ADVANCED BORON NITRIDE EPOXY FORMULATIONS EXCEL IN THERMAL MANAGEMENT APPLICATIONS

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Abstract

Epoxy based adhesives are prevalent interface materials for all levels of electronic packaging. One reason for their widespread success is their ability to accept fillers. Fillers allow the adhesive formulator to tailor the electrical and thermal properties of a given epoxy. Silver flake allow the adhesive to be both electrically conductive and thermally conductive. For potting applications, heat sinking, and general encapsulation where high electrical isolation is required, aluminum oxide has been the filler of choice. Today, advanced Boron Nitride filled epoxies challenge alternative thermal interface materials like silicones, greases, tapes, or pads. The paper discusses key attributes for designing and formulating advanced thermally conductive epoxies. Comparisons to other common fillers used in packaging are made. The filler size, shape and distribution, as well as concentration in the resin, will determine the adhesive viscosity and rheology. Correlation's between Thermal Resistance calculations and adhesive viscosity are made. Examples are shown that determination of thermal conductivity values in "bulk" form, do not translate into actual package thermal resistance. Four commercially available thermally conductive adhesives were obtained for the study. Adhesives were screened by shear strength measurements, Thermal Cycling (-55 °C to 125 °C) Resistance, and damp heat (85 °C / 85 %RH) resistance. The results indicate that low modulus Boron Nitride filled epoxies are superior in formulation and design. Careful selection of stress relief agents, filler morphology, and concentration levels are critical choices the skilled formulator must make. The advantages and limitations of each are discussed and demonstrated.

Introduction

For more than 30 years, epoxies have played a critical role in electronic assemblies. They were first introduced into the hybrid industry and enjoyed much success in bonding components, protecting devices, and hermetically sealing packages. Just as they provided an attractive alternative to eutectic bonding in hybrids, they were implemented in semiconductor packaging. Today, nearly 80% of the world die attach market for plastic encapsulated devices is solvent-less conductive epoxies [1]. Even further down the packaging hierarchy, epoxies have played a key role in board level assemblies; acting as encapsulants in advanced packaging techniques such as COB and TAB [2]; staking SMT components to PCB's [3]; silver filled conductive epoxies for solder replacements [4 - 6]; and lastly as thermal management for heat-sinking applications.

A few reasons why epoxies are wide spread and commonplace in electronic assemblies include: low temperature cure profiles allow for greater availability of substrates and temperature sensitive components; compliant nature of the polymer; low outgassing and good thermal stability at elevated temperatures; very good chemical and solvent resistance; 100% solid systems are environmentally benign; and epoxies readily accept fillers. ASTM D-883 defines fillers as "a relatively inert material added to a plastic to modify its strength, permanence, working properties, or other qualities, or to lower costs." Because they accept fillers, the formulator can

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tailor the electrical and thermal properties of the adhesive for a given application. This paper analyzes the performance of several commercially available thermally conductive adhesives, and provides a formulator's perspective as to the success in the design of the adhesive.

Results and Discussion

Because epoxies are insulators and very poor thermal conductors, fillers must be introduced into the epoxy in order to provide thermal transfer. The thermal conductivity of an epoxy will be determined by the choice of filler, the percentage of filler loading, and morphology of the filler particle; all of which play a critical role in the overall viscosity / rheology of the epoxy formulation. Table I lists typical fillers used by epoxy formulators and their respective thermal conductivity's [7]. For comparisons sake 2 epoxies are listed.

Table I. Thermal Conductivity of Typical Packaging Materials

Material	Conductivity (W / m-°K)
copper	393
gold	297
silver	418
alumina	30
boron nitride	600
organics	
conductive epoxy	5
FR-4	0.2

source: Microelectronics Packaging Handbook

A true vacuum (k=0) and a diamond (k=2300) are considered the limits of the thermal conductivity spectrum.

