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An alternative method to the curing study of polymeric die attach adhesives using dynamic mechanical analysis

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Abstract

This paper introduces an alternative way to the curing investigations of polymeric die attach adhesives using dynamic mechanical analysis (DMA). Proper curing of die attach adhesives is essential to provide adhesive strength and reliability of adhesive bonding between Si die and paddle in the microelectronic industry. The extent of cure of polymeric adhesives is typically studied with differential scanning calorimetry (DSC) which is a measure of exothermic heat generated during curing reaction. Nevertheless, mechanical properties of polymeric die attach adhesives are strongly related to the extent of cure on the manufacturing process in die attachment. Therefore, DMA was explored to the curing study of die attach adhesives. Materials for this study were: (a) raw die attach, and (b) prepared by curing raw die attach at schedules of 140, 155, 170, 185 and 200°C from 0 to 10 h in air. Viscoelastic properties of raw and cured adhesives over temperature at fixed oscillatory frequency were then investigated with 3-point bending mode of DMA. All specimens were heated and then followed by cooling and again reheating at a rate of 5°C/min under helium gas environment. Their storage moduli (E') drop in the orders of magnitude or phase angle (δ) change at temperature sweep addressed the transitions from glassy to rubbery state of the materials. Glass transition temperature (T_g) of the reheating process is higher than first heating from DMA studies, and it was noticed that this T_g difference of die attach adhesives was reduced while they were cured from low to high temperature and short to long duration. The extent of curing reaction of die attach adhesives was therefore determined by their T_g difference comparison of the DMA first heating and reheating processes with the raw specimen.

Keywords: Polymeric die attach adhesives; Curing study; Extent of curing; DMA

1. Introduction

Polymeric die attach adhesives are widely used for Si die-attachment onto leadframes of hermetic and plastic packages in integrated circuits industry [1,2]. The advantages are its lower processing temperature, lower die stresses and lower cost. Proper curing procedures are essential to provide enough strength and reliability of the bonding between dies and leadframes. The adhesives typically have to provide adequate strength to hold the assemblies and in some cases thermal conduction for heat removal. Curing schedules of these materials are always required to be modified so as to fit differences in users' process equipment and manufacturers' recommendations. Thermal analysis provides solutions to curing kinetics and thermodynamics information of these polymeric adhesives [3,4], and in a way to ascertain the effects of

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the curing process on adhesion and reliability, and to develop methodology for determining cure profiles in the die attachment process.

Thermal analysis has also been widely used for die attach adhesives characterization [4–7]. Extent of cure of die attach adhesives is typically studied with differential scanning calorimetry (DSC). It is calculated and compared from its enthalphic residual cure to the cure of raw materials. Furthermore, curing reaction of die attach adhesive is strongly related to its mechanical properties change. It is generally observed that high degree of cure is reflected by the increased T_g from either modulus (E') change or tan(δ) change of dynamic mechanical analysis (DMA) modulus plots. Extent of cure can be calculated from the T_g difference of the cured and raw specimens. This method of curing studies of die attach materials was, hence, investigated with DMA technique. The objective of our experiments is to explore the use of DMA with simple sample preparation to the curing study and determination of degree of cure of polymeric die attach adhesive in terms of its viscoelastic behavioral change as functions of temperature.

2. Experimental

Experimental matrix of cured specimens for this study was first determined from the curing peak temperature of the raw specimen using DSC (Perkin Elmer DSC7). The raw specimen was heated (in the temperature range below and above its curing peak) under N_2 purge environment with DSC. Specimens were then cured at temperatures every $\pm 15^{\circ}$C to its curing peak according to the following description.

