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DSC and DMTA studies of a thermal interface material for packaging high speed microprocessors

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Abstract

Thermophysical properties and cure behavior of a thermal interface material used in microelectronic packaging have been studied using DSC, DMTA and other thermal analysis techniques. Based on isothermal DSC results, the activation energy for the curing reaction is estimated to be 129 kJ/mol. When heated from −100 to 150 °C, the cured material exhibits a single endothermic peak near −45 °C, which corresponds to the melting of silicone oils in the sample. On cooling, the cured material crystallizes, but shows various degrees of undercooling depending on the cooling rate. Upon crystallization, DMTA analysis revealed that the storage modulus of the cured material increases dramatically, from several MPa to a few GPa. In the same process, the ultimate elongation decreases by almost a factor of 10. The impact of such static and dynamic mechanical behavior on packaging reliability will be addressed. The influence of curing on the mechanical modulus was also evaluated by DMTA. In addition, coefficient of thermal expansion (CTE) and thermal stability of this material will be discussed.

Keywords: DSC; DMTA; Thermal interface material (TIM)

1. Introduction

In the development of advanced microprocessors, the trend has been the continuous reduction in device size, coupled with increases in speed as well as power density. In 1994, it was predicted that the speed of microprocessors would reach 500 MHz in 2001 and 1 GHz in 2007 [1,2]. Today, the speed limit of 1 GHz has long been broken, and 2.4 GHz microprocessors are already commercially available. Furthermore, Intel has demonstrated the capability of microprocessors running at 3 GHz, and these high-speed microprocessors will be available in the near future.

Accompanying this trend of minimization, is the increasing challenge of thermal management for electronic packaging. For today's microprocessors, the typical core power dissipation is in the range of 60–120 W. The heat generated by the microprocessor can reduce the circuit efficiency and cause premature component failure, thus it must be effectively removed to ensure the performance and the long-term reliability of the device. Conventional methods of cooling electronic components through natural and forced convection air-cooling are no longer satisfactory for many applications. Cold plates, or heat sinks, are commonly attached to a silicon chip to reduce the temperature of the electronic component and provide greater reliability and longer service life [3]. To aid heat conduction and reduce the interfacial thermal resistance, a

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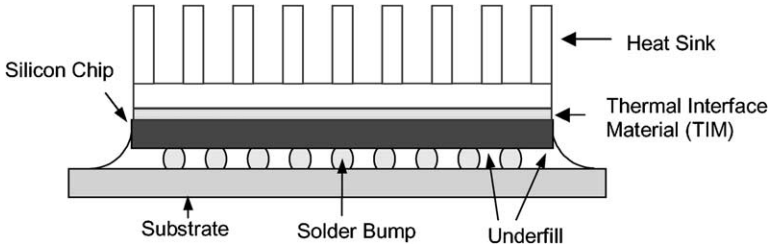

Fig. 1. A typical thermal management design for flip chip packaging technology.

thin layer of thermal interface material (TIM) is sandwiched between the silicon chip and the heat sink [4], as illustrated in Fig. 1. Thus, the development of high-performance TIMs is critical to meeting the thermal performance goals for Intel's advanced packaging technology.

Various TIMs have been developed for electronic packaging applications. These materials can be in the form of thermal greases, gels, phase-change films, or thermally conductive epoxies. All these materials are polymeric materials loaded with highly conductive fillers such as aluminum nitride (AlN), boron nitride (BN), or silver. These materials generally have low tensile and shear moduli to reduce mechanical stresses within the package. With light clamping pressure, these materials can form good contact with both surfaces, filling interfacial gaps and voids, thus minimizing thermal interface resistance.

Various techniques for thermal resistance measurement are now available [5], and will not be discussed here. This paper focuses on the thermomechanical properties of a thermal gel type of TIM, which is being evaluated as a candidate for use in Intel's high performance microprocessors. The curing behavior, phase transition of the cured specimen, dynamic and static mechanical properties, thermal expansion, and thermal stability of this material were investigated. In particular, the thermomechanical properties were evaluated at sub-ambient temperatures as well as at elevated temperatures. This is because although the typical operational temperature of a high-speed microprocessor is about 100 °C, reliability tests at much severe conditions are routinely conducted to accelerate possible material degradation. This would allow us to assess the long-term reliability and service life of the microprocessor under normal operational conditions. These data were used to predict thermal performance related package reliability and to aid root-cause analysis of failure mechanisms.