While it is true that boron nitride is a better thermal conductor than say, silver; it is not necessarily true that a boron nitride filled epoxy is more thermally conductive than the same silver counterpart. This is due to filler size and shape. Silvers typically are very fine two dimensional - like flakes associated with lubricants. When incorporated into an epoxy, the result can be a nice smooth, creamy, adhesive consistency. Boron nitride (BN) filler particles can be very large and amoeba-like. The overall adhesive consistency can be very viscous and dry. Because the BN filled epoxy is very viscous, and "bulky", it is difficult to handle, entraps air easily, and yields thick, voided bond layers. In contrast, the silver filled epoxy dispenses very well, with a uniform adhesive layer completely null of voids. The silver filled adhesive most likely will have better thermal transfer than the identical adhesive which uses boron nitride filler

The size, shape, and composition of the filler powders will determine the viscosity / rheology of the adhesive. In theory, the thinnest bond-line possible for an adhesive is the maximum size of the filler particle contained in that resin. Generally speaking, it is always advantageous for an adhesive bond-line to be kept to a minimum. Therefore, in designing an adhesive to act as thermal interface, formulators will avoid large particle size fillers at high concentrations in the resin, as they result in higher viscosity adhesives. For this reason, thermally conductive epoxy adhesives have been formulated with very fine filler particles at moderate concentrations. They will yield lower viscosity adhesives, resulting in thinner adhesive bond-lines. Silver, alumina, and boron nitride fillers are used most commonly while copper is avoided.

Some formulations exist with diamond fillers to promote the highest thermal conductivity but these applications are few. According to researchers at University of Arkansas High Density Electronic Research Center (HiDEC), examining the use of diamond in high performance MCM's, "although thermal analysis favors the use of diamond, stress analysis does not." Designers can only relax the induced stresses by careful thermal profiles after curing the adhesive [8]. Also, the cost of

diamond filled adhesives may be too great for them to be considered.

In choosing thermally conductive adhesives, engineers can be fooled by thermal conductivity values listed on adhesive supplier data sheets. First of all, thermal conductivity values are usually determined by the comparative method, which is performed on a "bulk" adhesive specimen. This method, ASTM E1225, does not take into account bond-line thickness, which will be critical in maximizing heat transfer. Secondly, the comparative method does not take into account possible void formation underneath the component. Air is a very effective thermal insulator, with a thermal conductivity of 0.02 W/m-°K. Therefore, void formation in the adhesive bond-line always impairs thermal transfer. Lastly, thermal conductivity values do not account for adhesion. The comparative method uses a rotary screw to clamp the vertical stack in place. For reasons above, thermal conductivity values can often mislead engineers. It is always advisable for the engineer to calculate the thermal resistance for the intended package.

Four commercially available adhesives were obtained for this study. All four adhesives contained boron nitride filler and the supplier of each described these as "thermally conductive" adhesives. A disinterested third party re-labeled these as adhesive's A through D , concealing their identities to the investigators. A description of each adhesive is summarized below in Table II. Performance and reliability testing for

Table II. Thermally Conductive Adhesive Description

Adhesive	Description
A	2 component, boron nitride filled, low modulus, epoxy
B	1 component, BN filled epoxy, high Tg, 85 Shore D
C	2 component, BN filled epoxy, high Tg
D	1 component, BN filled

each adhesive was carried out. Thermal resistance calculations, component shear strength, component shear strength after 85 °C / 85% RH, and component shear strength following 1000 thermal cycles were used for screening criteria.

Thermal Resistance

Thermal resistance can be simply calculated by knowing the intended bond thickness, thermal conductivity of the interface material, and surface contact area between component and substrate. The formula is shown below:

$$R = l / k A$$

where:
l = length of heat transfer path (i.e. bond thickness)
k = thermal conductivity
A = the effective surface contact area

In most cases, the expected thermal resistance differs from the actual calculated value. As an example, two boron nitride filled epoxy systems are analyzed below. A 5th adhesive, designated Adhesive E, was chosen only for the thermal resistance portion of the study, due to its unusually high thermal conductivity value published on a vendor's data sheet. Table III compares their properties.

