No.	Description	Nitrogen (%)	Oxygen (%)	Argon (ppm <sub>v</sub> )	Carbon Dioxide (ppm <sub>v</sub> )	Moisture (ppm <sub>v</sub> )	Helium (ppm <sub>v</sub> )	Hydrogen (ppm <sub>v</sub> )	Other (ppm <sub>v</sub> )
1	Common sealing atmosphere (dry nitrogen)	99.9	ND	125	<100	<100	ND	N/R	N/R
2	Glass-frit sealed ceramic packages/ eutectic die attach	81.0	17.9	9,221	1,100	541	N/R	N/R	N/R
		78.9	15.6	9,211	36,700	8,795	N/R	N/R	N/R
3	Glass-frit sealed ceramic packages/ eutectic die attach with polyimide barrier coating	86.1	5.09	9,808	54,900	2,207	N/R	12,900	Methane: 8,745
		94.8	1.55	724	30,500	642	N/R	N/D	Methane: 4,448
4	Solder sealed device/ eutectic die attach	99.4	N/R	N/R	154	473	N/R	5,845	N/R
5	Solder sealed device/ silver-glass die attach	99.0	N/R	N/R	3,420	439	N/R	5,556	N/R
		99.8	N/R	N/R	3,150	6,240	N/R	450	N/R
6a	Solder-sealed, low-temp. silver-glass adhesive, single cycle fired	97.1	N/R	N/R	14,300	12,600	N/R	1,985	N/R
6b	Solder-sealed, low-temp. silver-glass adhesive, double cycle fired	99.2	N/R	N/R	4,100	2,900	N/R	1,252	N/R
7	Solder-sealed packages/thermoplastic die attach	89.6	N/R	N/R	92,700	511	N/R	4,587	Hydrocarbons: 5,900

ND – None Detected; N/R – None reported. (Copyright © Oneida Research Services, 1994. Reprinted with permission.)

(cont'd.)

**Table 6.3. (Cont'd.)**

Case No.	Description	Nitrogen (%)	Oxygen (%)	Argon (ppm <sub>v</sub> )	Carbon Dioxide (ppm <sub>v</sub> )	Moisture (ppm <sub>v</sub> )	Helium (ppm <sub>v</sub> )	Hydrogen (ppm <sub>v</sub> )	Other (ppm <sub>v</sub> )
8	Seam-welded packages/epoxy cured with Dicy	91.0	N/R	N/R	2,091	1,680	8,340	N/R	Ammonia 3,161
9	Seam-welded packages/epoxy cured without Dicy	85.1	N/R	N/R	5,792	4,720	13,300	N/R	MEK 1,446 ppm <sub>v</sub> , Methanol 1,826, and THF 862
10	Seam-welded packages/epoxy and poor pre-seal bakeout	95.3	N/R	N/R	1,220	10,500	—	350	MEK 1.80%, Methanol 1.32%, and Hydrocarbons 3,250
11	Seam-welded packages/thermally overstressed epoxies	95.6	N/R	N/R	23,500	19,300	N/R	1,220	N/R
		92.0	N/R	N/R	20,700	18,900	N/R	9,780	N/R
12	Seam-welded packages/intermittent leak phenomenon	96.1	0.12	274	1,210	3,600	24,400	897	Fluorocarbons: 0.76%
		90.5	6.07	2,940	1,575	30,400	N/R	425	N/R
		87.7	4.87	2,415	2,750	27,200	30,700	890	Fluorocarbons 1.02%

ND – None detected; N/R – None reported. (Copyright © Oneida Research Services, 1994. Reprinted with permission.)

*Cases 6a* and *6b* show the importance of properly curing (processing) the silver-glass adhesive. The high carbon dioxide and moisture content of *Case 6a* indicates that the polymer binder or other organic constituents of the silver-glass were not completely burned off. After a second cure cycle was used, good RGA results were obtained (*Case 6b*).

In *Case 7*, a thermoplastic die-attach adhesive was used. The large amount of carbon dioxide indicates decomposition, but the small amount of moisture indicates that moisture may have been generated, but gettered by oxides or metals in the package. Often when moisture is expected to be high, but is low, and hydrogen is present, the moisture is believed to have reacted with oxides or metals to produce hydrogen.

*Case 8* shows evolution of ammonia that was common with some of the early epoxy formulations that were cured with Dicy. Once the Dicy-curing agent was replaced, results showed no ammonia (*Case 9*) although some alcohol and ketone were present; the source was residual solvents used in the new formulations.

Insufficient pre-seal vacuum bake is indicated in *Case 10* where large amounts of moisture were detected. Extended vacuum baking reduced the moisture content.

The presence of large amounts of carbon dioxide, water, and some hydrocarbons, as in *Case 11*, indicates decomposition of the epoxy adhesive possibly due to overheating.

In some cases, packages develop leaks because they were improperly sealed or subsequently stressed. These are evident from the presence of large amounts of oxygen together with argon. Since argon is present only in air, the detection of argon along with oxygen indicates the presence of air. In leaky packages, fluorocarbons may also be detected. The presence of fluorocarbons indicates an intermittent or a gross leak in which the fluorocarbon liquid used in testing for gross leaks has entered the package (*Case 12*). Fluorocarbon species may also originate from solvents used in cleaning that did not completely evaporate or somehow became tenaciously absorbed in the package.

### **6.1.6 Detachment of Adhesive Particles**

Particles of adhesive and filler can be generated from aggressive handling, during rework, or during vibration or mechanical-shock testing. Particles can dislodge from the adhesive fillets around devices or substrates. In sealed packages, loose conductive particles can become wedged be-

tween closely spaced conductor lines causing electrical shorting. Nonconductive adhesive particles and abrasive-filler particles, such as aluminum oxide, can collide with and damage thin wires, wire bonds, and thin-film metallization. Abrasive particles have been known to completely sever wires and wire bonds during vibration.

To assure the absence of particles in hermetically sealed single-chip or multichip modules, the Particle Impact Noise Detection (PIND) test<sup>[36]</sup> is employed. For high-reliability circuits such as Class K (space qualified) hybrid circuits, the PIND test is required of all circuits. To assure that particles are not generated subsequently to passing the PIND test, for example during vibration or mechanical shock, a particle-immobilizing coating such as parylene may be used. An alternate approach has been to apply a particle getter, usually a tacky silicone adhesive, to the inside center of the lid prior to sealing.<sup>[37][38]</sup>

## 6.2 SPECIFICATIONS

Besides an understanding of the basic failure modes and mechanisms, important in the initial selection of adhesives, qualification and strict adherence to materials and processes specifications and work instructions are an integral part of the reliability process. The process begins with the design guidelines and requirements for a specific application. Qualification criteria and test specifications must then be generated and the adhesives selected must be qualified. In addition, materials specifications or procurement documents are required to assure that the adhesive meets a minimum of quality assurance tests before acceptance from the supplier. A quality-control system should be in place that assures the material is properly stored and is still within its shelf life at the time of use. Once the adhesive is in use, process specifications, work instructions, and in-process controls are necessary to assure that the adhesive is properly dispensed and cured, and that the equipment used for processing and testing is calibrated. Finally, the completed assembly is inspected visually and some screen tests performed to assure that a known good product is delivered.

### 6.2.1 Qualification Based on Accelerated Testing

Materials are qualified by passing a series of tests as severe or more severe than those of the intended application. Generally, accelerated environmental and mechanical tests are specified and performed on actual

or simulated parts representative of the final product. Since the parts are subjected to accelerated tests, some of which are destructive, qualification parts are seldom deliverable items. Once an adhesive and process have been qualified, no changes in composition or processes are allowed without requalification. Testing at levels above the acceptance tests for an extended duration or number of cycles is necessary. The qualification tests for some applications, for example, for die and substrate attachment, have been specified in NASA and MIL specifications while those for other applications are being developed by industry and industry associations.

Qualification tests for adhesives are defined in Method 5011 of MIL-STD-883 and requirements for qualifying sealed hybrid microcircuits or multichip modules that contain adhesives are specified in MIL-PRF-38534. Space, automotive, and medical applications generally use the military specifications, but are modified or supplemented with additional tests and requirements for their particular application.

## 6.2.2 Qualification Based on Heritage Data

Some adhesives have been used successfully for over 20 years in specific applications and environments, and a reliability database is available (heritage data). These adhesives may thus be qualified for other applications by similarity of exposure and operating conditions. In general, the adhesive may be qualified and used if it had previously been used successfully in a proven, equivalent application for which the environmental conditions and tests were at least as severe as those required of the candidate application.

Reliability data are available for many adhesives used in space environments for different orbits, different radiation, and different thermal-vacuum conditions. These data are available from approved materials and processes lists from NASA<sup>[39]</sup> or from contractors for programs such as the Space Shuttle, Space Station, GPS, Hubbel telescope, and numerous satellite systems, some of which have been in orbit for over ten years. Adhesives used in military electronics have also been proven highly reliable in fighter planes, navy ships, ground and air communication systems, and navigation systems.

The reliability of silver-filled epoxy adhesives, such as Ablestik's Ablebond<sup>®</sup> 36-2 and 84-1, and Epoxy Technology's Epo-Tek<sup>®</sup> H20, and of insulative adhesives such as Emerson and Cuming's Eccobond<sup>®</sup> 104 and Ablestik's Ablebond<sup>®</sup> 84-3, has been demonstrated through many years of use in military, space, and medical electronics. During the period of

approximately 1970–1992, over 140,000 hybrid microcircuits of 525 part types were assembled by Rockwell (now Boeing) using Ablebond<sup>®</sup> 36-2 and Ablebond<sup>®</sup> 84-1 conductive die-attach adhesives and with Eccobond<sup>®</sup> 104 insulative substrate-attach adhesive. These hybrid microcircuits were delivered to the Air Force and NASA and are continuing to operate successfully today. Similar quantities have been produced by other aerospace manufacturers using the same adhesives or other qualified epoxy adhesives.

### **6.2.3 Receiving Inspection and Acceptance Testing**

Once qualified, acceptance tests are necessary on a batch-by-batch basis to assure that the supplier has not changed his formulation, and the adhesive is as good as that initially qualified. Adhesives should comply with the quality-assurance (QA) provisions of materials specifications or procurement documents. Source inspectors may also be used. Some simple tests that users perform include lap-shear strength measurements on each batch or an infrared spectrum comparison with an original “gold” standard. A Certificate of Compliance (C of C) provided by the supplier guaranteeing that the material sold is traceable to a batch that has been tested and meets the requirements of the user is yet another QA approach. Most adhesives suppliers will conduct the tests specified in Method 5011 of MIL-STD-883 and will provide a C of C. Some companies may want to perform their own receiving-inspection tests before accepting the product.

### **6.2.4 In-Process Controls**

In spite of all the precautions in selecting, qualifying, and procuring an adhesive, vigilance on the production line is still necessary to avoid failures. Process specifications and work-instruction documents provide step-by-step procedures to manufacture production quantities of parts in a manufacturing environment. A process specification often calls out sub-tier process documents such as cleaning, surface preparation, curing, and testing. The process should allow as much manufacturing freedom as possible commensurate with meeting the engineering requirements. For example, instead of specifying one cure schedule, a selection of several equivalent schedules should be permitted. Even better, a time-temperature curve of equivalent cures would give manufacturing greater freedom in meeting delivery schedules.

An essential part of the process specification that affects reliability, is the quality-assurance section. Quality-assurance provisions are usually

in-process controls and tests for the more critical steps. For adhesives, these may be periodically checking the viscosity and pot-life of the liquid adhesive, conducting bond-shear strength and hardness tests of cured samples, conducting tests to assure that surfaces are clean, and assuring that all processing and testing equipment are calibrated, especially those involving temperatures.

### 6.2.5 Screen Tests and Product Acceptance

Some customers require that a series of screen (nondestructive) tests be applied to the final product before delivery. These tests may consist simply of a few temperature cycles or a regimen of sequential mechanical and electrical tests as for Classes H and K of MIL-PRF-38534 for hybrid microcircuits.<sup>[40]</sup> The sequence of tests for Class H microcircuits consists of the following:

- Internal visual.
- Temperature cycling from  $-65^{\circ}\text{C}$  to  $150^{\circ}\text{C}$ , 10 cycles or thermal shock,  $0^{\circ}\text{C}$  to  $100^{\circ}\text{C}$ , 15 cycles.
- Constant acceleration, (3,000 g's in  $Y_1$  direction) or mechanical shock, (1,500 g's in  $Y_1$  direction). The  $Y_1$  direction is specified as the lid side of the package against the wall of the test chamber.
- Burn-in, usually 168 hours at  $125^{\circ}\text{C}$  with power.
- Electrical test.
- Fine and gross leak testing.
- External visual.

For Class K (space-grade), the additional tests of nondestructive wire bond pull, PIND, and radiography are imposed.

Screen tests assure the reliability of the entire electronic product of which the adhesive joints are a part.

### 6.2.6 NASA, Military, and Industry Specifications and Requirements

The first specifications for adhesives were generated by the staffs of NASA and the DoD who were prompted by the high reliability that was

required of microcircuits used in space and missile programs. These specifications covered primarily die and substrate attachments for hermetically sealed integrated circuits, hybrid microcircuits, and multichip modules. Subsequently, with the increased use of surface-mount adhesives in the assembly of commercial printed-wiring boards and underfills for flip-chip devices, industry associations took the lead in generating the requirements and test methods.

