THERMALLY CONDUCTIVE LIQUID MATERIALS FOR ELECTRONICS PACKAGING

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ABSTRACT

Electronics packaging has utilized one-part and two-part liquid adhesives and sealants for many years. Solid thermal interface pads or sheets have also been widely used in electronics applications. As the need for thermal management and heat dissipation increases due to the decrease in size and increase in power utilization of electronics assemblies, thermally conductive liquid materials have seen widespread implementation. Thermally conductive liquids are similar to their non-conductive liquid and conductive solid predecessors in many respects, but also differ in some very significant ways. The rheology, handling, and dispensing characteristics of these materials are quite distinct. The significant advantages of using thermally conductive liquids can best be realized when understanding some fundamental characteristics of these materials. We will present the performance, manufacturing, and reliability issues related to thermally conductive liquids. Significant differences with respect to solid pad like materials and unfilled liquids will be explored.

Keywords: Thermal conductivity, fillers, dispersions, rheology, dispensing, liquids.

INTRODUCTION

In any electronics assembly the thermal pathway between die and component, component and board, board and heat sink/chassis, inevitably contains interfaces or gaps. These interfaces are a potential barrier for heat flow which can affect both the performance as well as reliability of the electronics. Thermally conductive polymeric materials have been used in electronics assemblies to improve heat flow since the late 1980s when thermal management started to become more visible due to increasing power density in electronics [1,2]. Initially elastomeric gaskets with relatively higher modulus ((O) ~ 10^7 Pa) and lower thermal conductivity (< 1 W-m^{-1}-K^{-1}) than modern materials appeared in the market for limited applications that replaced the then standard mica/grease combination. As the power density and variety in electronics packaging exploded in the 90s, so did the development of thermally conductive materials in general. Increasingly, thermal management of electronics has become an important aspect of design activity rather than an afterthought [3, 4]. As a result, the design and usage of thermally conductive materials has also grown in sophistication.

Thermally conductive polymeric materials are now available in a variety of delivery formats and a wide range of properties. In the recent years, the use of dispense-in-place and/or cure-in-place liquids has become more popular as manufacturing volumes have grown. This change has occurred because significant efficiencies in material usage, production costs, manufacturing concerns regarding assembly stress, thermal performance improvement, and structural adhesion can be addressed with the use of thermally conductive liquids.

In this paper we will start with a general description of thermal interfaces. The two subsequent sections will then address the basic structure and properties of thermally conductive materials through a discussion of thermal conductivity and rheology. Next, we will detail issues relating to application performance and manufacturing contrasting the differences between pre-formed gaskets as well as non-conducting liquids. We will end with a summary of the most important aspects of thermally conductive liquid materials.

THERMAL INTERFACE MATERIALS

Thermally conductive polymeric materials or thermal interface materials (TIMs) are typically made of a polymer matrix that contains dispersed thermally conductive particles. Table 1 lists typical thermal conductivity values for some materials.

Table 1. Thermal Conductivity of Typical Materials

Material	Thermal Conductivity (W-m^{-1}-K^{-1})
Argon	0.018
Air	0.026
Typical Elastomers	0.1-0.2
Alumina	20
Aluminum Nitride	180
Boron Nitride	360 (in-plane); 1 (through-plane)
Aluminum	220
Copper	380
Pyrolytic Graphite	1500 (in-plane); 50 (through-plane)
Diamond	2000
Single Walled Carbon Nanotubes	6000 (along length)
TIM	1-10

The objective of thermally conductive materials is to eliminate air gaps between heat transfer surfaces. As Table 1 showed, the thermal conductivity of air is 2-3 orders of magnitude lower than that of typical thermal interface materials. Heat transfer can be improved significantly by eliminating this resistance to heat flow.

Variables other than thermal conductivity affect the ability to efficiently transfer heat in an assembly, a characteristic which is also known as thermal performance. If thermal conductivity was the only concern, sheets of metal or highly thermally conductive ceramic would be widely utilized as interface materials. The reduction of interfacial resistance using conformable materials that wet the interface surfaces is critical to success. The rheology of the TIM and the deformation behavior of the material under stress are very important to the quality of contact between the TIM and the substrate. The interface between surfaces has gaps on two different length scales. The first is small-scale roughness, as is seen in Figure 1, which is typically on the order of 1-10 μm from which air is eliminated by flow and wetting by the interface material.

