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Thermal analysis of encapsulants for tape automated bonded (TAB) applications [1]

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Abstract

The curing behavior of a filled epoxy phenolic material (epoxy H) was studied through TGA, DSC and DMTA. The lower temperature holds at 80°C and 100°C are key in eliminating most of the solvent and bubbling from the coating. The fractional conversion calculated from the enthalpies for the partial and total curing processes indicated some residual curing even after 60 min at 150°C. The degree of curing was also computed from DMTA by the relative moduli of the partially and fully cured samples and through an empirical relationship developed between percentage cure and hold time. Isothermal DMTA curves predicted the cure behavior well, including the regions of chemical and diffusion controlled curing processes. All these methods indicated that a minimum time of 4 h is needed to achieve complete curing at 150°C. However, a shorter time at 150°C is enough to develop a material with a T_g that lies outside conventional reliability test temperature ranges.

INTRODUCTION

Electronic packages provide the functions of signal distribution, heat dissipation, protection and signal timing for integrated circuit devices. There are two basic packaging types: tape automated bonded (TAB) and wire bonded packages. Wire bonded packages are fully enclosed in a plastic medium whereas many of the TAB packages have an incomplete shell with a cavity on top through which the encapsulant can be dispensed. Thus environmental protection is the primary function of an encapsulant in these packages. There are several candidate materials for TAB encapsulation. These materials fall into one of the following categories: epoxy resins; polyimides or silicone modified polysiloxyimides; silicones. The encapsula-

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tion of TAB devices has been a source of constant concern because materials under every one of these categories have specific reliability problems. Epoxies have good chemical resistance, adhesion and mechanical strength but poor stress relief and hence may not meet the more stringent reliability tests. Polyimides and polysiloxyimides accommodate thermal stresses better than epoxies but still have inferior chemical resistance and reliability properties. Silicones sometimes outperform the other categories in terms of reliability but are soft and do not have adequate solvent resistance. For these reasons, epoxies remain the most popular choice for encapsulation of TAB devices. Several epoxies have been specifically evaluated for this application. However, besides the reliability issues mentioned earlier, poor cosmetic appearance, non-homogeneous filler dispersion, non-uniformity and non-conformality still persist as other sources of concern in these epoxies. A recent material (epoxy H) has yielded superior results in terms of these problems. However, curing related issues such as undercuring due to loss of curing agent by outgassing, inconsistent curing and defects (cracks, voids and bubbles) during curing are still sources of concern.

This study was carried out to understand the curing mechanism through the evaluation of curing profiles and resultant mechanical properties. Thermogravimetric analysis (TGA) was used to determine the weight loss due to solvent evaporation associated with various curing schedules and establish the optimal conditions for achieving maximum solvent loss (related to completion of the curing process). Differential scanning calorimetry (DSC) was used to determine the various processes (such as volatilization (solvent loss) and vitrification) that occur during typical curing cycles and compute the energies of the corresponding reactions, the extent of residual curing with subsequent cure cycles and temperatures of interest (such as the glass transition temperature T_g). Dynamic mechanical thermal analysis (DMTA) was used to characterize the cure behavior by following the elastic and viscous strains, relaxation, internal molecular transitions and key thermomechanical properties (such as the modulus, loss tangent factor and glass transition temperature) after various curing treatments.

EXPERIMENTAL PROCEDURE

Epoxy H is a filled epoxy phenolic material, exhibiting considerable weight loss during curing due to solvent evaporation that results in a certain amount of bubbling in the coating. To minimize this effect, the curing was done in stages: 15 min at 80°C (optional step), 15 min at 100°C and for various times (15 min, 30 min and 60 min) at the final cure temperature of 150°C. TGA runs were carried out in a Perkin-Elmer TGS-2 system using 14.75 mg of the samples in a 4 mm diameter Al pan. The system was purged for 30 min at 25°C with dry N_2 prior to the runs.