2. Experimental

2.1. Material

The thermal interface material used in this study is a curable thermal gel material. It contains a large amount of thermally conductive filler (about 90 wt.%), silicone oils, as well as a number of additives and crosslinkers. The detailed chemistry of this material will not be discussed because it contains proprietary information. The unprocessed material is stored in a −40 °C freezer before use.

2.2. Cure

Before curing, the material was removed from the freezer and thawed at room temperature for 1 h. Samples were cured in a Teflon cavity mold at 125 °C for 1 h in an oven, or unless otherwise specified. The cavity of the mold is 25 mm in length and width, and 1 mm in depth.

2.3. DSC

Curing kinetics of the TIM was studied using a Perkin-Elmer DSC-7 system. Each sample was approximately 20 mg in weight and was sealed hermetically in an Al DSC pan. Both non-isothermal and isothermal experiments were conducted. Non-isothermal DSC experiments were performed at a heating rate of 10 °C/min from 25 to 200 °C. For isothermal measurements, the temperature was raised from 25 °C to a pre-selected isothermal temperature (e.g. 100 °C) at a

heating rate of 20 °C/min and then held at that temperature for up to 2 h. For each experimental condition, the measurement was repeated at least three times.

DSC experiments on cured TIM were carried out from −100 to 150 °C with a TA Instruments 2920 Modulated DSC operated in standard mode. A liquid nitrogen cooling jacket was used to cool the DSC cell. In these measurements, both heating and cooling rates ranged from 2 to 10 °C/min. Understanding low temperature phase transition behavior in the cured TIM is important because these transitions have a strong impact on material's mechanical properties and package reliability.

2.4. DMTA

Thermomechanical properties of the cured TIM were measured using a Rheometrics DMTA 3e operated under rectangular tension mode. The typical sample dimensions were 20 mm long, 2.0 mm wide, and 0.8 mm thick, whereas the DMTA gap size was maintained at 14 mm. During the dynamic temperature ramp experiment, the heating rate was 5 °C/min, and the frequency was 1 Hz. Static strain rate experiments were also performed at various temperatures with a strain rate of 0.001 s^{-1} to estimate the ultimate sample elongation. All DMTA experiments were repeated at least three times and the results were consistent.

2.5. TMA

To understand the thermal expansion behavior, the coefficient of thermal expansion (CTE) of the cured TIM was measured from −50 to 200 °C at a heating rate of 5 °C/min using a Perkin-Elmer TMA-7 system. During the measurement, a small loading force of 5 mN was applied to reduce the induced deformation. The typical specimen length used for TMA measurement is 4 mm. All TMA measurements were also repeated three times.

2.6. TGA

A TA Instruments 2950 Thermogravimetric Analyzer operated in an air atmosphere was employed to assess the thermal stability and degradation onset of the cured TIM. Isothermal TGA experiments were conducted near or above the operational temperature of the microprocessor to evaluate the long-term thermal stability of the TIM.

3. Results and discussion

3.1. Curing behavior

For thermal gels used as TIMs in microelectronic packaging, it is desirable that the material is compliant after it is cured. Therefore, the amount of cross-linking agent contained in these materials is usually small, resulting in a relatively low degree of cross-linking density in the cured state. The low modulus (both tensile and shear) of the cured material prevents excessive thermal stresses in the microelectronic packages.

Fig. 2 shows the DSC trace of the TIM scanned at a heating rate of 10 °C/min. The onset of the curing reaction is approximately 104 °C, and the peak is at 105.3 °C. The total amount of heat released during the curing reaction is about 1.2 J/g, which is quite small.

Isothermal DSC experiments were performed at several temperatures ranging from 60 to 100 °C. The results were plotted in Fig. 3. At 100 °C, the curing reaction started immediately when the isothermal temperature was reached, with the reaction peak being reached after 1.25 min. At 90 °C, the initial reaction rate was relatively slow. After about 2 min, the curing reaction began to proceed at an increasing rate, reaching a peak after 2.5 min. At 80 °C, there was a 7.6 min of ''incubation'' time before the reaction rate became significant, with the reaction peak being reached after 8.4 min. When the isothermal temperature was further reduced to 70 °C and then 60 °C, the ''incubation'' time increased to 27.5 and 95 min, respectively. At each temperature, the total heat of reaction is consistently around 1.2 J/g, in agreement with the non-isothermal DSC result.

