Polymer Adhesives and Encapsulants for Microelectronic Applications

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This article provides an overview of the use of polymer adhesives in microelectronic packaging, with key applications including die attachment, underfills, and encapsulants. For many applications, polymer adhesives provide several advantages over alternative materials, and polymers have been widely used for die attachment. In flip-chip devices, polymers are being used for electrical interconnects instead of metallurgical joints. Polymer encapsulants are widely used to package microelectronic and optoelectronic devices when hermeticity is not required. The various types of materials and their properties are presented along with the relative advantages and disadvantages. Processing and assembly steps, testing, and reliability issues also are discussed.

INTRODUCTION
Polymer adhesives and encapsulants are used in the electronics industry where lower temperature processing (typically <150°C), lower cost, and lower stress (attributable to lower rigidity) of polymeric materials provide an advantage over inorganic eutectics. Generic process steps for assembling various package types are given in Table 1. Polymer adhesives have been widely used for die attachment, in liquid crystal displays, and in smart cards, and they offer a more environmentally friendly alternative to Pb-based eutectics for electrical interconnections. Although the performance and long-term reliability of polymer adhesives have been lower than that of inorganic eutectics in flip-chip applications, the properties and performance of polymers have continually increased, and polymers are widely used depending on the particular device and application.

Polymer adhesives are commonly used as underfills in larger eutectic-bonded flip-chip devices in order to distribute stress in the solder/eutectic joints that occur during temperature cycling and results from coefficient of thermal expansion (CTE) mismatches at interfaces. Polymeric materials have been used for decades as encapsulants for electronic devices in which long-term hermeticity is not required. These types of encapsulants offer many advantages over hermetic packages with regard to size, weight, and cost, although hermetic devices are preferred for high-reliability applications. Polymers also are emerging as key materials within the optoelectronics
Polymer adhesives and encapsulants

In addition to adhesion and packaging applications, polymers are used for the fabrication of optical components, such as waveguides and interconnects.

Polymers for Die and Substrate Attachment

Polymer adhesives generally fall into three main categories or applications: (i) thermally and electrically nonconducting, (ii) thermally conducting and electrically nonconducting, and (iii) thermally and electrically conducting. Polymeric materials used for adhesive applications in electronic packaging are generally of two types: thermoset and thermoplastic. Thermoset materials become cross-linked and harder when subjected to elevated temperatures, whereas thermoplastic materials become softer at elevated temperatures. Typical polymers used in microelectronics are epoxies, silicones, acrylics, polyimides, cyanate esters, and various thermoplastic materials. The particle fillers include inorganic materials such as silica, alumina, aluminum nitride, diamond, and carbon nanotubes; metals such as Ag, Au, Cu, Ni, and Al; and metal-coated polymer spheres to provide some elasticity in special z-axis interconnection applications.

Polymer adhesives can be dispensed from tubes, screen-printed, or placed on substrates in a tape format (generally that is pressure-sensitive). Thermoset materials (e.g., epoxies, polyimides, and cyanate esters) require exposure to elevated temperatures to cure or induce cross-linking chemical reactions between the monomers. Depending on the adhesive chemistry, varying time periods are required to cure the polymeric system; cure schedules for epoxy formulations range from “snap cures” that require only a few minutes at 150–175°C to the more standard cure schedule of 0.5–2 h at 150–175°C; higher temperatures (e.g., 275°C) are required to cure polyimides. When used in hermetic packages, the materials are subjected to a bakeout (typically done in an inert environment such as flowing dry nitrogen or sometimes under vacuum) to outgas volatile components, and then the packages are sealed in dry nitrogen. To ensure a good interface between the adhesive and die or substrates, cleaning of the components often is required before assembly, and, in most cases, some chemical additives are present in the polymer formulation to improve the interface adhesion. Voids, especially at the various interfaces, are to be avoided, so volatile solvents generally are not used in the current generation of microelectronic adhesive formulations.

Thermoplastic materials include amorphous polymers (e.g., sulfone-based polymers, imide-based polymers, and polyarylates) and crystalline polymers (e.g., ketone-based polymers and polyphenylene sulfide). These materials do not require a cure and are processed by raising the temperature above a particular value at which the material becomes soft; this temperature is defined as the glass transition temperature, $T_g$. During the attachment procedure, the temperature is raised above $T_g$, therefore, rather high $T_g$'s are required in order for the adhesive joint to survive high-temperature exposure during subsequent processing. Despite simpler processing steps and the potential for rework, it should be noted that thermoplastic materials generally do not have mechanical shear strengths as high as those for thermoset materials.