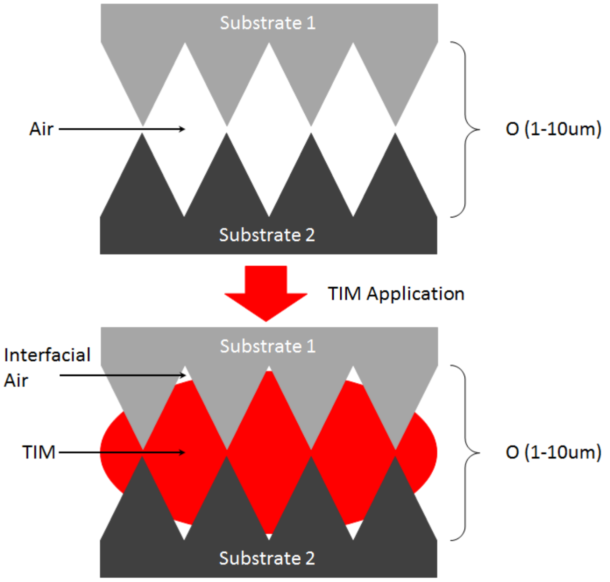

Figure 1. A Typical Thermal Interface

The second is related to larger gaps due either to the non-planarity of surfaces and poor co-planarity as can be seen in Figure 2. Thermal conductivity plays a more important role here but so does the rheology of the TIM. The thermal interface material needs to be able to conform to the surfaces, with a low external stress to produce deformation without straining the electronic components.

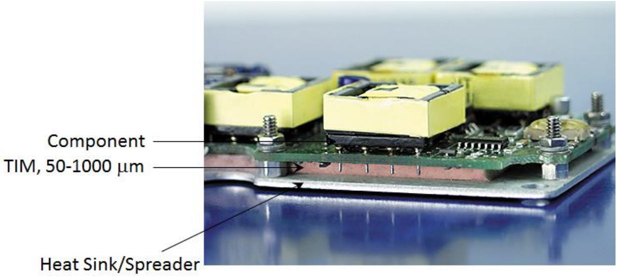

Figure 2. Representative Thermal Assembly

This is an area where liquid materials excel, when compared to pre-formed gaskets, since the component stress during assembly is orders of magnitude lower.

The key properties of liquid thermal interface materials, which affect the final performance, are thermal conductivity, rheology, and size of the particulates added to the material.

THERMAL CONDUCTIVITY

The thermal conductivity of a polymeric material that is filled with particles is naturally a function of the thermal conductivity of the filler and the polymer. In addition, the increasing proportion of filler increases thermal conductivity [5-7]. Finally, the morphology of the particles is key to determining the thermal conductivity of thermally conductive composites.

As seen in Fig 3 heat travels in pathways that are a combination of series and parallel steps through polymer (slow heat transfer) and filler (fast heat transfer). As the filler fraction increases, so does thermal conductivity, however it does not increase indefinitely.

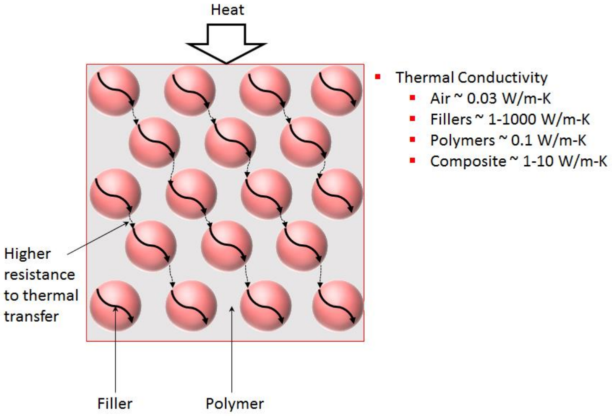

Figure 3. Thermal Transport in a Simplified TIM

This limitation occurs because filler particles are hard and therefore have a limiting volume fraction due to packing constraints. In addition, there are significant bottlenecks to heat transfer from particle to particle since heat, or phonons, must traverse the small polymeric region between particles. In cases where particle/particle contact occurs, the contact area is generally a small fraction of the overall filler surface area.