Table III. Material Properties for 2 BN filled Adhesives

	E	A
% Filler (by weight)	68	30
Mean filler size (μ)	300	3
Typical Viscosity (cPs)	250,000	17,000
Typical Thermal Conductivity (W/m-°K)	4	1.5

Assuming a 3.0 mil bond line and a bond area of 100 mm square, the calculated thermal resistance will be 0.19 °C / W for Adhesive E, and 0.5 °C / W for Adhesive A. The actual

measured thermal resistance for the former was 2 °C / W, while the latter 0.7 °C / W. One need not speculate why the two differ greatly. Simply put, listed thermal conductivity values do not take into account bond line thickness, possible void formation beneath the component, and adhesion. The measured thermal resistance for the Adhesive E significantly deviated from the expected value. This is due to the huge particle filler at a very high loading (Table III). The result is an adhesive that is extremely high in viscosity which traps air easily, and can not accommodate thin bond-lines. In short, thermal conductivity values should be used as a guide in selection only. What appears advantageous in "bulk" properties, can not model the intended application. Table IV summarizes the thermal resistance calculations of all the adhesives obtained for the study.

Table IV. Thermal Resistance (°C/W)

Adhesive	Expected (from Data Sheet)	Actual (from Package)
A	0.25	0.7-1.0
B	0.5	0.6-0.9
C	0.58	0.8-1.0
D	0.71	1.2-1.6

Aside from eliminating air gaps and voids, other factors to be considered in thermal management are ease of application, CTE's of component and substrate, and cost; however cost is best addressed in another forum and clearly not intended for discussion in this paper.

Application Method

Current methods of attachment are thermally conductive adhesives available in tapes or liquids, and non-adhesives. The former consists of silicones, epoxies, and acrylics, while the latter consists of thermally conductive pads, or greases [9]. The pads themselves can be used in conjunction with adhesives or mechanical fasteners. Most pads are silicone based interface materials, but others can be thermoplastic hot-melts; some pads are available with pressure sensitive adhesives for easy mounting, while others are clipped in place. Just like some of the pads, thermally conductive greases must be used with metal clips. The clips, which are usually stainless steel, provide easy attachment and resistance to the most demanding shock and vibration. They are most commonly used with microprocessors. Thermally conductive tapes have been formulated with polyimide or polyester supported films and pressure sensitive acrylic adhesives.

Epoxy adhesives, like tapes, can provide high thermal conductivity and electrical insulation making them ideal for bonding heat sinks to transistors, components, packages, and boards. Epoxy impregnated glass cloth is one such example. But epoxy preforms, like tapes, are usually hand applied. So although their attachment is simple, they require operators for manual hand placement. Thus, a benign process to an operator may come at the expense of overall product through-put. Manufacturing Managers must decide which is the best case for assembly; ready to fit precision epoxy films laid down by hand, or the variables, parameters and trouble-shooting common with automation?? Epoxy resin adhesive pastes must be considered since they allow for automated volume production. Acting as thermal interface material for component bonding, they are most commonly dispensed; while screen printing is the method of choice for high thermal conductivity epoxy dielectric coatings.

The data shown below in Figure 1 suggests that all four adhesives have a large processing window, making them suitable for dispensing or printing applications. Adhesives B and C can be used for 24 hours without compromising the bond strength. Adhesive D is the weakest of the 4 tested and also shows that component strength will decrease during the course of its pot-life. Adhesive A, on the other hand, had a similar processing window as D, but clearly was the strongest of the four adhesives tested. Thus, B and C seem more attractive for

manufacturing reasons, while A suggests the most robust adhesive joint.