<table>
<thead>
<tr>
<th>Package type</th>
<th>General steps</th>
<th>Plastic lead frame</th>
<th>Plastic ball and grid array</th>
<th>Hermetic</th>
<th>Flip chip</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inspection</td>
<td>Inspection</td>
<td>Wafer sorting</td>
<td>Wafer sorting</td>
<td>Wafer sorting</td>
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<tr>
<td>Wafer preparation</td>
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<td>Polymer adhesive</td>
<td>Wafer bumping</td>
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<td>Wire bonding</td>
<td>Wire bonding</td>
<td>Alignment</td>
<td>Reflow</td>
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<tr>
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<td>Encapsulate</td>
<td>Optical</td>
<td>Optical</td>
<td>Acoustic</td>
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<td>Packaging</td>
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<td>Encapsulate</td>
<td>Lid seal</td>
<td>Encapsulate with glob top</td>
<td>Acoustic</td>
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<tr>
<td></td>
<td>(mold compound)</td>
<td>(mold compound or glob top)</td>
<td>Ball attach and reflow</td>
<td>Leakage test</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. General assembly steps for various package types associated with semiconductor die devices.
Polymers filled with thermally conducting particles are used as thermal interface materials (TIMs) in applications where moderate, but not maximum, heat transport is required. Thermal conduction and the role of phonon transport at solid/solid interfaces are not well understood for TIMs. Comprehensive measurements, along with modeling, have recently been made on electrically insulating TIMs to determine the effect of the bulk thermal conductivity of filler particles, bondline thickness, and the various interfaces (substrate/polymer matrix, polymer matrix/particle, and particle/particle) on the overall thermal conductivity of the TIM. As the bulk conductivity of the filler particle increases, the thermal conductivity of the TIM increases, but the dependence is very nonlinear for high thermally conductive materials (i.e., not much is gained in going from aluminum nitride to diamond fillers). The thermal resistance of the TIM increases linearly with bondline thickness over the range studied (100–300 µm); hence, thinner bondlines are preferred for maximum thermal transport. However, it should be noted that measurements are needed for bondlines <100 µm to assess the overall performance (thermal and mechanical) of thin bondlines. Finally, it has been determined that the substrate/polymer matrix interface is more important than the particle/polymer matrix interface, in agreement with Putnam et al. Various approaches have been investigated to improve the thermal conductivity of polymeric TIMs. Recent investigations have been made by using electrospun fibers that were embedded with different thermally conductive particles, but the resultant TIMs did not have a significantly higher thermal conductivity than conventional materials. A new approach that appears promising involves low-temperature sintering adhesives in which a variety of low-melting-point and high-melting-point alloys were investigated (both Pb-containing and Pb-free). The fluxing and curing reactions occur at ~150°C, with the lowest melting point component at ~180°C, and the fully cured material exhibits a melting point of ~270°C. Because of the metallurgical bonds formed, the thermal conductivity of the TIM was in the range of 20 W/m·K, which is approximately one order of magnitude higher than conventional TIMs. Additionally, these materials appear to have good properties with respect to environment stress tests.

When thermal or electrical conductivity is not required, insulating polymer adhesives are used for bonding surface-mounted components to printed circuit boards, semiconductor die to substrates, substrates to packages, and lids to packages (where hermeticity is not required). The materials used are typically unfilled epoxies, although other polymers are used occasionally. A major application involves the use of adhesives as underfills for flip-chip devices to provide some stress relief of the solder joints during temperature cycling (see Underfill Materials for Flip-Chip Devices below). Another application of polymer adhesives, in particular benzo-cyclobutenes (BCB) and polyimides, is to serve as the dielectric layer/adhesive for redistributing the metal interconnection geometry on die (this application is not discussed in this article).

Electrically conductive adhesives typically have metallic fillers in the polymer matrix and generally are in two categories: isotropic and anisotropic. Isotropic conductive adhesives (ICAs) exhibit electrical conduction in all directions, whereas anisotropic conductive adhesives (ACAs) conduct in only one direction (generally referred to as the z axis); see Fig. 1 for a schematic of the cross-sectional bond. ACAs have a lower filler content than ICAs to minimize any conduction in the XY direction. A limitation of conductive adhesives is that they are not self-aligning (as is the case with solder), so accurate alignment of components is required. Filler materials include metal particles (typically silver), ferromagnetic metal particles (silver-coated nickel), and metal-coated polymeric spheres. The ferromagnetic particles are aligned in the z direction by applying an external magnetic field.

Figure 1. Schematic illustrating the die attachment process using an ACA. (a) ACA applied to substrate. (b) Chip placement onto substrate. (c) Cross-section of ACA bond after cure. (Reproduced with permission from Ref. 6 © 2006, IEEE.)
external magnetic field, as shown schematically in Fig. 2. The use of metal-coated polymer spheres enables height variations in the gap (noncoplanarity of the two surfaces) to be compensated via the elastomeric particle. ACA films are widely used in flat-panel-display applications. The ultimate pitch (spacing) of the interconnect array using ACAs is limited by the size of the metal particle filler. In most cases, the polymer matrix is electrically insulating, but recent investigations have been performed on polymers that are intrinsically conductive, such as polythiophenes and polyanilines. Given sufficient conductivity by the polymers, this approach might enable the metallic filler loading to be reduced dramatically. In addition to the anisotropic adhesive approach for achieving only \( z \)-axis interconnections, gold stud bumps are used with an electrically insulating adhesive (which will be discussed later).