**Specifications for die- and substrate-attach adhesives.** Although the original NASA specification for the qualification and acceptance of die- and substrate-attach adhesives has been inactivated and Method 5011 of MIL-STD-883 is now the dominant specification, some of the NASA tests that were not carried over are still useful for improved reliability assurance. For example, even though Method 5011 does not specify an infrared (IR) spectrum for incoming material, the IR spectrum is a quantitative, easy test to run to assure that the chemical composition of the adhesive has not changed. Further, the corrosivity test in which the adhesive is applied to an aluminized Mylar<sup>®</sup> film and examined for etching of the aluminum is also a rather simple and valuable test. A comparison of the requirements and test methods of Method 5011 with the original NASA specification is given in Tables 6.4 and 6.5.

**Specifications for surface-mount adhesives.** With the advent and wide use of surface-mount adhesives, several industry and industry-association documents have been generated. Examples include the following:

- IPC CA-821, General Requirements for Thermally Conductive Adhesives
- IPC 3406, Guidelines for Electrically Conductive Surface-Mount Adhesives
- IPC SM-817, General Requirements for Dielectric Surface-Mount Adhesives
- Siemens Standard SN 59651

Table 6.6 compares the requirements and tests for IPC CA-821<sup>[41]</sup> with those of Siemens SN 59651,<sup>[42]</sup> both of which are applicable to surface-mount adhesives.

**Specifications for underfill adhesives.** Table 6.7 summarizes requirements for underfill adhesives from the proposed JEDEC J-STD-030.<sup>[43]</sup>

**Table 6.4.** NASA MSFC SPEC-592, Requirements and Test Methods for Die- and Substrate-Attach Adhesives

Test	Requirement	Paragraph	Method	Paragraph
Visual	Uniform consistency, free of lumps or foreign matter	3.2.1	Visual examination at 30X	4.5.1
Pot life	≥1 hr	3.2.2	Vendor-established method	4.5.2
Shelf life	≥6 months	3.2.3	Properties meet requirements when tested at or before shelf life	4.5.3
IR spectrum	Disappearance/appearance of absorption bands (relative to baseline) criteria for requalification	3.2.4	IR spectrum of mixed or separate components	4.5.4
Cure schedule	≤165°C, ≤4 hrs	3.3.1	N/A	N/A
Outgassing	≤0.3% wt loss at 250°C	3.3.2	Thermogravimetric analysis	4.5.5.1
	3,000 ppm, moisture (maximum)	3.3.2	Packages with 10% of surface area of exposed adhesive analyzed after 24 hrs and 1,000 hrs at 150°C by RGA	4.5.5.2
Bond-shear strength	≥6.9 × 10 <sup>6</sup> N/m <sup>2</sup>	3.3.3	Shear test (die/substrate, @ 25°C)	4.5.6
	≥3.5 × 10 <sup>6</sup> N/m <sup>2</sup>		Shear test (die/substrate, @ 150°C)	
	≥10.3 × 10 <sup>6</sup> N/m <sup>2</sup>		Capacitors (@ 25°C)	
	≥5.2 × 10 <sup>6</sup> N/m <sup>2</sup>		Capacitors (@ 150°C)	
	≥0.7 × initial value, @ 25°C ≥0.8 × initial value, @ 25°C		After temperature cycling and solvent immersion After 1,000 hrs at 150°C aging	
N/A – Not applicable.				

(cont'd.)

**Table 6.4. (Cont'd.)**

Test	Requirement	Para-graph	Method	Para-graph
Corrosivity	No change in light transmittance of aluminized Mylar®	3.3.4	Sample on aluminized Mylar® (48 hrs)	4.5.7
Volume resistivity	$\leq 5.0 \times 10^{-4}$ ohm-cm (silver), to $\leq 15.0 \times 10^{-4}$ ohm-cm (gold)	3.3.5	4-wire probe measurement: 25°, 60°, 150°, and 25°C after 1,000 hrs aging at 150°C	4.5.8.1
	$> 1 \times 10^{13}$ ohm-cm (insulative, 25°C) and $> 1 \times 10^8$ ohm-cm (125°C)		ASTM D257	4.5.8.2
Thermal conductivity	$\geq 3.5 \times 10^{-3}$ cal/cm-sec °C (1.5 W/m-K) (conductive) and $\geq 4.0 \times 10^{-4}$ cal/cm-sec °C (0.17 W/m-K) (insulative)	3.3.6	Measured @ 121 ±5°C	4.5.9
Coefficient of thermal expansion	$\leq 65$ ppm/°C (below $T_g$ ), $\leq 300$ ppm/°C (above $T_g$ , $\leq 150^\circ\text{C}$ )	3.3.7	Thermomechanical analysis (TMA)	4.5.10
Electrical stability	Resistance change <5% (conductive only)	3.3.8	Gold-plated Kovar® tabs (wire bonded)	4.5.11
Ionic impurities	<1,000 ppm NaCl; pH 4.0–9.0; Cl⁻ $\leq 300$ ppm; Na⁺ <50; K⁺ <5 ppm	3.3.9	Federal Test Method Standard No. 406, Method 7071	4.5.14
Dielectric constant and dissipation factor	<6.0 (1 kHz and 1 MHz), <0.03 (1 kHz) and <0.05 (1 MHz)	3.3.10	ASTM D150	4.5.12, 4.5.13
N/A – Not applicable.				

**Table 6.5.** Method 5011, MIL-STD-883, Evaluation and Acceptance Procedures for Polymeric Materials

Test	Requirement	Para-graph	Method	Para-graph
Visual	Uniform consistency, free of lumps or foreign matter	3.4.1	Visual examination at 30X	3.8.1
Viscosity	Range established by customer and included in the procurement document	3.4.2	User and supplier agree to a method on reporting viscosity	3.8.2
Pot life	≥1 hr	3.4.3	User and supplier select the procedure to be used	3.8.3
Shelf life	≥12 mo @ -40°C for one-part systems; ≥12 mo @ 32°C for two-part systems. Shelf life is not extendable for Class K devices; may be extended once for Class H devices	3.4.4	Material, pot life, bond strength, and volume resistivity testing performed	3.8.4
Thermogravimetric analysis	≤1% wt loss at 200°C	3.5.2.1	10°C–20°C/min heating rate in nitrogen	3.8.5.1
	% filler acceptance ± 2% of certification lot	3.5.2.2	Heating from 25°C to 600°C at a 10°C–20°C/min heating rate in air	3.8.5.2
Outgassed materials	5,000 ppm <sub>v</sub> moisture (maximum)	3.5.3	Packages with an equivalent exposed adhesive to the application shall be analyzed after 24 hr and 1,000 hr @ 150°C	3.8.6
Ionic impurities	Total ionics ≤4.5 millisiemens/meter, 4.0 < pH < 9.0, Cl <sup>-</sup> ≤200 ppm, Na <sup>+</sup> , K <sup>+</sup> , and F <sup>-</sup> ≤50 ppm	3.5.4	Extract analysis on 3 grams of material (ground) added to 150 ml water and refluxed for 20 hr	3.8.7

*(cont'd.)*

**Table 6.5. (Cont'd.)**

Test	Requirement	Para-graph	Method	Para-graph
Bond strength	1.0X requirement of Fig. 2019.4 Method 2019 of MIL-STD-883	3.5.5	Bond strength of 80-mil-square tabs to gold or nickel-plated Kovar® @ 25°C and @ 25°C after 1,000 hr @ 150°C	3.8.8
Coefficient of thermal expansion	±10% of the value in the users material specification	3.5.6	Measured from -65°C to +15°C per ASTM D3386	3.8.9
Thermal conductivity	≥1.5 W/m·K for electrically conductive	3.5.7	ASTM C177 or ASTM C518	3.8.10
	≥0.15 W/m·K for insulative			
Volume resistivity	≤5.0 × 10 <sup>-6</sup> ohm-m (silver-filled), ≤1.5 × 10 <sup>-5</sup> ohm-m (gold-filled)	3.5.8	Strip of epoxy cured onto a glass slide  ASTM D257	3.8.11
	>1.0 × 10 <sup>11</sup> ohm-m (insulative) at 25°C and 1.0 × 10 <sup>6</sup> ohm-m (125°C)			
Dielectric constant	≤6.0 at 1 kHz and 1 MHz	3.5.9	ASTM D150	3.8.12
Dissipation factor	≤0.03 at 1 kHz and ≤0.05 at 1 MHz	3.5.10	ASTM D150	3.8.13
Sequential-environment tests	No evidence of mechanical degradation after screens	3.5.11	Screen testing per MIL-STD-883 [thermal shock (Method 1011), temperature cycling (Method 1011), mechanical shock (Method 2002), variable-frequency vibration (Method 2007), and constant acceleration (Method 2001)]	3.8.14

**Table 6.6.** Requirements and Test Methods for Surface-Mount Adhesives (IPC CA-821 and Siemens SN 59651)

Property	IPC-CA-821 (Jan. 1995)		Siemens Standard SN 59651 (1997)	
	Requirement (Paragraph)	Method	Requirement (Paragraph)	Method
Appearance	—	—	Homogeneous, void free, <50 µm particle size (3.1)	Visual (8X)
Shelf life	Specified by supplier (3.2.4)	Meets specification requirements	≥5 mos and storage conditions specified (4.1)	
Degree of fineness	Specified by supplier (3.2.5)	ASTM D1210	—	—
Viscosity	Range and speed agreed to by user and vendor (3.3.1)	ASTM D2556	Viscosity profile determined (3.2)	Casson viscosity (0–40 s <sup>-1</sup> )
Work time	Per supplier recommendation (3.3.2)		>8 days and tack time >8 hrs (4.2)	IEC 68-1
Spread or slump	—	Observe 3 dots dispensed (0.65 mm diameter and 0.25 mm thick) cured and uncured. Measure uncured dots after 70 mins	≤10% (5.6)	Average of 1.8 ±0.2 mm dots on FR4 epoxy with solder resist. Check after 3 mins uncured and cured.
Green strength	—	—	Device shift ≤0.15 mm (4.5)	Assembled and fixtured PWA slides down an incline 35 mm high and 400 mm long and strikes a stop.

(cont'd.)

**Table 6.6. (Cont'd.)**

Property	IPC-CA-821 (Jan., 1995)		Siemens Standard SN 59651 (1997)	
	Requirement (Paragraph)	Method	Requirement (Paragraph)	Method
Mass loss at temperature	—	—	<1%	Observed after 7 days at 85°C
Thermal conductivity	>0.4 W/m·K (3.3.3)	ASTM C177 or C518	—	—
Shear strength	<8.0 MPa (1,160 psi), removable grade; >8.0 MPa, permanent grade (3.3.4)	ASTM D1002 (A109 steel lap shear); conditioned per IPC-S-804 Methods 1, 2, 3, or 4	>5 N/mm <sup>2</sup> (825 psi) (5.7)	Die shear (25°C) after cure
Solvent resistance	No degradation or change in surface roughness, swelling, tackiness, blistering, or color change (3.4.2)	—	—	—
Hydrolytic stability	Stencil-applied coating, shall show no evidence of bubbles or voids (3.4.3)	IPC-TM-650, Method 2.3.10	—	—

*(cont'd.)*

**Table 6.6. (Cont'd.)**

Property	IPC-CA-821 (Jan., 1995)		Siemens Standard SN 59651 (1997)	
	Requirement (Paragraph)	Method	Requirement (Paragraph)	Method
Dielectric strength	Specify minimum requirements (3.5.1)	Not specified ASTM D149 (1 kHz, 1 MHz)	—	—
Dielectric constant	Specify minimum requirements (3.5.2 and 3.5.3)	0.38 ±0.05 mm sample, ASTM D149 (1 kHz, 1 MHz)	—	—
Volume resistivity	Specify minimum requirements (3.5.4)	ASTM D257	—	—
Surface resistivity	Specify minimum requirements (3.5.5)	ASTM D257	>10 <sup>10</sup> ohms (5.3)	40°C, 93% RH test
Moisture and insulation resistance	Specify minimum requirements (3.6.1)	IPC-TM-650, Method 2.6.3.1, 50 ±5°C and 90% RH	—	—
High temperature strength	No displacement (3.6.2)	IPC-TM-650, Method 2.4.42.1, solder float	>5 N/mm <sup>2</sup> (5.8)	Shear strength after solder float 255 ±3°C (1206 device)

(cont'd.)