Based on the isothermal DSC results, the activation energy E for the curing reaction can be estimated by plotting the time to reach the reaction onset or peak versus the inverse temperature, $1/T$, as shown in Fig. 4. The time t to reach the reaction onset or the peak has an Arrhenius dependence on temperature:

$$t = t_o \exp\left(\frac{E}{RT}\right)$$

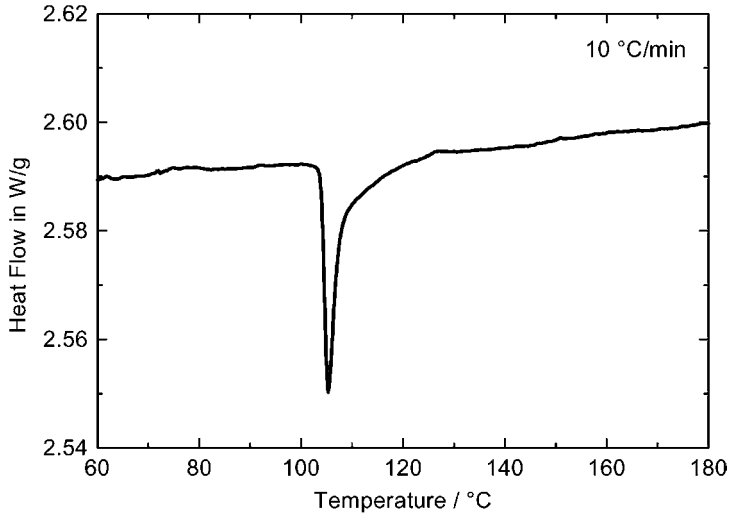

Fig. 2. Non-isothermal DSC curve of the thermal interface material.

where $R = 8.314$ J/(mol K) is the universal gas constant, T the absolute temperature and t_o a constant. In Fig. 4, $\log_{10} t$ versus $1000/T$ is plotted, thus, the slope of the linear fit gives $E/(1000R \ln 10)$. When onset time is used, the activation energy is calculated to be 129.3 ± 3.9 kJ/mol. When peak time is used, $E = 123.5 \pm 2.3$ kJ/mol. Using these data, it is estimated that at 25 °C, the time to reach the reaction onset is about 402 h or 16.8 days. Understanding the curing kinetics can help determine the material pot life at processing temperature, which in turn can help optimize material manufacturability.

From Fig. 3, it is clear that after about 30 min at $T = 80$ °C, the residual reaction rate becomes too slow to be detected by DSC. This does not mean that the cross-linking process has stopped. In fact, the curing reaction will continue even after 1 h at a higher temperature, such as 125 °C. At this later stage

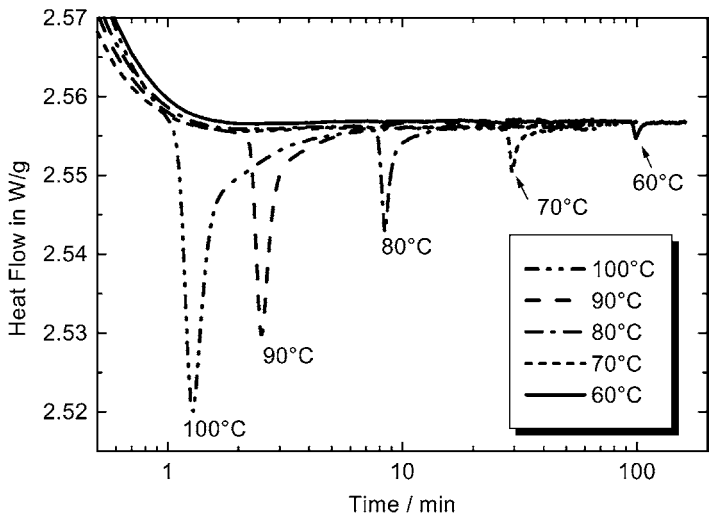

Fig. 3. Isothermal DSC results showing the curing behavior of the TIM at several different temperatures. The time needed to ramp from 25 °C to the isothermal temperature is excluded.