Various factors affect the overall conductivity of filled adhesives: polymer chemistry, the volume fraction of filler, and the filler properties (material type, coatings, particle morphology, and size distribution). The actual formulation chemistry of commercial adhesives is proprietary, and various additives are present at low concentrations to improve the performance of the adhesive. The electrical conductivity of the cured adhesive is generally described by percolation theory, with tunneling processes possibly occurring during the early stages of the cure. The particle fraction at which conductance first occurs is the percolation threshold, and it depends on the morphology and size of the metallic fillers. For isotropic conductive adhesives using spherical particles, the percolation threshold is 15–30% based on volume fraction; the corresponding mass loading of silver flake in commercial adhesives is ~80% by mass. For filler particles having a higher aspect ratio (e.g., flake geometry) or a mixture of large and small particles, the percolation threshold is somewhat lower.

Silver is the most common filler because its oxide is electrically conducting. In contrast, copper and nickel fillers are not as commonly used because insulating oxides readily form on the particles. Obviously, gold and palladium do not oxidize, but they are expensive. Various morphologies of silver fillers have been investigated over the years, but the most commonly used geometry is that of a flake. Recently, fillers consisting of a mixture of micrometer-sized particles and nanoparticles have shown improved performance. See Fig. 3 for a schematic of the packing of large and small particles, and see Fig. 4 for scanning electron micrographs of the surface morphology. Jeong et al. investigated an epoxy formulation that contained a mixture of 5-nm and 3-\( \mu \)m silver particles, with a total silver content of 92 mass %. They found that the optimum content of nanoparticles was 2 mass %. Das et al. investigated particle sizes ranging from 0.080 \( \mu \)m to 15 \( \mu \)m (the relative ratio of nanoparticles to microparticles was not given); the presence of nanoparticles resulted in a reduced sintering temperature relative to adhesives filled only with microparticles. The authors claim bulk resistivity values as low as \( 10^{-5} \ \Omega \cdot \text{cm} \). Another approach achieved very low silver loading (3.6 vol %, 40 mass %) by combining silver nanoparticles (60 nm) with larger polymer latex parti-

![Figure 2. Novel ACA before and after cure. (Adapted with permission from Ref. 7.)](image)

![Figure 3. Schematic of an adhesive bond cross-section illustrating the packing of large and small particles. (a) Schematic diagram of two particles with very different sizes dispersed in liquid media. (b) Schematic illustration of the packing of particles after drying. (Reproduced with permission from Ref. 11 © 2007, IEEE.)](image)
cles (0.1–5 µm). The latter create an excluded volume that decreases the percolation threshold of the silver particles. The nanoparticles are preferentially located in the interstitial areas of the large polymer particles (see Fig. 3). Scanning electron micrographs of the surface of conductive adhesives filled with nano/micro silver particles are shown in Fig. 4. By using silver particles <100 nm, the sintering temperature is reduced to 250°C, which is compatible with many polymers. The use of spherical nanoparticles by themselves does not lower the percolation threshold; consequently, the particle loading remains high.

Although Ag-filled conductive adhesives have been investigated for many years, the mechanism that leads to conductance in the cured material is not fully understood. Shrinkage of the polymer upon curing has been proposed as facilitating conductance, although it is not clear whether sufficient stress is generated to cause better particle–particle and particle–substrate contact. However, it is clear that the electrically insulating lubricant layer on the Ag filler particles must be removed to form a conductive network of particles. Lubricants and surfactants, such as stearic acid, are used in the mechanical milling of micrometer-sized silver flakes to minimize agglomeration and also to help disperse the flakes in the polymer formulation. Before the thermal cure, the Ag-filled adhesive has a very high electrical resistivity, on the order of 10⁶ Ω·cm, which decreases dramatically upon cure to values that approach 10⁻⁴ Ω·cm (for comparison, the resistivity of eutectic tin–lead solder is 1.5 × 10⁻⁵ Ω·cm).

Early hypotheses proposed that the lubricant layer vaporized during the cure, but this is unlikely because of the low vapor pressure of typical lubricants/surfactants. Investigations of the relationship between the flame surface chemistry and the evolution of electrical conductivity were made by using simultaneous measurements of electrical resistivity and Raman scattering. At room temperature in the high resistivity state, the Raman spectrum of the uncured adhesive exhibited spectral bands that were identified with a molecular species bound to the Ag surface via the carboxylate functionality of the lubricant adsorbate (stearic acid). During cure, the Raman data showed a partial decomposition of the carboxylate species and the formation of an amorphous carbon layer at the Ag surface; the development of high conductivity was correlated with the formation of the amorphous carbon layer.

As an alternative to using ACAs for z-axis interconnections, gold ball bonds are made on the substrate or die pads, truncated, and then coined (flattened), as shown in Fig. 5. The advantages of this ball-bumping process are that no expensive masks or chemical processing equipment are required, the assembly is straightforward, and, in contrast to using ACAs, the interconnects can carry higher current. The yields and reliability are high because the ball-bonding process is the same as the initial step in producing wire bonds. These gold ball bonds are coined to form stud bumps, which are an alternative to using ACAs for z-axis interconnections.