**Table 6.6.** (Cont'd.)

Property	IPC-CA-821 (Jan., 1995)		Siemens Standard SN 59651 (1997)	
	Requirement (Paragraph)	Method	Requirement (Paragraph)	Method
Fungus resistance	Non-nutrient (3.6.3)	Exposure to mixed spore suspension, IPC-TM-650, Method 2.6.1	Do not exceed limiting quality A1.4 (5.2)	—
Electro-migration	No tendency to migration (3.6.4)	IPC-TM-650, Method 2.6.14	Electrolytic corrosion: No green or other discoloration or dendritic growth	IEC 426 and IEC 68-3
Outgassing	Limits agreed upon (3.6.5)	ASTM E595	—	—
Self shimming	Report results (3.6.6)	IPC-TM-650, Method 2.4.51	—	—
Coefficient of thermal expansion (CTE)	Report results (3.6.7)	ASTM D3386	—	—

**Table 6.7.** Requirements and Test Methods for Underfill Materials (JEDEC J-STD-030)

Requirement	Paragraph	Requirement Description	Test Method	Paragraph
Filler size	6.1.1	Report maximum filler size	Sieve or particle-size analysis	Not specified
Filler type	6.1.2	Report filler type	Vendor data	Not specified
Filler loading	6.1.3	Report results (60%–75%, typical)	Thermogravimetric analysis	6.1.4
Underfill density	6.1.4	Report results (1.5–2.0 g/cm <sup>3</sup> , typical)	ASTM D792, or equivalent	6.1.4
Viscosity	6.2.1	Report viscosity and thixotropic index (0.5/5 rpm)	ASTM D2556 or other agreed to by vendor and supplier	6.2.1
Gel time	6.2.2	Report results(5–20 min @ 121°C, typical)	ASTM D2471, D4217, or IPC-TM-650, Method 2.3.18, or equivalent	6.2.2
Flux compatibility	6.3.1	Report adhesive strength	Adhesive strength to fluxed and nonfluxed surfaces	10.2.1 Die-shear, 10.2.2 Stud pull, and 10.2.3 ASTM D1002
Alpha particle emissions	6.4	Report results	Not specified	Not specified
Voids/bubbles	7.1.2	Free of bubbles that can induce voids	Visual examination of material between glass slides	8.6.1
Storage life	7.2	-40°C to -50°C	Supplier test methods	8.6.2
Viscosity change	7.4.1	20% to 50% change	ASTM D2556	6.2.1
Flow rate change	7.4.2	Usage-life limit classes: Class 1:50% reduced dispensing rate Class 2:40% reduced dispensing rate Class 3:30% reduced dispensing rate	Material dispense rate (8 hr period)	8.4.1, 8.4.2

*(cont'd.)*

**Table 6.7. (Cont'd.)**

Requirement	Paragraph	Requirement Description	Test Method	Paragraph
Settling test	7.4.3	Viscosity variation with dispensing (first and last part of syringe, report results)	ASTM D2556	6.2.1
Underfill flow rate	8.4.2	Report underfill flow rate	Coordinated between user/supplier; surfaces must be similar to actual use	Not specified
Spread/slump test	8.5	<10% increase in dot size	3-dot pattern (0.65 cm diameter, 0.25 mm thick) on 2 samples (1) 50–70 min @ 25°C and 50% RH	Not specified
Pot life	8.7	>8 hrs (25°C)	50% reduction in flow rate	8.7
Cure schedule	9.2.2	Specify cure cycle and ramp rate	Differential scanning calorimetry (DSC) to verify cure completeness	9.5
Die-shear	10.2.1	MIL-STD-883, Method 2019	6.35 mm <sup>2</sup> IC with 0.05–0.13 mm standoff; (25%–50% of the height filleting)	10.2
Stud pull	10.2.2	10.3–13.8 MPa region		6.2, 10.2
Lap shear	10.2.3			ASTM D1002
Shrinkage stress	10.3	Report radius of curvature	Supplier test	Not specified
Young's modulus	10.4	10–14 GPa		
CTE	10.5	>28 ppm/°C	Thermomechanical analysis (TMA)	Not specified
$T_g$	10.6	>150°C		

(cont'd.)

**Table 6.7. (Cont'd.)**

<b>Requirement</b>	<b>Paragraph</b>	<b>Requirement Description</b>	<b>Test Method</b>	<b>Paragraph</b>
Flammability	10.7	UL 94V-0 and 94V-1	UL 94	Not specified
Chemical stability, solvent resistance	10.8, 10.8.1	No evidence of chalking, tackiness, blistering, swelling, or color change	Immersion (ambient and 60°C ±5°C), 10–15 mins (Visual)	Not specified
Moisture absorption	10.9	Not specified	24 hrs immersion (boiling water)	Not specified
Hydrolytic stability	10.10	No evidence of cracking, chalking or general degradation	97°C ±2°C and 90% RH for 28 days. Potassium sulfate solution (saturated) is present (IPC-TM-650, Bellcore GR-78)	10.10
Fungus resistance	10.11	Non-nutrient	IPC-TM-650	2.6.1
Surface insulation resistance	10.12	Report results	IPC TM 650 (or equivalent)	2.6.3.1 or 2.6.3.2
Electrochemical migration resistance	10.13	No corrosion and metal migration <25% of conductor span	70 hrs at 85/85 conditions; 100 V DC ±10 V DC for measurements (IPC TM 2.6.14.1)	10.13
Volume resistivity	10.14	Not specified	DC electrical resistance (ASTM D257)	
Dielectric constant	10.15	Report results	AC loss characteristics, electrical insulation (ASTM D150C)	10.15
Ion contents	12.1	Na <sup>+</sup> , Cl <sup>-</sup> , K <sup>+</sup> <10 ppm <sub>v</sub>	121 °C, 20 hrs aqueous extraction	Not specified

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# 7 Test and Inspection Methods

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The reliability of electronic systems depends on extensive testing, inspection, and evaluation of all parts of the design and manufacturing process, including the adhesives used in the systems. Test methods for adhesives and adhesive-bonded assemblies may be generally classified as physical, electrical, environmental, thermal, mechanical or thermomechanical, and chemical (Table 7.1). This chapter summarizes most of the methods used to test and evaluate adhesives used in electronics. It is not intended to provide detailed instructions, but to lead the reader to the appropriate government or industry specifications, documents that are available from the various organizations listed in Table 7.2.

The test methods covered in this chapter are those most closely related to adhesives for die and substrate attachment, surface-mounting of components, underfill, and optoelectronic assembly. Some tests, such as bleedout and electrical stability, for which there are no standard test methods, are not covered since information for these procedures has already been addressed in other portions of this book, for example, in Secs. 2.1.1 and 6.1.4.

## 7.1 PHYSICAL TESTS

Physical-property tests are used to measure the properties of adhesives in the liquid or gelled states prior to curing and in the solid state after curing. Tests for the uncured state such as viscosity, visual examination, and surface energy or contact angle assure that fillers, if used, have not settled out, that the material has not exceeded its pot life or shelf life, and that the supplier has not changed the formulation. Visual examination and density after cure are performed to verify that voids are not present or, if present, meet specification requirements. Finally, light transmission and index of refraction measurements are important for adhesives used in optoelectronic applications.

**Table 7.1. Classification of Adhesive Test Methods**

Physical	Electrical	Environmental	Thermal	Mechanical/Thermo-mechanical	Chemical Analysis
<i>Viscosity</i> ASTM D2196 and ASTM D2556	<i>Volume resistivity</i> MIL-STD-883, Method 5011, (3.8.11.1), ASTM D257	<i>Solvent and chemical resistance</i> IPC-SM-817, paragraph 4.5.6	<i>Exotherm during cure</i> ASTM D2471	<i>Hardness</i> ASTM D2240	<i>Weight-loss during cure</i> No standard method
<i>Spread and slump</i> IPC-SM-817, Method 4.5.5 and IPC-SM-870	<i>Dielectric constant, dissipation factor</i> ASTM D150-81	<i>Corrosion or migration effects</i> IPC-TM-650, Method 2.6.14	<i>Gel time</i> ASTM D2471	Modulus ASTM D790 (flexural), ASTM D638 (tensile), and ASTM D412 (Young's)	Infrared spectrum (ASTM E1252 Practice for General Techniques for Obtaining Infrared Spectra for Qualitative Infrared Analysis) or Fourier Transform Infrared Reflection Spectroscopy (ASTM E1790-00 Standard Practice for Near Infrared Qualitative Analysis)
<i>Density</i> ASTM D1875 (uncured) ASTM D792-91 (cured)	<i>Dielectric breakdown voltage</i> ASTM D149	<i>Radiation effects</i> ASTM D1879-99 Standard Practice for Exposure of Adhesive Specimens to High-Energy Radiation	<i>Thermal conductivity</i> ASTM C177 and ASTM C518	<i>Elongation at break</i> ASTM D790 (flexural) and ASTM D638 (tensile)	<i>Gas chromatography, mass spectrometry</i> ASTM D6420-99 Standard Test Method for Determination of Gaseous Organic Compounds by Direct Interface Gas Chromatography-Mass Spectrometry
<i>Surface energy</i> (wettability, contact angle) No standard method	<i>Arc resistance</i> ASTM D495	<i>Fungus resistance</i> (IPC-TM-650, TM 2.6.1)	<i>Weight loss</i> (cured) ASTM D3850	<i>Coefficient of thermal expansion, glass-transition</i> ASTM D3386	<i>Ionic content</i> (total water extract conductance, pH, and specific ion contents) Federal Test Method Standard 406, Method 7071

(cont'd.)

**Table 7.1. (Cont'd.)**

Physical	Electrical	Environmental	Thermal	Mechanical/Thermo-mechanical	Chemical Analysis
<i>Visual</i> (MIL-STD-883, Methods 5011 and 2017)	<i>Electrical stability</i> (biased) (MSFC SPEC 592*, Method 4.5.11)	<i>Moisture absorption</i> (IPC-TM-650, TM 2.6.3.1, and ASTM D570)		<i>Bond strength</i> tensile pull (ASTM D1002), die shear (MIL-STD-883, Method 2019), flip-chip strength (MIL-STD-883, Method 2031), substrate strength (MIL-STD-883, Method 2017), and centrifuge (MIL-STD-883, Method 2001)	<i>Residual gas analysis</i> (MIL-STD-883, Method 1018)
<i>Light transmittance</i> (ASTM D1003-00)	<i>Current carrying ability, interconnect resistance</i> (N/A)	<i>Hydrolytic stability</i> (IPC-TM-650, TM 2.3.10)		<i>Voids, delamination</i> (acoustic microscopy) (MIL-STD-883, Method 2030)	<i>Total mass loss, water vapor recovery, and volatile condensable materials</i> (ASTM E595)
<i>Refractive index</i> (ASTM D542)				<i>Radius of curvature</i> (No standard method)	

\*NASA MSFC-SPEC-592 has been inactivated, but this method is described in this chapter.

**Table 7.2.** Sources of Government and Industry Documents

Organization	Address	Web Site
Military, Federal	DODSSP 700 Robbins Ave., Bldg 4D Philadelphia, PA 19111-5098	<a href="http://dodssp.daps.mil/">http://dodssp.daps.mil/</a>
ASTM	American Society for Testing & Materials 100 Barr Harbor Dr. West Conshohocken, PA 19428 (documents may be purchased from ANSI)	<a href="http://www.astm.org">www.astm.org</a>
ANSI	American National Standards Institute 1430 Broadway New York, N.Y. 10018	<a href="http://www.ansi.org">www.ansi.org</a>
IPC	IPC Association Connecting Electronics 2215 Sanders Road Northbrook, IL 60062-6135	<a href="http://www.ipc.org">www.ipc.org</a>
EPA	Environmental Protection Agency Ariel Rios Bldg. 1200 Pennsylvania Ave., NW Washington, D.C. 20460 <i>or</i>	<a href="http://www.epa.gov">www.epa.gov</a>
	Superintendent of Documents P.O. Box 371954 Pittsburgh, PA 15250-7954	
EIA	Electronic Industries Alliance 2500 Wilson Blvd. Arlington, VA 22201	<a href="http://www.eia.org">www.eia.org</a>
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ISO	Intl. Organization for Standardization 1, rue de Varembe, Case postale 56 CH-1211 Geneva 20, Switzerland	<a href="http://www.iso.org">www.iso.org</a>

### 7.1.1 Viscosity

*Viscosity*, a measure of the flow properties of a liquid, is important as an incoming receiving and acceptance test for adhesives. During automatic dispensing, measuring and monitoring, the viscosity of adhesives is also important to assure that the pot life has not expired and that reproducible high-yield results are achieved. Rechecking viscosity is also used as a criterion for extending the shelf life of an adhesive to verify that the material has not changed and will be within its working life when used.

Viscosity is the internal friction that results from intermolecular forces of attraction and interactions between fillers and resins in adhesives, a measure of resistance to flow. Most adhesives are non-Newtonian fluids that exhibit shear-thinning behavior, or decreases in viscosity with increasing shear rate. Exceptions to this general rule are the capillary-flow underfill adhesives that tend to be Newtonian in fluid behavior.

A property related to viscosity is the thixotropic index, a measure of the dependence of viscosity on shear-rate. The thixotropic index (TI) is the ratio of viscosities measured at speeds that have a ratio of 1:10 rpm, for example, at 2 rpm and 20 rpm. For non-Newtonian materials used in automated dispensing, shear thinning is apparent from TI values of 2–6. In general, capillary-flow underfills have thixotropic indices of 1, or close to 1.

