Beyond the Technical Data Sheet

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ABSTRACT

The traditional materials science tetrahedron emphasizes the interdependence of process, properties, structure, and performance. For instance, changing a process can affect a material's properties, or pushing a stretch performance requirement may require tradeoffs in manufacturability. This work explores the usefulness of the materials tetrahedron as it applies to the selection and processing of polymeric composite materials used in microelectronics. We will examine examples where changes in process can change the material properties or performance of polymer composites used in semiconductor packaging and board assembly, such as adhesives and encapsulants. While the technical data sheet is crucial for initial material selection and guidance on recommended processes, a deeper look at the interplay of process, properties, structure, and performance needs is worthwhile.

Key words: die attach adhesives, packaging, materials tetrahedron.

INTRODUCTION

The link between structure, properties, processing, and performance is widely used in materials and mechanical engineering colleges and universities [1-3]. Accurate mechanical properties such as coefficient of thermal expansion (CTE) and modulus that are necessary for predictive modeling, are often taken for granted, as fixed for a certain material and process. However, mechanical properties are affected by the processing of the materials. These processes can also affect the structure of the material. The ultimate performance of the materials that we use are intertwined with structure, properties, and processes.

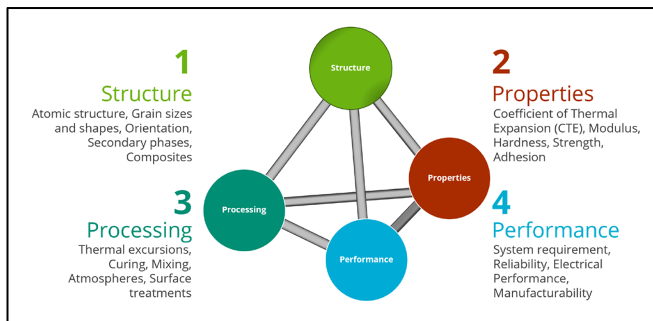

Figure 1. Materials tetrahedron

Microelectronics and semiconductor packaging have not escaped the materials tetrahedron's lessons. The example below elaborates the material tetrahedron-based relationships for silver-filled die attach adhesives, particularly the influence of the morphology of the filler.

RESULTS AND DISCUSSION

Influence of morphology of silver fillers in die attach adhesives

Silver filler is used commonly in die attach materials that require electrical conductivity. The silver lowers the CTE and increases the thermal conductivity and the electrical properties. Figure 2 shows significant differences of the structure of the silver flake. Three cross section Scanning Electron Microscopy (SEM) images of silver-filled die attach materials show fillers with a plate-like structure and a high aspect ratio (left), a significantly lower aspect ratio (middle), and a highly loaded smaller more rounded morphology (right).

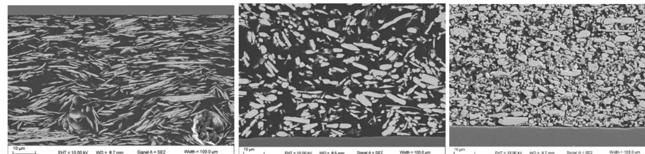

Figure 2. SEM cross sections of silver filled die attach materials

Surface area, morphology, size, variety of sizes, and % mass loading of the silver flake in die attach adhesives are very different. Each of these affect the properties, processability, and ultimately the performance of the package. For instance, the surface area of large plates is higher than spherical shapes per mass. The surface area may affect the dispensability. High mass loading of silver increases the thermal conductivity of the die attach, but it can lead to higher viscosity. Increasing diluents and solvents can help with dispensability, however it may lead to resin bleed, voiding during cure, or outgassing problems. Therefore, there are often tradeoffs that are in the purview of the material formulators and suppliers with respect to structure and process which can have significant effect on the properties and performance of die attach materials.

One such influential process factor is their curing schedule. For the same die attach adhesive cured following different schedules, properties and therefore, resultant performance can be significantly different. In this work, we focus on the effect of the cure schedule of die attach adhesives on their

outgassing behavior and influence on properties such as glass transition temperature (T_g) and adhesive shrinkage. The impact of this work is to highlight the influence of cure schedules in causing changes in die attach adhesive performance, which can lead to undesirable outcomes such as die warpage.

Effects of cure schedules on outgassing mass loss of die attach adhesives

Polymers such as adhesives, coatings, or in mechanical members can outgas small quantities of chemical species whose presence can affect performance of the component or device. For e.g., satellites are particularly susceptible to lens fogging due to condensed outgassing from materials. The criticality of outgassing for space applications requires testing of materials for total mass loss and for condensation.