Figure 4. SEM micrographs for the nano/micro-filled silver-based conductive adhesives. (A) Un-sintered at 200°C. (B) Sintered at 275 ± 10°C. (Reproduced with permission from Ref. 8 © 2007, IEEE.)

Figure 5. Image of gold ball bonds that are coined to form stud bumps, which are an alternative to using ACAs for z-axis interconnections. (Reproduced with permission from Ref. 17 © 1997, IEEE.)
stud bumps then are used with an insulating adhesive to bond the die and substrate under heat and pressure. The interconnect density (or pitch) is limited to that in which wire-bonding equipment can effectively bond gold wire to the metal pads. Depending on the pad metallization, intermetallics may form with gold and result in reliability problems. To avoid these problems, either a barrier metal layer can be deposited on the pad metallization or different metals and alloys can be used instead of gold wire.

**UNDERFILL MATERIALS FOR FLIP-CHIP DEVICES**

In the past decade, there has been significant growth in the research and development efforts devoted to flip-chip technology as a result of new requirements for package density, performance, and interconnection. A flip-chip device is defined as a die/chip mounted on a substrate by using various interconnection materials such as solder bumps, wire/stud bump interconnects, and ICAs/ACAs.

Underfill materials are primarily used to improve the reliability of the flip-chip solder interconnects. These materials fill the gap between the chip and substrate and surround the solder joints, thereby reducing any thermal stress that may be induced on the solder joint as, for example, a result of thermal cycling. The effect of die size in finite element modeling of the solder fatigue life often is expressed by the distance from the center of the chip to the corner-most solder bump; this is defined as the distance to the neutral point (DNP). As a rough rule, when the DNP is >7 mm (die size exceeds 10 × 10 mm), unfilled devices fail after a few hundred thermal cycles; consequently, underfills are used to minimize the thermal stress and thereby increase the reliability. Underfill materials generally consist of organic polymeric resins filled with inorganic particles and exhibit a high modulus after cure. Fillers are primarily used to reduce the CTE of the underfill to help in matching the CTE of the silicon chip and solder bumps. There are two general types of underflow materials: capillary flow and no-flow; these are discussed below.

**Capillary Flow Underfills**

Underfill materials that are deposited after flip-chip assembly must flow through the gap between the chip and substrate. The gap height typically ranges from 30 μm to 200 μm, and the underfill material flows via capillary forces (i.e., it is wicked) through the gap and around the solder bumps. The flow characteristics of underfills have been investigated, and a validated model was developed. The die size, solder bump pitch, gap height, presence of flux residue, and substrate wettability all affect underfill flow. The presence of flow voids (often resulting from flux residue and nonoptimized processing conditions) can lead to solder fatigue or solder bump bridging in flip-chip packages.

In traditional underfill applications, cleanable flux processes are designed to leave very little (if any) flux residue behind because the remnants have the potential to compromise the electrical interface. In some applications, however, an “effective” no-clean flux is used. No-clean flux is meant to leave a very small amount of flux residue after reflow. The residue resulting from the use of no-clean fluxes should be compatible with the underfill used for the package and should not impact the underfill capillary flow. Figure 6 shows a scanning acoustic microscope image of a package assembled with different no-clean fluxes. Figure 6a is assembled with an

![Figure 6. Scanning acoustic microscope image of a package assembled with an effective (a) and ineffective (b) no-clean flux. Panel b shows voids. (Reproduced with permission from Ref. 20 © 2006, IEEE.)](image-url)
effective no-clean flux, which shows no voids caused by flux residue, whereas Fig. 6b is assembled with an “ineffective” no-clean flux, which shows significant voids caused by flux residue.

**No-Flow Underfills**

As discussed above, capillary flow of the underfill is typically slow and can result in voids and inhomogeneities in the underfill, a particular problem with larger die and small gap heights. To overcome these limitations, no-flow underfill materials have been developed that have been regarded as a next-generation flip-chip technology because of its advantages. These advantages include the ability to assemble chips having fine-pitch, high-density arrays onto substrates with a narrow gap between the chip and substrate; the assembly steps are greatly simplified.21

Use of no-flow underfills eliminates the slow capillary flow step, and the underfill polymer can be cured during the solder reflow process. Because solder joints are formed after the underfill is applied, no-flow underfills need to possess self-fluxing capability. Organic carboxylic acids or anhydrides are typically used as fluxing agents to remove the metal oxide on the solder and substrate bond pad surface, which then allows the solder to spread during reflow and form metallurgical joints with the substrate.21 Cyanate ester-based materials offer several advantages (i.e., the cured polymer has a high $T_g$, high modulus, and low CTE) compared to traditional systems but lack the suitable fluxing chemistry required for no-flow underfill applications. As such, novel fluxing agents are needed that are solids at room temperature but rapidly melt and cause the solder balls to spread on the substrate at high temperature, as shown in Fig. 7. A shorter required fluxing time correlates with a more effective fluxing capability, and rosin gum is one of the most commonly used fluxing agents.