While various methods and equipment can be used to measure viscosity, the most common uses the Brookfield viscometer (Fig. 7.1). ASTM D2196, *Rheological Properties of Non-Newtonian Materials by Rotational (Brookfield) Viscometer*,<sup>[1]</sup> covers this method for Model LVF and Model RVF viscometers. Brookfield “LV” viscometers are used for low-viscosity materials, “RV” for medium-viscosity formulations, and “HV” for high-viscosity formulations. Test Method ASTM D2556, *Apparent Viscosity of Adhesives Having Shear-Rate Dependent Flow Properties*,<sup>[2]</sup> also specifies the Brookfield RVF viscometer for measuring viscosity and thixotropic index. Selection guidelines for the type of spindle and speed (rpm) are given for viscosity ranges. High viscosity (>500,000 cps) SMT adhesives, for example, typically use a Brookfield HAT with Helipath, and readings are taken at 1 and 10 rpm or at 2.5 and 20 rpm using Spindle “D”.<sup>[3]</sup>

The method and type of equipment used also vary with the type of adhesive. As an example, the viscosity of electrically conductive adhesives is measured according to ASTM D1824, *Apparent Viscosity of Plastisols and Organosols at Low Shear Rates by Brookfield Viscosity*.<sup>[4][5]</sup> The viscosity of typical electrically conductive die-attach adhesives is measured



**Figure 7.1.** Brookfield DV-111 Ultra-Programmable Rheometer.

with a Brookfield HBT viscometer with Spindle TB and Speed 5.<sup>[6]</sup> For higher-viscosity conductive adhesives and for underfill adhesives, a Brookfield RVT or RVF viscometer is used<sup>[7]</sup> with Spindles 6 or 7<sup>[8]</sup> at speeds of 4–10.4 rpm.<sup>[9]</sup> Another Brookfield viscometer, the “Cone-and-plate” viscometer with a CP-51 spindle is used for low-to-intermediate viscosity adhesives.<sup>[10]</sup> Finally, the Brookfield HAT and HBT instruments are used for the high viscosity (1–2 million cps at 1 rpm) adhesives typically used in SMT applications.<sup>[3]</sup>

Besides the Brookfield viscometers, the Haake rotoviscometer, (Fig. 7.2) PK10 M10/PK1 2 Cone, Casson Model is used to measure viscosity at shear rates of 0.4 to 30 s<sup>-1</sup>. This instrument is used alone or in combination with a Brookfield viscometer for SMT adhesives. The equipment is used not only to measure viscosities, but also to provide flow properties in the form of graphs of shear stress vs shear rate.

In addition to viscosity and thixotropic index, yield value (also known as yield point or yield stress) is measured. *Yield value* is the minimum force required to start the adhesive moving. Yield value may be measured by two methods. First, the yield value may be obtained from the curve of shear stress to shear rate.<sup>[11]</sup> The curve is extrapolated to give the shear stress at



**Figure 7.2.** Haake viscometer.

zero shear rate and the yield value is read off the y-axis. In a second method, a Haake low-shear viscometer, (CV-100) is used. The stress peak upon startup of rotation with the low-shear viscometer is a measure of the yield value.

### **7.1.2 Spread and Slump**

The degree to which an adhesive spreads after dispensing and the degree to which it slumps after curing are important parameters in achieving high yields in high-speed automated assembly. Adhesives must retain their dot or pattern shapes after dispensing. Excessive flow or spread in conductive adhesives may result in electrical shorting of adjacent conductors.

The spread and slump for surface-mount adhesives may be measured according to IPC-SM-817, Method 4.5.5.<sup>[12]</sup> According to this method, sets of adhesive dots (minimum three per set), 0.65 cm in diameter and 0.25-mm thick, are deposited (for example, by screen or stencil printing) on each of two frosted glass microscope slides. One sample is stored 50–70 minutes at  $25^{\circ}\text{C} \pm 5^{\circ}\text{C}$  and  $50\% \pm 5\%$  relative humidity and then measured for spreading of the uncured adhesive. The second sample is cured and measured for the

increase in pattern from the original dimensions. The acceptance criterion is an increase of less than 10% of the original diameter of the dot or pattern.

### 7.1.3 Density and Specific Gravity

The *density* of a material is mass per unit volume reported as gm/cm<sup>3</sup>. The density of uncured adhesives is useful in verifying the correct portion of liquid resin and filler ingredients of a formulation. The density of a cured adhesive is an indicator of the specific formulation and of completeness of cure.

The density of uncured liquid formulations is measured as specified in ASTM D1875, *Density of Adhesives in Fluid Form*. A weight-per-gallon cup whose volume is exactly 83.2 ml at 25°C is weighed to the nearest 0.1 gram, filled with adhesive, and reweighed.<sup>[13]</sup> The net weight of adhesive divided by the volume of the cup gives the density.

The density of a cured, solid adhesive may be measured by taking a small sample of the adhesive (any shape), weighing it (in grams), then immersing it in a graduated cylinder containing a known volume of water (in cm<sup>3</sup>). The volume of water displaced by the sample is equal to the volume of the sample, and density then equals mass/volume.

Test methods for the density and specific gravity of cured adhesives are specified in ASTM D792, *Density and Specific Gravity (Relative Density) of Plastics by Displacement*.<sup>[14]</sup> Specific gravity is the ratio of the density of a material to the density of water. For all practical purposes, density and specific gravity are the same, however, for high precision, the density of water must be taken into account. Specific gravity may be measured by weighing a piece of cured adhesive (at least 1 cm<sup>3</sup>) in air, submerging it in water at 23°C, and reweighing it while submerged. Specific gravity is then calculated as:

$$\text{Eq. (7.1)} \quad sg = w_a / (w_a - w_s)$$

where *sg* is specific gravity, *w<sub>a</sub>* is the weight of the sample in air, and *w<sub>s</sub>* is its weight when submerged in water. Taking into consideration the weight of the sinker and wire, if used to immerse the part in water, the equation becomes:

$$\text{Eq. (7.2)} \quad sg = w_a / (w_a + w - b)$$

where  $w_a$  is the apparent weight of the sample, without wire or sinker, in air;  $w$  equals the apparent weight of a totally immersed sinker, if used, and of partially immersed wire; and  $b$  equals the apparent weight of the sample and sinker completely immersed in water and of the partially immersed wire.

### 7.1.4 Surface Energy

A knowledge of the surface tension of the liquid adhesive and the surface energy of the substrate to which it will be applied is important in predicting the wettability and subsequent adhesion of the cured adhesive. As a rule, the surface tension of the adhesive should be less than the surface energy of the substrate. Additives are often added to adhesive formulations to reduce their surface tensions, while cleaning processes are used to increase surface energies of substrates.

The contact angle that a liquid makes with a solid surface is a measure of the wettability of the liquid to that surface as well as a measure of the cleanliness of the surface. The height of a water droplet on a surface relative to the base area it covers is indicative of the surface's affinity to wetting. Contact angles decreasing from  $90^\circ$  to  $0^\circ$  indicate progressive improvement in wettability with  $0^\circ$  being completely wettable. Contact angles increasing from  $90^\circ$  to  $180^\circ$  indicate progressively poorer wettability with  $180^\circ$  being completely non-wetting. Contact-angle meters, known as *goniometers*, are useful quality-control tools to assure that a cleaning process has removed hydrophobic residues or that a liquid coating will wet and adhere to a surface. Instruments to measure surface tensions and contact angles are available from Paul N. Gardner Co., BYK Gardner, and Ramé-Hart (Fig. 7.3).

### 7.1.5 Visual

Visual inspection of adhesives is performed on both uncured and cured samples. Uncured materials are inspected for uniformity of filler distribution, consistency, and adhesive coverage. Inspection methods are defined in paragraphs 3.4.1 and 3.8.3 of Method 5011.4 of MIL-STD-883F.<sup>[15]</sup>

Visual-inspection criteria for cured adhesives used for element or substrate attachment are specified in paragraph 3.1.2 of Method 2017, *Internal Visual (Hybrid)* of MIL-STD-883F.<sup>[16]</sup> Visual inspection criteria for adhesives are classified according to element and substrate attachment and according to coverage and defects.



**Figure 7.3.** Goniometer.

Elements bonded to substrates are visually examined at magnifications of 10X to 60X as stated in paragraph 3.1.4 of MIL-STD-883F, Method 2017. In order to meet Class H, adhesive attachment for non-end-terminated devices requires a minimum 50% filleting visible around the perimeter of the device unless the fillet is continuous on two full nonadjacent sides. To meet Class K, a minimum 75% of the fillet must be visible. This requirement also applies to end-terminated components such as capacitors. An exception to this rule is for an adhesive applied directly to more than 50% of the bond area on the substrate by using preform adhesives or screening or stencil printing paste adhesive directly to the bonding area. In such cases, mechanical strength measurements may be performed in lieu of direct visual inspection. Another exception to the rule is where the device or substrate is transparent and more than 50% coverage may be visually verified.

Failure criteria for element or die-attach defects include the following:

- Adhesive material that extends onto the top surface of the device.
- Cracks in the adhesive that are greater than 5 mils in length around the perimeter or 10% of the contact periphery, whichever is greater. Fissures and pulling back of the filler, however, are not considered cracks.

- Adhesive strings where the diameter at the attachment point is less than 50% of the maximum dimension of the string.
- Adhesive residue on a bonding pad.

Internal visual inspection for substrate attachment is also performed at magnifications of 10X to 60X. The 50% and 75% fillet rules also apply for element or die-attach adhesives.

Failure criteria for substrate-attach defects are as follows:

- Adhesive buildup that reduces separation to less than one mil between the mounting material and active metallization or between a mounting post not electrically common with the attachment.
- Any crack greater than 5 mil in length.
- Adhesive strings where the diameter at the attachment point is less than 50% of the maximum dimension of the string.
- Adhesive residue on a substrate bonding pad or package bonding post as evidenced by discoloration or adhesive residue on a substrate mounting post.

Inspection criteria for monolithic integrated circuits are defined in Method 2010.11 of MIL-STD-883F.<sup>[16]</sup> Failure criteria for die mounting are as follows:

- Adhesive that extends onto or vertically above the top surface of the die.
- Adhesive fillet not visible along 75% of each side of the die.
- Adhesive that bridges package posts or is on the post bond area.
- Separation, cracks, or fissures greater than 2 mils width in the adhesive, at the cavity wall or cavity floor.
- Transparent die with less than 50% of the area bonded.
- Flaking, lifting, peeling, or crazing of the die-attach material.
- Adhesive that is connected to the fillet or conductive cavity (e.g., metal package base or metallized floor of ceramic package) and extends up the cavity wall to within 1.0 mil of the package post.

### 7.1.6 Luminous Transmittance

Luminous transmittance is a measure of the amount of light that passes through a transparent material. Adhesives used in electro-optical interconnects must have a high transmittance. The *total light transmittance* through a material is equal to the total incident light less the light that is absorbed and light that is scattered.

A related property is haze or the scattering of light as it passes through a transparent material. The standard test method for measuring both transmittance and haze is ASTM D1003-00, *Standard Test Method for Haze and Luminous Transmittance of Transparent Plastics*.<sup>[17]</sup> Instruments that can measure transmittance, haze, and clarity are available from BYK Gardner, Paul W. Gardner Co., and Hunter Associates Laboratories. A typical test sample consists of a disk 50 mm or 100 mm in diameter although almost any flat sample can be used.

Ultraviolet-visible spectrophotometers can also be used to measure light transmittance over a wavelength range of 200 to 2,000 nm when samples are cast as films.<sup>[18]</sup>

### 7.1.7 Index of Refraction

When light traverses from air through a liquid, its *index of refraction* is the ratio of the sine of the angle of incidence to the sine of the angle of refraction. The index of refraction is a constant for each material and is greater than one when light enters a denser medium from a rarer medium as from air through a liquid. The index of refraction is important for adhesives used in the assembly of polymer optical fiber bundles and terminations where the index of the adhesive should match that of the silicon optical fibers. Furthermore, the index of refraction may be used as an indicator of the degree of purity of solids and liquids such as polymer resins, solvents, diluents, and mixed adhesive formulations. The refractive index is measured using a refractometer, of which the preferred method, ASTM D542, *Index of Refraction of Transparent Organic Plastics*, uses an Abbé refractometer.<sup>[19]</sup> Refractive indices ranging from 1.3 to 1.7 in increments of 0.001 can be measured with high accuracy.

## 7.2 ELECTRICAL TESTS

The main electrical properties related to organic materials are volume resistivity (for both conductive and nonconductive adhesives) and dielectric constant and dissipation factor (for insulative materials). Other electrical tests for conductive materials that are more application specific are electrical stability, current-carrying capacity, and interconnect resistance.

### 7.2.1 Volume Resistivity

*Volume resistivity* is a measure of the electrical conductivity of adhesives or the insulation resistance of a nonconductive material. Volume resistivity is used to qualify adhesives for electronics and also to evaluate long-term reliability after aging. Volume resistivity for conductive adhesives is given by the equation:

$$\text{Eq. (7.3)} \quad \rho = (R \times w \times t)/l$$

where  $\rho$  = resistivity in ohm-cm,  $R$  = measured resistance (ohms),  $w$  = width in cm, and  $l$  = length between the inner pair of probes, in cm.

This test is specified in Method 5011.4 of MIL-STD-883F in 3.8.11.1.3.<sup>[20]</sup> Volume resistivity is usually measured at 25°C, 60°C, and 150°C, and then measured at 25°C after 1,000 hours of aging at 150°C.

