Chapter

9

Adhesives, Underfills, and Coatings in Electronics Assemblies

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9.1 Introduction

Adhesives play an important role in the manufacturing of high-density surface mount assemblies. Adhesives are used to secure components during processing (chip bonders or surface mount adhesives), form an electrical or thermal interconnection (conductive), increase reliability (flip-chip and CSP underfill), and even protect the entire device once assembly is completed (conformal coating). This chapter will discuss some of the important physical properties related to these polymeric materials such as rheology, glass transition temperature (T_g) , coefficient of thermal expansion (CTE), and methods of curing. With respect to the various applications, a majority of the discussion will focus on the surface mount adhesives, but other applications will also be discussed.

When choosing an adhesive system to use within an application, several factors need to be considered. First are the properties of the uncured material, such as shelf life, pot life, and rheology. Second, the method by which the adhesive is processed, dispensed, and applied relates back to the rheology, and the method of curing must also be considered (e.g., heat or ultraviolet radiation). Finally, the properties of the final cured material are significant. Typically, one starts with the final item and works backward, but all three factors play an important role in selecting the correct material for an application.

9.2 Chapter 9

This chapter will first discuss these properties in detail to provide a better understanding of adhesives. Then, different applications using adhesive materials will be reviewed. Knowledge of these properties and an understanding of the applications will aid design and production engineers in selecting the right material for a particular product.

9.2 Rheology

Rheology is an often misunderstood but important property for adhesives used in electronics assembly. Rheology is the science of the deformation and flow of matter. Simply, how does matter react when you push it? Does it flow easily or with difficulty, or does it not flow at all but bounce back? The whole concept of rheology, flow behavior, and the terms involved can be summarized in Fig. 9.1.

Consider an amount of liquid of thickness *x* between two parallel plates. (For clarity, Fig. 9.1 shows this as a two-dimensional area.) The bottom plate is kept stationary while the top plate is forced to move. The liquid can be considered to be made up of layers that move relative to each other. This relative movement of layers is known as *shearing*. To characterize this process, only three parameters can be measured.

- 1. *Dimensions of the material.* This is trivial and is governed by the geometry of the particular system. Units are meters.
- 2. *Force appli*ed*.* This is how hard the upper plate is pushed. Units are newtons (N). The force required to move the upper plate is obviously related to the area of the plate. It is therefore conventional to divide the force by the area to give the *stress,* τ.

$$
Stress = \tau = \frac{Force (N)}{Area (m^{2})}
$$

$$
Units = N \cdot m^{-2} = Pa
$$

3. *Velocity.* This is the speed of the upper plate relative to the lower. Units are meters per second (ms^{-1}) .

The layered structure of the material is analogous to a pack of cards. The thicker the pack, the less each card moves relative to its neighbors for a given movement of the upper plate, and the lower the shearing. Thus, we can define a *shear rate, D* (or $\dot{\gamma}$), as

Shear rate =
$$
D = \frac{\text{Velocity (m \cdot s}^{-1})}{\text{Thickness (m)}}
$$
 Units = s⁻¹

The shear rate is obviously related to the shear stress in some manner. We define the ratio of these two to be the *viscosity*, η.

Viscosity =
$$
\eta = \tau/D
$$
 Units = Pa/s⁻¹ = Pa·s

So, it can be seen that the *viscosity is not a fundamental, measurable property of a material* in the same way that mass is. It is merely the constant of proportionality between shear stress and shear rate.

Some typical viscosities are shown in Table 9.1. Although the formal unit is Pas, it is common to see viscosity represented in mPa, because water has a viscosity of 1 mPa. Note that air has a viscosity of approximately 1/100 of that of water (0.01 mPa) even though it is a gas.

TABLE 9.1 Typical Viscosities

Viscosity/Pa
100,000,000
1,000
100
10
1
0.01
0.001
0.00001

Typical shear rates of some common processes are shown in Table 9.2. Processes that have very small sample thicknesses, such as brushing or rubbing, have extremely high shear rates, up to 10^6 s⁻¹. At the other extreme, sedimentation involves very small relative movement of layers and therefore is still a shearing process, with a typical value of 10^{-6} s⁻¹.

9.2.1 Rheological response and behavior

If a sample is sheared at different shear rates, and the corresponding stress required is measured, the data can be plotted to form a *flow curve* (see Fig. 9.2). This is basically a spectrum that can be used to characterize the flow behavior of a material. The simplest response is termed *Newtonian*. This designates that the shear stress varies linearly with shear rate over the entire range. If the corresponding viscosity is calculated and plotted, the resulting

Process	Shear rate/ s^{-1}	
Sedimentation	$0.000001 - 0.0001$	
Leveling	$0.01 - 0.1$	
Draining	$0.1 - 10$	
Chewing	$1 - 100$	
Brushing/pumping	$1 - 1,000$	
Rubbing	$10,000 - 1,000,000$	
Flow curve		Viscosity curve
З	η	З
D	1. Newtonian 2. Shear thinning	D
	3. Shear thickening	

TABLE 9.2 Typical Shear Rates

Figure 9.2 Simple rheological response.

graph is termed a *viscosity curve*. For Newtonian materials, the viscosity is constant at all shear rates. Examples of Newtonian fluids include water, ethylene glycol, simple oils, Loctite 270, and cyanoacrylate monomers.

3

The majority of fluids are not Newtonian. Most materials require less stress than might be expected at higher shear rates. The viscosity will therefore decrease with increasing shear rate. Such materials are described as being *shear thinning* or *pseudoplastic*. Examples are polymer melts, blood, and solder paste.

A wide variety of molecular arrangements can give rise to shear thinning behavior. Some of these are illustrated in Fig. 9.3. A common example occurs when irregularly shaped particles line up in the direction of the flowing liquid. They present a smaller surface area, there is less viscous drag, and consequently less shear stress is required than might be expected. As soon as the shearing is stopped, Brownian motion ensures that the particles become randomly oriented once again.

Other processes that can lead to shear thinning behavior are also shown in Fig. 9.3. These include stretching of long-chain polymer molecules, deformation of soft pliable particles, and the breaking up of agglomerates (disaggregation). A classic example of a shear thinning fluid is blood. On shearing, the red blood cells deform to thimble shapes. This reduces their diameter and facilitates passage through the smaller blood vessels.

9.2.1.1 Thixotropy. The shear thinning behavior described above is not time dependent. This means that the same viscosity is obtained at a particular

Figure 9.3 Shear thinning behavior of dispersions.

shear rate no matter how long the sample is sheared at this rate. In other words, there is no hysteresis in the viscosity curves for increasing or decreasing shear rates. The situation in which there *is* time dependency is called *thixotropy*. This is illustrated in Fig. 9.4. A material whose viscosity drops with time when held at a constant shear rate is termed thixotropic.

The effect on such a material of cycling the shear rate is shown in Fig. 9.4. Increasing the shear rate (*up curve*) gives rise to the normal shear thinning behavior. However, on subsequently decreasing the shear rate (*down curve*), much less stress is required. The result is a hysteresis or *thixotropic loop* between the two curves. An alternative way of detecting thixotropy is by plotting the viscosity at a constant shear rate as a function of time. A Newtonian or simple shear thinning product will show no change, but a thixotropic material will show a decrease in viscosity with time. Another characteristic of thixotropy is that a sample will regain its original structure when left unsheared for a while.

The standard everyday example of a thixotropic material is tomato ketchup. Ketchup is so thick that it will not pour out of the bottle. However, a few moments of rapid shaking (shearing) will reduce its viscosity sufficiently so that

Figure 9.4 Rheological response of a thixotropic fluid.

it can be poured. It is not simply shear thinning—the longer it is shaken, the lower its viscosity. When the ketchup is left for a few hours, the structure rebuilds. Cough syrup is also thixotropic. When it is formulated in the plant, it is capable of being pumped down pipelines into the bottles. Its thixotropic nature means that it rebuilds its structure in the bottle, thereby preventing sedimentation of the drug from the syrup.

Thixotropy is a very useful property in some adhesive products. Whenever there is a need to pump a high-viscosity paste through a nozzle, thixotropy is of great benefit. For example, epoxy chip bonders have very high viscosities, but they are capable of being pumped through syringe needles of 400 mm or less. They restructure rapidly to prevent slumping of the product on the circuit board. The rheology of SMA is discussed in more detail later (Sec. 9.3).

The most common raw material that imparts thixotropy (a *thixotrope*) is silica. This consists of roughly spherical silicon dioxide particles with diameters in the region of 100 nm. These do not exist individually but form *aggregates*. These in turn clump together to form *agglomerates*. When a dispersion of such agglomerates is left to stand, a three-dimensional network builds up (Fig. 9.5). This gives the product (which is now a *gel*) its structure, very much like reinforcements in concrete. The attractive forces between the agglomerates that drive this structuring can be either hydrogen bonding or Van der Waals' forces.

When the gel is sheared, the network breaks down and flow is facilitated. The cycle is reversible but *time dependent*. The longer the shearing, the more the structure breaks down. At rest the material gradually regains its structure until the entire network is rebuilt.

9.2.2 Measuring rheology

9.2.2.1 Brookfield viscometry. One piece of equipment used to measure viscosity is the Brookfield viscometer, shown schematically in Fig. 9.6. This consists of a disk, or spindle, which is placed in a beaker of the product (400 ml) in a wa-

Figure 9.5 Particle interactions in a silica dispersion.

Figure 9.6 Brookfield viscometer.

ter bath at 25°C. For the majority of instruments, the spindle can rotate at a limited number of defined speeds, and the instrument gives a reading of "viscosity." This is suitable for Newtonian products, but measurement of shear thinning materials presents problems.

This is shown by an examination of Fig. 9.6. The two parameters required for the determination of viscosity are shear stress, τ, and shear rate, *D*. The stress required to keep the spindle rotating at a particular rpm is measured accurately by a torque spring on the instrument. The shear rate, however, is more problematic. Recall that this is defined as the velocity, *v*, divided by the sample thickness, *x*. Neither of these parameters can be accurately measured. A rotating disk has a wide range of velocities, with the outside of the disk moving much faster than the inside. The thickness of a sample that is undergoing shear, x , is undefined. Hence, it is impossible for the shear rate, v/x , to be determined.

This is not a problem for Newtonian liquids, given that the viscosity is independent of the shear rate. In fact, the Brookfield system was developed for the petroleum industry, where many fractions of Newtonian oils of various viscosities need to be examined. However, for shear thinning materials, an undefined shear rate means that *the viscosity cannot be defined*. This is particularly relevant at low shear rates at which the viscosity declines rapidly.

Therefore, any measurement of Brookfield "viscosity" for non-Newtonian fluids is not an absolute value. It is only a relative number, which depends on the *particular spindle* used, the *spindle speed,* and the *time taken*.

9.2.2.2 Cone-and-plate (Haake) rheometry. Many of the problems with Brookfield viscosity, outlined above, can be overcome using a cone-and-plate system. There are a number of manufacturers of such equipment, including TA Instruments, Rheometrics, Bohlin, and Haake. Figure 9.7 shows a schematic diagram of the Haake configuration. The sample (1 to 2 ml) is placed between a cone and a plate that is thermostatically controlled to ± 0.1 °C. The plate is stationary, but the cone (which can be 2 to 5 cm in diameter, with an angle of 1° to

Figure 9.7 Cone-and-plate configuration.

4°) rotates at controlled, programmable rates. As in the case of the Brookfield, the stress required to turn the cone can be measured accurately.

Analysis of the shear rate measurement is shown in Fig. 9.7. As before, the velocity along the cone is greatest at the outside (i.e., $v_2 > v_1$). However, this time, the thickness of the sample is well defined and greater at the outside of the cone than the inside (i.e., $x_2 > x_1$). The angle of the cone is designed such that $v_2/x_2 = v_1/x_1$. In other words, the shear rate is precisely defined and con*stant throughout the whole of the sample.* The viscosity, τ/*D*, can therefore be calculated accurately and can be compared with the results obtained from any system that uses a well defined shear rate.