Figure 4 shows the structure of a thermal interface material where the particles and resin can be seen.

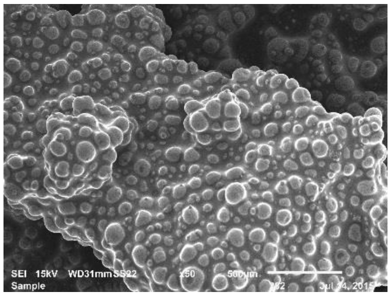

Figure 4. SEM image of TIM material, 50x

One model that has been widely used to predict thermal conductivity is the Nielsen model, which reproduces the basic behavior of filled polymer composites [7].

$$\frac{k_c}{k_p} = \frac{1+AB\phi}{1-B\psi\phi} \qquad \text{Eq. 1}$$

Here

k_c is composite thermal conductivity
k_p is polymer thermal conductivity
k_f is filler thermal conductivity
ϕ is filler content
A is a function of particle geometry

where

$$B = \frac{{k_f}/{k_p} - 1}{{k_f}/{k_p} + A}$$

$$\psi = 1 + \left(\frac{1-\phi_m}{\phi_m^2}\right)\phi$$

Table 2 depicts the typical value of A for various particle geometries. In many ways this value is very similar to a maximum packing fraction in rheological models.

Table 2. Typical Values of A for Different Particle Shapes

Aspect Ratio	Value of A	Description
1.0	0.68	Smooth spheres
6-8	0.44	Plates
18	0.32	Plates/rods
24	0.26	Rods
28	0.18	Fibers

RHEOLOGY

Various excellent reviews of the rheology of dispersions are available [8-10]. The rheological models for particulate dispersions have been around for some time starting with the simple Einstein type model for the relative viscosity of very dilute dispersions [11].

$$\eta_r = \eta/\eta_0 = 1 + 2.5\,\phi \qquad \text{Eq. 2a}$$

Where η is the viscosity of the dispersion and η_0 is the viscosity of the polymer liquid in which the particles are dispersed. However, thermally conductive liquids are rarely dilute. Several other models are available for more concentrated dispersions [12-15].

$$\eta_r = \frac{\eta}{\eta_0} = \frac{9}{8}\left[\frac{\left({\phi}/{\phi_m}\right)^{1/3}}{1-\left({\phi}/{\phi_m}\right)^{1/3}}\right] : \mathit{Frankel\ \&\ Acrivos} \qquad \text{Eq. 2b}$$

$$\eta_r = 1 + 2.5\phi + 10.05\phi^2 + A\exp\left(B\phi\right) : T\,\mathrm{hom}\,as \qquad \text{Eq. 2c}$$

$$\log\eta_r = \frac{5}{2}\left(\frac{\phi}{1-K\phi}\right) : Mooney \qquad \text{Eq. 2d}$$

$$\eta_r = \left(\frac{1}{1-{\phi}/{A}}\right)^2 : Ki\,\mathrm{tano}, et.al. \qquad \text{Eq. 2e}$$

Here ϕ_m is the maximum packing fraction. The equations above represent the "low shear" viscosity of dispersions, in other words, they apply to dispersions under very slow deformation. Typical trends for these models are shown in Figure 5.

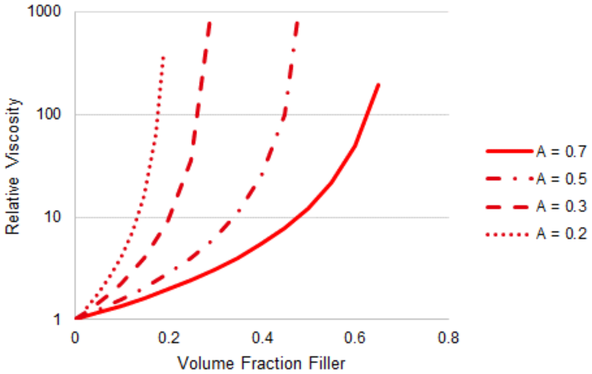

Figure 5. Theoretical Predicted Viscosities of Filled Dispersions

The structure of particulate dispersions can be very sensitive to shear rate. Typically, as shear rate increases the viscosity decreases. These fluids are non-Newtonian. The shear dependent behavior of such liquids can be modeled as a power law [10, 16].