*Insulation resistance* is the ohmic relationship of applied voltage to the total current between two electrodes in contact with a specific material. Insulation resistance is directly proportional to the length and inversely proportional to the area as follows:

$$\text{Eq. (7.4)} \quad IR = \rho l/A$$

where  $IR$  = insulation resistance (ohms),  $l$  = length (cm),  $\rho$  = volume resistivity, and  $A$  = area (cm<sup>2</sup>). Specifically, volume resistivity,  $\rho$  is ohmic resistance of a cube of bulk dielectric material one cm/side expressed as ohm-cm. Requirements for insulative adhesives are given in paragraph 3.8.11.2 of Method 5011.4 of MIL-STD-883F.<sup>[20]</sup>

## 7.2.2 Dielectric Constant and Dissipation Factor

Dielectric constant ( $\epsilon$ ) and dissipation factor (DF) are related to capacitance (C) and can be calculated from capacitance measurements. Capacitance, between a parallel-plate capacitor, is directly proportional to the dielectric constant of the insulator separating the conductors and the conductor area,  $A$ , and inversely proportional to the distance,  $d$ , between the conductors as shown in:

$$\text{Eq. (7.5)} \quad C = \epsilon A/d$$

If the gap between the plates is filled with a dielectric material, the capacitance increases by a constant factor characteristic of that material. The *dielectric constant*,  $\epsilon$ , is defined as:

$$\text{Eq. (7.6)} \quad C_m = \epsilon C_v \text{ or } \epsilon = C_m/C_v$$

where  $C_m$  and  $C_v$  are capacitance of the material and a vacuum, respectively. Because dielectric material affects the force with which two oppositely charged plates attract each other, the dielectric constant may also be defined as the relative effect of the medium on this force of attraction, according to Coulomb's equation:

$$\text{Eq. (7.7)} \quad F = QQ'/\epsilon d^2$$

where:  $F$  = force of attraction between the two plates

$Q$  = charge on one plate

$Q'$  = charge on the second plate

$\epsilon$  = dielectric constant

$d$  = distance between plates

Thus, the higher the dielectric constant of the material between the plates, the more attenuated will be the force of attraction between the plates. The dielectric constant of vacuum is 1. Of air, it is slightly above 1, which for all practical purposes is also taken as 1. This simplifies the measurement somewhat. Details of sample preparation, test methods, and equipment for measuring dielectric constants are given in ASTM D150.<sup>[21]</sup> Measurements are made at a standard frequency of 1 MHz for comparative purposes. Measurements at higher frequencies extending into the gigahertz range are necessary for high-speed and high-frequency circuits.

The dissipation factor,  $DF$ , is the ratio of the resistive (loss) component of current  $I_r$  to the capacitive component of current,  $I_c$ , and equals the tangent of the dielectric loss angle,  $\delta$ , as follows:

$$\text{Eq. (7.8)} \quad DF = I_r/I_c = \tan \delta$$

As for dielectric constant, test methods for dissipation factor may also be found in ASTM D150.<sup>[21]</sup>

### 7.2.3 Electrical Stability

Electrical-stability testing is essential for conductive adhesives used for electrical connections. Electrical conductivity can degrade at elevated temperatures, on aging with or without power, and on exposure to humidity and temperature. The specific test method used depends on the application. One test used for die-attach adhesives specified in NASA MSFC-SPEC-592 (now inactive) involves a series of gold-plated Kovar<sup>®</sup> tabs attached with conductive epoxy to metal pads on an interconnect substrate. In the test vehicle, a bias of 5 volts and current density of  $139 \pm 3.9$  amps/cm<sup>2</sup> (900 amps/in<sup>2</sup>) are applied to a series of wire-connected tabs, and the resistance change is measured after exposure to 150°C periodically up to 1,000 hours. The maximum allowable resistance change is 5%.

Electrically conductive adhesives that are used as solder replacements are evaluated for material characteristics and contact resistance on solder surfaces. In one study, the requirement for volume resistivity is given as 0.001 ohm-cm or less and for contact-resistance change as 20% or less after 500 hours of 85/85-exposure.<sup>[22]</sup>

### 7.2.4 Current-Carrying Capacity and Interconnect Resistance

Other characteristics of electrical interconnects are current-carrying capacity and interconnect resistance. Current-carrying capacity is important for the qualification of adhesives for flip-chip interconnects. Typical current densities for conductive epoxies used as flip-chip bumps are 10–20 amps/mm<sup>2</sup> and typical bump resistances are 12 mΩ.

No standard test method exists for these tests. According to the general guidelines of IPC-3406,<sup>[23]</sup> junction resistance shall be measured before and after performing the IPC aging tests on all surface materials that come in

contact with adhesives. Bond-joint resistance is measured by depositing a strip of adhesive 1 inch  $\times$  0.5 inch (minimum) onto gold-plated stainless steel and then applying a second gold-plated stainless-steel strip to give a one-half inch overlap.<sup>[24]</sup>

### 7.2.5 Metal Migration

Metal migration, especially silver migration, may be quickly tested by applying a drop of deionized water across two closely spaced silver or silver-filled conductors while a DC potential of 2–10 volts is applied. Catastrophic bridging and shorting of the conductors lines is visible at low magnification. The onset of migration is also indicated by the decrease in insulation resistance between the lines.

Other standard tests include UL 796 (Underwriters Labs.) and ASTM F1996-01.<sup>[25]</sup> According to the latter test, samples are prepared that represent the minimum circuit spacing and are energized with a DC or AC potential equal to the anticipated voltage rating for the PWB or interconnect substrate. Prior to humidity exposure the samples are subjected to a 60 second dielectric withstanding voltage of 40 V/mil to a maximum of 1,000 V. The samples are then exposed at 23°C, 95%–100% RH, energized for 1,344 hours, and examined for metal migration at 10X.

## 7.3 ENVIRONMENTAL TESTS

Adhesives may be exposed to solvents in subsequent assembly operations such as cleaning, and adhesive bonds are subject to elevated temperatures associated with wire bonding in packaged devices and surface-mounted parts. Adhesives in electronics are also bonded to different surfaces, and corrosion testing is required to verify the stability of cured adhesive interconnects. Adhesives alone or in combination with moisture can degrade the electrical stability over time. Adhesives on printed-wiring boards must also be resistant to fungus growth and be nonflammable. Finally, high-radiation and prolonged radiation exposures in space or satellite applications can result in reduced mechanical attachment and reduced high-temperature stability.

### 7.3.1 Solvent and Chemical Resistance

Cured adhesives must be resistant to the effects of solvents and chemicals used in subsequent cleaning and processing steps. Dissolving or swelling of adhesives degrades their mechanical, electrical, and physical properties. Adhesives' resistance to solvents is evaluated based on the function or application.

For example, solvent or chemical resistance of adhesives used in surface-mount assembly may be tested according to Method 4.5.6 of ANSI/IPC-SM-817, *General Requirements for Dielectric Surface-Mounting Adhesives*.<sup>[12]</sup> Although this method specifies specific solvents including isopropanol; 1,1,1-trichlorotrifluoroethane; an azeotrope of 6% methyl alcohol and 94% trichlorotrifluoroethane; and a 10% alkaline detergent solution (about pH 13), other solvents and chemicals encountered during manufacturing, screening, and rework processes should also be evaluated. Deposited dots of SMT adhesives exposed to the solvents for various periods of time are examined visually for physical changes or degradation.

### 7.3.2 Corrosion

The potential for corrosion caused by adhesives requires evaluations in both the cured and uncured state. In one test, developed for NASA MSFC-SPEC-592,<sup>[26]</sup> the adhesive components or the cured adhesive are applied to aluminized-Mylar<sup>®</sup> film and examined after 48 hours for etching or transmittance of light through the Mylar. A second test involves embedding copper wire with the adhesive and measuring corrosion by resistance changes in copper wire.<sup>[27]</sup> Because of the wide variety of tests and the fact that they are closely related to adhesive reliability issues discussed in Ch. 6, the reader is referred to that chapter.

### 7.3.3 Radiation Effects

Adhesives are used in satellite and missile applications that may be exposed to high-energy radiation. Evaluating the effect of total dose and dose rate on the mechanical, electrical, and chemical properties of adhesives is required for reliability. ASTM D1879, *Exposure of Adhesive Specimens to High-Energy Radiation*<sup>[28]</sup> defines conditions for exposure. Categories of dose rate exposure within this method are:

Gamma radiation, $x$ -radiation:	$10^5$ – $10^7$ rads/hour
Electrons (beta radiation)	
Radioisotopes:	$10^5$ – $10^7$ rads/hour
Accelerators:	$10^8$ – $10^{10}$ rads/hour
Reactor radiation:	$10^5$ – $10^7$ rads/hour
(neutrons and gamma radiation)	

The effects of a total dose of ionizing radiation from a cobalt-60 source may be measured by Method 1019.5 of MIL-STD-883F.<sup>[29]</sup> Although this method is intended for radiation effects on semiconductor devices, the radiation sources, doses, and procedures can be used to evaluate the effects on exposed adhesives, provided that changes in bond strength or other physical or electrical properties are measured.

### 7.3.4 Fungus Resistance

Fungus-resistance tests are used to determine the reaction of adhesives to several species of fungi under high humidity and a warm environment in the presence of inorganic salts. Testing for fungus resistance is more appropriate for exposed adhesives as in printed-wiring assemblies than for hermetically sealed devices or modules. One test method specified as Method 4.5.14 in IPC-SM-817<sup>[12]</sup> references Method 2.6.1 of IPC-TM-650, *Test Methods Manual*.<sup>[30]</sup>

According to this method, a test sample and a known nutrient control sample are inoculated with fungus spores and stored at 30°C and 90% RH for 20 hours followed by 4 hours at 100% RH. The samples are checked for fungus growth after 7 days. The control should show signs of fungal growth. If the test sample also shows fungus growth, the test can be stopped; if not, the test is extended to 28 days. The test adhesive is considered “non-nutrient” if no growth shows at the end of 28 days.

### 7.3.5 Moisture Absorption

Moisture absorption in uncured and cured adhesives is important for reliable adhesive bonding. Absorbed moisture in adhesives, particularly those used in surface-mounted parts, may result in voids in the bondline due to moisture desorption or entrapment. Absorption of moisture after cure also affects reliability. Popcorning, the cracking of plastic parts during solder reflow, is due to the rapid vaporization and expulsion of moisture retained by the die-attach adhesive or the plastic encapsulant.

*Water absorption* of a cured adhesive is the percent of water absorbed in a given period of time at a given temperature. Adhesive suppliers generally measure and report water absorption data based on exposure to water over 24 hours at room or elevated temperature based on ASTM D570, *Water Absorption of Plastics*.<sup>[31]</sup> Samples are usually preconditioned at  $50^{\circ}\text{C} \pm 3^{\circ}\text{C}$  prior to immersion. Moisture absorption may also be tested as specified in paragraph 3.3.10 of IPC-TM-650.<sup>[30]</sup>

### 7.3.6 Hydrolytic Stability

*Hydrolytic stability* is the resistance of a cured polymer material to reverting to a semisolid or liquid form when exposed to high humidity and temperature. Testing for hydrolytic stability is important for adhesives and other polymers that may be directly exposed to high humidity for long periods of time, as in tropical environments. Hence, testing applies more to printed-wiring assemblies than to hermetically sealed circuits. The hydrolytic stability test used for solder masks (IPC-TM-650 Method 2.6.11 as specified in IPC-SM-817 Section 4.5.15) may also be used to evaluate adhesives. Test specimens are prepared by stenciling adhesive 0.25 mm  $\pm$  0.05-mm thick. The specimens should be free of air bubbles or voids when examined under backlighting. Test samples are then exposed to 95%  $\pm$  4% RH and  $97^{\circ}\text{C} \pm 2^{\circ}\text{C}$  for 28 days and examined visually for evidence of reversion indicated by softening, chalking, blistering, cracking, tackiness, loss of adhesion, or liquefaction.

## 7.4 THERMAL TESTS

With increasing temperature, organic coatings and plastic materials, in general, undergo a variety of changes from simple changes of state (for example, melting, softening, subliming, or glass-transition phase changes) to catastrophic decomposition due to fracture of the polymer structure, oxidation, and outgassing of decomposition products. The thermal limits of adhesives should be known or measured to assure that the material will remain stable under the actual operating conditions or accelerated conditions, if those are used as screening or qualifying tests. Thermal testing of formulated, but uncured-adhesive materials include the measurement of heat absorption or heat evolution (exotherm) during cure, gel time at various cure

temperatures, and weight loss during cure. Cured-material thermal tests include thermal conductivity, CTE,  $T_g$ , and weight loss of the cured sample.

Key test methods for thermal stability include differential-scanning calorimetry (DSC) (also known as differential-thermal analysis, DTA), thermal conductivity, thermogravimetric analysis (TGA), gas chromatographic and mass-spectrometric analyses, and changes in mechanical properties such as tensile strength and elongation. These analytical methods may also be used to study chemical and physical changes that occur from exposure to various types and intensities of radiation. The degradation products of radiation often parallel those from thermal exposure.

### 7.4.1 Endotherm, Exotherm, and Gel Time

During the process of curing, adhesives, as well as other polymeric materials, undergo physical and chemical changes due to absorption of heat (endotherm) and evolution of heat (exotherm).

The *exotherm* (heat generated by uncured adhesives as they polymerize) is measured by adhesive suppliers for material characterization and the quality control of resins and curing agents. Users of adhesives may also measure the peak exotherm temperature and total energy to assure completeness of cure. Test method ASTM D2471, *Gel Time and Peak Exothermic Temperature of Reacting Thermosetting Resins*,<sup>[32]</sup> covers this measurement. Peak exothermic temperature is monitored using a temperature-sensitive probe; the highest temperature recorded is the peak exothermic temperature. Another, commonly used analytical method, is to run a differential-scanning calorimetry scan on a sample and report the peak exotherm.