Adhesive A, with a smooth creamy viscosity, allows for easy application by dispensing. Most production groups find it more cost effective for them to purchase a two component epoxy pre-mixed and shipped frozen in syringes. In this way they avoid operator variations in weighing, mixing, and transferring to syringes. Like all two part epoxies, pot-life and useable work time are critical in volume manufacturing. The convention for adhesive suppliers is to report pot-life as the time it takes for the material to double in viscosity. Because it was designed for dispensing methods, the pot life has been redefined to the time it takes the material to grow 10% in viscosity,

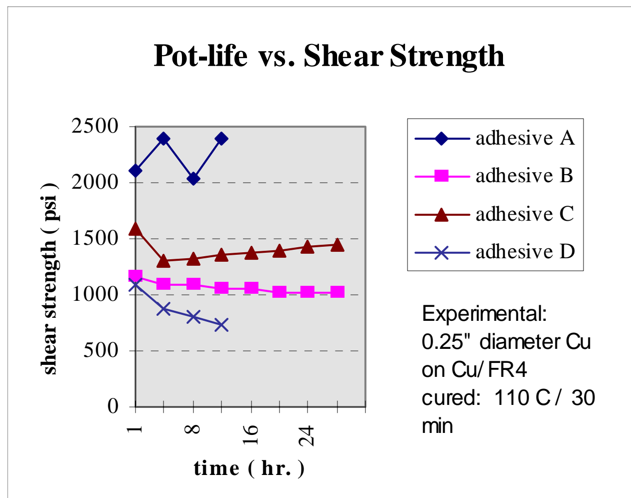

Figure 1. Shear strength versus pot-life for several commercially available thermally conductive adhesives. (reproduced with permission from G.F.C. Lijten, Philips Centre for Manufacturing Technology, Eindhoven, Netherlands)

as this will be significant enough to alter the dispense parameters and require operator intervention on the manufacturing line. Even though the pot-life for Adhesive A is listed on the data sheet as four hours, there is no drop off in shear strength over a 12 hour period. Thus, the short four hour pot-life for Adhesive A might be viewed as a negative, however, it clearly has little effect on its adhesive properties and this work suggests that reliable bonding can be realized in twelve hours.

CTE

Table IV lists the Coefficient of Thermal Expansion of common packaging materials [10]. An unfilled epoxy typically has a CTE value of 50-70 ppm / °C, acrylics and urethanes 180-250 ppm / °C, and silicones 800 ppm / °C. It is important to realize that adhesives used in electronic assemblies will never be CTE matching to the components and substrates which they bond. Stresses across the adhesive joint will be realized due to differing expansion rates between substrate and component. The incorporation of filler particles into an adhesive not only increases thermal conductivity, as previously discussed, but also lowers the CTE of the adhesive. An epoxy which is loaded 68% by weight of fused silica, yields a reduced CTE value of 24 ppm / °C. Rosler 1989 demonstrated that increasing filler particle loadings resulted in lower CTE values for epoxy molding compounds [11].

However, increasing filler loadings result in higher viscosity adhesives; and as previously shown, higher viscosity pastes can be troublesome in thermal management applications. Thus, low CTE adhesives are formulated at the expense of overall viscosity, which compromises thermal transfer. This poses a challenge to adhesive formulators. Lastly, increasing filler levels for the purposes of reduced CTE, causes the Modulus of Elasticity of the adhesive to increase.