One of the problems with no-flow underfills using conventional fillers is that the filler particles may become trapped at the solder-pad interface and interfere with the electrical connection. To overcome this problem, nanocomposite no-flow underfill adhesives (e.g., nanosilica fillers mixed with self-fluxing no-flow underfill polymers) have been developed.22 Nanosilica particles (120 nm) at 50 mass % were demonstrated to not interfere with the solder-pad bonding process and provided improved reliability. The presence of nanosilica filler enables the tailoring of key properties of the polymer formulation, including CTE, modulus, and viscosity, without dramatically affecting the curing behavior.22,23

**Disadvantages/Limitations of Underfill Materials**

As is the case with most polymeric adhesives, although there are many advantages to using underfill materials, there also are some disadvantages and/or limitations to their usage. Moisture in the underfill material may increase the dielectric constant, chemically attack bonds between the filler and the epoxy, or hydrolyze the epoxy matrix, thereby reducing the cohesive fracture strength and causing cracking and/or delamination as a result.24 Excess flux residue can cause underfill voids and also can cause delamination after underfill curing because of the lack of adhesion at the die/underfill or the underfill/substrate interfaces. Fluxing agents often have adverse effects on underfill performance. Traditional fluxing agents have the tendency to react with certain resins to generate volatile compounds at high temperatures, such as those required for lead-free solder reflow, and this can cause massive voiding. Fluxing agents also can act as plasticizers and result in a lower $T_g$ of the cured underfill resin. In addition, the acidity of fluxing agents also could lead to shortened work life of the formulation. Fluxing agent residue can cause defects in solder connections depending on the quantity of filler, which often results in lower reliability of the interconnections. A significant challenge presented by nanosilica technology is the viscosity increase in the material that is observed as the incorporated particles become smaller. No-flow underfill adhesives often are dispensed via syringe, and high-viscosity materials may not be amenable to this process.

**ENCAPSULANTS AND MOLDING COMPOUNDS**

Polymer encapsulants are materials that protect semiconductor devices and interconnects (e.g., wire bonding and solder bumps) from environmental factors such as moisture, corrosion-inducing contaminants, and ultraviolet radiation. They also protect the parts from mechanically induced damage such as bending, vibration, and material fatigue caused by thermal shock and...
Polymer-encapsulated microelectronics offer many advantages over hermetic packages in the areas of size, weight, cost, performance, and availability. As a result of these factors, plastic packaging accounts for >97% of the worldwide commercial chip-packaging market. The protocols associated with encapsulation, therefore, must address the operational requirements of assembly steps such as wire bonding and die attachment, in addition to those related to the formation of a highly protective polymer shell and reliable performance.

The various techniques of polymer encapsulation involve the infusion of a low-viscosity liquid resin mixture around a semiconductor device or assembly with a subsequent curing step that creates a mechanically and chemically protective polymer shell over the electrical components. For most commercial packaging applications, “transfer mold” encapsulation is preferred because of the high-volume capability of this approach.25,26 However, “liquid” encapsulation, which includes glob top, cavity filling, and dam and filling, is used for rapid, low-volume, and low-cost packaging applications.

The remainder of this section provides an overview of the two polymer encapsulation techniques, addressing topics such as benefits, risks, and challenges associated with polymer encapsulants. In assessing the reliability of these polymeric packages, a series of testing protocols that have been adopted by the electronics industry will be addressed in the next major section.27

Transfer Molding: Processing, Formulation, and Materials

Transfer molding is the most commonly used manufacturing process for the polymer packaging of electronic integrated circuit (IC) devices. It is a high-volume, reproducible process that is analogous to compression molding, where preforms of a molding compound, typically epoxy-based, are preheated and then transferred into the hot mold cavities over and around the substrates and devices. This approach is used to encapsulate both lead-frame and plastic ball-grid array (PBGA) packages. As illustrated in Fig. 8, the process involves heating, liquefaction, and transfer of powdered or pelletized mold compounds to a press, which produces a low-viscosity material that readily flows into the mold cavity and encapsulates the device.28 The cure reaction begins shortly after the transfer into the mold cavity, and the viscosity of the mold compound increases until the resin is hardened. Process parameters (e.g., transfer rate, temperature, and pressure) are optimized to ensure the complete fill of the mold cavity and the elimination of voids in the mold compound and at interfaces. Although not shown in Fig. 8, a series of runners and gates typically is designed to ensure that the flow of the molten resin into the mold cavity minimizes the formation of voids and prevents wire sweep that could result in electrical shorts inside the package.

An encapsulant formulation must address factors that are associated with both device assembly and subsequent operation. The components of a transfer mold mixture and their respective influence on encapsulation properties are shown in Table 2.25 As noted in the table, some of the key properties of the cured encapsulant are attributable to the filler particles, which are typically silica or alumina. The choice of filler material is based on the need to influence or control a wide range of parameters, including cost, thermal expansion, moisture absorption, thermal conductivity, electrical resistance, strength, and impact resistance.