In DSC or DTA, the heat input (endotherm) or heat generated (exotherm) of a material can be continuously monitored while it is subjected to a controlled temperature increase. The heat changes measured correspond to phase changes that occur at the indicated temperature; for example, they may consist of glass transitions, softening, melting, oxidation, sublimation, or decomposition: all characteristics of a given material.<sup>[33]–[35]</sup> Applications include determination of the degree of cure and thermal stability of polymeric materials. Like TGA, small sample sizes in the low milligrams are used. The heating rate may be 5°C to 20°C/min, and the thermal exposure may be conducted in an inert or air ambient.

Gel time is also used as a quality-control tool for formulated adhesives. During the cure of an adhesive, its surface is tested every 15 seconds with a clean probe. *Gel time* is defined as the time at which the adhesive no longer adheres to the probe.

### 7.4.2 Thermal Conductivity

Thermal conductance and conductivities are derived from the Fourier equation. The total amount of heat a material conducts is directly proportional to the surface area, the time of contact, and the temperature gradient and is inversely proportional to the thickness of the sample, according to:

$$\text{Eq. (7.9)} \quad Q \propto (T_2 - T_1)At/d$$

where:  $Q$  = total heat flow in joules, J  
 $A$  = surface area,  $m^2$   
 $d$  = thickness of sample,  $m$   
 $T_2$  = temperature of the hot surface,  $^{\circ}\text{C}$  or K  
 $T_1$  = temperature of the cold surface,  $^{\circ}\text{C}$  or K  
 $t$  = time, sec

When a proportionality constant,  $k$ , is introduced, the thermal conductivity equation becomes:

$$\text{Eq. (7.10)} \quad Q = k(T_2 - T_1)At/d$$

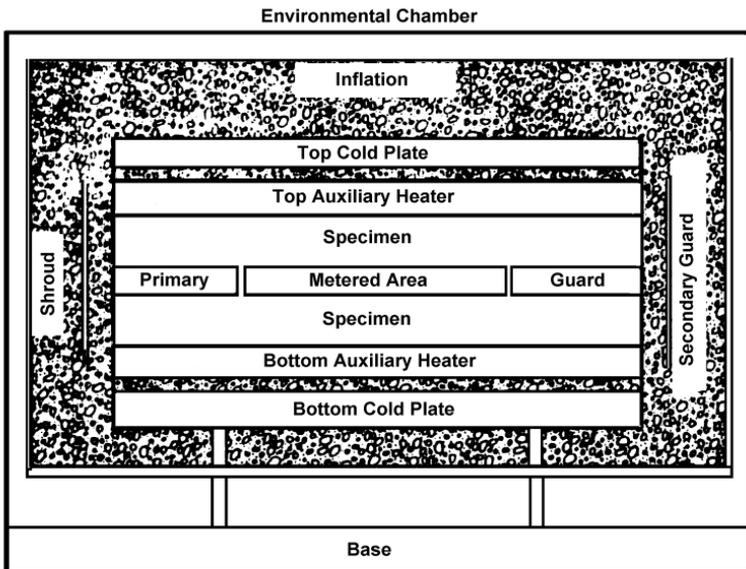
And rearranging to solve for  $k$

$$\text{Eq. (7.11)} \quad k = Qd/(T_2 - T_1)At$$

and the units become  $\text{W/m}\cdot\text{K}$ .

The constant,  $k$ , is a material constant called the *coefficient of thermal conductivity*. It is the time rate of heat flow under steady-state conditions through a unit area and unit thickness per unit temperature gradient. Several methods for measuring thermal conductance are available, of which the *guarded-hot-plate* and *heat-flow meter* methods are the most widely used. The most accurate method for plastics having thermal conductivities of  $3.4 \times 10^{-3} \text{ cal}/(\text{sec})(\text{cm})(^{\circ}\text{C})$  [ $1.4 \text{ W/m}\cdot\text{K}$ ] or less (most filled and unfilled polymers) is the guarded-hot-plate method as described in ASTM C177.<sup>[36][37]</sup>

**Guarded-hot-plate method.** Two types of guarded-hot-plate apparatus can be used. They are similar in principle, but differ somewhat in construction. One example, shown in Fig. 7.4, consists of three sections: a central heating plate, guard heating plates, and cooling plates. The guard portion insures unidirectional heat flow from the central heater and eliminates any influences from the edge of the sample. Thermocouples are located at various positions in the guarded-hot plate to measure the difference between the temperature of the guard ring and central heater and the temperature of the hot and cold surfaces. The central heating unit and cooling units are adjusted until the temperature drop through the two sides does not differ by more than 1% and the fluctuation over a one-hour period is no greater than 0.5% of the temperature difference between the hot and cold plates. When equilibrium is reached, measurements are taken of the temperature differences across specimens; the hot-plate temperature,  $T_2$ ; the cold-plate temperature,  $T_1$ ; and the electrical power input,  $Q$ , to the central heater. Knowing the thickness and area of the sample, the thermal conductivity can be calculated using the thermal conductivity equation given above. The sample thickness may vary with the maximum thickness based on calculations listed in ASTM C177.<sup>[36]</sup>



**Figure 7.4.** Schematic of guarded-hot-plate apparatus.

**Heat-flow-meter method.** The steady-state thermal transmission properties of an insulator can be measured using a heat-flow meter. This is a secondary or comparative method of measuring thermal conductivity since only the ratio of the thermal resistance of the specimen to that of a standard specimen is measured. According to this method, described in ASTM C518,<sup>[38]</sup> a sample is placed between a warm and cold plate. The meter measures heat flow through the specimen by generating a temperature difference across a slab of material of known thermal resistance. A calibration curve is generated using samples of known thermal conductivities. These samples should have thermal conductivities close to those expected of the samples tested. Sample thicknesses may range from 0.001 to 0.8 inches but, for accuracy, the value of thermal conductivity divided by the sample thickness should be less than 400 W/m·K. In the heat-flow-meter method, the spacing between the warm and cold plates is based on the theoretical maximum thickness of the specimens in the conventional guarded-hot-plate apparatus. Calculations of this spacing may be found in ASTM C518.

**Laser-flash method.** For high thermal-conductivity adhesives, such as the silver-glass compositions whose thermal conductivities are greater than 20 W/m·K, the indirect laser-flash method is used. Unlike the steady-state methods, the flash method does not measure thermal conductivity directly, but measures thermal diffusivity, from which thermal conductivity is calculated as follows:

$$\text{Eq. (7.12)} \quad k = DC_p d$$

where  $k$  = thermal conductivity,  $D$  = thermal diffusivity,  $C_p$  = specific heat capacity, and  $d$  = density.

The flash method, described in ASTM E1461, *Standard Test Method for Thermal Diffusivity of Solids by the Flash Method*,<sup>[39]</sup> is based on measuring the temperature rise of the back surface of the sample when the front surface is irradiated with a high-energy pulse from a laser or flash lamp. Thermal diffusivity is usually carried out by rapidly heating one side of the sample and measuring the temperature rise on the other side. Essentially, the temperature rise follows the propagation of the pulse pattern. Small sample sizes of 12.5 mm diameter and 1–2-mm thick can be used. The flash method is applicable only for homogeneous solid materials. For materials that are substantially inhomogeneous such as composite or anisotropic materials, the thermal diffusivity values may be erroneous.

### 7.4.3 Weight Loss of Cured Adhesive

Weight loss with increasing temperature is performed as a measure of the thermal stability of adhesives. Thermogravimetric analysis (TGA) has been used for many decades as a quantitative measure of the total weight loss of outgassed products from polymers as they are heated at a controlled rate. A TGA apparatus consists of a precision electrobalance contained within a controlled-temperature oven such that the change in mass of a sample can be dynamically measured as a function of increasing temperature. The temperature is increased at a programmed rate or the sample may be kept at constant temperature and weight changes recorded as a function of time (isothermogravimetric analysis). Sample weights of several milligrams to several grams can be accommodated and weight losses or gains as little as 0.5 micrograms can be measured. The programmed rate of temperature increase is normally 10°C per minute. Weight loss versus temperature curves (TGA curves, also known as *pyrograms*) are useful in determining the onset of outgassing, the weight loss at a specified temperature, and the temperature at which total decomposition occurs. TGAs may be conducted in nitrogen or, when thermal oxidative stability is being evaluated, in air.

Thermogravimetric analyzers may be connected to a variety of chemical analyzers to determine the exact composition of the outgassed materials as they are evolved. Among chemical analysis methods are gas chromatography, infrared spectroscopy, and mass spectroscopy; for example, a TGA apparatus may be coupled with a Fourier Transform Infrared (FTIR) spectrophotometer to measure the thermal oxidative stabilities of several fluorinated polyimides.<sup>[40]</sup>

TGA is used to qualify adhesives for use at process temperatures such as those experienced during belt-furnace sealing. The standard test procedure for this method is ASTM D3850, *Rapid Thermal Degradation of Solid Electrical Insulating Materials by Thermogravimetric Method*.<sup>[41]</sup> According to this procedure, a manufacturer's system is calibrated to within  $\pm 0.01$  mg and  $\pm 0.1$ °C. The purge rate is 40 to 100 cm<sup>3</sup>/min and the heat rate is set to 5°C/minute. Method 5011.4 of MIL-STD-883F, 3.5.2 also references this method. A maximum heat rate of 10°C/minute is allowed in a nitrogen atmosphere with 20 cm<sup>3</sup>/minute nitrogen flow.

## 7.5 MECHANICAL AND THERMOMECHANICAL TESTS

Mechanical and thermomechanical tests for adhesives are primarily used to evaluate the stress imparted by adhesives on bonded parts. Included in this category are physical characteristics such as hardness and modulus that are a measure of rigidity of the cured adhesive. Other mechanical properties used to evaluate and classify materials are modulus and elongation-at-break, as well as the coefficient of thermal expansion above and below the glass-transition temperature. A third general area of tests is bond strength that may include tensile shear as well as die-shear and stud-pull tests for devices and centrifuge for both devices and substrates. Finally, radius of curvature is used to characterize residual stress of devices imposed by adhesives as related to cure conditions and post-processing, such as wire bonding and plastic molding or encapsulation.

### 7.5.1 Hardness

Hardness is used both as a qualification and acceptance test for adhesives. It is a simple, low-cost test that can be used as a rough indicator of the degree of cure. There are several instruments for measuring hardness, but the most widely used are based on a spring-loaded indenter that is pressed into a sample. Small portable instruments such as the Shore Durometers give an analog or digital reading on a 0 to 100 scale. The Shore A Durometer is used for soft materials, Shore B for moderately hard, Shore C for medium hard, and Shore D for very hard materials. This method is defined in ASTM D2240.<sup>[42]</sup>

### 7.5.2 Modulus and Elongation (Flexural)

Flexural modulus is a measure of the strength of adhesives. Modulus data are most often used in stress analysis (one-dimensional or as an input to 3D-modeling). In addition to flexural modulus, elongation-at-break is also recorded. The standard test method is ASTM D790, *Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials*.<sup>[43]</sup> Two methods are specified. The first uses a three-point bending test; two supports hold the part and a load is applied with a single point to induce

flexure. In the second method, (four-point bending) the force is applied using two heads or points. The flexural modulus is calculated from the following equation:

$$\text{Eq. (7.13)} \quad E = L^3 F / 4bh^3 y$$

where:  $L$  = length of span  
 $y$  = distance covered by a load  $F$  during flexure, measured from the initial position  
 $F$  = load (in Newtons)  
 $b$  = width of test bar (in mm)  
 $h$  = thickness of test bar (in mm)

### 7.5.3 Modulus and Elongation (Tensile)

*Young's modulus*, also referred to as elastic modulus, tensile modulus, or modulus of elasticity in tension is the ratio of stress-to-strain and is equal to the slope of a stress-strain diagram for the material. In the standard test method, ASTM D412, a force is applied to a “dog-bone-shaped” sample of the cured adhesive. The force at elongation (strain) is measured. Most often, the elongation is 25%–30% although for elastomeric materials it may be 100% or greater.

Tensile and elongation characteristics of materials may also be evaluated according to ASTM D638-96, *Tensile Properties of Plastics (Metric)*.<sup>[44]</sup> According to this method, bi-axial strain gages are used to monitor axial and transverse strain in dog-bone test samples. Ultimate strength, modulus, Poisson's ratio, and percent strain at failure are determined.

### 7.5.4 Coefficient of Thermal Expansion and Glass-Transition Temperature

Thermomechanical-analysis (TMA) testing is used to measure a material's expansion coefficient above and below the glass-transition temperature or  $T_g$ . Thermomechanical analysis continuously monitors the expansion of a probe on a sample as a function of temperature. The standard test method for TMA is ASTM D3386, *Coefficient of Linear Thermal Expansion of Electrical Insulating Materials*.<sup>[45]</sup> In addition to the glass-transition temperature or  $T_g$ , the expansion coefficients above and below  $T_g$  are reported.

## 7.5.5 Bond Strength

Bond strength is measured to assure that bonding materials retain adhesion at temperature and after aging or thermomechanical stresses. Bond strength is measured as tensile strength for SMT adhesives and die-shear testing for component and substrate adhesives. Specialized adhesive test methods are also used for flip-chip and substrate strength, and centrifuge testing is used to evaluate both die and substrate adhesion.

**Tensile strength.** Tensile strength is evaluated by pull testing on metal “lap-shear” coupons, most often aluminum. The standard test method is ASTM D1002, *Apparent Shear Strength of Single-Lap-Joint Adhesively Bonded Metal Specimens by Tension Loading (Metal-to-Metal)*.<sup>[46]</sup> Aluminum coupons are overlapped by 1/2 in (typical) and a wire is used as a spacer to control bondline thickness. Method 5011, paragraph 3.8.8.2 of MIL-STD-883F references this specific method.