Table V. CTE of Typical Packaging Materials

Material	CTE (10 e-6 / °C)
copper	17
silver	19.7
kovar	5.3
aluminum	23
96% ceramic	6.6
silicon	2 - 7
FR-4	15
leadframe Cu alloy	17

source: Microelectronics Packaging Handbook

In overcoming the CTE mismatch, formulators have added flexibility and stress relief to the adhesives. A proposed solution is a moderately filled adhesive (yielding good thermal transfer) which is high CTE but slightly flexible. Flexible species, or low modulus adhesives, have the ability to store lots of mechanical energy. Given a certain applied stress, the resultant strain is very small. Low modulus species have the ability to absorb stresses due to dissimilar CTE's of components and substrates commonly found at all levels of packaging. An adhesive's job is not to support a load but to distribute the load. If the stresses are too severe, a delamination of the adhesive from the substrate will result. Therefore, the formulator will lower the modulus of the adhesive to compensate for the high CTE mismatch. A high modulus adhesive will have a difficult time absorbing the stresses associated with CTE mismatch, resulting in cracking, de-coupling, or delamination of the adhesive on 1 or 2 surfaces. Heavily filled adhesives can be so high in modulus that they do not respond well to thermal cycling, thermal shocks, and vibration. Impact resistance is very low with high modulus species.

Low modulus and flexibility is added to epoxies by incorporating plasticizers. The first stress relief agents were natural rubber, occurring in over 200 species of plants. However, synthetic rubbers, namely styrene butadiene elastomers (SBR) and acrylonitrile-butadiene copolymer elastomers (NBR) are used today. Other flexiblizers are silicones, and CTBN [12]. The adhesive is said to have been "toughened" when plasticisers and other stress relief agents are added to the formulation. It is commonplace that adhesive polymers can be toughened by either addition of compliant or rubber phase particles, rigid inorganic, or thermoplastic particles.

As early as 1994, it was found that adding rigid glass particles to an existing rubber modified polymer (i.e. combination of the two toughening mechanisms above), provided additional increase in toughness of the polymer. More recently, it was found that a special combination of rigid BN particles with CTBN provided fracture toughness greater than the additive effect of the two mechanisms separately [13]. This group has proposed the explanation in which the toughening mechanisms interact in a positive manner and the data agrees well with existing models. Simply put, the more toughened the adhesive, the greater the reliability of the adhesive joint. The joint will be much better equipped to survive accelerated environmental aging studies like thermal shocks and cycles, or vibrations, which it may encounter in the field or in the lab.

Adhesive A is characterized as a low modulus adhesive. Its flexibility was introduced by long chain aliphatic groups. Because this plasticizer lacks functionality, it impairs cross-linking of the primary resin. The lower degree of cross-linking results in more resiliency within the adhesive. The long chain flexible epoxy resin is reactive in a single phase within the epoxy matrix, unlike the inert rubber elastomers which are separate phase. The formulation design of Adhesive A was carefully chosen, and we wished to observe whether the BN epoxy could be as reliable as DiBerardino and Pearson, 1998. But, unlike them, the choice of the flexible species was not rubber based, but long chain aliphatic epoxy resins.

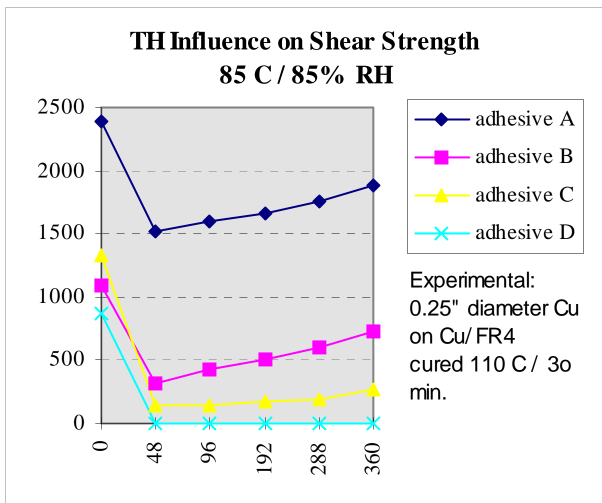

Figure 2. Shear strength as a function of environmental conditioning for several commercially available thermally conductive adhesives. (reproduced with permission from G.F.C. Lijten, Philips Centre for Manufacturing Technology, Eindhoven, Netherlands)

Just like filler loadings, aliphatic flexible epoxy resins do have limitations. They are never used alone due to lack of toughness, and sensitivity to moisture and water absorption [14]. Being used as additives in epoxy formulations, they can compromise the adhesive's ability to shed water and moisture. Formulators are challenged with adding flexibility at the expense of total water and moisture uptake. The blend of flexible epoxy resin to primary resin in Adhesive A may be considered ideal and efficient. Environmental conditioning suggests that it has not compromised the epoxy adhesive's overall sensitivity to moisture. Figure 2 shows the relationship of shear strength versus hours of dwell in a humidity chamber at elevated temperatures. Using adhesive shear strength to quantify overall product performance, it is clear that Adhesive A is superior. Its shear strength has been only slightly lowered.

Furthermore, a benefit of lowering the adhesive's modulus is that it increases the materials resistance to thermal fatigue. Figure 3 shows that Adhesive A can meet repeated thermal cycles without any reduction in adhesive shear strength.

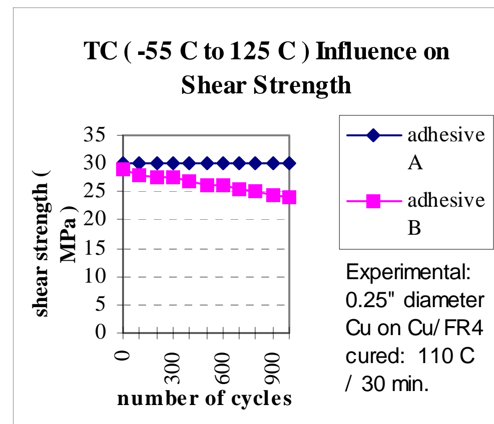

Figure 3. Shear Strength as a function of thermal cycling. Adhesives C and D were eliminated from the study due to their poor resistance to damp heat (reproduced with permission from G.F.C. Lijten, Philips Centre for Manufacturing Technology, Eindhoven, Netherlands)

This further illustrates the efficiency of a flexible-to-primary resin blend. Adhesive strength is not compromised at the expense of stress-relief additives.

Conclusion

Boron nitride filled epoxies must be considered for all thermal management adhesive applications. They allow for high volume, automated production, eliminating the need for operator hand assemblies associated with thermally conductive pads and tapes. Also, epoxies eliminate the need for metal clips to hold components together when used in tandem with pads or greases; thereby saving board space while reducing weight and minimizing costs. Generally speaking, an increase in filler loadings results in increased thermal conductivity but at the expense of viscosity and rheology. Adhesive formulators use fine fillers at moderate concentrations allowing for low viscosity pastes. These are very efficient in eliminating air gaps which impede thermal transfer. Thermal conductivity values listed on data sheets should be used as a guide only. They usually do not represent the true measured thermal resistance for the application.

Boron nitride filled epoxies are certain to play an integral role in replacing traditional thermal management methods. Electronic packaging is packing greater overall functionality and performance while minimizing space. With increasing pin counts and clock speeds at a fraction of size, heat dissipation in microprocessors will be significant. One group has addressed this issue by incorporating boron nitride into the epoxy molding compound [15]. In a 176 lead TQFP, they have shown that the boron nitride filled epoxy molding compound (EMC) has 2 °C cooler improvement than a traditional silica filled EMC with molded in heat sink. The boron nitride filler increases performance, with fewer purchased parts, resulting in overall lower costs.

Adhesive A, 2 part boron nitride filled epoxy is a novel thermally conductive adhesive formulation which provides maximum thermal transfer with low filler concentrations. The relatively high CTE of the adhesive is compensated by the addition of a flexiblizer. This allows bonding of large components, substrates, and other PC boards for heat sinking applications. The addition of a moisture sensitive flexiblizer has not compromised its reliability. It is a very attractive alternative to thermally conductive tapes, greases, pads, and diamond filled epoxies.

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