Cured specimens were simply prepared by sandwiching raw die attach adhesives between two rectangular Al foil strips. They were then cured at temperatures of 140, 155, 170, 185 and 200°C from 0 to 10 h in air. The viscoelastic properties of raw and cured adhesives were investigated with DMA (Perkin Elmer DMA7). The temperature was measured using a thermocouple, which is placed in close proximity to the specimen. The thermocouple of the analyzer was first calibrated with standard zinc metal melting temperature before analysis. Temperature profile for analysis was ramped up at a controlled heating rate of 5°C/min from temperature below glass transition to 250°C and then cooled and reheated at the same rate. All experiments were performed under helium gas purge environment. In our experiment, viscoelastic properties of die attach adhesives were characterized by 3-point bending mode at oscillatory frequency of 1 Hz and amplitude control of 1 μm as a function of temperature. Glass transition from glassy to rubbery state of polymeric die attach material was noted from the change of storage modulus and tan(δ); glass transition temperature was then determined. Calculation of extent of cure was based on T_g difference from storage modulus and tan(δ) between the cured and raw specimens.

3. Results and discussion

Fig. 1 shows the DMA plot of the raw die attach adhesive curing with tan(δ) and storage modulus (E') on the left and right *Y*-axis, respectively. Storage modulus (E') rises from the starting temperature (around -150°C) to -56°C and drops at -56°C indicating the specimen's glass transition. Glass transition of material is the transformation of glassy to rubbery state. Rise of tan(δ) associated to the glass transition is also observed from Fig. 1. A representative storage modulus (E') and tan(δ) change of first heat and reheat of the 185°C/30 min cured specimen is shown in Figs. 2 and 3, respectively, and glassy

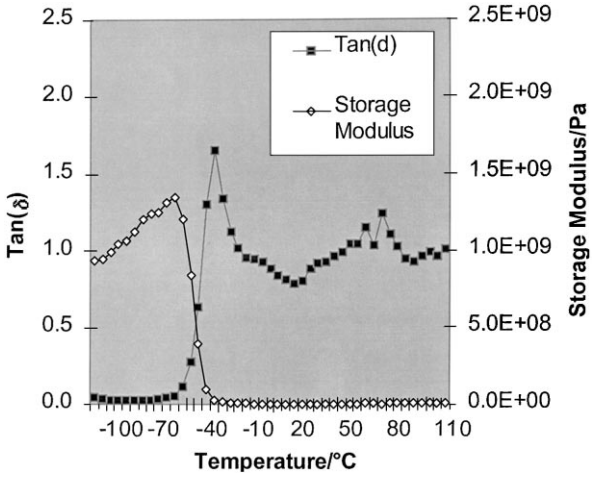

Fig. 1. DMA tan(δ) and storage modulus of raw die attach material curing.

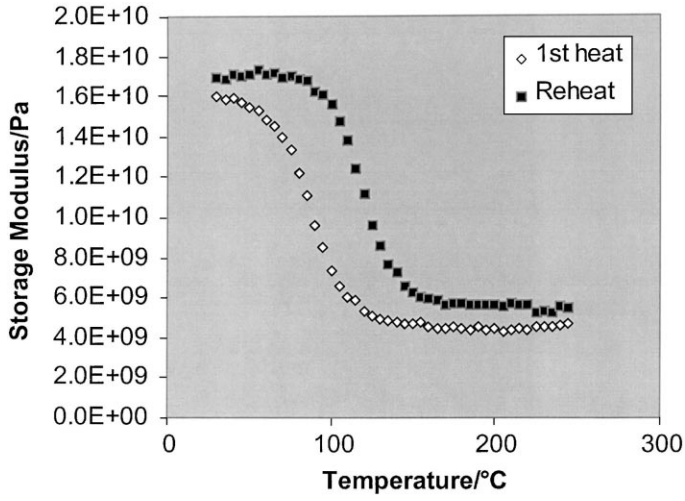

Fig. 2. DMA storage modulus plot of die attach material cured at 185°C for 30 min.

transition temperature (T_g) is determined from interception of slope change of storage modulus before and after the transition. It is always noted that T_g of reheat is higher than its first heat from storage modulus and tan(δ) of DMA sweeps. It is because further curing (cross-linking reaction) of die attach material happened during the DMA reheat process, which results in higher T_g than its first heat. T_g of first heat and reheat of the 185°C/30 min cured specimen are 71 and 101°C, respectively (Fig. 2). The tan(δ) of reheat peak is also at a higher temperature (130°C) than the first heat process (99°C) of the same cured specimen.