Epoxy resins are the dominant encapsulant material because of their inherently low viscosity, fast cure, low shrinkage during cure, excellent adhesion to the other device components, and good mechanical stability. They are manufactured with minimal levels of ionic contaminants and do not produce volatile byproducts during the cure reactions. During normal usage conditions, these cured thermoset resins resist hydrolysis, thermal degradation, and outgassing. Novolac resins are a commonly used monomer, and some resins are reacted with epichlorohydrin to produce epoxy novolacs. The novolac/epoxy resin ratio is usually near stoichiometric in the formulations. The preferred resins have the lowest possible molecular weight and narrowest molecular-weight distributions but still have at least two reactive groups per molecule.

In addition to epoxy-based transfer mold compounds, a number of alternative molding systems are used for packaging.25,26,29 Polyimides possess excellent thermal stability. They, along with BCB, form excellent interlayer dielectric insulators and also provide excellent step coverage, which is important in fabrication of multilayer IC structures. They require wet processes such as spraying or spin-coating and can be imaged by conventional
photolithography and etch processes. Polyurethanes are tough, elastomeric polymers made by reacting isocyanate
pendent molecules with polyols. The reaction is rapid,
but gaseous byproducts such as carbon dioxide can lead
to production of voids within the encapsulant. Silicones
were one of the first polymeric encapsulants used, and
they still find application where their low modulus mini-
mizes strain on the components. For most silicones, curing
occurs via a condensation reaction, where moisture-initi-
ated, catalyst-assisted cure chemistry generates water or
alcohol byproducts that can cause outgassing and voids.
Several thermoplastics, particularly poly(phenylene
sulfide) and liquid crystal polyesters, have attractive
properties for packaging. Being thermoplastic, molding
scrap from runners and culls is recyclable and can be
used again without refrigeration for storage. However,
the relatively high molecular weight of thermoplastic
materials (compared with uncured epoxy resins), along
with the higher temperatures and pressures associated
with injection molding, has always led to excessive wire
sweep in the past. Newer, low-molecular-weight liquid
crystal polyesters may allow injection molding of some
packages, particularly devices with robust wiring.

**Liquid Encapsulation: Processing, Formulation, and
Materials**

Liquid encapsulation is a relatively simple process in
which a dam, made of a viscous material, is dispensed
on the outside perimeter of the wire-bond pads. Its
role is to contain another material known as the filling
material. The latter is dispensed in a second step, after
the dam, and encapsulates the device and wires. Once
cured, the solidified plastic body provides protection
to the device and circuitry, as well as strength to the
package. One form of liquid encapsulation is referred
to as “glob top,” where the encapsulant is dispensed on
top of the semiconductor assembly and then solidified
by heat or radiation. Typically, this approach is utilized
in applications that have lower requirements regarding
visual appearance and reliability.

Liquid dispensing also is appropriate in some high-end
applications. Some designs for ball-grid array packages
mount the device into a cavity, which could not be filled
readily by transfer molding but does effectively contain
a dispensed liquid. Automated equipment controls the
dispensing by using syringes as the formulation reservoir
and hypodermic needles to deliver it to the proper posi-
tion (see Fig. 9). This equipment must visually identify
the application locations and paths, precisely position the
dispensing syringe needle in three dimensions, deliver a
precisely measured amount of liquid (often along a path),
and prevent drips into unwanted areas. Furthermore, the
equipment often must carefully preheat the compound
in the syringe and preheat the assembly region (often
in all three dimensions). This process involves rastering
the syringe and/or board assembly in a thermally con-
trolled oven while microdispensing the liquid, all under
sophisticated computer controls. Typically, the liquid
encapsulants are expensive and used only when transfer
molding is not a viable option. Furthermore, dispensing
is rather slow—virtually, one package at a time. Conse-
quentially, liquid processing is a good option for prototype
parts because machined molds are not required.

Similar to transfer mold compounds, liquid encapsu-
lant mixtures are a combination of polymer precursors
and fillers. In these epoxy systems, a hardener and epoxy
resin react at elevated temperatures to produce long
crosslink chains that are solid, cannot melt, and provide
good protection against most environmental damage.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Filler (&gt;70%)</th>
<th>Epoxy (~10%) and Hardener (~7%)</th>
<th>Elastomer (&lt;5%)</th>
<th>Catalysts</th>
<th>Flame Retardants and Scavengers</th>
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<td>+</td>
<td>+</td>
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</tr>
<tr>
<td>$T_g$</td>
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<td>0</td>
<td>-</td>
<td>-</td>
<td>0</td>
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<tr>
<td>Strength</td>
<td>0</td>
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<td>-</td>
<td>-</td>
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<tr>
<td>Moisture absorption</td>
<td>++</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Thermal conductivity</td>
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<tr>
<td>Electrical reliability</td>
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<td>0</td>
<td>0</td>
<td>+</td>
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</tbody>
</table>

+, positive influence; +++), strongest positive influence; −, unfavorable; 0, either favorable or unfavorable. Note: This table is a quick overview that shows the composition of typical EMCs by major components and the effect that each of these components has on the key performance properties (molding and cured properties).
Fillers, typically silica, are added to reduce the CTE. Surfactants and flow agents also may be added to assist in dispersing the encapsulant over the device.