The original outgas specification was initially written by NASA and is now an ASTM specification. The ASTM E595, Standard Test Method for Total Mass Loss and Collected Volatile Condensable Materials from Outgassing in a Vacuum Environment, is used to determine the levels of outgassing of materials [4]. The measurements in the specification are total mass loss (TML), collected volatile condensable material (CVCM), and water vapor regained (WVR). The specification prescribes TML <1% and CVCM <0.1% acceptable as a pass. WVR is for information only.

The ASTM E595 requires a specimen compartment, heater bar, collecting plate, collector chamber, and a cooling plate. The sample is first preconditioned at 23ºC and 50% relative humidity for 24 hours. Following the preconditioning, the sample chamber pulls a vacuum of 7x10-3 Pa, and then heats the sample to 125°C for 24 hours. Vapors from the heating process are collected on a cooling plate which is at 25°C. The mass of the condensed vapor is measured by weighing the cooling plate, and this with the mass of the sample is used to calculate the TML, CVCM and the WVR.

While polymeric materials including die attach adhesives, solder masks, encapsulants, and coatings can outgas, the quantity of outgassed species depends on the processing parameters. The cure schedule is a processing parameter that is critical to outgassing. NASA has public data on outgassing of several materials and their cure schedules [3] (https://outgassing.nasa.gov/). Tables 1 and 2 show some data from the NASA database, and that data highlights the importance of cure conditions for outgassing.

Table 1 shows the effect of cure time on the TML for two commonly used adhesives. For the cure schedules examined, the cure temperature is fixed at 65ºC, while the cure time was varied from 8 to 48 hours. For two separate samples of Material A that were cured following an 8-hour schedule, nearly identical results of 1.10 and 1.13% TML were obtained. For 24 hours of cure time of the same adhesive, the result was a substantially lower 0.79% TML. Doubling the cure time to 48 hours, however, does not improve the TML appreciably for the Material A indicating that a 24-hour cure at 65°C was sufficient towards removing a significant portion of the outgas species for this adhesive. The Material B die attach adhesive was cured following two schedules: 1.5-hour cure time at 82ºC and a 12-hour cure time at 80ºC. In this case, the TML was approximately halved when the 1.5 cure time was increased to 12 hours.

Table 1. Cure time effects on outgassing data

Adhesive Material	Cure Time (hours)	Cure Temperature (ºC)	Total Mass Loss (TML) (%)
Material A	8	65	1.10
Material A	8	65	1.13
Material A	24	65	0.79
Material A	48	65	0.78
Material B	1.5	82	2.49
Material B	12	80	1.11

Given this data in Table 1, it is possible that cure times longer than 12 hours may result in removing more outgas species in the Material B. In a different approach, Table 2 shows the effect of increasing the cure temperature on outgassing for the Material B. Cure times varied from 1-2 hours and cure temperatures examined were 82ºC, 100ºC, and 150ºC. The TML decreases incrementally from 2.49 at 82ºC, TML 1.18 when cured at 100ºC, and TML 0.76 when cured at 150ºC.

Table 2. Cure temperature effects on outgassing for Material B die attach adhesive

Cure time (hours)	Cure temperature (ºC)	Total Mass Loss (%)
1	150	0.76
2	100	1.18
1.5	82	2.49

Effects of cure schedules on glass transition temperatures of die attach adhesives

A series of differential scanning calorimetry (DSC) tests were performed at Sandia National Laboratories on a commercial die attach adhesive, commonly used in industry, to evaluate the degree of cure from the specified cure schedules. All samples of this adhesive were subjected to different first cure schedules followed by an identical secondary cure schedule. The secondary cure schedule included a ramp up from room temperature to 175°C with a hold for 5 hours at this temperature to simulate an encapsulation process followed by a post-mold cure. After all samples were run, they were subjected to an additional ramp up to 175°C 1 hour to

determine differences in the final cured sample. Table 3 shows the different first cure schedules for the adhesive. Descriptions for the individual Method/Cure schedules show the ramp rate, the temperatures and dwell times, and the measured T_g values.

Cure 1 is a low temperature cure at 125ºC for 2 hours, with a ramp rate of 3ºC per minute. Cure 2 is a standard temperature cure at 150ºC for 2 hours, with a ramp rate of 3ºC per minute. Cure 3 is a low temperature cure at 125ºC for 2 hours, with a slow ramp rate of 0.25ºC per minute. The slow ramp rate and low peak temperature can reduce stress. Cure 4 is a standard temperature cure at 150ºC for 6 hours, with a ramp rate of 3ºC per minute. Kinetics modeling suggests that this will give a full cure of this material. Cure 5 is a step cure, with a low temperature cure at 125ºC for 3 hours, with a slow ramp rate of 0.25ºC per minute, followed by an increased temperature to 135ºC for 3 hours, followed by an increased temperature to 150ºC for 3 hours, with a slow ramp rate of 0.25ºC per minute. This overnight cure in theory would provide the lowest stress cure for a "full" cure.