There are a number of advantages of the cone-and-plate system.

- As outlined above, the shear rate, and therefore the viscosity, are precisely defined.
- A very small sample size is used.
- The temperature of the sample is controlled very precisely, and temperature equilibrium is reached within a matter of minutes.
- A wide range of shear rates is possible—up to 1,000 s^{-1} . The shear rates are programmable, so a continuous "spectrum" can be obtained.
- It is possible with the cone-and-plate system to perform a number of sophisticated measurements, such as yield point determination, pipe flow prediction, and temperature profile.

An example of the importance of using this method with a non-Newtonian fluid is the type of output obtained from the cone-and-plate rheometer of an SMA material in Fig. 9.8. Clearly, this is a dramatically shear thinning product, so the question, "what is the viscosity of this SMA?" is meaningless unless the shear rate is specified. The Brookfield viscometer will give a number, but what does that mean? The shear rates involved in the Brookfield are low (ap-

Figure 9.8 Viscosity curve for a chip bonder.

prox. 1 to 10 s^{-1}). This is where the curve is most steeply sloped and therefore where the greatest error occurs. The Brookfield and cone-and-plate systems are compared in Table 9.3.

Haake cone-and-plate	Brookfield		
\cdot Small sample size (2 ml)	\cdot Large sample size (400 ml)		
\cdot Shear rate defined	\cdot Shear rate undefined.		
• Wide range possible	• Single "point" measurement only		
• Rapid temperature equilibration	• Long temperature equilibration time		
• Yield point	• Cheap (approx. $$3,000$)		
• Temperature profile			
• Pipe flow prediction			
\cdot Expensive (approx. \$40,000)			

TABLE 9.3 Comparison of Brookfield and Cone-and-Plate Systems

9.2.2.3 Yield point measurement. If the viscosity curve of Fig. 9.8 is replotted as a flow curve (stress versus shear rate), the result is Fig. 9.9. Again, it is clearly shear thinning behavior; however, the most obvious feature is the fact that there is a distinct intercept on the y-axis. This intercept is termed the *yield point,* τ_0 , or *yield stress*, and can be defined as the minimum stress required to get the material to flow. It can be thought of as being the material's inertia. It is analogous to the force required to push start a motorbike (low τ_0) compared to a Mercedes car (high τ₀).

Examination of the flow curve of Fig. 9.9 shows that stresses of up to 400 Pa are insufficient to get the sample to move. This is particularly evident when

Figure 9.9 Flow curve (linear) for a typical chip bonder.

the data are replotted on a logarithmic scale (Fig. 9.10). Above 500 to 600 Pa, a low shear rate is achieved. The value of τ_0 is therefore somewhere between 400 and 600 Pa. Calculation of the yield point is not particularly straightforward. Figure 9.9 indicates that the curve is very rapidly changing at low shear rates. Therefore, an intercept cannot be manually read from the graph; some sort of mathematical equation must be used.

There are quite a number of mathematical models describing rheological behavior, the simplest of which is Newtonian $(\tau = \eta D)$. Table 9.4 shows just some examples. The Haake software can be used to fit the data from a flow curve to a model. Often, a number of different models fit the data equally well. So which one should be used? An equation that may be used to calculate the yield point is the *Casson model*. This is partly because it generally fits the data very well, but it is also used for reasons of consistency. The yield points derived from different equations cannot be compared to one another. Therefore, once it

Figure 9.10 Flow curve (logarithmic) for a typical chip bonder.

has been decided to use a particular model to characterize a particular adhesive, it makes sense to continue to use it.

The Casson model predicts that the square root of shear stress varies linearly with the square root of shear rate. When the data of Fig. 9.10 are plotted in this way, the result is Fig. 9.11. A straight line is indeed obtained. The intercept, $\tau_0^{-1/2}$, is just above 20, which gives a yield point of just over 400 Pa as expected.

A word of caution about yield point: the estimated value of τ_0 depends to a large extent on the experimental conditions. When a force is applied against any material, it will eventually flow or deform if the time scale of the experiment is sufficiently long. For example, even though a glacier is a mass of solid ice (which apparently would have a huge yield point), it still flows like a river on geological time scales. Also, it is well known that glass can flow. Windows in very old buildings are significantly thicker at the bottom than at the top, as a result of the "solid" glass flowing merely under the force of gravity. There-

Figure 9.11 Casson plot data.

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9.12 Chapter 9

fore, there is no absolute value of yield point for a material. Its significance lies in comparing values of different materials under the exact same experimental conditions. For an example of how this parameter is useful in predicting material behavior, see Sec. 9.7.1.10.

9.3 Curing of Adhesive Systems

The adhesive and polymer systems discussed in this chapter all start as a liquid or a paste that must be cured to achieve the final properties presented in their respective technical data sheets. Polymers can cure via a number of mechanisms. The most common with regard to the materials used in the assembly of high-density electronic devices are thermal, ultraviolet, room-temperature vulcanization (RTV), and catalyzed (two-part). Also, the path and/or conditions of the cure will affect the final properties of the material.

9.3.1 Thermal cure

Many polymer systems used in high density electronic assemblies are cured via thermal energy. This can include curing during a solder reflow profile (e.g., Loctite 3515), multiple hours in a batch oven (e.g., potting compounds), or seconds on a hotplate or curing station (e.g., QMI SkipCure[™] systems). Also, some curing reactions that will progress at room temperature can be accelerated through the application of thermal energy. The data sheets supplied with these materials often contain the optimal cure profile. Deviations from that profile will result in the final properties of the material being different from those of materials cured at a different temperature. The most notable affect is on the glass transition temperature $(T_g,$ see Sec. 9.4).

The most common heat-cured system are premixed frozen epoxies (e.g., SMAs and underfills). These materials have already begun to cure once they are mixed, but to obtain the optimal properties (and also to achieve reasonable cycle time), heat cure cycles are used to complete the curing. The higher the temperature, the more rapid the cure time, but there is a trade-off. Higher temperatures result in a larger stresses and can quickly evaporate volatile materials, leading to voids. On the other hand, with too low a temperature, you may not achieve sufficient temperature to "kick-off" the reaction, leading to long cycle times and unfavorable final properties.

As an example of a heat-cure system, let's examine a surface mount adhesive (SMA). Most surface mount adhesives are one-part, epoxy-based, heatcure materials that are liquid or paste-like at ambient temperature. However, when exposed to relatively high temperatures, they will harden to a tough glass-like polymer within minutes. The active raw materials in the adhesive (from the point of view of curing) are the epoxy resins (Fig. 9.12) and the curing agent (latent hardener), typically an amine.

The curing agent, or latent hardener, is normally dispersed as a very fine powder into a specific blend of various epoxy resins of different viscosity (chosen to give an overall target viscosity that is suited to the rheological requirements of the particular mode of application). Under ambient temperature

Adhesives, Underfills, and Coatings in Electronics Assemblies 9.13

Bisphenol A Epoxy Resin

conditions, minimal chemical reaction occurs between the curing agent and the epoxy groups. To effect cure, the adhesive must be heated to elevated temperature—i.e., sufficient energy must be applied for the latent hardener to undergo a melting process/phase change such that it can chemically react by a ring-opening of the epoxy as illustrated in Fig. 9.13.

The latent hardener usually possesses more than one active site that is capable of reacting with an epoxy group. A particular epoxy resin chain also usually possesses more than one epoxy group; for example, bisphenol A diglycidyl ether is difunctional. Hence, the adhesive initially consists of a blend of lowviscosity, multifunctional epoxy resins and a dispersed, powdered (of fine particle size) latent hardener. No chemical reaction takes place between the hardener and the epoxy groups under ambient temperature storage conditions. As heat is applied to the adhesive, the hardener starts to dissolve, and the reactive sites on the latent hardener start to chemically react with the epoxy groups on the individual epoxy resin chains such that these chains become increasingly chemically linked. This chain growth process is accompanied by an increase in viscosity.

Once ring-opened by chemical reaction with the hardener, the epoxy group is converted to a new chemical entity known as an alkoxide (-0^-) . Such alkoxide groups are themselves reactive toward other epoxy groups (if heated to sufficiently high temperatures), and this results in the formation of new ether linkages between adjacent polymer chains; i.e., polyetherification. This pro-

Figure 9.13 Ring-opening of epoxy by curing agent RNH₂.

cess produces a highly cross-linked three-dimensional network. As the number of cross-linked chains increases, the viscosity of the adhesive increases until the adhesive eventually becomes a solid polymer when cure is complete. The cure process is illustrated in Fig. 9.14. As the adhesive approaches 100 percent cure, it assumes 100 percent of its cured properties. Incomplete cure will reduce the cured properties of the adhesive.

A typical oven temperature profile for heat curing the epoxy chip bonders is shown in Fig. 9.15. This shows a residence time of 65 sec above 150°C and 130 sec above 125°C with a peak of 155°C. This is more than adequate to fully cure the adhesive. The cure profile can be further optimized to reduce dwell time in the oven and peak temperature by monitoring the effect on bond strength

The degree and rate of cure are most often modeled using differential scanning calorimetry (DSC). An isothermal DSC curve gives a measure of the time required to achieve 100 percent cure when heated at a constant temperature. In this test, the adhesive sample is heated up at a rapid rate $(100\textdegree C/min)$ to a target temperature (e.g., 125°C) and then held at this temperature over a period of several minutes. The degree of conversion of the adhesive from the uncured, liquid state to the cured, solid state can then be expressed as a percentage degree of cure for different time periods of, for example, 3 min, 4 min, 5 min, etc. A typical isothermal DSC curve is shown in Fig. 9.16 as a graph of percent conversion (%) against time (minutes).

The isothermal curve indicates how long the adhesive should be heated at a certain fixed temperature to achieve full cure. The curing oven must be set

Figure 9.14 Illustration of the curing process.

Figure 9.15 Typical oven profile for curing chip bonders.

Figure 9.16 DSC curves illustrating the effect of temperature on degree of cure on an underfill material.

and maintained to give a temperature-time profile that matches or exceeds the heat input required by the adhesive. Although the heater panels of a typical conveyor oven may be set to attain a certain target temperature, the actual temperature that the adhesive experiences will depend on several factors. These include the heat capacity of the PCB and the individual components, the component population density on the PCB surface, and the conveyor belt speed (which depends on the total number of boards to pass through the oven). Consequently, the actual temperature achieved on the board should be measured against time to produce a cure profile. The temperature-time profile of

the cure station should be checked regularly to confirm adequate curing conditions. It is important to measure the temperature of the adhesive at the bondline of a fully populated PCB so as to take into account all thermal transfer effects. The bond-line temperature of components located in regions of the board adjacent to large heat sinks (such as large PLCC components) should be checked to confirm that they are receiving the minimum cure requirement.

DSC can also be run in a dynamic mode to measure changes in the heat flow characteristics of an adhesive when the material is heated under precisely controlled conditions. It measures the heat of reaction generated when a liquid adhesive product is converted to a cured or solid state. In a dynamic DSC run, the temperature of a liquid adhesive sample is ramped up at a rate of (typically) 10° C/minute, from room temperature to 250° C, and the heat of reaction is measured. Three key pieces of information are available from dynamic DSC tests.

- The temperature at which the adhesive starts to undergo cure or polymerize (*Tonset*)
- **•** The temperature at which the maximum rate of reaction is achieved (T_{peak})
- The total amount of heat evolved in the polymerization reaction (∆*H*, in joules per gram of product)

A typical dynamic DSC curve is shown in Fig. 9.17.

The dynamic DSC trace illustrates the reaction profile of a typical surface mount adhesive, and it indicates that a certain minimum threshold temperature is required to initiate the cure mechanism.