$$\eta = K\dot{\gamma}^{n-1} \qquad \text{Eq. 3}$$

Where,
K is a constant, $\dot{\gamma}$ is the shear rate and n is a constant indicative of shear dependent behavior (n < 1 for shear thinning fluids, n = 1 for Newtonian fluids, n > 1 for dilatant or shear thickening fluids). While mostly one observes shear thinning behavior, at high particle packing and high shear rate a shear thickening effect can occur. This phenomenon is the result of the particles inability to slip past each other as well as disruption of long range order in the filler packing. Figure 6 demonstrates these behaviors.

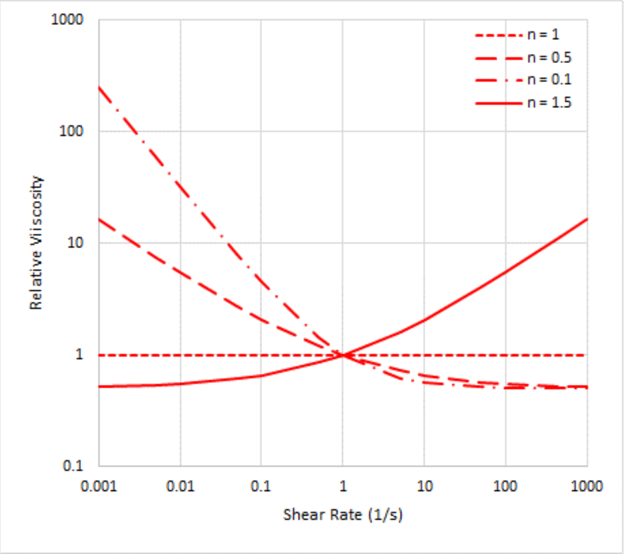

Figure 6. Viscosities of Shear Thinning and Thickening Dispersions

An understanding of the shear thinning behavior can be critical in applications where the fluid goes through a range of shear rates. The fluid is at rest in the package or drum, flows at high shear rate during pumping and dispensing, and again experiences no shear once it has been dispensed in the application. Figure 7 displays some of these shear regimes.

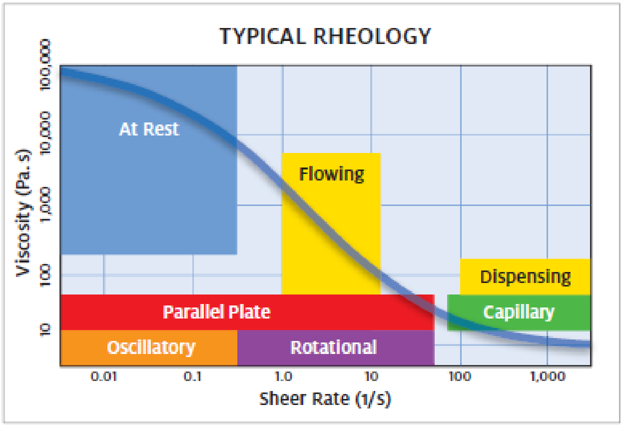

Figure 7. Typical Shear Regimes Experienced by a TIM

Long chain polymers, either entangled or crosslinked, tend to be viscoelastic, i.e. they show both elastic and viscous behavior under various time dependent stress or strain regimes. These materials tend to show more elastic behavior at higher frequencies and more viscous behavior at low frequencies or steady shear. The relative magnitude of these behaviors is represented by the storage modulus G′ and loss modulus G″. These terms indicate the energy stored elastically or lost through viscous dissipation per strain cycle. Most thermally conductive dispersions do not contain long chain polymers but do show some viscoelastic behavior due to the structure induced by hydrodynamic interactions between particles. One such model due to Faulkner and Schmidt [17] shows:

$$G_R' = 1.0 + 1.8\phi \qquad \text{Eq. 4a}$$

$$G_R'' = 1.0 + 2.0\phi + 3.3\phi^2 \qquad \text{Eq. 4b}$$

The subscript R denotes reduced, i.e. normalized to the properties of the polymer liquid matrix.