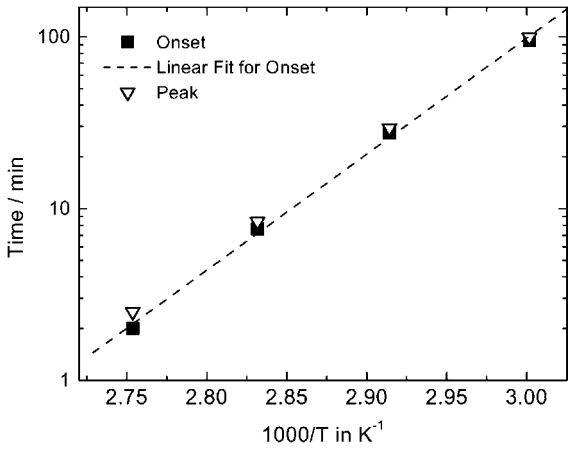

Fig. 4. Reaction onset time and peak time as a function of 1000/*T*. The data point at $T = 100\ ^{\circ}C$ is not included in the plot because the reaction rate at this temperature is too fast.

in the reaction, the heat-releasing rate is too small to be detected by DSC. However, this increase in cross-link density can be readily detected by monitoring the mechanical properties of the material, as will be discussed later.

3.2. Phase transitions

As one of the reliability requirements, assembled microprocessors must go through a large number of temperature cycles over a specified temperature range without failure. Thus, it is essential to understand phase transformation behavior of the TIM within the temperature range of interest, which is typically from -50 to 125 °C.

Fig. 5 shows the DSC curves of the cured thermal interface material scanned at several heating rates. From this figure, it is clear that the only observed transition between -100 and 100 °C is an endothermic transition. This peak, which is reversible, is attributed to the melting of silicone oils in the cured TIM. As shown in Fig. 5, the peak position is not affected by varying the heating rate. At 10 °C/min, the onset and peak temperatures of this endothermic reaction are -49 and -43.7 °C, respectively. At 2 °C/min, the melting peak appears at -43 °C and the transition completed at -39 °C.

On cooling, however, the DSC curves of the cured material showed a different behavior. Fig. 6 plots

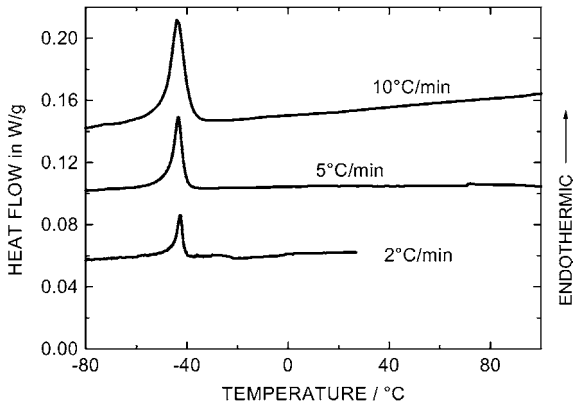

Fig. 5. DSC heating curves of the cured TIM. At 2 °C/min, the melting transition completed at -39 °C.

several cooling curves obtained at cooling rates of 2, 5, and 10 °C/min. The exothermic peak, which corresponds to the crystallization of silicone oils, appears at a lower temperature than that of the corresponding melting peak. This is not surprising, and it can be attributed to supercooling. At temperatures slightly below the equilibrium melting temperature, the energy barrier for nucleation is large compared to the thermodynamic driving force for crystallization. This results in slow nucleation kinetics, and the material can remain in its supercooled liquid state for certain period of time without crystallizing. Isothermal DSC results (not shown) revealed that at -62 °C, it takes approximately 5.5 min to reach the maximum crystallization rate, and 15 min to complete the crystallization process.