VERSION: V5.44

Figure 9.17 Dynamic DSC trace.

Adhesives, Underfills, and Coatings in Electronics Assemblies 9.17

Ideally, the recommended cure conditions should be observed, with the understanding that the true bond-line temperature of the adhesive may not necessarily be identical to the oven set temperature. If a cure profile other than the recommended one is needed, DSC studies can be used to determine the appropriate cure schedule, and the final physical properties of the cured material should be determined with the cure schedule being utilized.

9.3.2 Ultraviolet (UV) curing

An ultraviolet light curing material has a curing mechanism that is initiated with exposure to ultraviolet and/or visible light. Within the electromagnetic spectrum, ultraviolet light refers to the wavelengths in the range of approximately 200 to 400 nm, whereas visible light encompasses those from 400 to 750 nm (Fig. 9.18). The wavelength of light is inversely proportional to energy. Therefore shorter wavelengths (e.g., UV) possess higher energy.

$$
\lambda = h \nu
$$

where $v = \text{frequency}$

```
\lambda = wavelength
```
 $h =$ Planck's constant, 4.135×10^{-15} eV-sec

Polymerization begins when the energy from light of a specific wavelength contacts the photointiators present in the resin. The free radicals that form as a result initiate polymerization reactions between the monomers of the resin leading to varying degrees of cross-linked polymer chains.

The cure begins at the surface and continues as far as the wavelengths can penetrate the material. Curing starts instantly and can occur over a time span as short as 1 or 2 sec, depending on the intensity of light and volume of material. The chemical type of these adhesives includes acrylates, modified acrylates, acrylated urethanes, modified acrylic esters, epoxies (cationic), plus many others.

Figure 9.18 The electromagnetic spectrum.

9.18 Chapter 9

Two important process demands that must be addressed when using a UV cure material are depth of cure and surface cure. When a deeper cure of the UV material is needed, high-intensity light ranging between 300 to 400 nm is required. The longer wavelengths are able to penetrate father into the material, yielding a higher cure depth. It is also important to note that, if the UV material is colored, this will significantly inhibit the depth of cure because of a boundary layer of dark, cured material forming on the surface that blocks any further light penetration.

On the other hand, if a hard, tack-free surface is required, it is necessary to expose the material to high-intensity light in the wave bands below 300 nm. The shorter wavelengths will provide the energy needed to polymerize the surface of the material.

When using a UV cure material, it is important to choose a UV curing system that is capable of delivering both the proper intensity and wavelength needed to cure the material in question (for examples of UV curing systems, see Fig. 9.19). Most UV curing materials cure on the order of seconds at an intensity of in the range of milliwatts per square centimeter (given a thickness on the order of 0.1 mm) *at the photoinitiator wavelength*. Specifications for a UV curing system may list an intensity on the order of hundreds of watts per square centimeter. At first, this appears to be more than sufficient—several magnitudes above what is needed. This output is measured over the entire spectral output of the bulb. Therefore, before choosing a UV curing oven, it is important to know the spectral output (what wavelengths are emitted by the bulb) and the intensities at the wavelengths of choice.

One common observation with certain UV-cured materials is that the surface may be tacky to the touch after irradiation with UV light. Some UV photo initiators experience what is termed *oxygen inhibition*. This is caused by the oxygen molecules in the atmosphere interacting and "using-up" the cure initiator at the surface of the material being cured. This can be alleviated in three ways. First would be to blanket the material in an oxygen reduced atmosphere (e.g., nitrogen). This can be costly to set up and operate with large batches of materials. Second would be to have a secondary cure mechanism available (e.g., heat, moisture, and so on) that can complete the curing on the surface. Finally, sometimes this can be overcome through the use of a higher-intensity and/or higher-energy light source.

Some materials may be cured by both UV and other mechanisms, and these are termed *dual-cure systems*. These materials, first partially cured using UV

Figure 9.19 Sample UV curing systems.

Adhesives, Underfills, and Coatings in Electronics Assemblies 9.19

light, are subsequently fully cured using another mechanism. These secondary cure mechanisms include heat, activators, ambient moisture, and resin/ hardener mixtures. In some cases, photoinitiators are added to an already existing technology (e.g., silicones or epoxies) so as to achieve dual cure mechanisms.

Multiple curing mechanisms are important for many reasons. The most important of these is the need to cure the material in areas where the light cannot penetrate or in shadowed areas. In these cases, the UV light is used to immobilize the material initially, thus enabling the assembly to be moved to another stage in the process. This increases production throughput, preventing a bottleneck in the system.

Another benefit gained by adding photo initiators to other materials revolves around the fact that one is able to take advantage of the inherent properties of these materials. Epoxies, silicones, and cyanoacrylates are all examples of existing technologies that have been fused with UV technology to gain the benefits of both.

Another approach to curing epoxies with UV light is by means of a technology referred to as *cationic UV curing*. These are typically one-part epoxies that exhibit extremely low outgassing during cure. Once cured, these cationic UV epoxies can provide high-temperature bonds that demonstrate toughness and high peel and high impact resistance.

The cure of these epoxies is initiated by UV light. However, the cationic curing mechanism differs from typical UV cure in the fact that, once the cure is initiated, it will continue even if the UV light is removed. These products also require less UV energy to cure than other UV curable materials, so it is not difficult to find a UV light that will provide enough energy to initiate cure.

9.4 Glass Transition Temperature

The glass transition temperature (T_g) of an adhesive indicates the temperature at which the adhesive changes from being a glassy solid to a "rubbery" material. There is often a significant increase in the coefficient of thermal expansion on passing through the T_g (often a two- or threefold increase). If the T_g is within (or near) the operating temperature of the assembly, the reliability of the assembly can be adversely effected. Even within the same sample, the glass transition occurs within a range of temperatures and not as a single point. Factors such as intrachain stiffness, polar forces, and co-monomer compatibility can affect the size of the glass transition region.

Differential scanning calorimetry (DSC) is the quickest and simplest method to measure T_{g} . The method requires extremely small samples (typically 5 to 20 mg) that require no special preparation, and material from components on processed boards can be utilized. The method consists of heating the sample in a closely calibrated thermocel, where the temperature of the sample is compared to the temperature of a blank reference point within the same cell. Thermodynamic transitions such as melting points and reaction exotherms are easily measured, and the change in heat capacity at the T_g is seen as a shift in the baseline for cured materials (see Fig. 9.20).

Figure 9.20 Example of DSC to measure *Tg*.

Unfortunately, this fast and convenient method is not universally applicable to all materials. High filler loadings, high crosslink densities, and other thermomolecular processes can mask the shift resulting from the T_g and make the transition difficult or impossible to identify.

Thermomechanical analysis (TMA) is the test used to determine thermal expansion coefficients. Because there is a shift to a higher thermal expansion coefficient above the T_g resulting from changes in molecular free volume, the method can also be used to measure the glass transition temperature as shown in Fig. 9.21.

The technique simply consists of heating the sample on an expansion-calibrated platform and measuring the dimensional change of the sample with an instrumented probe. The method will also easily follow cure-stress relaxations in and around the glass transition region, which sometimes leads to ambiguity in assignment of a specific T_g and can yield a different value for the same

Figure 9.21 Thermomechanical analysis used to measure T_a .

specimen if measured at a different point. (For example, the cure stress may be significantly different when measured near the edge of a sample rather than its center.)

Dynamic mechanical analysis (DMA) consists of oscillating flexure energy applied to a rectangular bar of the cured material. The stress that is transferred through the specimen is measured as a function of temperature. Components of material stiffness are separated into a complex modulus and a rubbery modulus. The technique is highly accurate and reproducible, although the T_g can be defined in different ways, which will result in different values as illustrated in Fig. 9.22. Large samples that must be accurately machined, coupled with longer setups, make this test relatively expensive to run.

Each of these methods will produce different data for the same material. For example, a single specimen of a developmental epoxy encapsulant material was cast and cured for 2 hr at 145°C after gelling at 100°C for 1 hr. It was then machined into specimens for DSC, TMA, and DMA analysis. The results show T_g values ranging from 130°C for the TMA to 146°C for the DMA measurement, as shown in Table 9.5.

TABLE 9.5 Instrument Effect on *Tg*

Instrument	T_g in $^{\circ}$ C
DSC	142
TMA	130
DMA	137 (G") 146 (tan delta)

Figure 9.22 Dynamic mechanical analysis used to measure T_g .

9.5 Coefficient of Thermal Expansion

The coefficient of thermal expansion is a measure of the fractional change in dimension (usually thickness) per degree rise in temperature. For microelectronics encapsulants, it is often quoted in ppm/ ${}^{\circ}C$ (value $\times 10^{-6}$ ${}^{\circ}C$). Chemical composition, filler loading, and cure cycles all affect the value. For typical materials that have nonlinear expansion, the specified temperature range will also have an effect on the data, with measurements out closer to the T_g yielding higher values than those quoted across lower temperature. This is shown in Fig. 9.23.

The CTE of adhesives used in microelectronics assembly is often a critical parameter. The different polymer systems used in electronics have vastly different CTEs for the base system. These CTEs can be modified from this base level through the addition of fillers, changes in the backbone chemistry, and changes in the hardener system. For example, most underfill materials are used to mitigate the CTE mismatch between silicon die (1.8 ppm/°C) and the FR-4 substrate (15 ppm/°C). Therefore, the CTE of the base epoxy is often manipulated with the addition of fillers. This effect can be observed by examining a matrix consisting of a standard epoxy anhydride that is loaded with a proprietary mixture of low-expansion fillers. All samples were cured for 2 hr at 145°C after gelling for 1 hr at 100°C. CTEs decrease rapidly, and the viscosity increases, as shown in Table 9.6.

TABLE 9.6 Effect of Filler on CTE

Filler loading	CTE (TMA method)
60%	$34.5~\text{ppm}/\text{°C}$
65%	$28.8~\mathrm{ppm}/^{\circ}\mathrm{C}$
70%	$24.1~\text{ppm}/\text{°C}$
75%	$20.0~\text{ppm}/\text{°C}$

Figure 9.23 Effect of temperature on CTE.

Also, the CTE is often increased (sometimes as much as three-fold) after passing through the glass transition temperature. These values are often defined as α_1 , below T_g , and α_2 , above T_g . When looking at a material and the amount of stress it may impinge on a system or the amount it can absorb, it is useful to examine the CTE, T_g , and modulus together when choosing a system.

9.6 Young's Modulus

Young's modulus is the same as tensile modulus. Tensile modulus is the ratio of stress to strain within the elastic region of the stress-strain curve (prior to the yield point). Young's modulus characterizes the elastic properties of the material under tension or compression irrespective of the sample geometry. Typically, the lower the modulus, the more elastic the material. Thus, a material with a low modulus can be considered to be very rubbery and can absorb more stress before fracturing.

To measure tensile modulus, the stress is gradually increased on a sample, and a measurement of the elongation the sample undergoes at each stress level is recorded. This is continued until the sample breaks. Subsequently, a plot of stress versus elongation is produced, such as shown in Fig. 9.24.

This plot is called a stress-strain curve. (*Strain* is any kind of deformation, including elongation. *Elongation* is the word we use if we are talking specifically about tensile strain.) The height of the curve when the sample breaks is the tensile strength, of course, and the tensile modulus is the slope of this plot. If the slope is steep, the sample has a high tensile modulus, which means it resists deformation. If the slope is gentle, then the sample has a low tensile modulus, which means it is easily deformed.

Figure 9.24 Example of a strain-stress measurement for determining modulus.

9.24 Chapter 9

Modulus is measured by calculating stress and dividing by elongation, and it would be measured in units of stress divided by units of elongation. But because elongation is dimensionless, it has no units by which we can divide. Therefore, modulus is expressed in the same units as strength, such as $N/cm²$.

9.7 Applications

9.7.1 Surface mount adhesive

SMT encompasses two fundamentally different manufacturing processes, one incorporating the use of solder paste (or cream), the other incorporating surface mount adhesive (SMA). The first of these processes involves screen printing a solder paste onto the solder pads on the surface of the PCB. A surface mount device (SMD) component is then placed on the solder paste, and the connections are reflow soldered. The second type of process recognizes the fact that, most commonly, PCBs contain a mixture of SMDs and through-hole components. Such through-hole components are attached to the PCB by a wave soldering process wherein hot molten solder is deposited between the lead connector and the hole. SMDs can also be attached to the PCB using this same wave soldering process; however, the components must be bonded to the bottom side of the board to keep them from falling off and into the solder wave. This bonding process, a critical step to the overall process, is displayed schematically in Fig. 9.25.

In this process, the adhesive is dispensed directly onto the substrate PCB between the solder pads, and the component is placed on the adhesive dot that is then heat cured. The cured adhesive must have sufficient strength to bond the components to the board surface during the next step of (manual) insertion of through-hole components. The board is then flipped by 180° and passed through the wave solder.

9.7.1.1 Process requirements of the SMA. Adhesive is used to bond the body of the SMD to the PCB between the solder pads. The adhesive must have the correct rheology (see Sec. 9.2), or flow characteristics, to permit deposition of

Figure 9.25 Illustration of a mixed-technology process.

Adhesives, Underfills, and Coatings in Electronics Assemblies 9.25

accurate quantities of adhesive dots in precise locations between solder pads on the PCB surface. Adhesive can be applied to the PCB using one of several methods: stencil printing, pin transfer, or (most commonly) a syringe dispensing system, either pressure/time or volumetric. After the SMD is placed, the wet adhesive must have sufficient wet, or "green," strength to hold the SMD in position until cured (see Yield Point, Sec. 9.2.2.3). The cured adhesive must then have sufficient strength to hold the SMD to the PCB during the solder wave operation. After soldering, the adhesive must not affect operation of the circuit in any way. To meet these demands, the product must satisfy the following requirements:

- The packed adhesive must be free of contaminants and air bubbles.
- It must have a long shelf life.
- The adhesive must enable high-speed dispensing of very small dots.
- It must exhibit consistent dot profile and size.
- It must have a high dot profile, nonstringing.
- The color must allow visual and automated detection.
- It must have high wet strength.
- It must provide rapid curing.
- It must be nonslumping during the cure cycle (heating).
- It must have high strength combined with flexibility and resistance against a thermal shock/solder wave.
- Good electrical properties must result when the adhesive is cured.

9.7.1.2 Dispensing methodology. High-volume surface mount assembly is a very competitive industry, with product designs changing rapidly. To remain profitable, it is vital for PCB assembly manufacturers to maintain a high quality standard without compromise in throughput and flexibility. SMT placement equipment manufacturers continually meet the challenges of this fast-paced industry by developing new and improved placement equipment, which now offers ability to place more than 70,000 SMD components per hour. The most common method of adhesive deposition is by high-speed automatic dispensing, which provides excellent control of adhesive deposit volume and dispense location. However, the speed of most automatic dispensers is limited to up to 50,000 dot placements per hour. This limitation can potentially produce a bottleneck in a high-throughput assembly line environment. It is therefore vital to develop both new and faster methods of deposition and new adhesive materials that possess the required rheological properties to permit increasingly faster rates of deposition.

Surface mount adhesives are applied to the surface of a PCB by one of three methods.

1. Syringe dispensing

- 2. Stencil printing
- 3. Pin transfer

More than 80 percent of the total surface mount adhesives used are currently dispensed by syringe. Syringe dispensing can be further divided into two subgroupings.

- 1. Pressure-time systems
- 2. Volumetric systems

Pressure-time syringe dispensing (Fig. 9.26) is the most common method used, and it employs a pressure/time system to dispense adhesives at high speed. This is a conventional system used by many of the major equipment manufacturers such as Fuji, Sanyo, Panasert, and others. On a pressure-time system, the amount of adhesive dispensed will depend on the nozzle size, the temperature of the adhesive, the dispense pressure, and the dispense time. Volumetric dispensing systems are based on one of two principles: Archimedes screw or piston (positive displacement) as shown in Fig. 9.27.

Pin transfer is a high-speed alternative to automatic syringe dispensing that uses an array of pins that dip into a tray of adhesive and then transfer the suspended adhesive drops to the PCB surface. However, this method is not without limitations. Deposition locations are fixed in complex and expensive tooling plates that make changeovers slow. This in turn makes product design changes expensive and difficult to implement. Less than 10 percent of total adhesive is dispensed by the pin transfer method.

Stencil printing has been widely used for many years as an efficient and cost-effective means of dispensing solder paste and, with increasing component counts and faster placement equipment, it has become increasingly popular to use the same technology as a means of adhesive deposition that is both

Figure 9.26 Pressure-time automated syringe dispensing.

Figure 9.27 Archimedes screw and positive displacement systems.

faster and more flexible than either automatic syringe dispense or pin transfer. New equipment developments have overcome some of the earlier limitations of this technique and, while stencil manufacturers have developed new stencil technologies designed for adhesive printing, adhesive manufacturers have responded with the development of new printable adhesives with rheological properties specifically preengineered for stencil printing applications. Newer SMAs have been developed that possess a rheology such that the same material can be both dispensed and screen printed.

9.7.1.3 Dot profile. Each of the above dispensing techniques is used to apply adhesive dots to the board surface. The actual shape of the dot (dot profile) produced by a particular adhesive grade will be influenced by the various adhesive rheological parameters such as thixotropic recovery rate, viscosity at zero shear rate, surface tension, and wetting characteristics (see Sec. 9.2). The actual dot shape (Fig. 9.28) may be peaky-conical (associated with very high yield point values), Hershey kiss, or rounded hemispherical (associated with lower yield point values).

The dot profile is also defined by nonadhesive (machine-related) parameters such as dot volume, dispense needle diameter, and needle standoff height. For a given adhesive grade, it is possible to produce exaggeratedly high, narrow

Figure 9.28 Illustration of various dot profiles.

dots and low, wide dots by adjusting these parameters (particularly stand-off height).

It is important to dispense the adhesive accurately, and consideration must be given to the dimensions and location of the solder pads. The adhesive dot must be high enough to bridge the gap between the surface of the PCB and the underside of the SMD body, yet not so high that it will contaminate the component placement head. The gap to be bridged by the adhesive will depend on the height of the solder pad above the PCB solder mask surface and the gap created by the difference in end metallization and body thickness of the SMD. This gap can vary from less than 0.05 mm for flat chips to more than 0.3 mm for large SOs and QFPs.

Considering these wide ranging demands, it is generally best to get reasonably tall dots to ensure good adhesive coverage on the underside of components with high stand-off space; at the same time, the dot can be squeezed out between low stand-off components without risk of pad contamination. Quite often, two separate sets of dispense parameters are used side by side for a single grade, one producing a high, large volume dot for high stand-off components and the other producing moderate height and volume dots for flat chips and MELFs.

The question often arises as to when a single dot or a dual (twin) dot configuration should be used. The main process issues influencing whether a single or dual dot configuration is used are the size of the component being bonded, the board component population density, and the board design/pad spacings. (The adhesion of the surface mount adhesive to the particular solder mask may also play a role.) The size of the component imposes restrictions on the maximum size of the adhesive dot diameter, because the dot must be smaller than the spacing between the solder pads. As components get larger, they do so more through increasing thickness, so certain components have a higher mass but similar spacing between solder pads. As the mass of the component increases, it becomes more susceptible to movement. This affects both the green strength and the cured bond strength of the adhesive in its ability to hold a larger, heavier component. It is therefore necessary to use more adhesive to hold the component in place and minimize component skewing. Similarly, larger, heavier components are subject to stronger forces during the wave soldering step. To prevent component loss, greater bond strength is required. Because adhesive bond strength is also related to the total bond area, the bond area should be maximized. Again, this can be done by increasing the amount of adhesive under the component. Because of restrictions imposed on the adhesive dot diameter by the solder pad spacings, the only viable way of increasing the amount of adhesive under the component is by using a twin adhesive dot configuration (Fig. 9.29). The figure illustrates the amount of adhesive that can be put under a component with a single dot versus a twin dot and the amount of coverage (bond area) that each dot configuration will afford when compressed by the component (assuming a 3-mil stand-off height to the component and pad widths matching the component) (see Fig. 9.30).

Obviously, for an 0805 component, a twin dot will afford greater adhesive coverage under the component as compared to a single dot, and this will result

0.875

0.750

Figure 9.29 Component stand-off height and adhesive dot height.

PLCC

Figure 9.30 Single and dual dot pattern.

in both better green strength and better cured bond strength. As the mass of the components and the tolerance between the solder pads decreases (i.e., 0603 and 0402 components), single dots should be sufficient for good bonding. However, other process issues, such as adhesion to board surface, may dictate use of twin rather than single dots.

9.7.1.4 Dispense parameters. The adhesive must have the right rheological characteristics to give good dot shape control. However, good dispensing does not depend on the adhesive alone. For pressure-time syringe dispensing, the machine-related factors that will influence dispensability and good dot formation are needle size, PCB-to-needle stand-off, temperature, dispense time and pressure, and dispense cycle profile.

The inner diameter of the needle is critical. It must be significantly smaller than the diameter of the dot on the board. As a guide, the ratio should be 2:1. For example, for dot sizes of 0.7 to 0.9 mm, the needle I.D. should be 0.4 mm; for dot sizes of 0.5 to 0.6 mm, the I.D. should be 0.3 mm. Different adhesive dispensers make use of different designs and needle lengths, and these will also affect dispensability.

The stand-off, or *stopper,* height is also critical. This will control the height of the dot produced. However, it must be appropriate for the quantity being dispensed and the needle inner diameter. For a given adhesive volume, the height-to-width ratio of the adhesive dot will increase with the stopper height. Typically, the maximum stopper height is half the needle I.D. (Fig. 9.31). Beyond this point, the adhesive dot diameter will be too small relative to the needle I.D., and this will cause inconsistent dispensing and stringing.

The temperature of the adhesive will affect viscosity and, consequently, dot shape. Figure 9.32 illustrates how the viscosity of a typical surface mount adhesive varies with temperature.

Most modern dispensers use some sort of temperature control, either on the dispense nozzle or dispense chamber, to maintain the adhesive at a set tem-

Figure 9.31 Stand-off height, needle I.D., and adhesive dot diameter.

Figure 9.32 Temperature-viscosity curve.

Adhesives, Underfills, and Coatings in Electronics Assemblies 9.31

perature above ambient*.* However, the temperature of the PCB should also be considered. Dispensing on hot boards, warmed from previous processing, can change the dot profile.

The majority of syringe dispensers use *air-over* pressure systems. The volume of adhesive dispensed is then controlled by a combination of pressure and time. Very short dispense times with high pressures may be attractive to speed up the cycle time, but the ability of the pressure regulation system to respond must be considered. High pressures (4 to 5 bar) will, in theory, allow shorter dispense times; however, this leaves little scope for pressure adjustment to compensate for viscosity variations and also can cause the air temperature behind the piston to rise faster and higher. In practice, machine operators usually set the pressure to a mid-point value (approx. 2 to 3 bar). The dispense time is then set according to the size of dot required, which in turn is dependent on the SMD component. Although there are guidelines for the different dot sizes, the actual size used will depend on the sizes and mix of components being bonded, the pad spacing, and the in-house limits of acceptable variation. Often, this is established by trial and error and previous experience.

More recent high-speed dispensers use dispense cycles (Fig. 9.33) wherein the dispense pressure can be timed to start before the nozzle has arrived at the dispensing position. The speed at which the nozzle retracts, the retraction height, and the delay between end of dispensing and the start of nozzle retraction all will affect dot shape control and possibility of stringing.

9.7.1.5 Common dispensing defects. Several types of dispensing defect may lead to final process defects. (The presence of a dispensing defect does not imply that a defective SMD joint will occur, but it does increase the risk of such a defect.) These are stringing (or tailing), inconsistent dot size, and missed dots. Each of these defects is discussed briefly here.

Stringing is probably the most common defect, and it can result in contamination of the solder pads and, ultimately, poor solder connections (Figs. 9.34

Figure 9.34 Illustration of the stringing defect.

and 9.35). In some cases, stringing is caused by the adhesive not having time to wet out onto the PCB surface or time to recover from being sheared in the nozzle. In these cases, an increase in the *delay after* often can solve the problem. (The *delay after* is the time, typically 10 to 20 ms, during which the nozzle rests in position above the PCB after the adhesive shot has been dispensed. It allows the adhesive time to wet onto the PCB substrate and restructure itself after being sheared in the nozzle.)

If increasing the delay after has no effect, particularly for larger dot sizes, then breaking off of the adhesive dot from the nozzle may be the problem. If there are satellites (or spattering, Fig. 9.36) associated with the stringing, then an increase in the Z-safe height (Z-retract height) will allow the nozzle to retract further after dispensing giving the adhesive dot a better chance to break cleanly off from the nozzle. Increasing either the delay after or the Zsafe reduces the incidence of stringing at the expense of dispense speed, as both increase the overall dispense cycle time. However, it is possible to achieve an optimal balance of dispense quality versus dispense speed.

If adjustment of either the delay after or the Z-safe has only a minor effect on stringing, then a different nozzle configuration (nozzle I.D./stand-off ratio) may be required. If the dispense volume of adhesive is too small for the nozzle diameter and stand-off height, resulting in a very tall, thin dot, then the risk of stringing is high. The correct solution here is to use a smaller needle diameter/stand-off height combination. Stringing sometimes can also be caused by poor board support or board warpage, or by the nozzle stopper (or stand-off post) landing on the solder pads and giving an incorrect stand-off height. (This problem may be solved by reindexing the nozzle by turning it through an angle of 45° or 90° to keep the stopper from contacting the solder pads.) In addi-

Figure 9.35 Photo of a stringing defect.

Figure 9.36 Splattering or satellite dots.

Adhesives, Underfills, and Coatings in Electronics Assemblies 9.33

tion, stringing can sometimes be caused by electrostatic buildup on areas of the board. In this case, the strings characteristically are generally small and all point in one direction on the board (not always the direction of nozzle travel). This often occurs during dispense trials wherein the same boards are repeatedly dispensed onto and wiped clean, leading to a buildup of electrostatic charge on the PCB surface. This phenomenon can be eliminated through use of proper precautions such as static mats.

Inconsistent dot sizes is also a commonly observed defect. Differences in dot size can occur from several causes.

- The dot size may be too small for the needle diameter, resulting in poor wetting of the PCB. An increase in the dot size or use of a smaller needle often can solve this problem.
- Temperature changes can cause adhesive viscosity variations. Use temperature control and vision system feedback to control dot quantity.
- Pressure variations can occur, particularly due to changing air volume and temperature behind the piston. Use vision feedback control of dot quantity. More recent dispensers now enable the air to be vented back out of the syringe between "dispense-on" signals. This eliminates buildup of air temperature and speeds the recharging of pressure between dispense shots as the syringe empties.
- Partial blockage or buildup on the walls of the needle can occur. Clean the nozzles.
- There may be an imbalance in flow through multiple-needle nozzles. Clean the nozzles and check for damage.
- The third most commonly observed defect is missed dots. Missed dots can occur for one of two reasons,
	- Blockage of a nozzle may be caused by a large particle or foreign material. Every effort is made to ensure that such particles are not present in the adhesive, but it may happen occasionally. Foreign particles may also be trapped in the adhesive during nozzle attachment. One common source of blockage is old partially cured adhesive on unclean nozzles and adapters that falls into the nozzle during the reattachment of nozzles to syringes.
	- Air bubbles can cause missed dots. Although most surface mount adhesives are packaged bubble-free, a potential source of air bubbles is when air is entrapped during the attachment of nozzles and adapters to the syringe. Care should be taken when attaching nozzles and adapters to avoid introducing air, and the nozzle should be purged to clear any product that contains entrapped air bubbles.

Needles and stoppers can become damaged, bent, or worn, which will negatively affect dispensing. They should be checked regularly. Excess adhesive on the outside of a needle can interrupt smooth and consistent dot formation. In extreme cases, the adhesive may bridge over to the stopper pin and totally disrupt dispensing. The exterior of the nozzle should be kept as clean as possible. **9.7.1.6 Adhesive wet (green) strength.** Before passing through the curing oven, PCBs are exposed to various chip placement machines that deposit surface mount devices onto uncured adhesive dots on the board surface. Many such high-speed chip placement machines use X-Y table movement to position the circuit board under the static cam-controlled placement head (e.g., Fuji CP-6 chip placement machine). Such X-Y table movement subjects the components and uncured adhesive to rapid acceleration/deceleration forces as the board is moved rapidly to correctly position the placement sites on the board surface with the static placement head. *Green* or *wet strength* refers to the ability of the adhesive in the uncured state to maintain the positional alignment of the SMD device with the solder pads on the surface of the PCB prior to the curing process. If the adhesive does not have sufficient green strength, the forces generated by the machines can cause misalignment of component leads with the solder pads.

The green strength of the adhesive depends on the degree of contact between the adhesive and the component as discussed in Sec. 9.7.1.3, and it is yield point dependent (see Sec. 9.2.2.3). An adhesive with too low a dot profile will not make good contact with the component, and this reduces the ability of the uncured adhesive to hold the component in place. This causes misalignment of the component with the solder pads, which in turn may result in higher process failures.

Poor green strength may also arise, even if the adhesive has good contact to the SMD but possesses a low base viscosity. In this case, the SMA is of too thin a viscosity to resist the directional forces experienced by the board and to hold the component in place.

The green strength of an adhesive can be tested using the Siemens standard SN59651, "Acceptance of SMD Adhesives," which involves sliding a populated PCB down a steel ramp of fixed incline (Fig. 9.37) into a stopper at the base of the ramp. The position of the various components on the PCB surface is noted before and after the test, and displacement is measured. According to the Sie-

Figure 9.37 Sliding ramp for green strength test.

mens test, the adhesive must not allow the component to shift position by more than 150 μ m (corresponding to half the track pitch on a standard 0.3mm pitch component). Some typical green strength values for five different Chipbonder[®] adhesives are shown in Fig. 9.38.

9.7.1.7 Moisture absorption. An important step in the SMT PCB assembly process is the dispensing of an appropriately sized dot of adhesive onto the exact location on the PCB surface. The next step involves placement of the various SMT components onto the adhesive dots before passing the entire board through an oven wherein the adhesive undergoes cure. Quite often, there is a time delay between dispensing of the adhesive and component placement. This results in the uncured adhesive being exposed to whatever temperature and humidity are prevalent under normal factory operating conditions. Because surface mount adhesives are used worldwide, there can be considerable variation in the factory conditions of ambient temperature and humidity. It is very important that the SMA have no inordinately high tendency to absorb moisture from the surrounding atmosphere when left exposed in the uncured state. Moisture pickup of this type can cause a problem known as *popcorning*. Popcorning occurs when the SMA absorbs moisture from the atmosphere. When the component is then placed onto the adhesive dot and the PCB is passed through the cure oven at temperatures >100°C, the moisture absorbed by the adhesive vaporizes and boils off. This can manifest itself in any of the following ways:

1. There can be a formation of numerous bubbles or voids (Fig. 9.39) on the surface of the cured adhesive. The cured adhesive takes on a honeycomb appearance. This can reduce the area of contact between the cured adhesive and the underside of the SMT component, resulting in weaker bond

Figure 9.38 Green strength of five surface mount adhesives.

Figure 9.39 Photographs of void formation caused by popcorning.

strengths. The reduction in bond strength can result in component loss during the manual insertion or wave soldering steps.

The effect of such popcorning on the resultant bond strengths is illustrated in Fig. 9.40. This illustrates the effect of different humidity exposure times on torque strength for two surface mount adhesives with different moisture tolerances. The required adhesive dots were dispensed onto a bare FR-4 board, and 1206 capacitors were either placed and cured immediately (exposure time $= 0$), or the dots were exposed for the various time periods (5, 15, 30, and 60 min) to 30°C/85 percent RH before placing the components and curing $(180 \text{ sec}, 2125^{\circ} \text{C})$. The result-

Figure 9.40 Adhesive bond (torque) strength after humidity exposure.

ant bond strengths (off torque, N-cm) were then recorded for each exposure condition.

In the case of adhesive B, the effect of humidity exposure is clear, with a dramatic decrease in torque strength evident after only 5 min exposure to 30°C/85 percent R.H. Adhesive A, on the other hand, is resistant to the effects of the humidity exposure. Adhesive B would almost certainly cause an increase in PCB defect rates when used in warm or humid environments.

- 2. The voids/bubbles are so large as to form channels through which solder can flow during wave soldering, resulting in solder bridging and component/device failure (Fig. 9.41). During the preheat flux cycle, it is possible for solder flux to penetrate the voids in the cured adhesive dot (Fig. 9.42). Because flux materials are commonly acid based, they can subsequently cause corrosion/surface insulation resistance failures.
- 3. The moisture boils off so quickly (because of a high ramp rate in the cure oven) that the SMT component actually gets blown off the board surface, resulting in missing components.

Figure 9.41 Solder bridging.

Figure 9.42 Flux penetration.

The tendency of the adhesive to pick up moisture from the surrounding atmosphere is a result of the use of hygroscopic raw materials in the adhesive formulation. Therefore, it is important to screen surface mount adhesives to eliminate any that may cause popcorning problems through excessive moisture pickup. A screening test known as the *glass sandwich test* (Fig. 9.43) is quite useful for studying the tendency of a particular adhesive to pick up moisture. This test involves stencilling a series of five controlled dots (4 mg each) of adhesive onto a glass slide and exposing the adhesive dots to various temperature/humidity conditions, which are dictated by the typical environmental conditions the SMA is expected to endure (e.g., 1 hr ω 30°C/80 percent R.H.).

After complete exposure of the dots to the required environmental conditions, a second glass slide is placed over the adhesive dots to form a sandwich. The dots are spread out by placing a weight on top of the glass slide sandwich, which is then placed onto the surface of a flat aluminium hotplate at 165°C for 90 sec. This results in cure of the adhesive dots. Any moisture absorbed by the adhesive during exposure to the environmental test condition boils off during cure, causing the formation of voids within the adhesive between the glass slides. The amount of voiding is noted and rated on a scale of 0 to 10, with a 0 rating equivalent to no void formation and a rating of 10 equivalent to serious void formation. This test is very useful, because it can be used to quickly screen surface mount adhesives that may have moisture uptake problems.

9.7.1.8 Cure speed. The cure speed of a particular adhesive can be measured by recording off-torque values for the adhesive when cured for variable periods of time at different temperatures as described in the following test procedure.

A bare FR-4 board populated with 1206 capacitors is placed in a specially machined hotplate as shown in Fig. 9.44. An IR lamp is moved into position

Figure 9.43 Glass sandwich moisture absorption test.

Figure 9.44 Test rig for measuring cure speed by off-torque.

over the board. The IR temperature is controlled by a thermocouple on the board surface, switching the IR lamp in and out as required. Two heat sources are used to produce as rapid a ramp rate as possible. This ensures that the *residence time at the target temperature* does not include excessive time between the start of cure and the target temperature. After cure at the required time and temperature, the board is cooled, and the components are torqued off 24 hr later. In practice, components can be torqued once the board is cooled. These data are used to build up a cure curve. Tables 9.7 through 9.9 show the off-torque values for five Chipbonder[®] products, A through E, under test at temperatures of 100, 125, and 150°C.

Off-torque (N-cm)	SMA A	SMA B	SMA C	SMA D	SMA E
60 sec @ 100° C	Fixture	Fixture	Fixture	Fixture	2.96
120 sec @ 100° C	0.76	1.29	0.4	0.69	4.34
180 sec @ 100° C	2.17	2.7	1.48	2.16	4.2
300 sec @ 100° C	4.77	5.64	3.05	4.13	5.01
600 sec @ 100° C	6.28	5.95	4.71	6.23	5.61

TABLE 9.7 Off-Torque Strengths for Chipbonders® A–E @ 100°C

The data presented in Tables 9.7 through 9.9 can be used to generate a curespeed-versus-temperature graph (Fig. 9.45). This shows the typical increase in strength (torque) with time at different temperatures. The time shown is the residence time and does not include the heat-up time required to reach that temperature. This heat-up time can vary significantly, from 15 sec to several minutes, depending on the temperature and oven configuration. The cure

	SMA A	SMA B	SMA C	SMA D	SMA E
15 sec $@125°C$	2.18	4.41	1.14	0.82	3.09
30 sec $@125°C$	2.78	4.76	1.73	1.43	3.41
60 sec @ 125° C	3.37	5.28	3.03	4.46	4.74
90 sec @ 125° C	4.25	6.14	3.93	5.60	5.30
120 sec @ 125° C	5.11	5.68	3.54	5.65	5.44
300 sec @ 125° C	6.64	6.31	5.26	7.24	5.86
600 sec @ 125° C		6.57			

TABLE 9.8 Off-Torque Strengths for Chipbonders® A–E @ 125°C

TABLE 9.9 Off-Torque Strengths for Chipbonders® A–E @ 150°C

	SMA A	SMA B	SMA C	SMA D	SMA E
15 sec $@150°C$	4.41	5.48	2.89	3.48	3.63
30 sec $@150°C$	5.25	6.09	3.71	4.54	3.88
60 sec $@150°C$	5.34	6.19	4.07	5.6	4.91
90 sec $@150°C$	5.96	5.92	4.55	5.87	3.66
120 sec @ 150° C	6.29	5.92	4.48	5.86	4.58
300 sec $@150°C$	6.00	5.97	4.57	6.05	4.61

curve shows the times required to reach full cured strength at each temperature. In practice, these are conservative guidelines, because the adhesive will also receive heat during warm-up, and quite often the oven profile does not maintain exactly the cure temperature but reaches a higher peak value. In addition, some users find that achieving 90 percent of full cured strength is adequate for the process. The curing temperature and speed can also be related to DSC results.

9.7.1.9 Electrical characteristics. After the wave solder step, the function of the surface mount adhesive has ended. However, the adhesive remains on the printed circuit board for the life of the product and may be subjected to harsh environments, such as high temperature and humidity, combined with electrical loading across the adhesive. It is therefore vital that, under such environmental conditions, the adhesive does not break down during the functioning of the board and cause electrical failure due to corrosion, short circuits, or current leakage across terminals or tracks. The modern SMA must be able to withstand high electrical loadings under increasingly demanding environ-

Figure 9.45 Typical cure-speed-vs.-temperature graph.

mental conditions of high temperature and humidity. A series of electrical tests are available to ensure the adhesive does not modify the electrical characteristics of the components with which it comes in contact.

Surface insulation resistance (SIR) is the most commonly known type of environmental test for chip bonders, solder paste fluxes, and board coatings such as solder resist and conformal coatings. The adhesive is coated across an interlinking comb pattern of bare copper tracks (Fig. 9.46).

Track width and pitch, as well as applied bias voltage, test voltage, and adhesive thickness requirements, differ from customer to customer. Environmental conditions and test duration differ also, with many automotive telecom and companies requesting 85°C/85 percent R.H. for 1000 hr. Again, the test setup is allowed to come to temperature in the chamber before the humidity is switched on, to prevent condensation on the test combs.

Typical test conditions are summarized in Table 9.10. The cured adhesive must maintain a minimum resistance value after 1000 hr with an applied bias voltage of 16 VDC in an 85°C/85 percent R.H. humidity cabinet. The adhesive must prevent the type of corrosion illustrated in Fig. 9.47.

Another common test related to SIR is a test for electrolytic corrosion. This test is a measure of the ability of the cured adhesive to cause corrosion on PCB

Figure 9.46 SIR test comb pattern (left) and SIR test vehicle (right).

TABLE 9.10 SIR Test Conditions

Figure 9.47 Effect of yield point on chip bonder dot profile.

pads when subjected to high humidity and electrical loading (4 days @ 40°C, 92 percent RH, with 100 VDC applied voltage). A strip of cured adhesive acts as a bridge between brass foil electrodes, with 100 VDC potential across them. Test conditions are 4 days @ 40°C, 92 percent RH. The test setup is allowed to come to temperature in the chamber before the humidity is switched on, to prevent condensation on the test piece. After the test, the foils are checked for tarnishing and corrosion and rated against standard foils.

9.7.1.10 Yield point and surface mount adhesives. So what use is this Casson yield point? A useful application of the Casson yield point is for the characterization of surface mount adhesives. Chip bonding involves placing very small dots, each weighing approx. 80 mg, precisely between metal pads (solder lands) on a printed circuit board. The shape of these dots depends very much on the yield point (see Fig. 9.48).

A high τ_0 produces a conical dot. This holds its shape with time, because the yield point is large enough to resist the force of gravity on any realistic time scale. Too low a yield point, and the dot spreads out, giving a low, rounded appearance. If it spreads too much, it can cover the solder lands and prevent good contact with the SMD.

Surface mount adhesives are formulated to give very specific rheological, or flow, properties to allow rapid and controlled dispensing of the adhesive onto very precise locations on the PCB surface as adhesive dots of very defined shape. SMAs have the ability to change their viscosity when a shearing stress is applied to them. During dispensing, a shear stress is applied to the adhesive (such as the application of a pulse of air pressure that forces the adhesive from a syringe through a narrow nozzle, or the shearing effect of a squeegee dragging the adhesive across the surface of a stencil and forcing it into the stencil apertures and in contact with the PCB surface). Consequently, the viscosity decreases, permitting easier flow of the adhesive. Once the adhesive drop has reached the PCB board surface, the shearing action is removed, and the adhesive quickly restructures and rebuilds its viscosity. This feature is referred to as *thixotropy,* and it ensures that adhesive dots with well defined profiles are achieved and that, once dispensed, the adhesive dots maintain this profile. Maintenance of dot profile is particularly important when one considers that a typical PCB will be populated with a variety of SMD components, each with different standoff heights from the PCB surface and each requiring an adhesive dot of different size.

9.7.2 Underfills

Underfill materials are polymer systems (filled and unfilled) that are used to increase the reliability of a variety of area array packages used in high-density electronic assemblies. Underfill systems are typically epoxy-based chemistries (e.g., bisphenol and cycloaliphatic epoxies) that sometimes have a filler

Figure 9.48 Effect of yield point on chip bonder dot profile.

added. There are two main reasons for using an underfill material. First, it is used to relieve stress from the large CTE mismatch between a silicon device (e.g., flip-chips) and the substrate to which is bonded (e.g., FR-4). Second, it is used to increase the reliability of the component, such as a chip-scale package, with respect to physical shock and vibration.

Underfill materials are used to increase the reliability of a variety of component types, including flip-chips, chip-scale packages, ball grid arrays (BGAs), and micro BGAs. Most manufacturers that use flip-chips on board (FCOB) underfill them to deal with the large CTE mismatch between the silicon die and the FR-4 substrates typically used in manufacturing these products. The other packages may be underfilled only if there is either a perceived risk to the products (e.g., a cell phone may undergo frequent drops) or it they are intended for a high-reliability application (e.g., avionics). The CTE matching of the underfill materials is typically achieved through the addition of silicabased fillers. This addition lowers the CTE to provide a gradient between the silicon chip and the substrate. Underfills used to provide physical protection to other packages typically have higher T_g , but they have a modulus that is better suited for that function. The need for a low CTE in an underfill is an often misunderstood concept. Not all underfills necessarily need to have a low CTE to provide reliability enhancement to all devices. The balance between CTE and modulus should be examined to provide the highest reliability enhancement possible. A graphic showing the relationship between modulus, CTE, and two common failure modes is Fig. 9.49. As this figure illustrates, understanding the failure mode of the device is critical in choosing a material with the right properties. Also note that using a material with a low CTE does not guarantee an increase in reliability if the device is susceptible to fatigue cracking. Figures 9.50 and 9.51 illustrate the reliability of various underfill

Figure 9.49 Graph showing the relationship between CTE, modulus, and failure modes.

Adhesives, Underfills, and Coatings in Electronics Assemblies 9.45

Figure 9.50 Reliability of various underfill materials with respect to drop tests.

BGA / CSP-testboards after 2000 thermo-cycle (-65°C / +125°C)

Figure 9.51 Underfill reliability with respect to thermal cycling.

9.46 Chapter 9

materials under drop testing and thermal shock, respectively. The materials tested included two fast-flow snap cures (FFSCs) and two reworkable underfills.

9.7.2.1 Capillary underfill. These low-viscosity liquids are designed to flow under a component by capillary action, wetting to the chip and substrate surfaces and encapsulating the solder joints. Underfills designed for assemblylevel flip-chip generally cure in 5 min or less at 165°C to form a hard seal with high adhesion to both the component (flip-chip or CSP) and the substrate. Underfills designed for package-level assemblies offer improved assembly reliability but generally require more time to flow under the die and to cure. Faulty or skewed components must be detected before underfill cure, because most all capillary flow underfills are permanent (see Sec. 9.7.2.3 for reworkable underfills).

Underfill is applied close to the edge of a flip-chip or CSP to enable capillary forces to encapsulate the gap between the component and the board. Dispensing capillary underfill materials requires specialized equipment to achieve the accuracy and precision required for high-volume assembly. At a minimum, the dispenser must reproducibly position successive assemblies and apply a predetermined volume of underfill to the edge of the component. Heating the substrate is a common secondary requirement that accelerates capillary flow. Cure is usually accomplished in belt-style reflow or curing ovens.

Several dispensing patterns are used for applying underfill to die and packages. The simplest pattern involves applying underfill to a single side and maintaining a reservoir as material wicks between the package and substrate. If necessary, underfill can be applied to the remaining three sides using a "U" pattern to form a fillet. With newer-generation materials, the filleting step can be eliminated.

Another common flow pattern recommended for fast processing of smaller or simpler devices involves dispensing an "L" of material (two sides), waiting for the flow out, and then dispensing an inverted "L" to complete the fillet, if needed. Other patterns can be used, but the line/L, double L, and their variations are most common today.

The underfill flow rate or underfill time is one of the key attributes of an underfill encapsulant. Suppliers typically use smooth or frosted glass slides with a predetermined gap established by shim stock to evaluate underfill times. In some cases, a fixture is used to maintain a stable gap and provide a more efficient (more than one slide assembly can be prepared at a time) means of running the test.

The fixture is placed on the hotplate and monitored for the selected underfill temperature (typically, 60 to 100°C). When the selected temperature is reached, underfill material is dispensed at the gap area. The flow front is timed to determine the time required to reach 1 cm. Information regarding underfill time and voiding predisposition can be obtained.

Other methods, such as glass slides set up with a variable gap that runs from ~0.13 mm to 0 (creates a wedge shape), can be used to expeditiously de-

Adhesives, Underfills, and Coatings in Electronics Assemblies 9.47

termine the compatibility of an underfill with various gap sizes. Another approach that may be utilized more by IC manufacturers is the use of a quartz bumped die that is consistent with the IC size to be used in the application. Different combinations of substrates with slides such as FR-4, silicon, and so on can be evaluated. The predisposition to voiding can also be assessed before and after cure. The glass slide/quartz die tests are not designed to reflect underfill times in specific applications, because solder masks, chip size, chip passivation coating, bump count, bump spacing, bump location, and surface cleanliness will all have a dramatic effect on underfill times. This test may be used to compare alternative encapsulant suppliers, alternative underfill temperatures, and the shelf life/pot life of underfill encapsulants.

9.7.2.2 Fluxing (no-flow) underfill. Fluxing, or so-called "no-flow," underfills are an attempt to make underfill processing more compatible with conventional surface mount assembly processes by eliminating the dedicated oven required for cure. A fluxing function incorporated into the underfill combines the component attachment and underfill cure processes.

Fluxing underfill is applied directly to the attach site on the substrate preceding component placement. The flip-chip or CSP is then placed into the underfill. During reflow, the underfill acts as the flux, enabling interconnect formation and self-centering before curing of the underfill. Ideally, underfill cure is completed in the reflow oven. Otherwise, subsequent reflow or deliberate heat treatment is required to complete underfill cure.

Fluxing underfills are different from capillary flow materials in several ways. Viscosities are typically much higher than that of capillary underfills. Because inorganic fillers in the underfill will generally impede essential contact between the CSP solder balls and the attach pads, fluxing underfills are unfilled, which results in a higher CTE. The entire board must be discarded if defective or skewed components are detected, because the underfills are not removable.

9.7.2.3 Removable/reworkable underfill. Occasionally, malfunctioning flip-chip or CSP components are discovered in the factory or in the field. Conventional underfills are not removable once cured, requiring that a malfunctioning assembly be discarded, sometimes at considerable cost. Removable underfill enables repair of the assembly.

Removable underfill is typically dispensed and processed much like other underfills. Extra functionality enables them to soften or degrade when sufficiently heated. The assembly repair process is similar to that of other solder SMT components with the exception of an extra step or extra time required to remove residual underfill.

9.7.2.4 Staking or corner bond underfill. An alternative approach to complete underfilling of chip-scale package devices for increased reliability with respect to shock and drop is to bond the corners or edges of a CSP (see Fig. 9.52). Some materials can be applied after the device is soldered to the substrate, and some can be dispensed with the solder paste before reflow. The advantage with these materials is that you can reduce the capital equipment expense by eliminating a curing oven and a separate dispenser, and reduce cost by using less material—four to eight dots versus the entire surface area under the package. There is a limit to the mass of components whose reliability can be enhanced; if the mass of the component is too great, the adhesive may not hold. Also, when dispensing corner dots with packages that have corner bumps, care must be taken not to interfere with the reflow soldering process.

9.7.2.5 Molded underfill. Costs related to use of liquid flip-chip underfill on high-volume manufacturing lines have driven development of underfills that are processed using high-throughput molding equipment. A solid mass of underfill is heated and softened then forced under pressure into a molding cavity containing one or more flip-chip assemblies. The process is very fast and capable of processing many assemblies simultaneously.

9.7.2.6 Wafer-applied underfill. Costs related to use of liquid flip-chip underfill on high-volume manufacturing lines have driven development of underfills that are applied to an entire wafer of flip-chip components before wafer dicing. Underfill dispensing during flip-chip assembly is eliminated. Wafer-applied underfills and accompanying application and assembly processes are under development by a number of organizations.

9.7.3 Electrically conductive adhesives

Continuing improvements in adhesive technology have enabled adhesives to replace solder in many electronic assembly applications. There are three types of electrically conductive adhesives formulated to provide specific benefits where an electrical interconnect is desired.

Figure 9.52 Corner bonded CSP.

Adhesives, Underfills, and Coatings in Electronics Assemblies 9.49

- 1. *Isotropic* materials, which will conduct electricity along all axes, are able to replace solder on thermally sensitive components and can also be used on devices that require a ground path.
- 2. *Conductive silicones* help protect devices from environmental hazards such as moisture, and they shield electromagnetic and radio frequency interference (EMI/RFI) emissions.
- 3. *Anisotropic conductive polymers*, which allow electrical current to flow only along a single axis, provide electrical connectivity and strain relief for flip-chip devices.

All electrically conductive adhesives have two common qualities: they provide a chemical bond between two surfaces, and they conduct electricity.

9.7.3.1 Isotropic materials. Electrically conductive isotropic epoxies can be used for electrical interconnect on nonsolderable substrates such as glass and ceramic, or to replace solder on thermally sensitive components that cannot withstand the 200°C processing temperatures of typical solders. Traditional applications for isotropic epoxies include bonding the flex circuit of a glass LCD to the mating trace on a PCB and attaching a component lead to a matching land on a thermally sensitive printed circuit board. Isotropic electrically conductive epoxies offer nondirectional, or all-directional, conductivity by incorporating conductive particles such as silver, nickel, or gold into the adhesive formulation. These particles carry electrical current through the epoxy resin. The most popular filler material is silver because of its moderate cost and superior conductivity. Isotropic silver-filled epoxies are available in heator room-temperature curing and single- or two-component formulations. Because electrically conductive epoxies require temperatures of only 150°C or less to cure, and room-temperature curing is a viable option, isotropic epoxies provide an ideal alternative to solder on thermally sensitive parts. Several varieties of silver-filled, isotropic epoxies are available to electronic device manufacturers. General-purpose, silver-filled room-temperature and heat-curing epoxies have been formulated specifically for rework and repair applications on large-pitch interconnects. For example, if the trace on a circuit board's surface gets gouged, selected versions of these epoxies may be used to repair the circuit in place of the original solder. These adhesives can also be used as solder substitutes on through-hole components. Certain grades of silver-filled epoxies are "die attach grades," designed to provide an electrical ground path and transfer heat from the chip to the substrate. Both electrically and thermally conductive, these epoxies develop strong, durable bonds on many different substrates, including metals, ceramics, glass, laminates, and molded plastics. Room-temperature-curing, flexible silver-filled epoxies have been formulated for electronic interconnect applications that require high flexibility, such as assembly and repair of flexible circuits or bonding flexible substrates and connectors. Gold bonders are heat-curable epoxies formulated to offer enhanced adhesion to gold-plated devices and other high-end metal surfaces such as palladium. These adhesives offer enhanced shear strength and are formulated to absorb the stress associated with extreme thermal mismatch between dissimilar substrates. Typical adhesives on the market today cure in 30 min at 150°C, or in 1 hr at 125°C. Certain grades of silver-filled epoxies are specifically formulated for direct use on the die and are aptly referred to as die attach grades. These adhesives are formulated to provide an electrical ground path and transfer heat from the chip to the substrate. A variety of formulations are available, offering benefits such as high purity and low ionic content, a long working life, and snap heat cures of 3 min or less.

9.7.3.2 Conductive silicones. New conductive silicone materials allow device manufacturers to shield EMI/RFI emissions and seal electronic enclosures, protecting them from environmental hazards. Conductive silicones can be applied directly to areas that require environmental sealing and EMI/RFI shielding, and cured in place to form a customized gasket that eliminates the need to inventory cut gaskets.

A number of conductive fillers can be incorporated into gasketing formulations. These materials are available with varying levels of attenuation and different cure methods, including heat cure and room-temperature vulcanization. In addition to environmental protection and EMI/RFI shielding, conductive silicones can also be used to provide ground paths for electronic devices that require high flexibility. For example, on video touch screens, silicone conductive adhesives are used to bond wire. Certain grades of *silver-filled epoxies* are *die attach grades* designed to provide an electrical ground path and transfer heat from the chip to the substrate leads, to a ground strip on the back of the screen, providing an electrical interconnect that communicates the request for information from the touch screen to the circuits inside the computer. Whereas solder and most other adhesives would be too rigid to hold up against the constant contact required by the touch screen, highly flexible and resilient silver-filled conductive silicones easily survive high-impact applications.

9.7.3.3 Anisotropic conductive polymers. Anisotropically conductive adhesives consist of mixtures of conducting fillers in an insulating matrix, just like isotropic conductive polymers. The ability of the these materials to conduct in one axis (the z-axis) while remaining insulators in the x-y plane is governed entirely by the loading, particle size distribution, and dispersion of the conductive filler. The aim with these adhesives is to trap (at least) one conductive particle between conductive bumps on the flip-chip and the corresponding pads on the substrate while preventing bridging between pads.

Figure 9.53 shows a diagram of a cross section through a fine-pitch assembly. Clearly, if the filler loading is increased, the probability of shorts between adjacent pads is dramatically increased. When the filler level is too low, there is a probability that no particles will be trapped between conductors, and open circuits will occur. In most anisotropic materials, the particles are randomly distributed in the matrix material. This in itself can cause problems (particu-

Figure 9.53 Illustration of an anisotropic adhesive.

larly for very fine-pitch applications), because there will always be local variations in particle concentration throughout the material, which can result in an open or short circuit. Various methods have been tried to address this random particle distribution.

The insulating matrix will be either thermoplastic or thermosetting, depending on the final application of the assembly. Although thermoplastics have some advantages (reworkability and assembly speed), they are not normally chosen as matrices for anisotropic adhesives; the robustness afforded by a thermosetting system (resistance to heat, moisture, and mechanical stress) means that they are the more common choice. Epoxy resin-based adhesives are a particular class of thermosetting material that has found wide acceptance in the electronics industry. A broad range of desirable properties are achievable with these epoxy-based systems (adhesion to a variety of substrates, toughness, and corrosion resistance), and the final material properties can be tailored to the final application.

A number of conductive fillers have been used to impart conductivity to the (insulating) matrix. The filler is generally spherical in nature and is often monodisperse; examples include gold-plated polymers, solid gold, silver, nickel, and Sn-based alloys.

9.7.4 Thermal management

Thermal management is a growing challenge in the electronics industry. As the overall size of electronic devices grows smaller, the enclosed electronic assemblies operate at higher frequencies and generate more heat. Increasing input/output (I/O) counts, which make devices faster in cycles per second, also cause electronic devices such as ASIC and other hybrid devices to generate greater amounts of heat. This heat, which can decrease the effectiveness and shorten the component's overall life, must be quickly and effectively dissipated for devices to function effectively. Electronic device manufacturers rely on heat sinks attached to ICs to diffuse excess heat. These heat sinks can be attached using mechanical fasteners, thermally conductive adhesives, greases, tapes, or pressure-sensitive pads. Not all of these methods are equal in their operating effectiveness, thermal management capabilities, or ease of application.

Of all the available methods of thermal management, thermally conductive adhesives are the most process friendly. When applied correctly, adhesives produce minimal air voids, resulting in consistent heat diffusion.

Adhesives can be used on any shape or size device and, in addition to providing a permanent bond, will add structural support to the device. Adhesives provide excellent electrical isolation and will not migrate or loosen during normal application or use. Adhesives are single-component materials that do not require temporary or permanent fixturing with mechanical fasteners; as such, they require little inventory. Because they are versatile and simple to use, adhesives can be dispensed using a manual process or may be automated with a robotic gantry to pick, place, and orientate the preactivated parts (heat sinks). An added programmable syringe dispenser can apply the set amount and pattern of adhesive to the opposite side (component) of the preprogrammed site, or vice versa.

Thicker adhesive bond lines result in improved thermal shock resistance. For consistent performance, it is important to ensure consistent bondline thickness. Adhesive formulators have developed self-shimming adhesives that incorporate tiny, 5-mil (.005-in) glass beads into the resin to ensure a minimum 5-mil gap thickness. Adhesive resins are not thermally conductive by nature. Fillers must be added to the resin base to make the adhesive transport heat more effectively. The most popular thermally conductive filler is currently aluminum oxide, which offers excellent conductivity (70 W/m-K) and low cost. Aluminum nitride and boron nitride offer higher conductivity (150 W/m-K) and higher strength but are also more expensive. Other popular fillers include metals such as steel, nickel, aluminum, and silver, which offer higher thermal conductivity than alumina. Of these, silver has the highest thermal conductivity. However, these metals are also more likely to separate from the resin as a result of their higher density.

Adhesives are easy to adapt for the specific needs of an application; typical alumina fillers can be easily replaced with a substitute filler that will remove heat faster in more demanding environments. Depending on the gap thickness that the adhesive must fill and the speed at which the heat must travel between substrates, the percentage of filler in thermally conductive adhesive resins is typically 40 to 60 percent.

9.7.4.1 Thermal adhesive chemistries. Thermally conductive adhesives are available in several chemistries, appropriate for different applications. For an effective and lasting bond to be established, adhesives require solidification or "cure" to take place. Cure times and methods vary, depending on the adhesive chemistry used.

Single-component silicone adhesives are ideal for environments that undergo extreme temperature cycling (below -55° C to above 200 $^{\circ}$ C). By nature, silicones have low cohesive strength and, therefore, are excellent for repair and rework applications. As they are low-modulus materials, silicones offer limited adhesion and limited abrasion resistance. Most of these materials require exposure to heat to cure, but other available curing mechanisms include room-temperature cure, ultraviolet (UV) light cure, and activator-induced curing. Depending on the adhesive formulation and the temperature required, the electronic component can spend several minutes to several hours in an oven for cure to be completed. Single-component acrylics are general-purpose adhesives that offer good adhesion to many substrates as well as good cohesive strength. These adhesives can withstand normal operating environments in the range of −40°C to 125°C. Acrylics typically require an activator or a chemical that initiates solidification to be applied up to 24 hr before the adhesive is applied. Activator-initiated acrylics fixture between 30 sec to 5 min, with full ambient cure in 24 hr. Activator cured acrylics are very popular in the electronics industry, because many devices cannot withstand the temperatures required for heat cure, and effective light cure is often difficult. Available grades of acrylic adhesives can be easily reworked using a thermal parting tool and mild mechanical action. Acrylics can also be formulated to achieve partial cure or fixturing on exposure to UV light. Because electronic devices seldom incorporate one transparent substrate capable of transmitting light, UV-fixturing acrylic adhesives are formulated with a secondary heat cure mechanism that will complete the cure process in shadowed areas. Epoxies are highly durable adhesives that offer good thermal and chemical resistance, good cohesive strength, and high adhesion to a wide variety of substrates. Available as single- and two-component systems, epoxies will withstand operating temperatures slightly higher than 125°C and cure on exposure to heat or to a two-part catalyzed reaction. Rework is extremely difficult, and sometimes impossible, because of the structure of the epoxy. Techniques used to get the epoxy to revert to a reworkable state will usually destroy the board or the components, which are usually also made from epoxy material. Additional available adhesive chemistries include urethane, polyester, and other thermoset elastomeric systems.

9.7.4.2 Phase-change thermal interface materials. Phase-change technology is the latest development in thermally conductive materials. These materials are generally high-melting waxes that contain conductive fillers. They offer most of the advantages of thermal greases in terms of wetting, bond filling, and conductivity, but they will not migrate. These materials are typically preapplied on the heat sink or arrive from the supplier in the form of a coated pad. When the entire apparatus is heated during the manufacturing process, the phase change material melts (typically in the range of 50 to 60°C) and pro-

9.54 Chapter 9

vides void-free gap filling. Over the next five years, adoption of phase-change technology into the assembly process is expected to grow by 40 percent per year, in large part because of the products' excellent thermal conductivity, ease of application, low cost, and ability to be repaired and reworked.

9.7.5 Conformal coatings

Conformal coatings are polymeric materials used to protect electronic assemblies from a wide variety of life-cycle contaminants. Conformal coatings provide a high degree of insulative protection and are usually resistant to many types of solvents and harsh environments encountered in the product life cycle. The coating materials also act to immobilize various types of particulate on the surface of the PCB and function as protective barriers to the various devices on the board.

They are resistant to moisture and humidity and are often applied as an afterthought (not part of the initial design) to quiet down electrical bias and potential arcing during high-humidity operating conditions, especially on finepitch assemblies. They can also remedy other electrical problems on the board that can occur as a result of the environment in which the electronic device must perform.

The primary traditional classifications are as follows:

- $AR = \text{acryclic}$
- \blacksquare ER = epoxy
- Π UR = urethane
- $\overline{\text{SR}}$ = silicone
- $\text{XY} = \text{parylene}$

These systems are primarily made up of monomers, oligomers, defoaming agents, fillers, and wetting agents. Various combinations of each are added to the formulations to adjust the cured and uncured properties. Solvents were, and still are, typically added to adjust application viscosity. They "flash off" by solvent evaporation, leaving a resin matrix to initiate the cure. The volatile organic compound (VOC) emissions associated with this type of cure created a need for more environmentally acceptable production chemistries and cure mechanisms. Presently, solvent-based conformal coating chemistries exist that are exempt from environmental regulations.

All resins except for acrylic resins are cured by an irreversible polymerization reaction with a varying degree of cross-linking (thermoset polymers). The cross-linking of the epoxy, urethane, and silicone polymers provides very good chemical resistance but also makes it difficult to remove the coatings when performing repair work. No polymerization reaction is taking place when applying acrylic coatings. Therefore, it is misleading to say that acrylic coatings are cured. Most of them are formed by drying a solution of already formed acrylic polymer chains dissolved in a solvent (thermoplastic polymer). Hence,

acrylic coatings are easily dissolved in many organic solvents, providing poor chemical resistance but facilitating repair work. Consequently, most acrylic materials are solvent based.

All except the paraxylylenes have traditionally been solvent based until the 1990s, when environmental issues dictated a need to change. Now, many materials are solvent-free chemistries (100 percent solids). The ability to effect an ultraviolet (UV) cure is commonplace. This new generation of conformal coating materials has also given birth to hybrid coatings that contain two or more systems to achieve superior properties, i.e., acrylic resin and urethane resin (ARUR) chemistries.

The chemical categories discussed above break down into two liquid families, organic and silicone.

9.7.5.1 Conformal coating application. Conformal coatings can be sprayed, either manually or automatically. In manual operations, aerosol cans or handheld sprayguns can be used. To automate a spray process, one of two methods can be employed: a reciprocating spray system or a selective coating unit.

Any application method brings health and safety concerns to the user. Manual operations must address operator issues even more seriously, as the employee will have direct contact with the spray process. In aerosol or manual spray operations, it is suggested that the operator be supplied with adequate respiratory equipment.

Aerosol spray methods are typically used in lower-volume applications rather than for high-volume production. Aerosols have a low solids content (less than 5 percent), so ventilation of the spray area is paramount. Spray in a horizontal position to prevent the flow of coating into undesirable areas and to assist in producing a consistent film build. Masking is required. To ensure total coverage, apply a thin coating (approximately 0.001 in) during each one of four coats, rotating the board 90° after each cycle. Although initial startup costs for an aerosol application system may be low, efficiency is a concern. Material utilization for aerosol applications is typically 25 to 40 percent.

Manual spray operations can be very similar to aerosol applications. Proper ventilation must be ensured. Again, the spray application should be completed in a horizontal position in four thin (0.001-in) passes, rotating the board 90° after each cycle. Masking is required. A manual spray operation should consist of a spraygun, a material reservoir, and a cycle actuation device (trigger assembly, valve controller, and so on). Fluid and air pressure can be regulated to produce a fine, atomized spray. When using a material reservoir, be sure to pressurize your conformal coating material with dry, unlubricated air or nitrogen. This is especially prudent for moisture-cure coatings that may take on cured characteristics if exposed to unfiltered air for a prolonged period of time.

Care should also be given to UV-curable coatings. Because of the presence of UV in sunlight and other light sources, steer away from using clear feed lines from the reservoir to the spray head. Black tubing can easily eliminate any concerns over UV light penetrating and contaminating your coating process.

Manual spray operations can be a quick, relatively inexpensive avenue into a conformal coating process. Spray heads can accept higher-viscosity fluids than aerosols and may not require dilution. A more controlled spray process can result in greater transfer efficiencies; however, this depends on time and the complexity of each assembly. In bulk spray applications, material utilization may be relatively similar to aerosols. If greater care is taken, utilization can improve to 50 percent or better.

A reciprocating spray system provides a method that incorporates at least one spray valve; more often, many more exist in an automated in-line process. A reciprocating sprayer incorporates a paper belt conveyor that will transport a masked board into the spray area. There, a bank of spray heads will move back and forth over your assembly, producing an even film build. Material tanks will feed each spray head in a similar fashion to the manual process described above. The same considerations for material chemistry and curing mechanism should be observed. Proper ventilation through the spray area must be achieved.

Reciprocating systems offer advantages over manual spray operations. Automating provides increased throughput capabilities and a more uniform coating. However, an investment must still be made in masking or shielding devices, as well as in the automation equipment itself. Material utilization is still an issue, as waste is applied to masking components and the paper belt conveyor.

Variables such as temperature; valve, air cap, and nozzle design; atomization pressure; humidity; and flow rate will all have an impact. Generally, viscosity for spraying is lower than for dipping.

Dipping is a low-cost, efficient way to apply a conformal coating. This method consists of the immersion of an assembly into a bath of coating to supply coverage. Masking of sensitive areas is required. Assemblies should be dipped vertically as opposed to horizontally. Coating thickness, and the inevitable success or failure of this method, relies heavily on the immersion and withdrawal speed. Typically, immersion speeds are recommended to be between 6 and 12 in/min. An applicable speed should be chosen to allow displacement of air surrounding all components and to prevent are entrapment Once immersed, the assembly should remain in the bath until all bubbling has ceased.

The withdrawal speed from the dipping process should be slower than the cascade effect of the coating. This typically can be equated into 1 to 6 in/min. Remember, the slower the withdrawal speed, the thinner the coating.

Slower withdrawal speeds and lower-viscosity materials may cause coating to flow and can produce an uneven coating over the assembly. This is simply a product of gravity and must be evaluated prior to implementation. Transfer efficiencies of 50 to 75 percent can be achieved in a dipping operation.

To coat a limited quantity of board assemblies, a brushing technique may be utilized. This is a labor-intensive operation that may not be suitable for high production rates. This application method consists of manually using a brush or similar device to "paint" the coating on an assembly. This can reduce some masking by virtue of the controlled nature of the process; however, hoping for

a mask-free environment would be optimistic. Brushing is most often used in a repair or touch-up mode. Obtaining uniform film builds over an entire assembly is difficult in this method.

Be wary of air bubbles forming during the application process. It may be necessary to restrict yourself to only one or two strokes of the brush to reduce the possibility of air introduction.

Considerations must also be given to moisture cure coatings that may change in viscosity during application. Use an appropriate solvent or cleaning agent to remove coating from a brush that may be hardened by the cured material.

Polymer films can be deposited on a substrate in a vacuum by the following methods:

- 1. Vaporizing the polymer via sputtering or evaporation (physical vapor deposition)
- 2. Chemically reacting volatile compounds to form a polymer (chemical vapor deposition)
- 3. Reacting two or more volatile metal organic compounds (metal organic chemical vapor deposition)
- 4. Plasma polymerization of stable organic compounds (plasma enhanced chemical vapor deposition)
- 5. Laser polymerization of stable organic compounds

The major techniques are physical vapor deposition and chemical vapor deposition; all other vacuum deposition techniques are special cases of the two major ones. The major advantages of vacuum film deposition are as follows:

- 1. It provides rapid processing.
- 2. The substrate coverage is conformal.
- 3. Vapor penetrates small interstices.
- 4. No liquid sheath is present on substrates.
- 5. Films can be highly cross-linked.
- 6. The growth rates can be controlled.
- 7. Sterile films are produced.
- 8. Multilayered films are readily deposited.
- 9. Because thin films can be readily prepared, polymer usage is minimized.

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