It is useful to make a comment on the common usage of terminology. The terms thixotropic and rheopectic describe respectively thinning and thickening behavior over time i.e. they describe time dependent behavior rather than steady shear behavior. In common industrial usage the term thixotropic is also used to describe shear thinning behavior, which is a typical behavior of particulate dispersions.

BONDLINE AND INTERFACE THICKNESS

An important factor in the ultimate thermal performance and reliability of an adhesive, paste or cure-in-place gasket, is the bondline. This value is the thickness of the interface after the manufacturing operation.

Sometimes the bondline is dictated by the mechanical and electrical requirements of the final application. In this case the rheology of the material is tailored to suit the manufacturing requirements. One may have a highly shear thinning material that is dispensed in place and does not flow away or one that is self leveling and exhibits low viscosity even at low shear.

If the bondline is not set by external mechanical constraints, then the final interface thickness is determined by one of the following factors: (1) External force on the interface and the yield stress of the material or (2) largest particles in the particulate dispersion.

Particulate dispersions can behave like plastics that need a minimum stress to deform. This plastic behavior can be modeled by, among others, the Herschel-Bulkely model [18].

$$\tau = \tau_0 + K\dot{\gamma}^n \qquad \text{Eq. 5}$$

Where τ_0 is the yield stress. The Herschel-Bulkley model reduces to the familiar Bingham plastic model when n = 1.

As an example, a material with a $\tau_0 < 50$ Pa is easy to pour like milk and is self leveling; between 50-120 Pa the dispersion is a thick but pourable material; between 150-250 Pa the dispersion will hold its shape when dispensed. Higher yield stress materials can create a problem if proper pumping equipment is not chosen. Voiding can occur in the material as it will not reflow into any disturbed areas.

If the external stress is sufficient to deform the liquid, the size of the particles, their concentration, and their modulus determines the final bondline. The ceramic or metal particles used in thermally conductive liquids are typically high in modulus and crush strength. Therefore, it becomes very difficult to get below the thickness of roughly D_{90} of the particle size distribution – 90% of all particles are below this particle size. In some cases, especially at high filler loadings, the particles may not flow past each other and form a single layer. In this case one could get stacking of particles 3-4 deep as is seen in Figure 7.

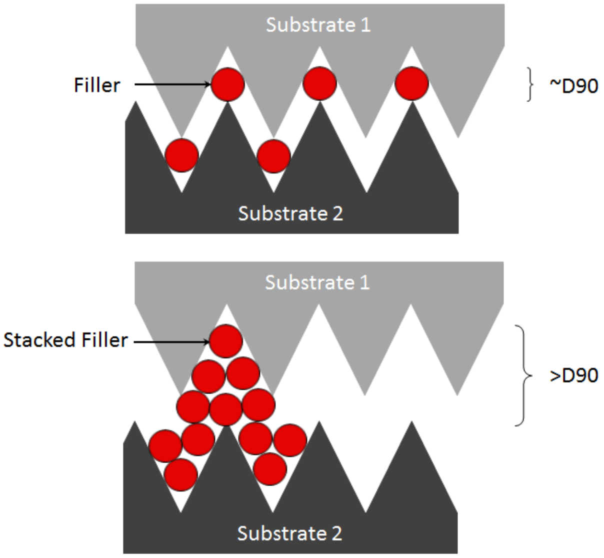

Figure 7. Bondline Limitations from Particle Size and Loading

APPLICATION PERFORMANCE

Issues related to the thermal performance of pre-cured solid materials have been described in detail in many other texts [3,4]. In this section, we will highlight those features of thermally conductive liquids that distinguish them from solid materials.

Material Categories

Firstly, liquids are available in various formats depending upon suitability in an application. These include the following general categories:

Thermal Greases: These are relatively lower viscosity polymer liquids that have been loaded with thermally conductive particulates. These are thermoplastic, i.e. they will deform continuously under external stresses without limit until the dimensions of the application approaches those of the fillers.