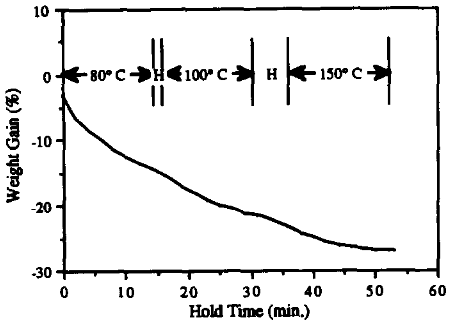

Fig. 1. Weight loss as a function of hold time and temperature.

The heating rate used was 10°C/min^{-1} and the weight loss was determined as a function of time starting from the time the samples reached 80°C. DSC runs were performed in a Perkin-Elmer DSC-2 system using 10.5 mg of the material in Al pans similar to the ones used in the TGA runs. The heating/cooling rates used for all heats were 10°C min^{-1} and 320°C min^{-1}, respectively and the temperature range over which the experiments were conducted was −20°C–300°C. DMTA runs were carried out using a PL Thermal Sciences system and $0.25 \times 1 \times 10$ mm^3 samples on Teflon sheets. The samples were subjected to known sinusoidal force and the strain response was continuously monitored as a function of both the frequency of loading and temperature at various heating rates. From these parameters, all desired properties (such as storage modulus E', loss modulus E'', and loss tangent tan δ) were calculated.

RESULTS AND DISCUSSION

The weight loss that occured during the various stages of curing during an 80°C per 15 min–100°C per 15 min–150°C per 15 min curing cycle was monitored continuously through the TGA and the results are shown in Fig. 1. The general shape of the curve indicates an exponential relationship between the weight loss rate vs. time of hold and temperature. The total weight loss in the samples was 27.1%, with a combined 69% of it occurring after the 80°C and 100°C holds. The importance of the lower temperature holds in eliminating most of the solvent (and thus the bubbling associated with it) is immediately apparent. Even short time holds at 80°C ($<$ 2 min) and 100°C ($<$ 5 min) should assist in the removal of a significant amount of the solvent. In any event, the 80°C hold should not be eliminated from the curing cycles for this material if minimizing bubbles and associated voids and cracks is desirable. At 150°C, after 12 min no further drop in weight is noticed, indicating that the solvent loss is complete. No further benefit occurs by holding the samples for longer than 12 min (strictly in terms of solvent loss considerations).

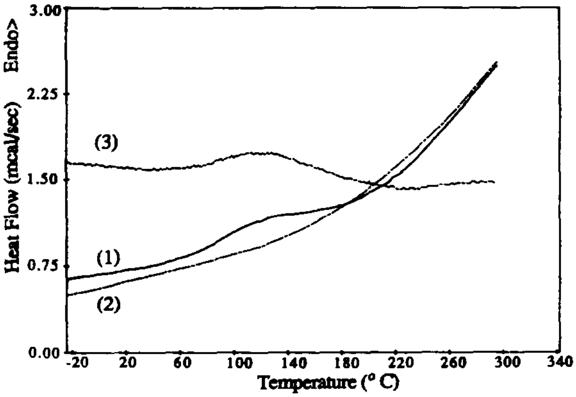

Fig. 2. Heat flow as a function of temperature.

Figure 2 traces the rate of heat evolution (exothermic) and heat absorption (endothermic) as a function of temperature (−20°C–340°C) for a sample that had been initially heated at 80°C for 30 min. Curve 1 is the first heat trace and curve 2 is the second heat trace after the sample had been quenched to −20°C after the first heat from 307°C. Curve 3 is the difference in heat evolution or absorption (curve 2 − curve 1) plotted on a relative scale. The major peak in Fig. 3 is assignable to the solvent loss (an endothermic reaction). The integrated area under this peak (67°C–207°C) gives the enthalpy of the solvent loss reaction (ΔH_{rs}). This parameter is important because it measures the relative ease of removal of the solvent and predicts its chemical nature. The degree of curing is minimal after only 80°C treatment, as evidenced by the residual curing (exothermic peak) that is seen around 227°C. The enthalpy of this reaction (ΔH_{rc}) can be computed as before by the integrated area under the residual curing peak. Similar results were obtained for samples held for 30 min at 80°C followed