**Die-shear strength.** Die-shear testing is performed both for qualification and quality assurance testing of adhesive-attached semiconductor die and other chip devices. MIL-STD-883F, Method 2019.7<sup>[47]</sup> defines the test method most commonly used. A uniform force is applied to the edge of the die using a die-contact tool. The tool loads against the edge of the die perpendicular to the mounting plane (substrate). A lateral force is applied sufficient to shear the die from the substrate. Failure criteria are given as the minimum force in kilograms required to detach the die based on the area of the die. Graphs of failure criteria are provided in Method 2019 for minimum strength, 1.25 times minimum, and 2 times minimum strength as a function of die area. Most wire-bond pull testers are now also equipped for die-shear testing.

**Die and substrate strength.** Another method for measuring either die- or substrate-attach adhesion strength involves attaching a contact tool to the top of the die or substrate with an adhesive that is stronger than that of the die-attachment adhesive. The tool applies a vertical force until the die detaches from the substrate or until a minimum specified strength is achieved. The test method and failure criteria are specified in Method 2027 of MIL-STD-883F.<sup>[48]</sup>

**Centrifuge testing (constant acceleration).** Centrifuge testing, also known as constant acceleration, is applicable to both die and substrate adhesion and is defined in Method 2001 of MIL-STD-883F.<sup>[49]</sup> According to this method, parts assembled with adhesives are centrifuged in the  $Y_1$  direction with the die-side against the wall of a spinning test chamber

(centrifuge). The centrifugal force pulls against the attached devices. Parts may be centrifuged to a known “G” load or until failure occurs. Centrifuge testing is widely used as a 100% screen test for hermetically sealed hybrid microcircuits and multichip modules for both Class H (military) and Class K (space). In both cases, according to MIL-PRF-38534E<sup>[50]</sup> modules must pass 3,000 G without any detachments. In addition, for qualification, modules must pass 5,000 G in the  $Y_1$  direction.

Mechanical shock Method 2002.4 of MIL-STD-883<sup>[51]</sup> may be used as an option instead of constant acceleration as the screen test, but both mechanical shock and constant acceleration must be used for qualification.

### 7.5.6 Acoustic Microscopy

Scanning acoustic microscopy (SAM) is an ideal nondestructive method for revealing internal flaws within materials or between material interfaces. SAM is extensively used in detecting voids, delamination, and other separations that can occur in adhesive-attached parts, especially after thermal cycling. SAM is particularly useful in the analysis or evaluation of many types of electronic parts, including ceramic and plastic-encapsulated ICs, plastic-encapsulated microcircuits (PEMs), hybrid microcircuits, CSPs, PBGAs, and printed-wiring boards.

The acoustic microscope produces an image by mechanically scanning with an ultrasonic transducer in an  $X, Y$  pattern over the test specimens. This “scan” is performed in a vessel filled with deionized water or other liquid that couples the ultrasonic energy from the transducer to the part. Water is the most effective medium but, where the electronic part is sensitive to moisture, other liquids such as alcohols can be used. The transducer emits a short ultrasonic pulse and then detects the echo. If the part is free of defects, there will be two signals, from the near and far surface. If there is an internal defect, such as a void or delamination, the transducer will detect an additional return signal. This signal has a direct relationship to the depth of the defect. Moreover, acoustic images from several depths can be acquired simultaneously, revealing defects at each interface in an electronic device.

Images are typically displayed as either C-scans or B-scans. A C-scan is an overall  $X, Y$  view of the test specimen at a particular depth or interface. A color scale or black and white image displays signal amplitude. B-scans display an image of a cross-sectioned view at a chosen location with the scan indicating signal amplitude. Acoustic microscopes have the flexibility to adapt different transducers for different applications from low-frequency

transducers (1 through 15 MHz), used for detecting large flaws in thick materials (through which sound travels slowly) to 50 MHz transducers that can examine thin Kovar<sup>®</sup> of 30 mils or aluminum up to 200-mils thick. Higher frequency transducers are needed for thin substrate materials such as alumina or gallium arsenide. The high-frequency transducers allow finer resolution and greater detail, but do so at the expense of penetrating power.

The acoustic microscope has the software to analyze the image once the scan is completed. Analysis tools include: histogram (for percentage of voids), vertical and horizontal profile, zoom, manipulation of color scale, measurements, and multiple scans. The system also has the capability to print either in color or black and white, or to transmit images electronically over the network.

Although there is no standard test method for acoustic microscopy, Method 2030, *Ultrasonic Inspection of Die Attach* of MIL-STD-883F<sup>[52]</sup> is used to nondestructively detect unbonded regions and voids in IC die-attachment materials. Parts are rejected if a single void larger than 15% of the contact area is present (>10% at a corner) or more than 70% of any given quadrant is detached.

### 7.5.7 Radius of Curvature

The ability of an adhesive to absorb stresses associated with bonding large devices to substrates with mismatched expansion coefficients is directly measured by the radius of curvature. Radius of curvature of a device bonded to a leadframe is determined in order to predict relative stress absorption capabilities of materials. There is no industry standard for this test, and measurement techniques vary by vendor. The radius of curvature is used in determining the bending stress as defined below:

$$\text{Eq. (7.14)} \quad \text{Bending stress} = Eh/2Yr$$

where:  $E$  = Young's modulus,  $h$  = thickness of the specimen,  $Y$  = Poisson's ratio, and  $r$  = radius of curvature.<sup>[53]</sup>

Typically, an automatic dispenser is used to apply enough adhesive to completely cover the underside of a die. Bondline thicknesses of 1.0 to 1.5 mils and fillets of 50% to 75% of the die thickness are recommended. The star pattern of dispensing is suggested to achieve optimum coverage. A surface-roughness tester, such as a Brown & Sharpe Surface Roughness Measuring

Instrument Model Surfcom 120A or equivalent, is used to measure the profile of the cured sample.<sup>[54]</sup>

Radius of curvature,  $r$ , is determined as (see Fig. 7.5):

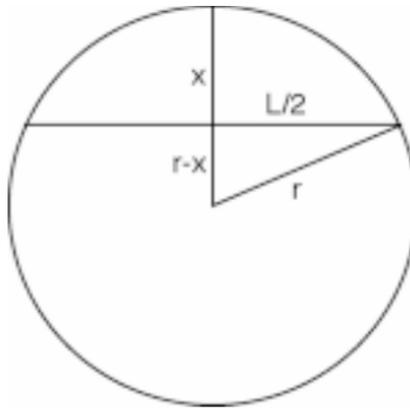
$$\text{Eq. (7.15)} \quad r^2 = (r-x)^2 + (L/2)^2$$

And rearranging:

$$\text{Eq. (7.16)} \quad r = [x^2 + (L/2)^2]/2x$$

where:  $r$  is the radius of curvature in millimeters,  $x$  is the maximum amplitude ( $\mu\text{m}$ ) from the printout, and  $L$  is the traversed length of the specimen.

Laser interferometry can also be used to measure the radius of curvature. Changes in surface deflection are detected from the angle of reflection, and the radius of curvature is determined.



**Figure 7.5.** Radius of curvature diagram.

## 7.6 CHEMICAL ANALYSIS

Many chemical and analytical or instrumental methods are available for analyzing adhesives for chemical structure and composition, outgassing, decomposition products, and ionic impurities.

### 7.6.1 Weight Loss During Cure

*Weight loss during cure* is a measure of the amount of volatiles given off during cure. High-weight loss is a concern in contaminating curing ovens and subsequently redepositing onto critical surfaces of circuits, such as wire-bond pads. There is, as yet, no industry standard for this test. Some adhesives' suppliers use "simulated" silicon die attached to a glass microscope slide and accurately weigh the glass slide, the silicon chips, and the adhesive-bonded samples; then, by difference, calculate the initial weight of uncured adhesive used. After curing, the test coupons are reweighed and, by difference from the original sample weight, the weight loss and percent loss are calculated.<sup>[55]</sup>

### 7.6.2 Infrared Spectral Analysis

Infrared spectroscopy (IR) is an excellent method for determining chemical changes that occur in organic materials through decomposition, oxidation, polymerization, reactions with other compounds, or changes in the formulation. Infrared spectroscopy is also a valuable tool for detecting and identifying organic compounds, polymer types, impurities in compounds, and for quantitative analysis of mixtures of compounds. Infrared spectra result from different modes of vibration and rotation within a molecule. Pure rotational spectra occur at the long wavelengths (greater than 25  $\mu\text{m}$ ). At shorter wavelengths, the radiation has sufficient energy to cause changes in vibrational levels of the molecule. Thus, the frequencies of vibration are related to the masses and binding forces of the atoms that become the basis for infrared in determining the structure of a compound. The region of most interest for the analysis of organic materials lies between 2  $\mu\text{m}$  and 15  $\mu\text{m}$  where specific groups absorb at definite frequencies or wavelengths.

The percent absorption or transmission of infrared radiation by a material when scanned over wavelengths of approximately 2  $\mu\text{m}$  to 15  $\mu\text{m}$  provides a "fingerprint" of the material that is useful in determining the exact nature of the compound. Absorptions at specific wavelengths in the near infrared are indicative of various groups within a molecule such as amino, carboxyl, keto, or hydroxyl groups, while absorption in the far infrared is indicative of the nature of the molecule as a whole. The spectrum obtained may also be compared with spectra of known compounds as recorded in the literature.<sup>[56]</sup> The standard test method for IR analysis is ASTM E1252.<sup>[57]</sup>

### 7.6.3 Gas Chromatography

In gas chromatography, the components of a mixture are separated by volatilizing the sample and passing the gases through a column of solid porous material of 20 to 200 mesh or onto thin layers of finely divided solids. In one method, gas-liquid chromatography, the surface of the packing is coated with a nonvolatile liquid (the stationary phase). If the liquid is not present, the process is called gas-solid chromatography. The principle of chromatography is based on the different rates at which the chemical components pass through the packing material, and their detection as separate species as they exit the column. The components may be detected by thermal conductivity changes, density differences, or by ionization detectors.

### 7.6.4 Mass Spectrometry and Residual-Gas Analysis (RGA)

The main source of moisture and other outgassed compounds in hermetically sealed ceramic or metal packages is from adhesives and other polymer materials used in the assembly of the electronic devices. Even though the assemblies are extensively vacuum baked prior to sealing and even though they are sealed in dry nitrogen, outgassing of moisture, greater than the 5,000 ppm<sub>v</sub> allowed by MIL-PRF-38534, can occur after burn-in or after temperature cycling.

Mass spectrometry is an excellent analytical method to quantitatively measure moisture and trace amounts of low-molecular-weight organic species. In RGA, the outgassing from adhesives and other organic materials such as moisture, carbon dioxide, carbon monoxide, and low-molecular-weight hydrocarbons can be measured in low parts per million.

By mass spectrometry, molecules are first activated and dissociated into ionic fragments that are then separated according to their charge-to-mass ratios. Mass spectrometers essentially consist of four parts: equipment to ionize the sample, an ion accelerator, an ion separation system, and a detection system. The sample may be ionized by bombardment with electrons from a heated filament or by several other means. The ions produced are then accelerated and focused electrostatically and separated according to their atomic masses while traveling through a magnetic field.

A variation of magnetic-separation equipment, widely used today, is the quadrupole mass spectrometer. This equipment consists of four cylindrical

rods arranged in an orthogonal array. Opposite rods are electrically connected and opposite voltages applied. The positively charged pair acts as a low-mass pass filter while the negatively charged pair acts as a high-mass pass filter. By adjusting the voltages on the two pairs of rods, the quadrupole is made into a narrow, bandpass-mass filter. The separated ions are then detected electrically. The ion beams are scanned across a collector where they pick up electrons and generate an electric current that is amplified and analyzed by computer. As with infrared spectra, an extensive database of mass spectra of chemical compounds is available and can be used to compare with the mass spectrograph of an unknown to verify its nature.<sup>[58]</sup>

The standard test method for RGA is Method 1018.4 of MIL-STD-883F<sup>[59]</sup> according to which mass spectrometry is used to detect moisture and other volatilized compounds present in sealed microcircuit packages. The sealed modules are first preconditioned to remove external contaminants and adsorbed moisture by prebaking for 16–24 hours at  $100^{\circ}\text{C} \pm 5^{\circ}\text{C}$  then placed in a vacuum holding chamber that is attached to the spectrometer. The device and chamber are then pumped down and stabilized at  $100^{\circ}\text{C} \pm 5^{\circ}\text{C}$ , after which the lid of the device package is punctured and internal gas from the package allowed to enter the mass spectrometer.

In qualifying adhesives for outgassing, an amount of adhesive and surface area representative of that to be used in actual devices or modules is cured in gold-plated or nickel-plated lead-less packages. After vacuum baking, the samples are sealed in dry nitrogen, leak tested, heated for up to 1,000 hours at  $150^{\circ}\text{C}$  and analyzed. Moisture must be no greater than 5,000 ppm<sub>v</sub> for both Class H and Class K parts. If a moisture getter is used, the moisture requirement is less than 3,000 ppm<sub>v</sub> after the 1,000-hour exposure.

Because of the expensive equipment involved and the expertise required for accurate analyses, moisture and gas analysis is generally outsourced to laboratories that are certified.