Thermal Pastes or Gels: These are relatively higher viscosity materials with a higher molecular weight linear or branched polymeric matrix. This gives them a certain rheological stability and some elastic properties. Ultimately these materials behave like greases, but with a higher yield stress.

Curable/Reactive Liquids: These may be either adhesives or form-in-place gaskets (gap fillers) and may be one component (1-k) or two component (2-k). These are thermoset materials that crosslink into a network that will initially deform in response to external stresses until the internal stress in the material resists further deformation.

Thermal Impedance

The thermal impedance between two points in any electronics assembly refers generally to a measured temperature difference and power dissipation. For a general overview of thermal management

$$\theta = (T_1 - T_2)/P \qquad \text{Eq. 6}$$

Here θ is thermal impedance, T_1 and T_2 are temperatures measured at two different locations and P is the power output from the electronic device or package. This thermal impedance is can be roughly modeled as:

$$\theta \approx \theta_C + l / K.A \qquad \text{Eq. 7}$$

Where θ_C is the contact impedance, which is a function of the surface roughness, wetting and flow between surfaces. *l* is the bondline thickness which is a function of the application geometry, material rheology, particle size of dispersion, and external stress. K is the thermal conductivity of the dispersion and A is an effective area for heat transfer between surfaces.

Typical gasketing materials may have a modulus ranging between 10^5-10^7 Pa whereas liquid dispersions have a yield stress significantly below 10^3 Pa. Therefore, the assembly stress needed for achieving similar bondlines is at least two orders of magnitude less for liquids than it is for typical gaskets. As a result, for a given assembly stress which is dictated by the component or board mechanical strength a thinner bondline can be achieved with liquids. This lower bondline then leads to a lower thermal impedance. In addition, this significantly lower yield stress allows liquids to flow and wet out the surface better thereby reducing the contact resistance, θ_C, significantly over gaskets.

Mechanical Performance

Curable liquids, especially adhesives, couple stresses between two surfaces much better than the combination of gaskets and mechanical fasteners or laminating adhesives due to better wetting and flow. This result means that liquid adhesives can provide better adhesion strength when applied at lower pressures compared to laminating adhesive gaskets or pressure sensitive adhesives. One property worth noting is elongation to break or toughness. As the filler volume fraction increases above a critical volume fraction, the elongation to break of the final cured gasket decreases significantly. The higher the aspect ratio, the lower this critical fraction. It is typical to have elongation to break below 10% above this loading. These properties are of deep interest for adhesive applications where power or thermal cycling produces deformation of the interface due to coefficient of thermal expansion, CTE, mismatch.

Property Optimization

To achieve better thermal conductivity, the dispersions need to contain a large concentration of particles. However, this change also leads to a higher yield stress and potentially a higher bondline, which have an adverse impact on thermal performance. Additionally, higher filler loading leads to poor contact resistance as well as poor wet out and lowers toughness and strength as can be seen in Figure 8. All these also impact thermal and mechanical performance adversely.

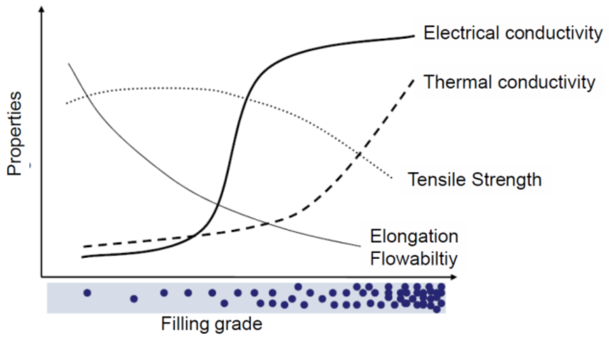

Figure 8. Variation in Material Properties with Filler Loading

The design of thermally conductive liquids must be tailored to the application. The liquid properties need to be optimized based on performance trade offs as well as manufacturing and reliability considerations.