Table 3. DSC methods and analogous cure schedules

Cure Schedule	DSC Method
Cure 1 • Room temperature to 125°C at 3°C/min • 125°C for 2 hours	**Method 1** • Ramp from 25°C – 125°C at 3°C/min • Isotherm at 125°C for 2 hours • Ramp from 125°C – 25°C at 3°C/min
Cure 2 • Room temperature to 150°C at 3°C/min • 150°C for 2 hours	**Method 2** • Ramp from 25°C – 150°C at 3°C/min • Isotherm at 150°C for 2 hours • Ramp from 150°C – 25°C at 3°C/min
Cure 3 • Room temperature to 125°C at 0.25°C/min • 125°C for 2 hours	**Method 3** • Ramp from 25°C – 125°C at 0.25°C/min • Isotherm at 125°C for 2 hours • Ramp from 125°C – 25°C at 3°C/min
Cure 4 • Room temperature to 150°C at 3°C/min • 150°C for 6 hours	**Method 4** • Ramp from 25°C – 150°C at 3°C/min • Isotherm at 150°C for 6 hours • Ramp from 150°C – 25°C at 3°C/min
Cure 5 • Room temperature to 125°C at 0.25°C/min • 125°C for 3 hours • 135°C for 3 hours • 150°C for 3 hours	**Method 5** • Ramp from 25°C – 125°C at 0.25°C/min • Isotherm at 125°C for 3 hours • Isotherm at 135°C for 3 hours • Isotherm at 150°C for 3 hours • Ramp from 150°C – 25°C at 3°C/min

The glass transition temperature after the first cure was determined in the final ramp for all methods except Method 1. The Method 1 material was sufficiently under-cured that the reaction exotherm interfered with an accurate analysis of T_g. Each sample was also evaluated for T_g following the second cure. Figure 3 shows the first cure cycles as a function of time for both the ramps and the isotherms, and Figure 4 shows the ramps as a function of temperature.

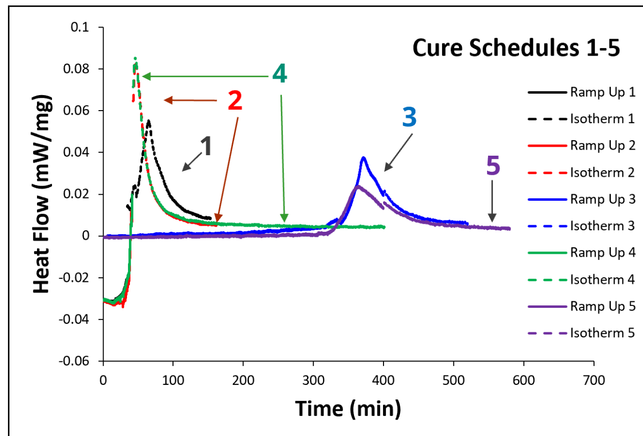

Figure 3. The first cure schedule as a function of time for all methods, not including cooling. The solid lines are the ramp up portions and the dashed lines are the isothermal portions.

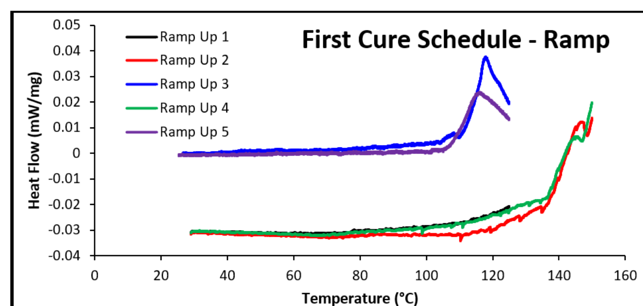

Figure 4. The ramp up portion of the first cure schedule as a function of temperature for all methods.

The DSC data for the second cure ramp (Fig. 5) and the ramp after the second cure step (Fig. 6) are used to determine the level of cure following the first cure schedule and the T_g of the final cured material respectively.