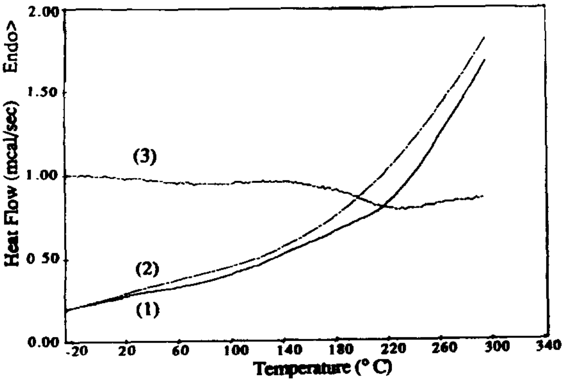

Fig. 3. Heat flow as a function of temperature.

TABLE 1

Variation of T_g and percentage cure with time of hold

Property	t (min)		
	15.0	30.0	60.0
$T_{g,dsc}$ (°C)	21.0	37.0	38.0
$T_{g,dmta,1\ Hz}$ (°C)	56.5	105.5	126.5
$T_{g,dmta,10\ Hz}$ (°C)	63.5	112.0	134.0
x_{dsc} (%)	49.0	65.0	74.0
x_{dmta} (%)	54.0	66.0	84.0

by 30 min at 100°C. The amount of outgassing due to solvent evaporation is smaller than that in Fig. 2 due to the additional hold at 100°C. Significant residual curing is still seen. Similar results are shown in Fig. 3 for a sample held at 80°C for 15 min, 100°C for 15 min and 150°C for 60 min. Solvent loss and residual curing are still present (at reduced amounts).

In TAB bonding with Sn-plated Cu leads, the propensity for the formation of undesirable Cu–Sn intermetallics increases directly with the time of hold at temperatures above 150°C. One of the objectives of this study was to determine the minimum time needed at 150°C to achieve complete curing. Insufficient curing, besides causing instabilities in properties with respect to time and temperature, will also result in cracks and voids in the coating due to subsequent solvent loss and curing. Experiments were conducted with curing schedules similar to the one used in obtaining Fig. 3 but varying the hold times at 150°C between 15 and 60 min. To monitor the degree of cure, another parameter (ΔH_t, the total heat of reaction) was determined the same way as Δh_{rc}, but using an initial uncured sample. The fractional conversion x was then computed from the relationship [1]

$$x_{dsc}\ (\%) = ((1 - \Delta H_{rc})/(\Delta H_t)) \times 100 \qquad (1)$$

Table 1 lists the percentage values computed using eqn. (1). These values indicate that even after 60 min hold at 150°C, complete curing is not achieved. The glass transition temperature T_g was computed for these DSC plots using the mid point of the endothermic step change in the DSC scan over the temperature range of the glass transition in the first heat curves. The computed value from Fig. 3, for example, is 37°C.

The transition temperatures and the heats of reaction are somewhat difficult to identify and quantify through DSC, especially because the cross link density increases with curing, due to the highly ordered nature of the structure and the low heat capacity. However, because T_g increases nonlinearly with the degree of conversion in these crosslinking systems, it is more sensitive in the later stages of cure (the critical stages) and hence can be measured with relatively better accuracy than the heat of reaction. Thus, T_g can be used to monitor the cure process in this material (100% cure is

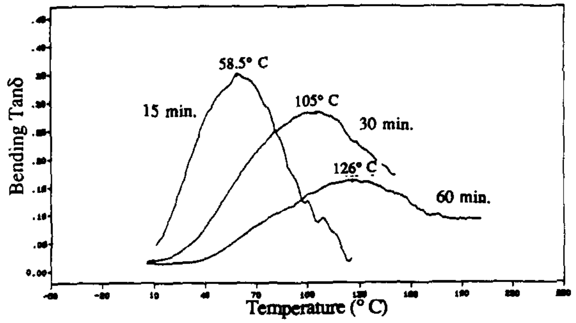

Fig. 4. Relaxation behavior as a function of hold time at 150°C.