MANUFACTURING CONSIDERATIONS

1-k or 2-k liquids can be applied in a variety of ways to an application. Much depends upon factors like volume usage, packaging, shelf life, and application requirements. One advantage of using liquids, besides performance as noted above, is the fact that the material usage is targeted and optimized leading to lower materials and operating costs. A given gasket must be purchased at a thickness larger than the designed gap to accommodate compression, but a smaller volume of liquid can perform as well or better.

Leveling/Shear Thinning

Depending upon the geometry and the time between dispensing and final assembly the liquids may need different rheology. For thick bondlines and longer open time between dispensing and assembly, there would be need for a material with high yield stress that will flow easily when stressed i.e. a shear thinning material. For a complicated geometry where liquid needs to flow and wet out a varying topology there will be a need for a self-leveling material i.e. one with a yield stress below that caused by gravity.

Assembly Stress

While a liquid dispensed material will apply less stress to an assembly, there is nonetheless stress when pressure is applied to cause the material to flow. If the rheology of the material allows it to flow easily under pressure then one option may be to dispense a bead using a thin nozzle. Typically, a bead traces a pattern on one surface that allows all active areas to be covered once the assembly is made. Various patterns are evaluated, and visually inspected for efficient materials usage, by using a transparent cover to simulate the other surface. This method can be seen below in Figures 9 and 10.

Figure 9. Dispensed Bead of Liquid Paste

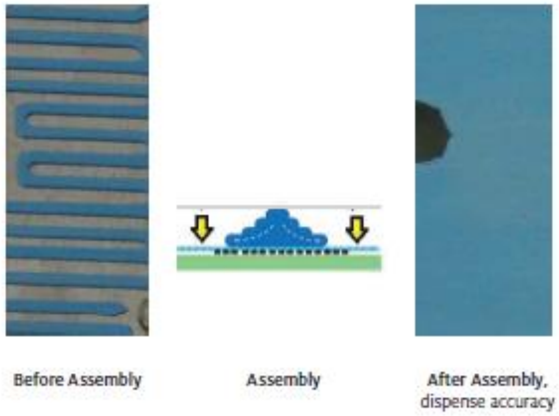

Figure 10. Material Patterning and Assembly

In some applications, either due to higher viscosity or fragile components like LTCC or thin ceramic boards the material may be applied in a more uniform pattern to reduce localized stress build up. It may also be possible to automate dispensing in a dot or line pattern as seen in Figure 11.

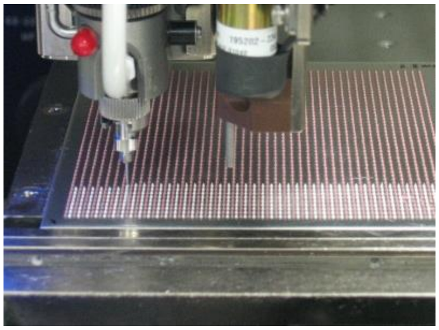

Figure 11. Dispensed Pattern

Other options include screening the liquids or stenciling them if their large particle size does not allow easy screening. Below in Figure 12 is an example of liquid gap filler stenciled in various patterns.

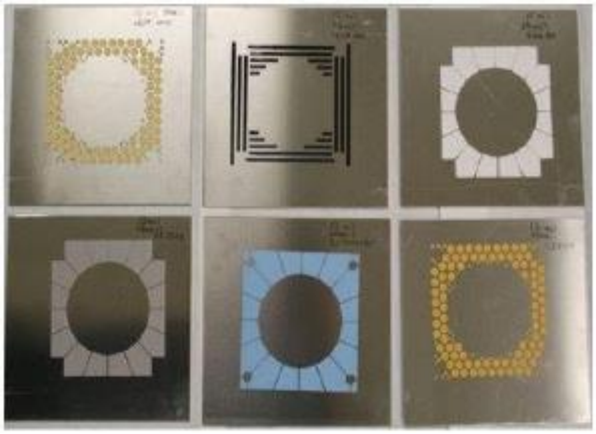

Figure 12. Stenciled Liquid Gap Filler

Abrasion

Typical thermally conducting liquids contain abrasive ceramic particles. In pumping these materials there is abrasion of moving parts that come into contact with the liquid and particles. As such the manufacturing process must account for wear and replacement of worn parts or invest in up front fixed costs in abrasion resistant parts. Many equipment manufacturers of pumping and dispensing equipment have addressed these issues and supply equipment made from or coated with wear resistant materials.