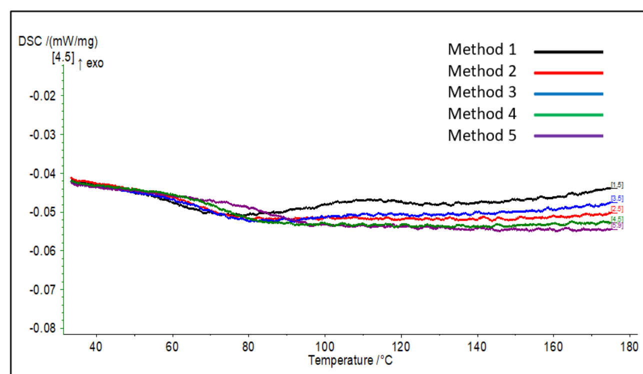

Figure 5. The second cure ramp as a function of temperature for all methods. These data were used to determine the level of cure following the first cure schedule.

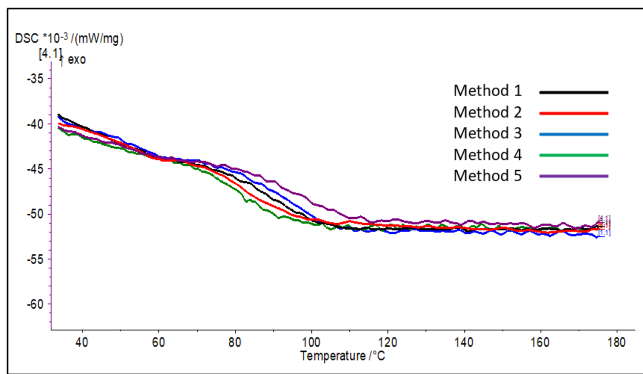

Figure 6. Ramp after the second cure step as a function of temperature for all methods. These data were used to determine the final cured material Tg.

The results of the T_g after the initial epoxy cures and the T_g after the second cure are shown in Table 4.

Table 4. Glass transition temperatures after initial cure and the second cure

Cure or Method	Tg After Initial Epoxy Cure*	Tg After Second Cure ***
1	Unknown **	94.7°C
2	69.1°C	82.6°C
3	70.6°C	95.3°C
4	72.5°C	82.3°C
5	89.5°C	98.4°C

* See Table 3 for the Cure/Method details
** The T_g was unknown because the material was insufficiently cured to measure Tg
*** 2nd cure dwelled at 175°C for 5 hours after initial cures

Method 5 showed the most complete cure for this material. The T_g was highest for this method (89.5°C), a step cure with a slow ramp of 0.25°C per minute and incremental steps of 125°C, 135°C, and 150°C for the first cure. The second cure increased this T_g to over 98°C. Method 1 and Method 3 produced similar glass transition temperatures to each other in the first cure but these were a few degrees lower than Method 5. The T_g for Methods 1 & 3 after the second cure increased to ~ 95°C for both samples. Methods 2 and 4, both of which ramped immediately up to 150 °C for their isothermal hold, exhibited the low levels of cure in the first cure indicated by lower glass transition temperatures, and continued to be on the lower side, even after the post-cure. It is important to note that for Methods 2 and 4, the slow ramp rate of 0.25°C/min, can shift thermal transitions to a lower temperature, and any error in measurement signal intensity can introduce a certain degree of error in the determination of the exact glass transition temperature. Evaluating the degree of cure on samples that went through the initial cure schedule showed a different order for degree of cure. The increased heat flow following the transition can be linked to crosslinking activity in the material. No sample was completely cured after the initial cure schedule, because all samples exhibited an increase in T_g during the second cure step. This evaluation demonstrated the importance of not blindly following the technical data sheet prescribed cure schedules for adhesives and always making sure that the optimum cure schedules are determined for every die attach adhesive prior to being used in manufacturing.

Effect of cure schedule-driven glass transition temperature changes on die warpage

The cure cycles evaluated for this standard die attach adhesive in our study changed glass transition temperature significantly, but knowing the impact of this change on die adhesion and stability would be critical in manufacture. For this, a silicon die was die-attached to a Plastic Ball Grid Array (PBGA) substrate, using the same die attach material. The same cure cycles 1-5 in the DSC data were used for the silicon die attached parts. Sample sizes for each of the five cure cycles were 32 to 36. After the initial cure and post cure, the warpage of each part was measured optically using a Keyence VR-5200. The warp (edges to center) was measured for each die and plotted in Figure 7.

A higher warp indicates a higher stress on the die. Cure 2 and cure 4 have an average die warp of slightly above 0.14 mm. The cures of 1, 3, and 5 are significantly lower, between 0.115 – 0.125 mm average warp. Cures 2 and 4 were initially cured with a 3°C/minute ramp up to a 150°C cure. The initial cures for 1, 3, and 5 all had a long enough dwell at 125°C to cross link at a lower temperature. This effort demonstrated the impact of selecting the right ramp rate to the right cure temperature and allowing for sufficient dwell times at the same to minimize stresses within the material during manufacturing processes.