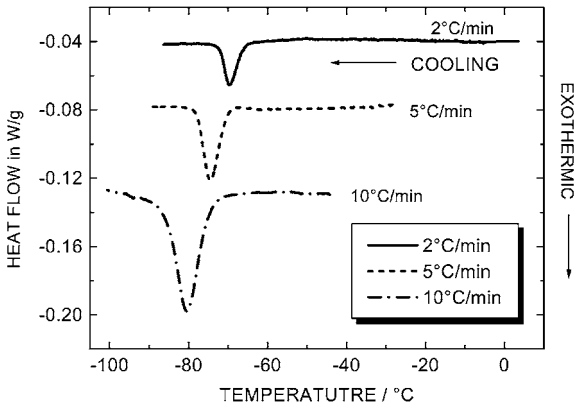

Fig. 6. DSC cooling curves of the cured samples measured at cooling rates of 2, 5, and 10 °C/min.

As the cooling rate increases, the degree of supercooling also increases, as shown in Fig. 6. For the three cooling rates shown in Fig. 6, the corresponding onsets of crystallization were detected at −65.9, −70.4, and −74.9 °C, respectively, and repeated measurements revealed that these temperatures were quite consistent. The peak temperatures for the same cooling rates were observed at −69.7, −74.5, and −80.5 °C, respectively. This melting-crystallization transition has a strong impact on the material's thermomechanical behavior at low temperatures, as will be discussed below.

3.3. Dynamic and static thermomechanical behavior

During temperature cycling, large thermal stresses can develop in the microelectronic packages as a result of the mismatch of the coefficients of thermal expansion (CTE) of the various materials in the package. During the cooling process, the substrate, which has an in-plane CTE of $20 \times 10^{-6}\ K^{-1}$, and the underfill materials, which has an in-plane CTE of $\sim 25 \times 10^{-6}\ K^{-1}$, will attempt to contract much more than the silicon chip does, since Si has a CTE of only $2.8 \times 10^{-6}\ K^{-1}$. Such thermally induced stresses can cause warpage of the silicon chip and the substrate at temperatures well below the processing temperature [6]. As this warpage develops, thermal interface material near the corners and the periphery of the chip will be under high tensile and shear stresses, which could lead to bond failure such as material delamination during temperature cycling. This will significantly increase the interfacial thermal resistance and result in a deteriorating thermal performance [7]. For this reason, it is necessary to understand the dynamic and static mechanical behavior of the thermal interface material over a broad temperature range.

Fig. 7 shows the DMTA curves of the TIM after it was cured at 125 °C for 1 h. In this figure, the storage modulus (E'), the loss modulus (E'') and the loss tangent (tan δ) curves were plotted. At –80 °C, E' of this material is as high as 6 GPa. When temperature increases to near −50 °C, E' starts to decrease by nearly a factor of 100 over a narrow temperature interval. This is again caused by the melting transition of the silicone oils in the TIM. This transition behavior is consistent with the DSC results. At −35 °C, E' is ∼ 47 MPa, and at 25 °C, E' is approximately 15 MPa.

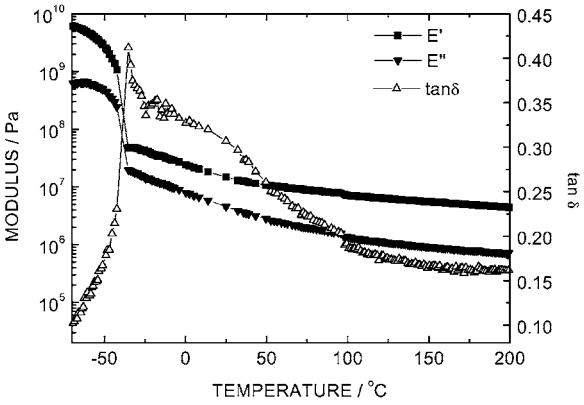

Fig. 7. DMTA curves obtained at a heating rate of 5 °C/min and a dynamic frequency of 1 Hz. This sample was cured at 125 °C for 1 h.