Similar experiments for specimens cured at different temperature and duration were performed with DMA analysis. Curing experiments were performed at duration from 0 to 600 min and temperature at 140, 155, 170, 185 and 200°C. Figs. 4 and 5 show the T_g onsets of storage modulus (E') vs. curing time of the

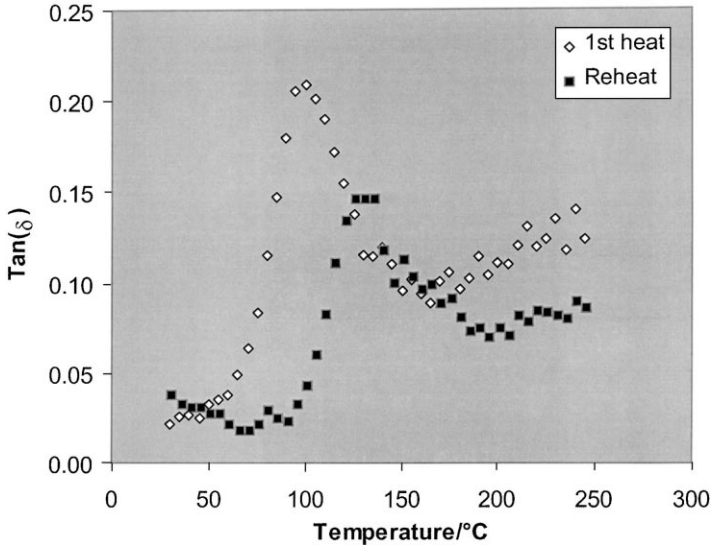

Fig. 3. DMA tan(δ) plot of die attach material cured at 185°C for 30 min.

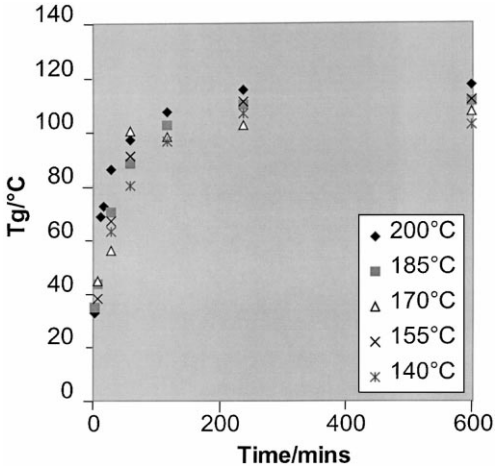

Fig. 4. Plot of T_g onset from DMA storage modulus first heat vs. curing time.

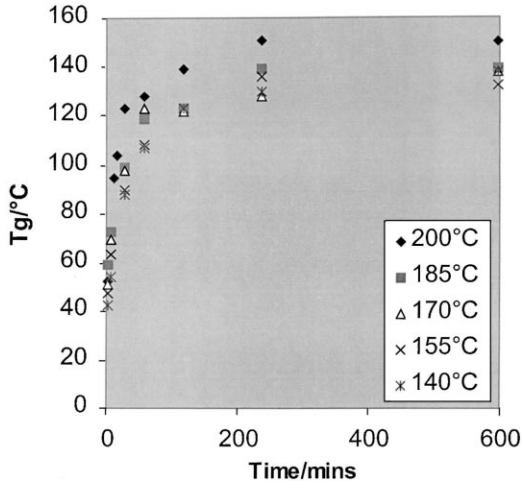

Fig. 6. Plot of T_g from DMA tan(δ) first heat vs. curing time.