given by the maximum T_g measurable in the material). To resolve the T_g values with minimal error, DMTA runs were made for a similar set of samples. The results are given in Fig. 4, which shows tan δ (the ratio of the loss to storage modulus) as a function of temperature for the three hold times at 150°C at a test frequency of 1 Hz. These relaxation curves are related to the damping characteristics of the material and the intensity of the most significant peak in these curves is a measure of the ability of the material to dissipate energy as heat during the deformation cycle. This peak value T_g is in turn relatable to the cross link density and thus the fractional conversion after a given cure cycle. If the sample is uncured, the relaxation curve will exhibit a larger damping peak at T_g than when the sample is totally cured. The measured values of T_g are indicated in the curves and included in Table 1. T_g values measured similarly at 10 Hz are also included in Table 1. The effect of higher frequency is to shift the T_g values to higher temperatures, a phenomenon explained elsewhere [2]. As the degree of conversion increases, the intensity of the tan δ peak decreases and the peak width increases. Hence T_g can be used to predict the degree of curing. A decrease in peak height and an increase in peak width at constant frequency imply an increase in the cross link density and in turn, a decrease in the number of molecular segments involved in the transition and a corresponding decrease in molecular mobility. An increase in T_g implies an increase in cross link density or an increase in the activation energy for the molecular segmental motion. The increase in peak width can also be attributed to an imperfect network caused by unreacted epoxy molecules.

There is some discrepancy in the T_g values measured by DSC and DMTA. The values measured by DSC are subject to errors associated with locating the mid and end points of the endothermic step change corresponding to the glass transition. Furthermore, the DSC is a static method, whose values will always be lower than those from the dynamic method. Beyond these factors, the two methods actually measure different parame-

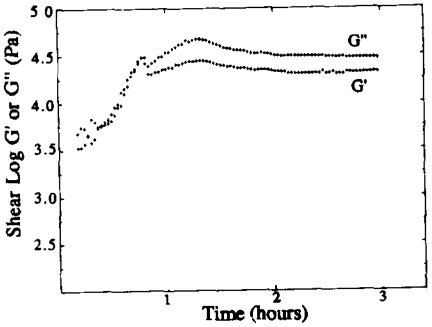

Fig. 5. Isothermal scans at 100°C.

ters. When the thermodynamic glass transition is traversed, there is a change in the state of the material with respect to temperature, pressure and internal parameters of order. DSC measures this thermodynamic glass transition temperature. However, as time or frequency is changed, as in the DMTA, although material response changes from glasslike to rubberlike behavior, there is no change in the thermodynamic state of the material. The transition corresponding to this change in time or frequency is what is measured by the DMTA.

The cure kinetics of the epoxy was monitored in the DMTA shear mode. Figure 5 traces the shear storage and loss modulus at 1 Hz as a function of hold time at 100°C. The change in the modulus with time of hold is able to fully explain the cure behavior at this temperature. The behavior is similar to that exhibited by most thermosetting epoxies [3]. The cure process starts by the formation of "A stage" monomers which start to link up and form the basis of the molecular chains of the final cured material. This first stage is characterized by a rapid increase in the modulus with time of hold (to about 30 min). The next stage is characterized by the linear growth and branching of the monomers to a "B stage" material below the gel point (at approximately 45 min). As the reaction proceeds, gelation with incomplete cross linking of the networks occurs. This point is very critical and is characterized by the crossover of the modulus curves. Beyond the gelation point, the molecular weight increases rapidly and several chains link up to form networks of very large molecular weight (fully cured "C stage" thermoset). There is a sudden and irreversible transformation from a viscous liquid to an elastic gel at this gelation point. The polymer no longer flows, it is not processable beyond this point and the modulus does not change beyond this point appreciably, indicating that no further curing occurs at that temperature (additional curing might occur at higher temperatures). Gelation does not inhibit curing and the reaction rate remains unchanged, so techniques sensitive only to chemical reactions such as DSC cannot detect this phenomenon. However, from a processing standpoint it