## 7.6.5 Total-Mass Loss and Water Regained

Another variation on outgassing is total-mass loss of cured-adhesive materials. Outgassing and subsequent condensation of volatiles is a concern, for example, in optical and space applications. A standard test method is ASTM E595, *Total Mass Loss and Collected Volatile Condensable Materials from Outgassing in a Vacuum Environment*.<sup>[60]</sup> Three measurements are made in this test: total mass loss (TML), collected-volatile condensable materials (CVCM), and water-vapor regained (WVR). Historically, maxi-

imum values of 1% TML and 0.1% CVCM have been used to qualify materials for spacecraft applications. TML and CVCM are determined after 24 hours exposure at  $5 \times 10^{-5}$  Torr and 125°C. Water vapor regained is determined by reweighing after storage in a 23°C and 50% RH environment. Samples are normally mixed in 10-gram batches and cured specimens are cut into cubes 1.5 to 3.0 mm/side. Adhesive films may be applied to surfaces to simulate use conditions.

### 7.6.6 Ionic Content

The total ionic content and the amounts of specific metal ions such as sodium and potassium greatly affect the electrical properties of an insulative adhesive and of the electronic function of a circuit. A simple test to determine the total ionic content of a polymeric material is to digest a weighed, powdered sample in deionized water and to measure the resistivity of the water extracts after refluxing for 20 hours. This test gives a rough idea of the extent of ionic contaminants in the sample. For example, a drop in resistivity from 10 megohm-cm to 10,000 ohm-cm indicates a considerable amount of ionic species. The total ionic content is reported as ppm of equivalent NaCl:

$$\text{Eq. (7.17)} \quad \text{Total ionic content} = 23.47(L_2 - L_1)/W$$

where:  $L_2$  = specific conductance in micromho/cm. of a sample

$L_1$  = specific conductance in micromho/cm. of a blank

$W$  = sample weight in grams

23.47 = the constant  $A/L_s$  where  $A$  = grams of NaCl in 50 cm<sup>3</sup> of a 0.0005N NaCl solution

$L_s$  = specific conductance of the 0.0005N NaCl solution

Exact elemental analysis can then be performed by evaporating the water and analyzing the residue by atomic absorption spectroscopy or flame photometry. These are emission spectrographic methods whereby the atoms or molecules of the sample, on being excited by energy input from an arc, spark, or flame, emit wavelengths of radiation as they return to the normal state. These wavelengths indicate qualitatively and quantitatively the atomic species present in the sample. The spectra of the elements consist of lines of distinctive color, for example, the yellow D line for sodium. The spectra of molecules consist of groups of lines called bands. The number of lines present in an emission spectrum depends on the number and position of the outermost

electrons and the degree of excitation of the atoms. Element analysis may also be performed by ion chromatography.

Standard test methods and requirements for total ion content and specific ions such as chloride, sodium, fluoride, and potassium are given in Method 5011.4, paragraph 3.8.7.3.<sup>[20]</sup>

A simple qualitative test for chloride ions consists of immersing or swabbing the part in deionized water and adding a few drops of 0.1N silver nitrate solution to the water extracts. A white turbidity or precipitate indicates that an insoluble silver chloride has formed and that chloride ions may have been present. The test, however, is not entirely specific for chlorides since a few other anions, such as sulfate, also form white insoluble precipitates that must then be distinguished by other qualitative or quantitative methods.

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# Appendix

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## CONVERSION FACTORS

**Table A.1.** Thermal Conductivity Units and Equivalents

Cal/ (sec · cm · °C)	BTU/ (hr · ft · °F)	W/ (m·K)	W/ (cm · °C)	W/ (in · °C)
1	241.9	418.6	4.186	10.63
$4.13 \times 10^{-3}$	1	1.73	0.0173	0.044
$2.39 \times 10^{-3}$	0.578	1	0.01	0.0254
0.239	57.8	100	1	2.54
0.094	22.74	39.4	0.394	1

**Table A.2.** Dimension Units and Equivalents

<b>Mil</b>	<b>Inch</b>	<b>Centimeter</b>	<b>Millimeter</b>	<b>Angstrom</b>	<b>Micrometer</b>	<b>Microinch</b>
1	0.001	0.00254	0.0254	254,000	25.4	1,000
1000	1	2.54	25.4	$2.54 \times 10^8$	25,400	$1 \times 10^6$
394	0.394	1	10	$1 \times 10^8$	$1 \times 10^4$	$3.94 \times 10^5$
39.4	0.0394	0.1	1	$1 \times 10^7$	$1 \times 10^3$	$3.94 \times 10^4$
$3.94 \times 10^{-6}$	$3.94 \times 10^{-9}$	$1 \times 10^{-8}$	$1 \times 10^{-7}$	1	$1 \times 10^{-4}$	$3.94 \times 10^{-3}$
0.0394	$3.94 \times 10^{-5}$	$1 \times 10^{-4}$	0.001	10,000	1	39.4
0.001	$1 \times 10^{-6}$	$2.54 \times 10^{-6}$	$2.54 \times 10^{-5}$	254	0.025	1

**Table A.3.** Pressure and Force Conversion Factors

To Convert From:	To:	Multiply By:
Pascals (Pa)	Pounds per in <sup>2</sup> (psi)	$1.45 \times 10^{-4}$
Pounds	Newtons	4.44
Dynes/cm <sup>2</sup>	Pounds per in <sup>2</sup> (psi)	$1.45 \times 10^{-5}$
Newtons/mm <sup>2</sup>	GigaPascals (GPa)	$1 \times 10^{-3}$
MPa	Newtons/mm <sup>2</sup>	1
Pascals (Pa)	Dynes/cm <sup>2</sup>	10

**Table A.4.** Viscosity Conversion Factors

To Convert From:	To:	Multiply by:
Poise	Centipoises	100
Centipoises	Poise	0.01
Poise	lb/(sec · ft)	0.0672
Poise	lb/(hr · ft)	242
Poise	Pa sec	0.1
Pa sec	Centipoises	1,000
Poise = gm/(sec)(cm)		

## ABBREVIATIONS, ACRONYMS, AND SYMBOLS

**Table A.5.** Abbreviations, Acronyms, and Symbols

ACA	Anisotropic Conductive Adhesive
ACS	American Chemical Society
AEW	Amine Equivalent Weight
ANSI	American National Standards Institute
ANTEC	Annual Technical Conference (of SPE)
ASIC	Application Specific Integrated Circuit
ASTM	American Society for Testing and Materials
BCC	Bumped Chip Carrier
BGA	Ball-Grid Array
BT	Bismaleimide Triazine
CAF	Conductive Anodic Filament
C of C	Certificate of Compliance
CERDIP	Ceramic Dual-In-Line Package
CFC	Chlorofluorocarbon
CHMT	Component, Hybrid, and Manufacturing Technology
CMOS	Complementary Metal Oxide Semiconductor
COB	Chip-on-Board
CCD	Charged Coupled Device
COG	Chip-on-Glass
COL	Chip-on-Lead
COS	Chip-on-Substrate
COTS	Commercial Off The Shelf
CPGA	Ceramic Pin-Grid Array
CPMT	Components, Packages, and Manufacturing Technology
cps	Centipoise
CSP	Chip Scale Package
CTE	Coefficient of Thermal Expansion
CVCM	Collected Volatile Condensable Materials

(cont'd.)

**Table A.5.** (Cont'd.)

DADS	Diaminodiphenyl Sulfone
DeI	Deionized
DGEBA	Diglycidylether of Bisphenol A
DGEBF	Diglycidylether of Bisphenol F
Dicy	Dicyandiamide
DIP	Dual-In-Line Package
DoD	Department of Defense
dph	dots per hour
DRAM	Dynamic Random Access Memory
DSC	Differential Scanning Calorimetry
DSCC	Defense Supply Center, Columbus Ohio
DTA	Differential Thermal Analysis
EDX	Energy Dispersive X-Ray
EEPROM	Electrically Erasable Programmable Read Only Memory
EEW	Epoxy Equivalent Weight
EIA	Electronic Industries Alliance
EMI	Electromagnetic Interference
EMTA	Emerging Markets Trade Association
EPA	Environmental Protection Agency
ESD	Electrostatic Discharge
FCIP	Flip-Chip in Package
FCOB	Flip-Chip on Board
FCOF	Flip-Chip on Flex
FDA	Food and Drug Administration
FEP	Fluorinated Ethylene Propylene
FPD	Flat-Panel Display
FTIR	Fourier Transform Infrared
GPS	Global Positioning Satellite

(cont'd.)

**Table A.5.** (Cont'd.)

HAST	Highly Accelerated Stress Test
HCFC	Hydrochlorofluorocarbon
HDI	High Density Interconnect, <i>also</i> Hexamethylene Diisocyanate
HFC	Hydrofluorocarbon
HFE	Hydrofluoroether
HHPA	Hexahydrophthalic Anhydride
HTC	High Temperature Cofired Ceramic
IC	Integrated Circuit
ICA	Isotropic Conductive Adhesive
ID	Inside Diameter
IEC	International Electrotechnical Commission
IEEE	Institute for Electrical and Electronics Engineers
IEMT	International Electronics Manufacturing Technology
IMAPS	International Microelectronics and Packaging Society
I/O	Input/Output
IPA	Isopropyl Alcohol
IPC	Institute for Interconnecting and Packaging Electronic Circuits (formerly Institute of Printed Circuitry)
IR	Infrared (also Insulation Resistance)
ISHM	International Society for Hybrid Microelectronics (now IMAPS)
ISO	International Standards Organization
ITO	Indium Tin Oxide
JEDEC	Joint Electronic Device Engineering Council (now Solid State Technology Association)
K	Kelvin
KB	Kauri-Butanol
LC	Liquid Crystal
LCD	Liquid-Crystal Display
LED	Light Emitting Diode
LMI	Low Mobile Ions

(cont'd.)

**Table A.5.** (Cont'd.)

LOC	Lead on Chip
LSI	Large-Scale Integration
LTCC	Low Temperature Cofired Ceramic
MCM	Multichip Module
MCOT	Modified Cyclo-olefin Thermoset
MELF	Metal Electrode Leadframe
MEMS	Micro Electromechanical System
MEPTEC	Microelectronics Packaging and Test Engineering Council
MOE	Modulus of Elasticity
MPa	Megapascal
MPC	Microphase Cleaning
MSDS	Material Safety Data Sheet
MSFC	Marshall Space Flight Center
MSL	Moisture Sensitivity Level
MVTR	Moisture Vapor Transmission Rate
N	Newton
NC	No Clean
NCMS	National Center of Manufacturing Science
NFFUF	No-Flow Fluxing Underfill
NFU	No-Flow Underfill
NMP	N-Methyl Pyrrolidone
OA	Organic Acid
OD	Outside Diameter
ODA	4,4' Oxydianiline
ODS	Ozone-depleting Solvent
OE	Optoelectronics
OSHA	Occupational Safety and Health Administration
OSP	Organic Solderability Preservative
Pa	Pascal
PA	Phthalic Anhydride

(cont'd.)

**Table A.5.** (Cont'd.)

pbw	parts by weight
PCB	Printed-Circuit Board
PCMCIA	Personal Computer Memory Card International Association
PDA	Personal Data Assistant
PDIP	Plastic Dual-In-Line Package
PEEK	Polyaryletherether ketone
PEM	Plastic-Encapsulated Microcircuit
PFI	Polymer Film Interconnect
PGA	Pin-Grid Array
phr	parts per hundred of resin
PIND	Particle Impact Noise Detection
PLCC	Plastic Leadless Chip Carrier
PMDA	Pyromellitic Dianhydride
ppm	parts per million
ppm <sub>v</sub>	parts per million by volume
PTFE	Polytetrafluoro ethylene
PTMEG	Polytetramethylene ether glycol
PWA	Printed-Wiring Assembly
PWB	Printed-Wiring Board
QFP	Quad Flat Pack
RGA	Residual Gas Analysis
RH	Relative Humidity
RIE	Reactive Ion Etch
R	Rosin
RA	Rosin Activated
RMA	Rosin Mildly Activated
ROSE	Resistivity of Solvent Extracts
rpm	revolutions per minute
RT	Room Temperature
RTV	Room Temperature Vulcanizing

(cont'd.)

**Table A.5.** (Cont'd.)

SAM	Scanning Acoustic Microscopy
SAMPE	Society of Aerospace Materials and Processes Engineers
SCF	Super Critical Fluid
SDRAM	Synchronous Dynamic Random Access Memory
SEM	Scanning Electron Microscopy
SIP	System-in-Package
SIR	Surface Insulation Resistance
SMA	Surface-Mount Adhesive
SMT	Surface-Mount Technology
SOIC	Small Outline Integrated Circuit
SOT	Small Outline Transistor
SOP	Small Outline Package
SPE	Society of Plastics Engineers
SRAM	Static Random Access Memory
TAB	Tape Automated Bonding
TCR	Temperature Coefficient of Resistance
TDI	Toluene Diisocyanate
TGA	Thermogravimetric Analysis
TI	Thixotropic Index
TO	Transistor Outline
TMA	Thermomechanical Analysis
TML	Total Mass Loss
TSOP	Thin Small Outline Package
UV	Ultraviolet
VCM	Volatile Condensable Material
VFM	Variable Frequency Microwave
VLSI	Very Large Scale Integration
VOC	Volatile Organic Compound
WI	Wetting Index
WLU	Wafer-Level Underfill
WS	Water Soluble
WVR	Water Vapor Regained

# Index

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