Conformal Coatings

Conformal coatings encapsulate circuit boards and their electronic components in order to minimize the permeation of moisture and prevent the ingress of fungus, particles (dust), and other environmental contaminants. Parylene, a poly(para-xylylene) used for conformal coating applications, was first developed by Union Carbide Corporation. The deposition process is done at below ambient pressure and uses a thermal reactor to first vaporize and pyrolyze the di-para-xylylene and then polymerize the dimer into polymer at room temperature. This room-temperature deposition is a very attractive encapsulation process, especially for temperature-sensitive, low-T_g substrate materials. There are no solvents, catalysts, or other impurities in the final film. Parylene deposition provides excellent step coverage with conformal film thicknesses ranging from 2 µm to 50 µm. Because it is a room-temperature and a gas-to-solid deposition process, encapsulated electronic parts experience minimal stress. The deposited film is very uniform without the formation of pinholes or micro-cracks, resulting in a low permeation rate of water vapor. In addition, these films typically have excellent electrical properties and excellent chemical resistance. Regarding limitations of parylene, the deposition process requires a vacuum environment to ensure both uniform and effective coatings. Additionally, the deposition is typically not confined to a single component or location; rather, multi-components of varying functionality are simultaneously coated with the parylene film. Finally, because the coating is chemically impervious to room-temperature organic solvents, rework of a coated device is problematic and requires either mechanical or thermal treatment for device removal. In a recent packaging application, a parylene coating was used as the sole package protection for a microelectromechanical system (MEMS) flip-chip assembly. However, the high cost of the starting dimer and the deposition equipment prohibits its wide use in consumer electronic applications.

Emerging Applications

In addition to traditional semiconductor devices, chip-level packaging of MEMS occasionally involves the use of encapsulants to minimize the impact of environmental factors on the micrometer-scaled movable elements. In most applications, polymer encapsulation of MEMS devices protects movable fragile parts during wafer handling, wafer dicing, or plastic molding. Encapsulation provides a more robust device for transportation and handling without altering the performance of the devices. Several MEMS packaging techniques have been reported involving wafer-to-wafer bonding and thin-film sacrificial-based sealing methods. As shown in Fig. 10,
a sacrificial polymer placeholder is first patterned on top of the MEMS component of interest, followed by overcoating with a low-dielectric-constant polymer overcoat. The sacrificial polymer decomposes at elevated temperatures, and the volatile products from the sacrificial material permeate through the overcoat polymer, leaving an embedded air cavity around the MEMS structure. Thus, the device is released from the sacrificial polymeric material and housed in a protective overcoat. The protected MEMS device can then be handled and packaged like an IC.

Another emerging application area is the use of polymer adhesives in optoelectronic devices. Over the past decade, the introduction of miniaturized optical components and interconnects within microelectronic devices has led to the development of new processes for polymer-based packaging (see Fig. 11). Although most development efforts have focused on the fabrication of polymer-based optical components, packaging issues associated with interconnect alignment and encapsulation also are critical to device performance. For the latter, conventional electronics packaging technologies (e.g., automatic pick-and-place and transfer molding) are being used in the mass production of optoelectronic devices that include optical transceivers.

**RELIABILITY ISSUES, TESTING, AND CHARACTERIZATION**

A reliable microelectronics package performs its electronic function properly throughout its expected lifetime in its normal ambient environment. Failures in microelectronic packages containing polymeric materials depend on the properties of the organic materials and interfaces, along with factors associated with the assembly process. As a result of device complexity and potentially harsh operating environments, the electrical and mechanical integrity of microelectronic packages becomes critical. In an attempt to standardize the evaluation of an encapsulated device under realistic environments, a number of accelerated testing protocols have been developed to assess the effects of stress factors on the electrical performance of the device and evaluate the reliability. These tests include burn-in or high-temperature soak (typically 500 h at 125°C), thermal cycling (typically −65°C to +125°C), 85/85 testing (85°C/85% relative humidity), and the highly accelerated stress test (HAST) (typically 145°C/85% relative humidity at a pressure of two atmospheres). In many cases, these tests are conducted with the devices under bias (applied voltage). It should be noted that predicted lifetimes based on accelerated tests should be used with caution because there is the possibility that new failure mechanisms may occur with harsher test conditions. In addition to materials properties and process parameters, there are a variety of environmental factors that may affect the performance and reliability of a packaged device. These include moisture, heat, thermal cycling, chemical contaminants, and mechanical stress. Typical reliability issues are listed below:

1. **Moisture-Induced Assembly Failure**
   Polymers absorb moisture and are not impermeable to moisture. Moisture diffusing through the polymer can transport ions to the die surface and other interfaces and possibly cause electrical current leakage or corrosion. Furthermore, this moisture can rapidly vaporize during solder reflow at board assembly and result in delamination of interfaces; the term “popcorn effect” refers to such an explosive phenomenon. In addition to moisture absorption and process-induced contamination, some polymer formulation constituents themselves can supply harmful chemical species.