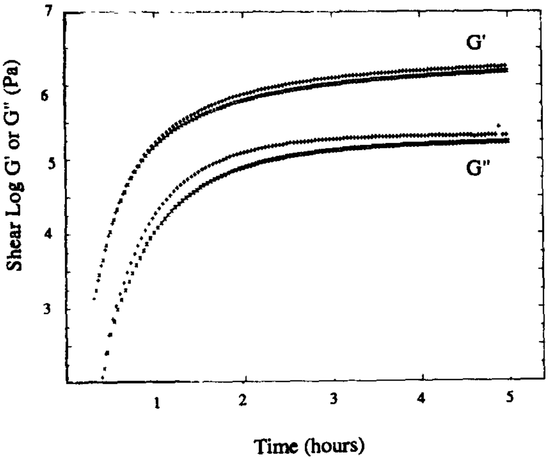

Fig. 6. Isothermal scans at 150°C.

is very important to determine the gelation point. Beyond this point, the reaction proceeds towards the formation of one infinite network possessing the dimensions of the reaction vessel and with substantial increase in cross link density T_g and ultimate physical properties.

Another phenomenon that occurs in this material is vitrification, as indicated by a second broader peak at about 75 min. This transformation from a viscous liquid to a glass occurs as the glass transition and cure temperatures coincide. Further curing is extremely slow but the process is reversible (by subsequent reheating, the partially cured thermoset can be devitrified and the curing process resumed). Vitrification also indicates the transition from a chemically controlled to a diffusion controlled mechanism in the curing process and is characterized by a gradual decay of the reaction rate.

Isothermal DMTA plots were also generated at 150°C (Fig. 6). A frequency effect was incorporated by conducting the runs at 1 Hz and 10 Hz. The effect of higher frequency is to merely shift the corresponding reactions to higher hold times. At 150°C, the gelation point is no longer seen, indicating that the transformation from A to B to C stages is almost instantaneous. This process only takes a few minutes because the temperature of hold is above the cure initiation temperature. The vitrification point is still seen. The curing process slows down beyond the vitrification point and is over almost completely after 4 h. The cure time can be defined as the minimum time needed to achieve the desirable properties at that temperature. The increase in cross link density (and thus the percentage cure) can be monitored by following the modulus curve. As the modulus reaches its equilibrium value T_g approaches the hold temperature and a high degree of conversion ($>$ 95%) is achieved.

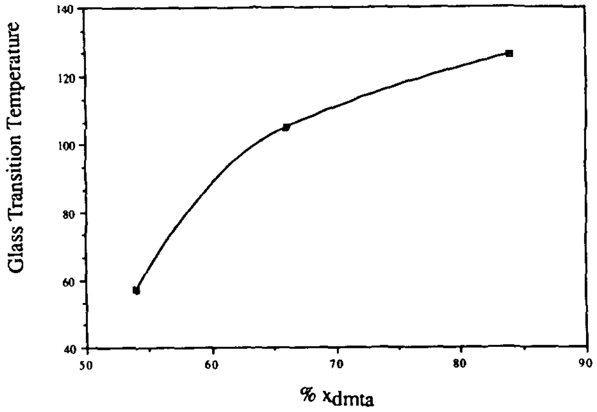

Fig. 7. Glass transition temperature as a function of percentage cure.

Assuming that 95% curing is achieved after a 4 h hold at 150°C, it is possible to calculate the percentage cure (DMTA) after various hold times at this temperature from the equation