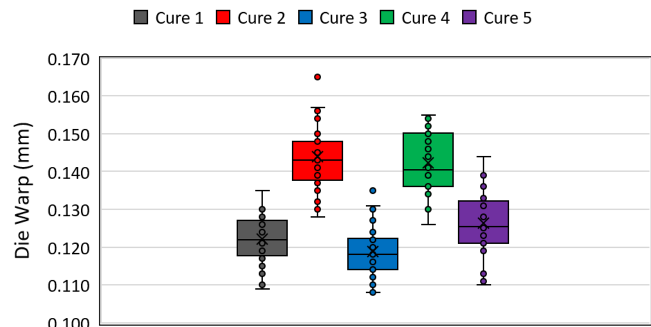

Figure 7. Die warp for cures 1–5 measured on silicon dies attached on substrate, without encapsulation.

Effects of cure schedule on shrinkage of die-attach adhesives

Epoxy materials, such as those used in the adhesives for the die attach process, typically show some amount of volumetric shrinkage during cure. This shrinkage can lead to an increase in stresses within the material. Development of a method to measure shrinkage of the various adhesive candidates, using a small amount of adhesive and a straight-forward, easily

reproduced technique, would allow for selection of an adhesive with minimal shrinkage during cure.

Through adaptation of a method found in literature [5], the material was measured using a rheometer (TA Instruments DHR-1) using 8 mm aluminum parallel plates to minimize the amount of material required for the measurement. The heated cure as described on the adhesive technical data sheet was applied using a ramp of 10°C/min to the isothermal hold of 1 hour at 150°C. The gap between the parallel plates was controlled at 1000 µm until the epoxy reached the gelation point determined via modulus crossover (approximately 16 minutes into the isothermal hold), after which the gap was controlled via maintaining the axial force at 0 N, allowing the gap to shrink or expand with the epoxy. Volumetric shrinkage was then calculated from the change in gap length during the isothermal portion of the cure.

The results from duplicate shrinkage measurements of a commercial die attach adhesive can be seen in Figure 8 below. The measurement showed excellent reproducibility and an average volumetric shrinkage of 1.34% during the isothermal cure. The material shows additional shrinkage during the cooling ramp back to 25°C, which would be expected due to thermal contraction of the epoxy. The corresponding expansion during the initial heating ramp to 150°C was not observed as the epoxy was not yet gelled, so any expansion of the material would cause it to flow out from between the plates fixed at the 1000 µm gap rather than push the plates apart.

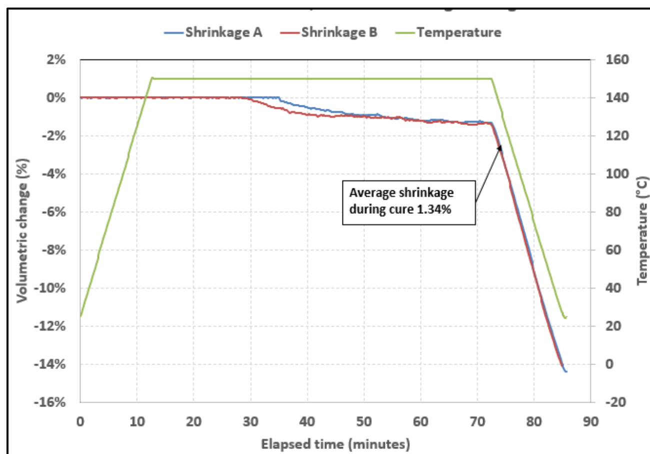

Figure 8. Volumetric shrinkage measured in die attach adhesive during thermal cure

The results from this initial set of measurements showed that this rheometer technique can be used to compare the thermal cure shrinkage of various die attach adhesive candidates. This shrinkage data can be used to select an adhesive with minimal shrinkage, thus decreasing the internal stress that will form in the bond between the die and the substrate. The shrinkage data can also be used in modelling efforts, allowing for a more robust adhesive recommendation. This technique can also be used to evaluate various adhesive cure schedules, in a further effort to minimize shrinkage.

CONCLUSIONS

While technical data sheets on die attach adhesives provide a wealth of necessary information on these materials to the end-user, it is critical to evaluate selected materials with the prescribed cure schedules and make necessary adjustments prior to incorporation in one's manufacturing processes. Understanding the influences of cure schedules on glass transition temperatures and volumetric shrinkage of die attach adhesives can be critical to avoiding issues such as die warpage. This can ensure product quality and performance of the component while avoiding poorly made parts, reducing wastage, and increasing yield.

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