   For encapsulated devices, test protocols were developed by the Joint Electron Device Engineering Council (JEDEC) and employ severe conditions of temperature, humidity, and bias that accelerate the penetration of moisture through the external protective material (encapsulant or seal) or along the interface between the external protective material and the metallic conductors that pass through it. The test conditions are intended to activate the same failure mechanisms as the 85/85 Steady-State Humidity Life Test (JEDEC Standard No. 22-A101). This test is used to identify failure mechanisms internal to the package and is destructive. Excellent demonstrations of using HAST on encapsulated devices have been performed by Emerson et al., which involved the use of Sandia assembly test chips (ACT01 and ACT04) in evaluating the effects of both moisture penetration and mechanical stress within mold transfer and liquid encapsulants.
Stress

Shrinkage of the polymer during cure as well as thermal expansion mismatches with the die, substrate, or lead frame create mechanical stresses. The greatest source of stress at the die/substrate interface is the result of a thermal expansion mismatch between the components. The silicon die has a CTE of ~2.3 ppm/K, while unfilled polymers typically have values of 10–25 ppm/K. The value for lead–tin solder is 21 ppm/K, the lead frame metals have values of 4–20 ppm/K, and printed circuit boards have values near 15 ppm/K. For encapsulated devices, the polymer generally transfers the stresses from the low-expansion silicon chip to the high-expansion printed circuit board. To compensate for stress within a device, a design engineer must account for all interfaces and structures within the electronic package. Finite element calculations are used extensively to model and optimize designs. Moiré fringe analysis and stress sensors provide direct stress data. Manufacturers test real package electrical performance after extensive cold–hot temperature cycles.

Intermetallic Bond Failure

Although most semiconductor die have aluminum metal conductor traces, other metallizations also can be present. Gold wire bonds, various types of solder, and conductive adhesives are used as interconnections between the die and substrate. In the case of gold–aluminum bonds, the nature of the interconnect can lead to a classic failure mechanism at the metallic interface, which results from the formation of a brittle gold–aluminum phase. This phase depletes the surrounding region of metal, thereby creating voids that lead to bond weakening.

Although this problem can occur in bare-wired devices, it is accelerated in the presence of the molding compound in encapsulated devices. This effect is attributable to the release of ions from the brominated resins used as flame retardants in the encapsulant. Encapsulant formulators mitigate these effects by minimizing the bromine resin levels, adding insoluble salts called scavengers or getters to chemically or physically trap the bromine-containing species and using polymeric systems with high $T_g$ to retard molecular diffusion. Regarding the latter, biphenyl resin chemistry is particularly prone to problems because of its low $T_g$. The addition of antimony oxides enables the concentration of brominated resin to be reduced significantly because there is a synergistic flame-retarding effect when compounds of antimony and bromine are both present.

Corrosion

Corrosion refers to the degradation of the semiconductor metal traces on or within the die surface. This corrosion involves water and usually an ionic species that catalyzes the metal oxidation to a nonconductor. For epoxy molding compounds, the ionic species of greatest concern is the chloride ion, which is always present as an epoxy resin contaminant because of chemical reactions involving epichlorohydrin. Commercial polymer resins have tolerably low chloride levels, but other ions can come from the environment, typically from solder fluxes and other processing chemicals. These ions can quickly enter the package along any delamination pathway. Scavenger ions or getters help immobilize these corrosive species. Accelerated testing is used to assess corrosion resistance, and most tests use heat and moisture applied to devices that are operating at direct current voltages to encourage ion migration. The most severe is the HAST, which usually operates at a couple of atmospheres of unsaturated steam pressure at the corresponding temperature (typically 145°C). Devices that survive over a couple of hundred hours under such corrosion stress generally provide excellent real-world corrosion resistance performance.

Additional Challenges

A major challenge for the over-mold process used with new ultra-fine-pitch PBGA packages (encapsulated according to the previously explained injection processes) is the wire-sweep criterion. Wire sweep has always been one of the most important parameters in process optimization and has become increasingly important as the wire spacing is reduced with finer device pad pitches (see Fig. 12). Current studies on wire-sweep reduction have been focusing on the wire length or molding control, along with various methods of increasing wire-bond stiffness. Latter approaches involve changing the wire material type and alloy/dopant concentration to increase wire strength. Other approaches provide guidance in modifying the mold encapsulation formula or flow characteristics through thermomechanical simulation and modeling.

Figure 12. Wire sweep after transfer molding for wire length 4.57 mm by using a 50-µm pitch test chip. (Reproduced with permission from Ref. 41 © 2005, Elsevier.)
SUMMARY

An overview has been provided of the general types of materials used to formulate polymer adhesives for die attachment, underfills, and encapsulants, along with their properties. Typical processing steps were presented for various applications, and the advantages and disadvantages of polymer adhesives were discussed in relation to applications, processing, performance, and reliability. Recent improvements in the materials as a result of the incorporation of nanoparticles in the polymer formulation have been highlighted. Polymeric materials continue to offer advantages over inorganic materials for particular applications, and they provide a more environmentally friendly alternative to lead-based materials for electrical interconnections.

REFERENCES

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References: