THE CHEMISTRY & PHYSICS OF UNDERFILL

Dr. Ken Gilleo
ET-Trends
gilleo@ieee.org

Abstract

Underfill is today's polymer magic that enables the increasingly popular 2nd generation Flip Chip - lower cost assembly on organic substrate. This paper will provide a basic understanding of the chemistry of underfills and the physical properties that are important to their successful use. Underfills are a carefully formulated composite of organic polymers and inorganic fillers. Fillers are the most important single ingredient in the modern underfill. We must therefore examine the affects of filler characteristics on underfill pre-cured and post-cured properties in some detail. Finally, we will investigate the total rheology of underfill in order to understand the material-machine interface and better define the underfill process.

Introduction

Underfill was originally tested as a sealant to protect Flip Chip (FC) joints from corrosion on IBM mainframe computer modules. This early work led to the unexpected discovery that thermomechanical fatigue could be reduced. The improved thermocycle performance, while of small value for already robust ceramic FC systems, is absolutely essential for reliable FC-organic systems with their significant thermomechanical mismatch.

Low expansion silicon-based FCs assembled to much higher expansion organic Printed Circuit Boards (PCBs) result in high stress on solder joints during each temperature excursion. Heating causes the PCB to expand at a significantly greater rate than the chip causing destructive strain on joints. Exposure to low temperatures produces excessive contraction of the circuit board that again deforms joints. Relatively short Weibull lifetimes (thermal cycles where 63.2% of parts fail) result thus supporting the conclusion that Flip Chip is impractical on organic substrate.

Fortunately, the placement of a strongly adhering material with the correct physical properties, increases the thermomechanical life to a totally adequate level. The hardened underfill takes on an expansion rate approximately equal to that of the chip in the plane of the chip interface. This reduced expansion rate is then transmitted to the surface of the PCB thereby constraining the previously excessive movement in the X-Y plane. The locked-in-step results in very little differential movement between substrate and chip thus preserving the integrity of the joints. The thermomechanical stress is dissipated in the PCB in the form of non-destructive strain within the organic material.

The principle is reasonably simple, but the required properties of underfill present a significant challenge to the formulator. Pre-cured and post-cured

properties are at extreme ends of the materials spectrum. The pre-cured underfill is expected to flow like water under the smallest gaps, now well under 1 mil (<25 microns) for some of the flex-based packages. The cured underfill is expected to assume rock-hard, inorganic like properties, while bonding strongly to inorganic silicon and organic substrate. The interface is further complicated by the presence of various passivation materials on the chip and any number of solder mask types to the board. And if that were not enough, the modern process line demands that the highly-loaded underfill completely fill the chip-to-board gap in seconds without producing voids. Finally, the conversion from easily flowable liquid to rock-hard solid is expected to occur in only a few minutes under the influence of heat. The resulting underfill interface ridgidizes and protects the joint, whether it is metallurgical, polymer or a combination, as graphically depicted in Figure 1.
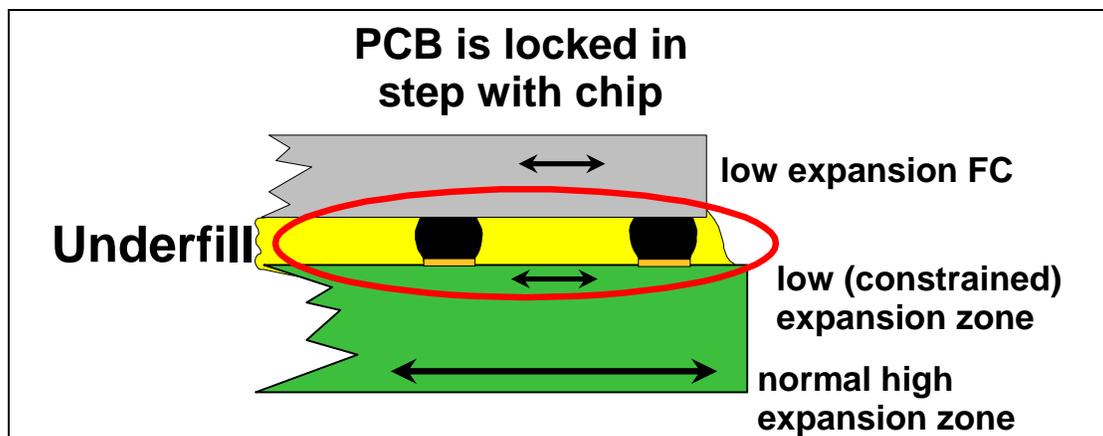
PCB is locked in step with chip

Underfill

low expansion FC

low (constrained) expansion zone

normal high expansion zone

Figure 1 - Role of Underfill

We will first examine the chemistry of underfills and then explore the affects on properties produced by the all-important filler. The affects of filler loading, size, shape, distribution, smoothness and surface treatment will be presented. These filler properties have a profound affect on flow rate and pattern. Flow vs. Temperature will be examined as a means of achieving faster processing.

Polymers

Electronic Polymers, including substrate, die attach adhesives, solder masks, encapsulants and wire insulation, are absolutely essential for modern electronics. Several key properties of polymers make them the only viable materials for many electronic applications. Desirable properties include easy conversion from liquid to solid phase, excellent electrical insulation characteristics, low moisture absorption, high thermal stability and excellent mechanic characteristics. However, one of the most important characteristics of polymers is their capacity to be highly tailored to the required properties.

While literally thousands of polymers are used today, a narrow group is used for underfills. Thermosets, those polymers that are permanently hardened

into non-melting solids, are dominant materials in electronics and the only present choice for underfills. Epoxy systems are preferred for underfills because of their balanced properties, long-established safety record, wide availability, high versatility and general characteristics that are desired in this product area.

Epoxies are typically used as A-B polymer type systems where resin and hardener combine in approximately equal stoichiometric proportions to produce polymer chains made up of both constituents. This provides even higher formulation versatility since properties are contributed by both the resin and hardener unlike homopolymers where only the resin (monomer) dictates properties. Epoxy resins are available in a wide range of properties from higher melting solids to water-thin liquids. The lower viscosity liquid resins, of course, are the ingredients sought for flowable, "capillary" underfills. A variety of co-reactant hardeners are also available, but it is the low viscosity liquid types that are used for underfills.

The most common hardeners for epoxy-based encapsulants and underfills are anhydrides. Low viscosity anhydrides react with the epoxide rings of the resins to form the highly stable polyester group. Each anhydride ring opens to provide two reactive sites for epoxides. The epoxy resins are selected with two or more reactive sites so that long repeating chains of anhydride and epoxy components are produced. Linkages between adjacent polymer chains also result. These cross-links produce excellent mechanical and thermal stability. Cross-linking, configuration that is found in all thermosets, rigidizes the entire structure into permanently-shaped super-molecule (essentially one giant 3-dimensional molecule made up of millions of atoms). Figure 2 shows the polymerization reaction and Figure 3 is a graphical representation of a thermoset structure.
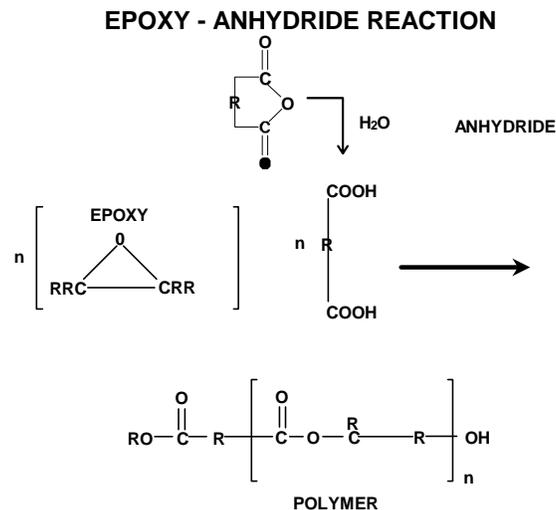
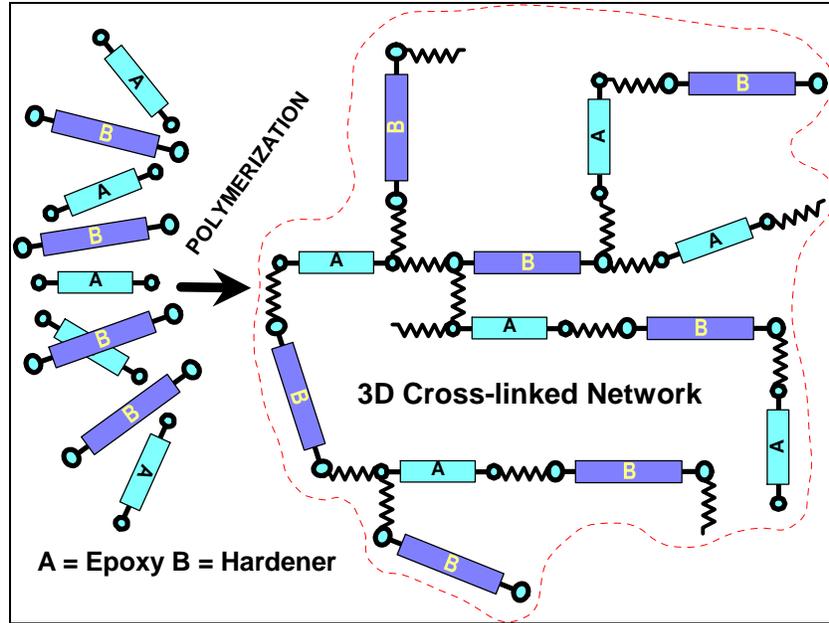**EPOXY - ANHYDRIDE REACTION**

Figure 2

Figure 3 - Molecular Structure of Thermoset Polymer

Underfill Composition

Polymers generally have a relatively high Coefficient of Thermal Expansion (CTE)[1]. Common epoxy systems range around 70 - 80 ppm/^{o}C. Silicon has a CTE value of 2.3 while eutectic solder is around 25 ppm/ ^{o}C. Although thermal expansion of underfill is constrained in the X-Y plane by the Flip Chip, expansion in the Z-direction is unrestricted. Underfill made with resins only will have a CTE that is about three times greater than that of the solder joints. This means that the solder joint will be placed in tensional mode when the FC-PCB assembly is heated and in compression on cooling. The net result will be that the unfilled underfill places destructive forces on the Flip Chip joints. The practical underfill must have a CTE that is reasonably close to that of the Flip Chip joints, 25 ppm/^{o}C, in the case of eutectic solder. Actually, one detailed study has found that the optimum CTE for underfill should be nearly 10ppm/ ^{o}C lower than that of the joint[2], but more on this later.

The simplest means of reducing the CTE of the underfill is to add low expansion filler. Fused silica is the preferred filler because of lower expansion, compatibility with the silicon chip, excellent dielectric properties and high chemical and thermal stability. Virtually all underfills use silica filler to reduce the CTE. The filler is the most important single ingredient in underfill compositions and the area where much of the recent underfill progress has been made. We will now investigate the affects of silica filler on polymer properties in some detail.

Addition of silica to polymers reduces the CTE in a linear manner as shown in Figure 4. We can observe from the graph that more than 60%, by weight, of silica is needed to move the underfill CTE into a practical range. Even if we assume that the CTE value should only match that of solder, about 65% filler is required. There is one major drawback in adding a substantial amount of

solid filler to liquid underfill monomers, however. Viscosity increases dramatically as filler loading is increased. Higher viscosity generally translates to a slower flow rate under the die. The formulator is thus faced with a balancing act of adding filler to achieve an acceptable CTE while still retaining the right rheology for reasonably quick processing. Figure 5 shows the affect of viscosity on filler loading. But there is much more to fillers than just the loading factor.
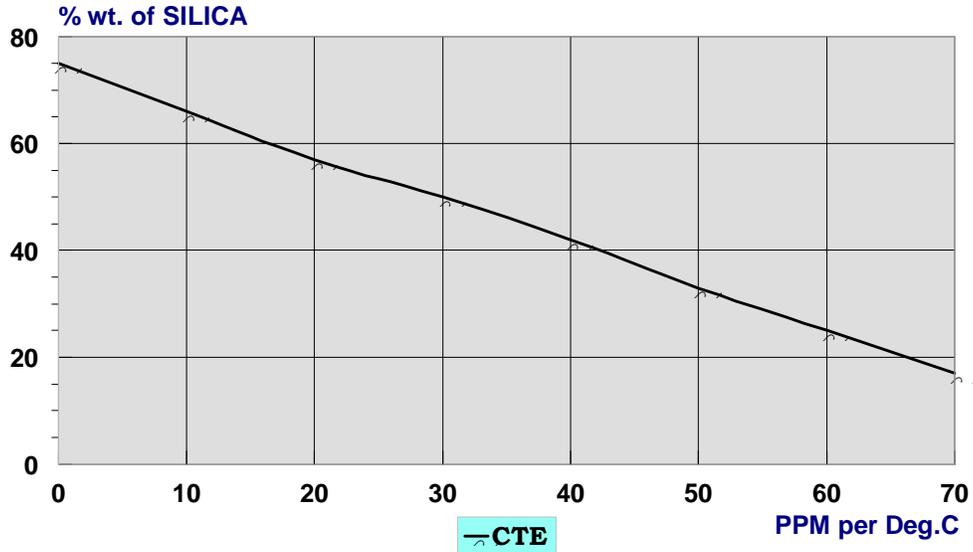
Silica Level vs. CTE

Figure 4

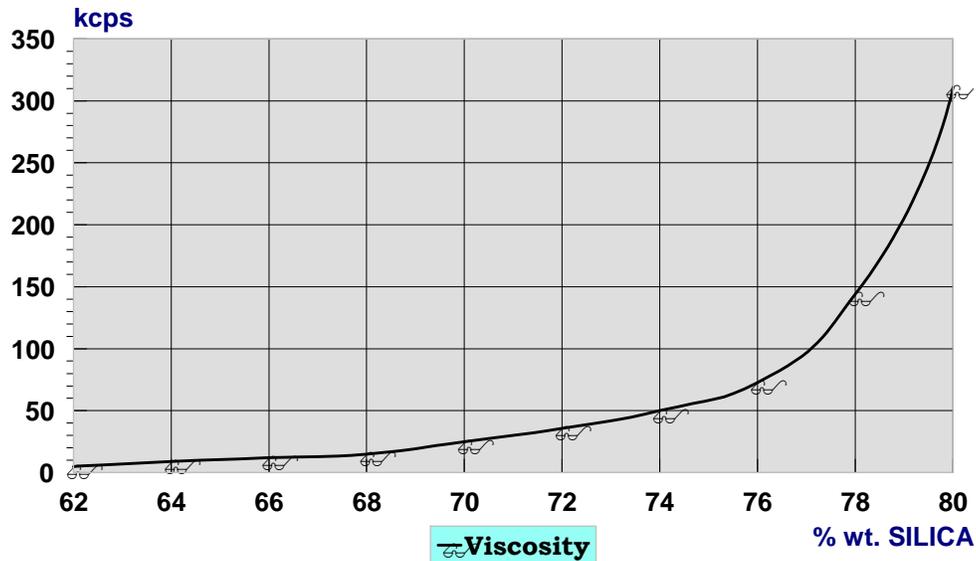# Silica Level vs. Viscosity

Figure 5

The Science of Fillers and Flow

Solid fillers impede the flow of liquids by adding resistance, the subject of many books and articles within the science of rheology. Since the loading of filler is dictated for a particular resin system by the CTE reduction requirement, we need to look at the characteristics of fillers that affect rheology. Any factor that reduces flow resistance should improve underfill flow. A spherical shape is much more conducive to flow than an irregular one which should be somewhat intuitive. An irregular particle sweeps out a much larger effective diameter than a sphere as shown in Figure 6. Spherical fillers are absolutely essential for underfills. A nearly perfect spherical particle will produce a lower viscosity than an "egg shaped" particle and ground mineral fillers are impractical since they produce non-flowing pastes.

Effective Rotational Diameters
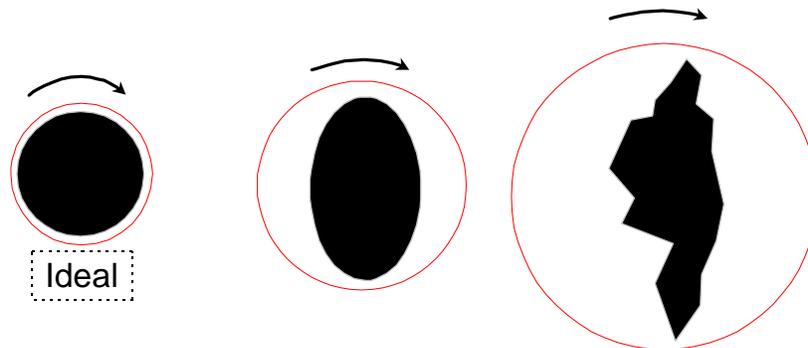
filler particles of equal volume
Figure 6 - Filler Morphology Affects

Even with an essentially spherical shaped particle, surface smoothness is very important. Progress has been made, just in the last year, in terms of producing very smooth surfaces on the microspheres. The surface smoothness becomes increasingly more significant as smaller particle sizes are used. Very fine fillers of less than 8 microns in diameter can produce high viscosities with impeded flow unless the very smoothest materials are used. Before moving on, lets examine the relation between filler size and rheology.

Viscosity increases as the filler size is reduced when weight loading is kept constant. This is because reduction of diameter for a given weight of filler increases total surface area. The more solid surface area in contact with the underfill liquid resin system, the greater the drag. The affect filler of size on underfill rheology is well behaved but non-linear as seen in Figure 7. This is predicted by rheological equations which need not be covered here. The simple answer to faster flow would appear to be the use of larger diameter particles. However, the gap size dictates the maximum particle size that can be used. Let's see why.
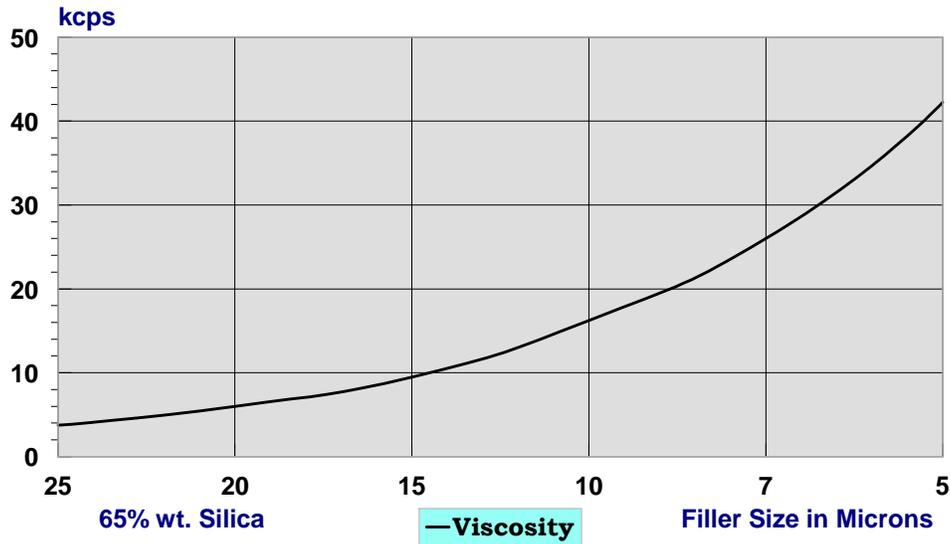
Viscosity vs. Filler Diameter

Figure 7

Gap Size Constraints

Flip Chip gap sizes range from a high of up to 12 mils (for solder bumped PCBs) down to a low of about 15 microns for thermocompression bonded chips on flexible substrate. The gap, of course, can not be smaller than the particle diameter if any filler is to flow under the chip. However, we have found that the practical diameter must be considerably less than the gap. Empirical tests have shown that flow is greatly restricted unless that gap is more than twice the particle diameter. For example, when the gap height is about 2.1 times the maximum particle diameter, underfill will flow between the chip and substrate under ideal circumstances. Tests with glass slides and precision spacers verifies this rule of thumb. However, if a glass slide is placed over a PCB, surface roughness comes into play and a 3:1 gap to filler size is recommended. The probability of 3 particles getting trapped, shown in Figure 8, is unlikely. Conversely, there is no benefit in reducing the ratio much beyond 3:1. For example, a 6:1 ratio will not have a problem with clogging, but the unnecessarily small particles will restrict flow as was shown in Figure 7. Our recommendation is to select a filler diameter of between 3:1 and 4:1 gap-to-filler.
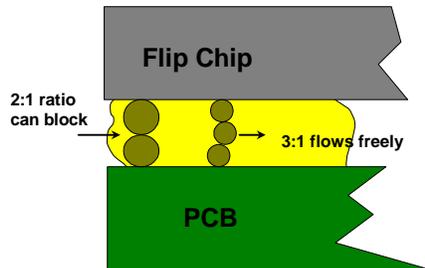

Figure 8 - Gap vs. Diameter

Heating vs. Flow

There are process solutions to the predicament caused by the need for a substantial amount of small diameter filler. Fortunately, the viscosity of most liquids drops with an increase in temperature. Monomers can be even more sensitive to heating. Figure 8 shows the change in viscosity with temperature. However, although flow rate and viscosity go hand in hand, the more useful measurement is flow rate vs. Temperature. Figure 9 shows flow vs. temperature using glass microscope slides heated on a digital hot plate.
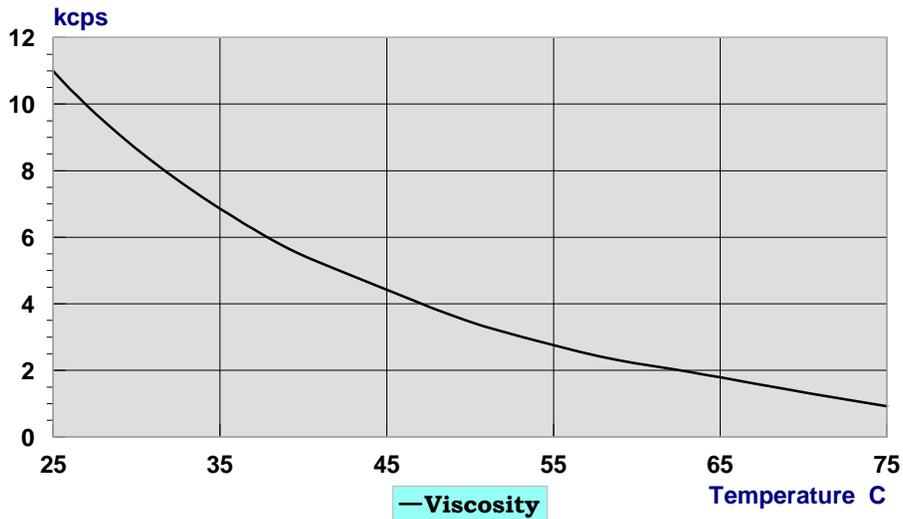
Viscosity vs. Temperature

Figure 9
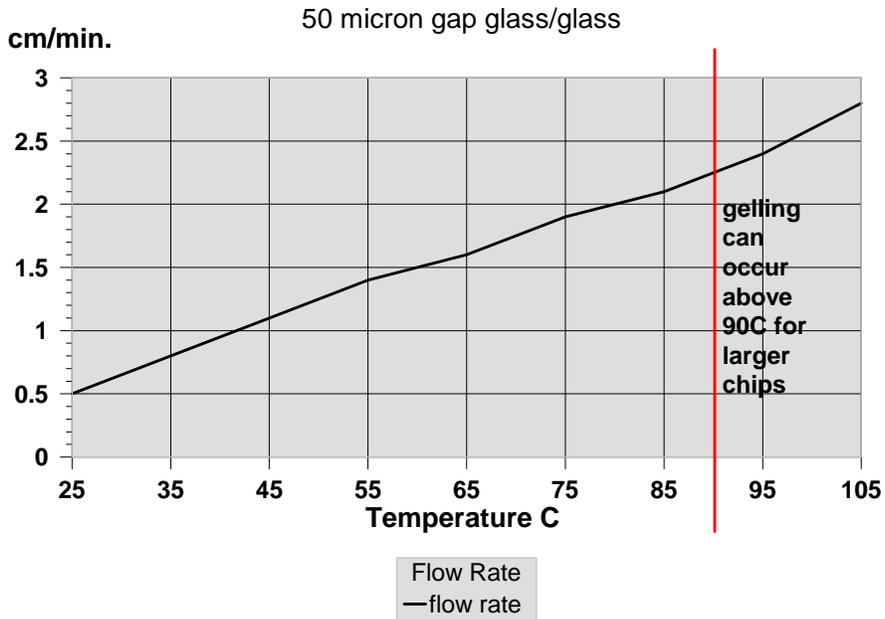

50 micron gap glass/glass

Figure 10 - Flow Rate vs. Temperature

The great boost in flow rate produced by heating underfills has prompted dispensing equipment manufacturers to add heaters to their equipment. Many units have substrate heaters or preheating chambers that can be used to accelerate underfill flow rates. This topic is covered in other papers in the proceedings dealing with dispensing and the related equipment.

One more important factor for flow rate is surface tension of the underfill relative to the surface energy of the die and substrate. Wetting occurs when the surface tension of the underfill fluid is lower than the surface energy of the solid surfaces to be wet. The lower the surface tension of the underfill, the lower the liquid contact angle with the solid surface and the faster the wetting. In fact, a non-wetting situation occurs when the surface energy of the substrate is lower than the liquid and a receding contact results instead of the desired advancing contact angle. This phenomenon is seen when high surface tension water (72 dynes-cm) contacts low energy surfaces like Teflon. Wetting does not occur and no adhesion results.

Since low surface tension results in more rapid wetting with faster flow and is a prerequisite for adhesion, underfills are designed to have low surface tension values, typically under 25 dynes-cm compared to board materials around 35 - 40 dyne-cm. Additionally, wetting agents that are specific to silicon can also be added. Silane compounds with an affinity toward silicon and the ability to chemically bond to that surface are commonly employed. Proper use of such wetting agents can also allow the underfill to flow up the side of the Flip Chip to form a fillet, hence the term self-filleting may be applied. However, self-filleting underfills do not produce complete symmetry around the die edges and some may chose use the dispensing process to produce a more robust fillet. Once the underfill has been dispensed along the edge(s) of the die and flow to all edges is complete, a filleting, or sealing step, may be added. Filleting, or sealing involves adding more underfill to the edges opposite and adjacent to the fill side. This can increase thermocycle performance, especially for larger die. Figure 10 shows the filleting step.
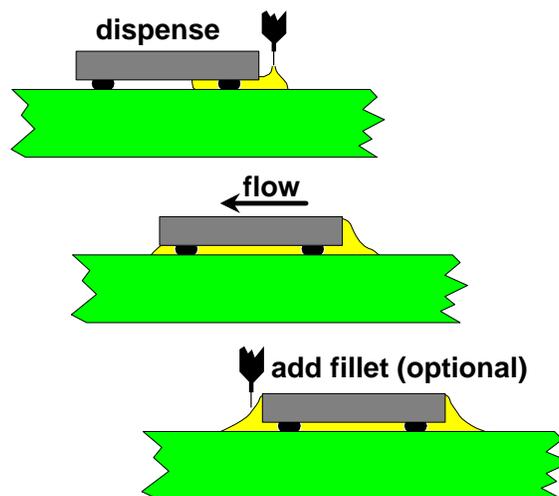

Figure 10

Post-Cured Properties

Once underfilling is complete, the liquid is hardened by the application of heat, although radiation curing with UV or microwaves may be feasible. Epoxy resin-anhydride systems are notoriously slow to polymerize, but accelerators have been discovered that reduce cure times down to 5 minutes or even less. Most underfills following a very behaved reaction rate equation where cure time is proportional to the inverse log function of temperature. An increase of 10 degree C in temperature approximately doubles the reaction rate thereby cutting the cure time in half. Thermal lag must be factored in especially when accessing snap cure (~ 5 minute) systems. Cure rates can be accurately measured using Differential Scanning Calorimetry (DCS) where energy input/output is measured as the underfill is heated to its polymerization point. Since epoxy polymerization is exothermic (produces heat), the end of the reaction is signaled by the absence of additional heat output as shown in Figure 11. The underfill shown in figure 11 is a state-of-the-art *snap cure* system that displays an end of reaction at between 4 - 5 minutes at 165°C.
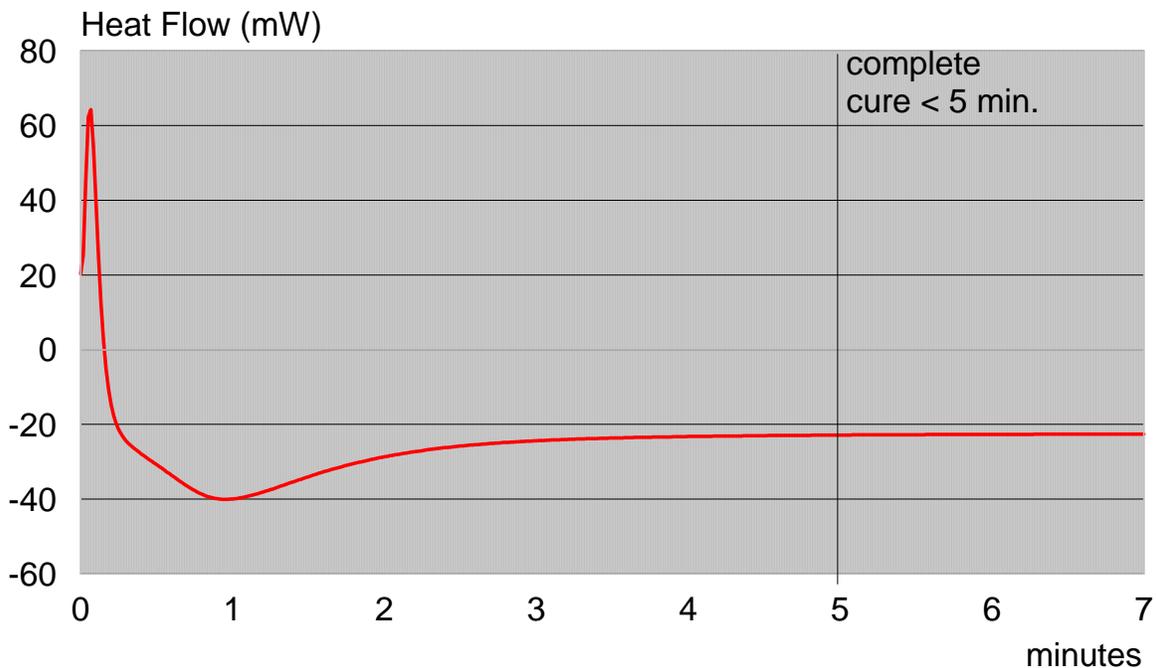
DSC Curve - Time of Cure @ 165C

Figure 11

Glass Transition Temperature (Tg)

Most underfills display a Glass Transition Temperature (Tg) where a major phase change occurs. Above the Tg there is enough heat (increased molecular motion) to allow the polymer chains to move slightly apart and gain additional degrees of freedom (axis of movement). The polymer can not melt because the cross-links prevent the long polymer chains from slipping over one another

thereby changing the bulk shape. The added molecular motion also causes the CTE to increase. The CTE above the T_g, called α_2, may be 3 or 4 times higher than below. This means that a well designed underfill with a CTE of 20 - 25 ppm/^{o}C, displays an excessive expansion rate, up to 100 ppm/^{o}C above T_g. This higher CTE value would produce severe Z-axis strain on the joints leading to thermomechanical failure. This is why the T_g value for most (but not all) underfills should be well above the intended use and test maximum temperature. A T_g of 150 ^{o}C or higher is considered adequate since use and testing is below that value for most systems.

The cure temperature affects the T_g value. A general rule is that T_g will not be much higher than the maximum cure temperature. The snap cure systems may achieve a T_g value of 8 to 10 ^{o}C higher than the cure temperature, however. Since a higher cure temperature usually increases the T_g while reducing the cure time, the industry has attempted to push the maximum temperature. The generally accepted maximum cure temperature for tin/lead eutectic solders is approximately 165 ^{o}C, a temperature that can be handled by the advanced substrate materials being used in Flip Chip applications.

Affect of Temperature on Other Properties

Higher cure temperature was seen to have a positive affect on T_g and cure schedules, but what about other important underfill properties? Adhesion is also enhanced with higher temperatures and strong adhesion to substrate and chip improves reliability. A higher cure temperature may allow chemical bonding to certain PCBs, solder masks and polyimides used as chip passivation and as substrate for flexible circuitry. In every case, with every substrate, including ceramic, we found a boost in adhesion at higher cure temperatures. Longer cure schedules did not have a significant affect once the underfill was thoroughly cured. Moisture absorption was also reduced at higher cure conditions as would be expected due to slightly higher cross-linking density. As would also be anticipated, modulus was slightly increased while CTE was slightly reduced. No negative factors were found by moving from the once-common 150°C cure to the now accepted 165°C schedule.

Undercuring can be very detrimental, whether caused by the wrong oven profile, equipment failure or some type of polymerization inhibition. Poorly cured underfills can have significantly reduced adhesion leading to early thermocycle failure. The importance of adequate curing has prompted some of the leading suppliers of underfill to introduce *polymerization end-point color indicators*. One system is shown in Figure 12 where a color change results during the last 5% of polymerization.
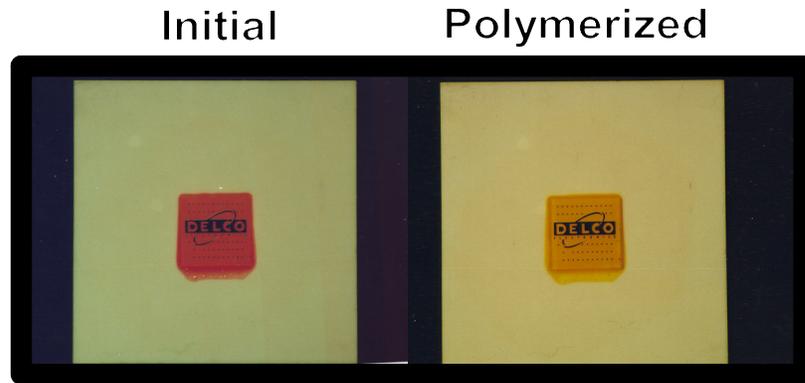
Figure 12 - Color Change on Cure

Conclusions

Flip chip is becoming a main-stream micro-assembly method as the infrastructure rapidly build and technical hurdles are overcome. Flip Chip on organic substrate generally requires underfill to reduce joint fatigue. State-of-the-art underfills have achieved rapid flow, snap cure and the capability of flowing under the smallest gaps. The science of underfill is a multidisciplinary realm embracing both chemistry and physics. Understanding the dynamics of underfill is a prerequisite to the efficient application of this class of materials on modern automated dispensing machines. Fortunately, underfill materials follow the laws of science and the most important relationships have been present here.

Summary

Underfills have come a long way since the days when flow could take minutes and curing required up to 6 hours. The best materials flow rapidly, up to 3 or more cm/minute and cure in about 5 minutes. Advances in filler technology allow underfills to be made that can flow under gaps of well under 1 mil.

Underfills are well behaved in terms of their chemistry and physics. Science can and must be applied to the use of underfills as the "art" content continues to be reduced. Simplified property and use rules can be applied that have a firm basis in chemistry and physics as well as the specialized areas of surface chemistry, rheology and fluid dynamics. The optimum material-machine interface requires that the science of underfills be applied to the technology of dispensing and curing equipment.

References

1) See terminology section at end of paper for definitions.
2) Popelar, S., "A Parametric Study of Flip Chip Reliability Based on Solder Fatigue Modeling", IEEE/CPMT International Electronics Manufacturing Technology Symposium, pp. 299-397, 1997.

Terminology

CTE; Coefficient of Thermal Expansion: change in length of a material per degree C often expressed in parts per million/^{o}C or ppm/ ^{o}C.

T_g; Glass Transition Temperature: a phase transition that occurs at a specific temperature in a hardened polymer from the hard glassy state to the rubbery state. Most materials have lower strength and exhibit a higher CTE above the T_g.

DSC; Differential Scanning Calorimetry: measurement of heat flux (absorption/release) over time especially of reactive materials that can be used to study the onset of polymerization and the end point or completion.