Static stress–strain behavior was measured using DMTA operated in the strain rate mode at −80, −40, −25, 0, 25, and 150 °C. The results are plotted in Fig. 8. At −80 °C, the ultimate elongation is only 2%, which is rather limited. Above the liquidus temperature of the silicone oils T_L, the ultimate elongation increases to approximately 20%, and it is not very sensitive to the temperature as long as $T > T_L$ ($T_L \approx -39$ °C). Thus, at temperatures above −39 °C, this material exhibits a significant amount of elongation. At −40 °C, it is expected that the equilibrium

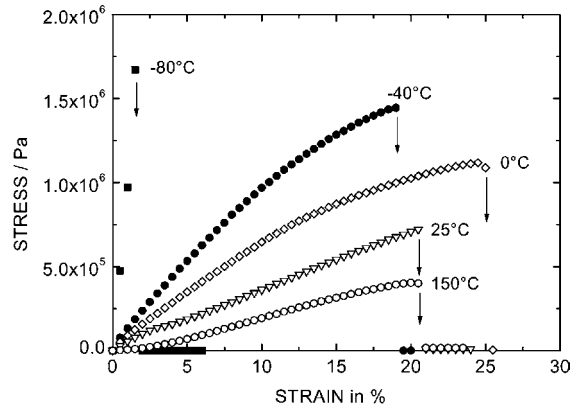

Fig. 8. Static stress–strain curves at several temperatures obtained by using DMTA strain rate mode. The strain rate is 0.001 s^{-1}. The measurement at −40 °C was conducted immediately after the temperature equilibrium was reached. All samples were cured at 125 °C for 1 h.

volume fraction of the crystalline phase is rather small, and the material should still have substantial strain. This feature, together with its low modulus, allows this TIM to be able to sustain relatively large strain during temperature cycling between −40 and 150 °C without bond-failure. Below −80 °C, however, the TIM will fully crystallize in a short time, resulting in an increased modulus. This leads to an increased thermal stresses in the microelectronic package, which in turn increases the danger of bond-failure in the heat sink-TIM-silicon chip interfaces.

3.4. Temperature effect on mechanical modulus

Based on DSC results (Figs. 2 and 3), it seems that this TIM can be cured in a short time at 100 °C. However, we have noticed that in a real package, the mechanical properties of the cured TIM continue to change at elevated temperatures. Because the mechanical properties have a strong impact on package reliability, an investigation was conducted on the effect of temperature on the mechanical properties of cured TIM.

The samples were cured at 100 °C for 4 h and then examined using DMTA. The storage modulus E' as a function of time was monitored at 125 and 150 °C, respectively, as shown in Fig. 9a and b. During these measurements, the dynamic strain was kept at 0.5%. As indicated by these figures, E' decreases rather rapidly at first during the initial ramping segment when the temperature was increased from room temperature to the isothermal temperature. Once the isothermal temperature is reached, E' starts to increase slowly, indicating continuous hardening or stiffening of the TIM. For example, when the cured sample was held at 125 °C (Fig. 9a), E' was determined to be 6.80 MPa at the beginning of the isothermal segment. After 5 h at 125 °C, E' increased to 7.83 MPa, which represents a 15.2% increase in modulus. Similarly, when isothermally held at 150 °C, E' increased from 5.70 MPa in the beginning to 7.28 MPa after 5 h (Fig. 9b), which is a 27.7% increase. This is a substantial change in material's mechanical property. Similar changes in storage shear modulus G' have been detected in rheological analysis.

Samples were also cured at 150 °C for 4 h and then examined using DMTA at 125 and 150 °C, respectively. Continuous hardening at these temperatures

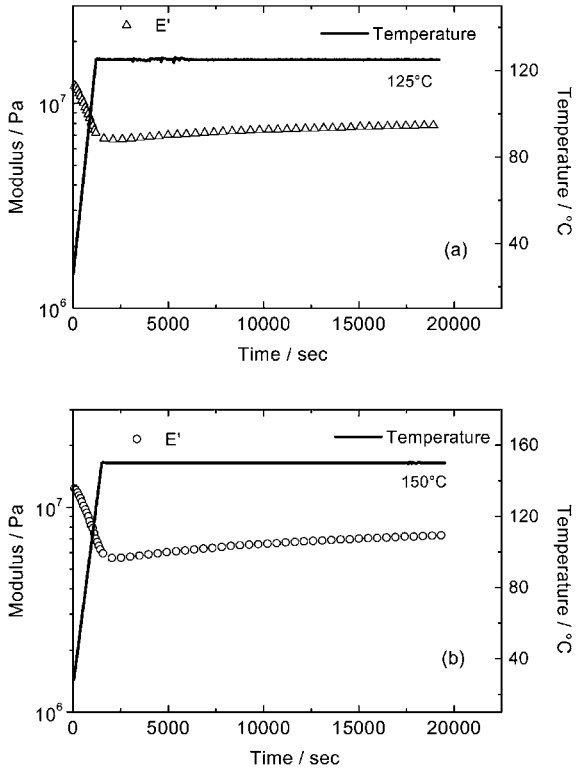

Fig. 9. Storage modulus of the TIM cured at 100 °C for 4 h and measured with DMTA at (a) 125 °C; and (b) 150 °C for up to 5 h. The initial ramping rate from room temperature to the selected isothermal temperature is 5 °C/min. The dynamic strain is kept at 0.5% and the dynamic frequency is 1 Hz.