first heat and reheat, respectively, from DMA analysis. T_g of DMA first heat increases sharply from 0 min to below curing time of 100 min at all the constant curing temperatures. Higher curing temperature also results in higher T_g value at the same curing time. Changes of T_g as functions of curing time become less significant after curing time of 100 min (Fig. 4). However, T_g of DMA reheat increases slowly and is approaching a constant value (e.g. around 118°C for 200°C/600 min but only ~106°C for 140°C/600 min cured specimens) between 200 and 600 min. It is because of the slow diffusion-controlled cross-linking reaction of further cross-linking reaction that happened at the reheat process. The temperature onset of storage modulus (E') of reheat varies from ~106 to 118°C at 600 min and is reaching maximum of 118°C for the specimen cured at 200°C/600 min. Similar T_g response to curing temperature and time was also observed from tan(δ) plots of DMA first heat and reheat (shown in Figs. 6 and 7). Rate of T_g increase (in terms of tan(δ)) is also rapid for the first 100 min and slows down after that. Glass transition temperature from tan(δ) is nearly

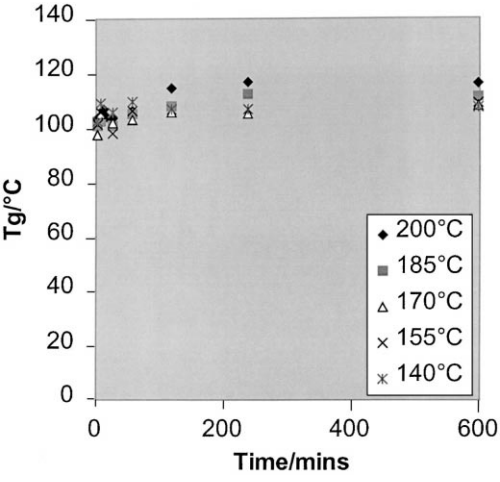

Fig. 5. Plot of T_g onset from DMA storage modulus reheat vs. curing time.

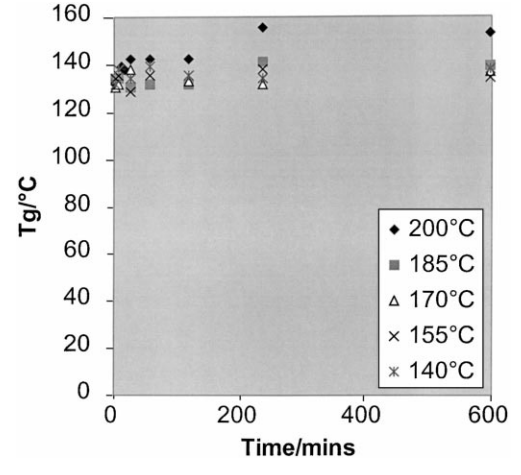

Fig. 7. Plot of T_g from DMA tan(δ) reheat vs. curing time.

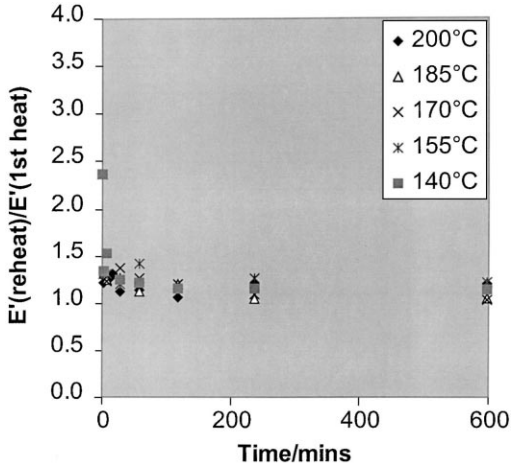

Fig. 8. Plot of E' (reheat)/E' (first heat) vs. curing time.

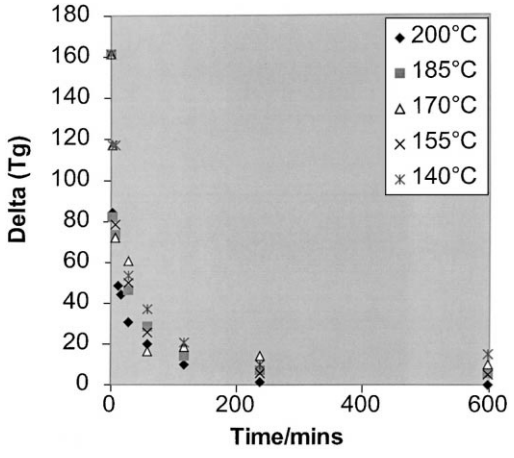

Fig. 9. Plot of ΔT_g from storage modulus onset vs. curing time.

constant after 240 min cured for all specimens from 140 to 200°C at constant curing time. Furthermore, specimens cured at higher temperatures always result in higher T_g values. T_g's increase slowly from 0 to 240 min for the DMA reheat analysis (Fig. 7) and become constant after 240 min curing at the 200°C cured schedule.

The difference between storage modulus ratio of DMA first heat and reheat was also observed. Fig. 8 shows the storage modulus ratio of reheat to first heat processes of specimens that had been cured at different temperature as a function of the curing time. The ratio is decreasing from >2 to ~1 as 600 min curing time is approaching. Close saturation of cross-linking reaction is indicated by the E' (reheat)/E' (first heat) ratio approaching unity. Therefore, it was observed in Fig. 8 that E' (reheat)/E' (first heat) was close to unity after a curing time of at least 100 min.

Figs. 9 and 10 show the T_g difference of DMA first heat and reheat process from storage modulus and tan(δ), respectively. T_g difference is close to 0 as the specimens were cured at longer time and higher temperature. Extents of cure of specimens at certain curing conditions were then evaluated and calculated based on the above observation. It is assumed that die attach material is fully cured under the condition of 200°C for 600 min. In fact, this assumption is acceptable as the (a) T_g of reheat process is approximating constant, (b) T_g difference of first heat and reheat is close to 0, and (c) E' (reheat)/E' (first heat) ratio is close to 1. Degree of cure (α) is then calculated by Eq. (1) below

$$\alpha = \frac{\Delta T_{g,\ \text{raw specimen}} - \Delta T_{g,\ \text{cured specimen}}}{\Delta T_{g,\ \text{raw specimen}}} \times 100\% \quad (1)$$

where

$$\Delta T_{g,\ \text{raw specimen}} = (T_{g,\ \text{reheat}} - T_{g,\ \text{first heat}})_{\text{raw specimen}},$$

$$\Delta T_{g,\ \text{cured specimen}} = (T_{g,\ \text{reheat}} - T_{g,\ \text{first heat}})_{\text{cured specimen}}$$

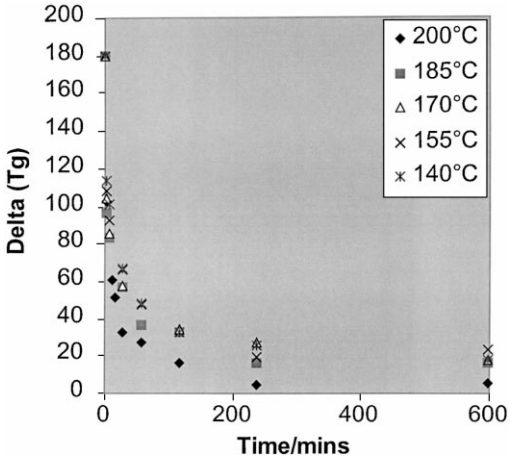

Fig. 10. Plot of ΔT_g from tan(δ) vs. curing time.

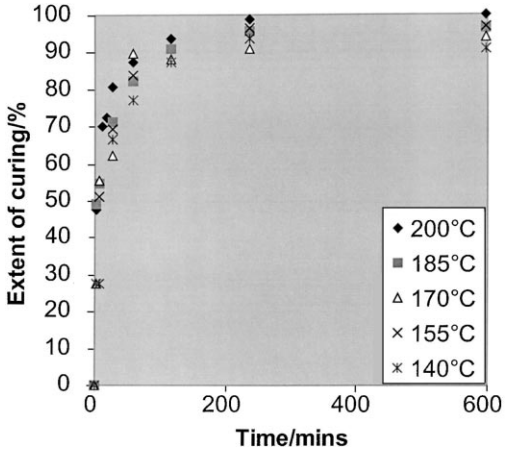

Fig. 11. Plot of extent of curing (T_g onset from storage modulus) vs. curing time.

Extents of die attach adhesive curing as functions of time at constant temperature were then calculated and compared. Figs. 11 and 12 show the extents of curing vs. time at different constant temperatures calculated based on the T_g difference from storage modulus onset and tan(δ), respectively. The plots of extent of curing from the T_g difference of storage modulus (Fig. 11) and tan(δ) (Fig. 12) are very similar except that extents of curing of specimens at longer than 100 min calculated from storage modulus T_g difference is ~6–10% higher than those calculated from tan(δ). For the same

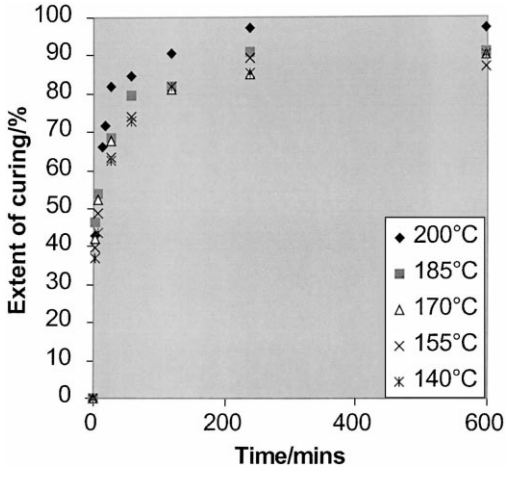

Fig. 12. Plot of extent of curing (T_g from tan(δ)) vs. curing time.

curing time, higher curing temperature results in higher extent of curing of the specimens. The same degree of curing can then be achieved at lower temperature for longer curing time or higher temperature for shorter curing time. Degrees of curing for the first 30 min are very rapid at all the isothermal conditions. However, they start to slow down after specimens were about 70% cured. It is also observed that the extents of curing at any temperature below 170°C are close and always around 90% (Fig. 11) and 80% (Fig. 12) even cured for longer times such as 600 min. However, it is achieving close to 100% cured when the specimen was cured at >185°C for around 240 min. Therefore, these types of plots help determine degrees of curing of polymeric die attach adhesives.

4. Summary

This paper demonstrated the use of DMA technique with a simple 3-point bending mode to investigate cross-linking curing reaction of polymeric die attach adhesives for die-attachment to leadframes in electronic packaging industry. Proper curing of die attach adhesives is a result of both curing temperature and time which results in increase of its modulus. DMA with 3-point bending mode is therefore pursued as a complimentary tool to the typical DSC for die attach materials curing study. It was observed that glass transition temperature (T_g) of reheat is always higher than its first heat for both storage modulus (E') and tan(δ) plots. Extents of curing (in terms of percentage) of die attach materials that had been cured under various temperature and time were calculated and plotted as functions of curing time. Higher curing temperature (or longer curing time) results in higher T_g value for the same curing time (temperature). Rate of T_g increase is rapid for the first 100 min and increases slowly until 600 min reached. The E' (reheat)/E' (first heat) decreases from >2 to ~1 as curing time approaches, where cure saturation of cross-linking reaction was indicated. From the plots of extents of curing vs. time, it is always observed that higher curing time results in higher degree of curing. The same degree of curing can be achieved at lower temperature for longer curing time or higher temperature for shorter curing time. Moreover, degree of

curing for the first 30 min is very rapid at all the isothermal conditions, results of which are used to design cured schedules in order to fit users' process environment and manufacturer's recommendation.

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