$$x_{\mathrm{dmta}}\ (\%) = (G_t'/G_{\mathrm{f}}') \times 100 \tag{2}$$

where G_t' and G_{f}' are the modulii after t min of hold and 4 h (final value) respectively. The x_{dmta} percentage values calculated from eqn. (2) are included for 15, 30 and 60 min of hold at 150°C in Table 1. The degree of conversion should be directly related to the T_g shift as mentioned earlier. Assuming a 54% cure after 15 min at 150°C, it was empirically determined that a ± 3°C change in T_g corresponds to a ± 1% change in the degree of conversion. This is consistent with other findings, wherein it has been demonstrated that in a similar epoxy–glass system, a ± 1% change in the degree of cure corresponds to a ± 1–4°C change in T_g [4]. The percentage cure values computed on this basis are included in Table 1. Figure 7 is a plot of $T_{g,\mathrm{dmta}}$ as a function of x_{dmta} (%). The usefulness of Fig. 7 lies in its ability to predict the time needed for 100% cure (particularly for quality control applications). Although stress relief, physical aging and other factors could alter the T_g values, this method can be applied to ensure $> 95\%$ curing. A better method for representing the cure data is to plot x_{dmta} (%) as a function of the time of hold t at 150°C (Fig. 8). The various stages of the cure phenomenon, including the chemical and the diffusion controlled regions, are observed clearly in Fig. 8. The plateau region corresponds to the fully cured state. An empirical relationship that can be developed from Fig. 8 for predicting the amount of cure for various hold times is given by

$$x_{\mathrm{dmta}}\ (\%) = 41.187 + 1.008t - 0.007t^2 \quad (15 < t < 240) \tag{3}$$

where t is the hold time in min.

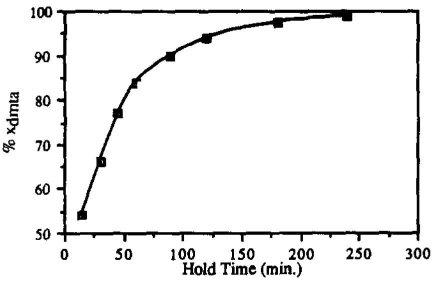

Fig. 8. Dependence of degree of cure upon hold time at 150°C (eqn. (2)).

The fractional conversion computed from the two DMTA and the single DSC methods all agree relatively well. The DSC values are underestimated because the ΔH_t values were computed using a sample that was initially held at 100°C for 30 min as opposed to a totally uncured material. This was done to prevent overlapping of solvent loss and residual curing peaks. The DMTA methods are very consistent and the modulus method in particular reflects more precisely the degree of curing in the material.

All these methods of calculating the degree of cure indicate that a minimum 4h hold is needed to achieve almost complete curing ($>95\%$). However, complete curing may not be needed if thermal stability and time independent properties of the coating are achievable within the normal service temperatures and times at these temperatures. For example, if the field temperatures do not exceed 150°C for 10 min or 100°C for 30 min, then a curing schedule that results in only 65% curing may still be acceptable. Another factor that is important is the relative position of the transition peak with respect to operational or test temperatures. If the thermal cycle test range is between 0°C and 100°C, a 30 min hold at 150°C would yield a T_g that lies outside this range and hence an acceptable coating from the thermomechanical point of view.

CONCLUSIONS

The curing behavior of epoxy H was studied through TGA, DSC and DMTA. TGA revealed a total weight loss of 27.1%, with a combined 69% of it occurring after the 80°C and 100°C holds. The lower temperature holds are key in eliminating most of the solvent and bubbling (with associated cracks and voids) in the coating. Further, even short holds at 80°C (<2 min.) and at 100°C (<5 min.) are helpful in removing a significant amount of the solvent. At 150°C, after a 12 min hold no further drop in weight occurred, indicating that solvent loss was complete. The enthalpies of solvent loss and curing reactions were calculated from the integrated areas under the respective reaction peaks in the DSC scans. The fractional conversion calculated from the enthalpies for the partial and total curing processes indicated significant undercurring even after 60 min hold at 150°C. The degree of curing was also computed from DMTA by the relative modulii of the partially and fully cured samples and through an empirical relationship developed between T_g and hold time. Isothermal DMTA curves predicted the cure behavior well, including the gelation and vitrification points and the regions of chemical and diffusion controlled curing processes. Relaxation curves indicated the transition peak positions and widths to be directly related to the degree of cross linking and hence to the amount of cure. All these methods indicated that a minimum of 4 h is needed to achieve complete curing at 150°C. However, a 30 min hold at 150°C is enough to develop a material with a T_g that lies outside a temperature cycle test range of 0–100°C.

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