Filler Separation/Caking

As noted earlier, under high shear the particles may not be able to flow past each other and start aggregating. In addition, if there are sharp corner or fittings, the particles may separate under centrifugal action and accumulate in dead spaces. Figure 13 shows an example of a desirable sweeping elbow fitting as opposed to a problematic sharp corner fitting.

Figure 13. Curved and Sharp Corner Fittings

Finally, if the fitting the not designed well for the pressure needed for pumping, the polymer fluid may leak slowly and cause the local concentration of filler to build up until a cake forms as shown in Figure 14.

Figure 14. An Elbow Fitting Exhibiting Caking

All these issues can cause the clogging of tubing and fittings [19]. Loose fittings or sharp corners are the most commonly implicated components in poor pumping performance. Equipment manufacturers are now taking these factors into account to produce robust pumping systems.

Open/Working Time

The issue of open time is applicable mainly to curing materials where the rheology changes with time. Open time refers to the time window available after dispensing when the final assembly needs to be completed. When the lag time between dispensing and assembly is large, there will be a need for long open time. Another related concept is pot life, which refers to reactive material that is pre-mixed before application. Sometimes adhesives or gap fillers may be pre-mixed before screening or stenciling. In this case there is limited time before the liquid viscosity increases and makes it unworkable, which is the pot life.

Shelf Life

Unfilled liquid polymer systems have storage or shelf life limitations based on the lifetime of reactive species. Over time reactivity is lost and the materials do no cure to the same final properties. Thermally loaded polymer systems also have similar limitations. In addition, filler settling imposes another limitation on shelf life. Most ceramics are denser than the polymer liquid they are dispersed in and hence settle over time. The settling rate depends upon the liquid viscosity, particle size, concentration, and density difference between the particles and the polymer liquid. Settling velocity of particles, which is inversely proportional to shelf life, can be approximated as

$$v \approx \frac{1}{t_{shelf}} = \frac{2}{9}\frac{r^2 \Delta\rho g}{\eta} \qquad \text{Eq. 8}$$

Where $\Delta\rho$ is the density difference, g is gravitational acceleration, η is the viscosity of the dispersion (which depends upon local particle concentration according to Eq.2) and r is particle radius. Over time there is some stratification if the dispersion is left undisturbed. Shelf life is typically defined as the time until less than 0.5 vol.% of the dispersion has separated and the final properties of the material in the application are unchanged. Figure 15 shows separation in a TIM material stored in a 5 gallon (20L) pail.

Figure 15. Separation in a TIM Material

There are also procedures for remixing if the material is otherwise chemically stable although care must be taken to avoid incomplete mixing or air entrainment.

Volumes

For high volume usage as defined as 5-10 cc per application and 10^6-10^7 applications per year it is economical to package the material in pails or drums and use some pumping equipment to deliver the material on an assembly line. This option requires higher fixed costs in capital and lower operating expenses. For moderate usage such as ~ 1 cc, 10^4-10^6 applications per year the liquids can be pre-packaged in 1-k or 2-k cartridges, which can be used in simple automated machines that essentially push the material out of the cartridge and through a static mixer using a piston. In this case, the operating expenses may be slightly higher due to extra packaging but the fixed costs are lower. Finally, for smaller volumes still, packaging in small cartridges and dispensing through manual piston systems is a possibility.

CONCLUSIONS

In this paper the main thrust has been to focus on the physics, which underlies the properties of thermally conductive polymeric dispersions. As these materials become more ubiquitous it is imperative to understand not only the important factors that a thermal design engineer may focus on but also the manufacturing engineer who will implement these materials in volume usage. Significant cost and performance benefits can be realized with liquid thermally conducting materials mainly due to lower stress during assembly, better wet out, and more efficient material usage. For greater success, attention must be paid to the storage, handling, and dispensing of these materials due to the unique challenges presented by their large concentration of particulate fillers. These issues are being directly addressed by equipment manufacturers and now have technically and economically viable solutions on the market.

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