was also observed for these specimens. After 5 h at 125 °C, the storage modulus increased by 9.3%, even though this temperature is lower than the cure temperature. After 5 h at 150 °C, E' increases by 10.9%. These results indicate that even after the samples were cured at 150 °C for 4 h, continuous cross-linking can still take place at elevated temperatures, although the rate of modulus increase is much reduced.

In reality, this TIM was cured at $T < 150$ °C for less than 4 h for manufacturing reasons. It is thus expected that the modulus E' of this material will continue to increase during temperature cycling or during operations when the microprocessor temperature is sufficiently high. Such change in mechanical properties needs to be closely monitored. As long as such changes in mechanical properties do not lead to degradation in thermal performance, one can expect this material to pass reliability tests.

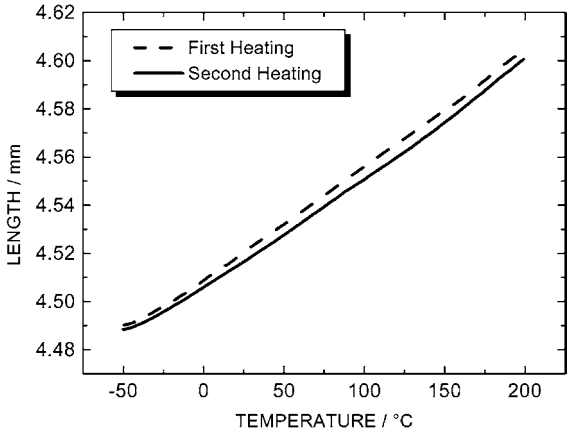

Fig. 10. Thermal expansion behavior of the TIM. The heating rate was 5 °C/min.

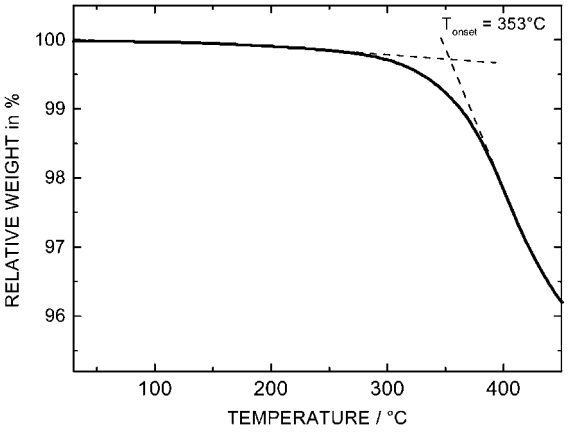

Fig. 11. TGA curve of the TIM measured with a heating rate of 10 °C/min.

3.5. Thermal expansion

Thermal expansion is always a key parameter for electronic packaging materials. Fig. 10 shows the thermal expansion curve of the thermal interface material. Between −30 and 50 °C, the average CTE is $(120-140) \times 10^{-6}\ K^{-1}$. As shown in Fig. 10, the CTE value of this material is not very temperature-dependent over the range of measurement. Although the CTE of this TIM is relatively high, its low modulus helps to reduce thermal stresses by decoupling the CTE mismatch between the silicon chip, the substrate, and the heat sink.

3.6. Thermal stability

Fig. 11 is a TGA weight loss curve. It shows that the degradation onset of this material is ∼353 °C, at which the sample loses 0.8% of its original weight. It demonstrated that this material is very stable and no substantial weight loss will occur at processing or operational temperatures.

Fig. 12 is an isothermal TGA curve obtained at 150 °C for 12 h in an air environment. At the end of the experiment, this material loses only about 0.21% of its original weight, and most of this weight loss occurs in the first 30 min. The relative sample weight W can be

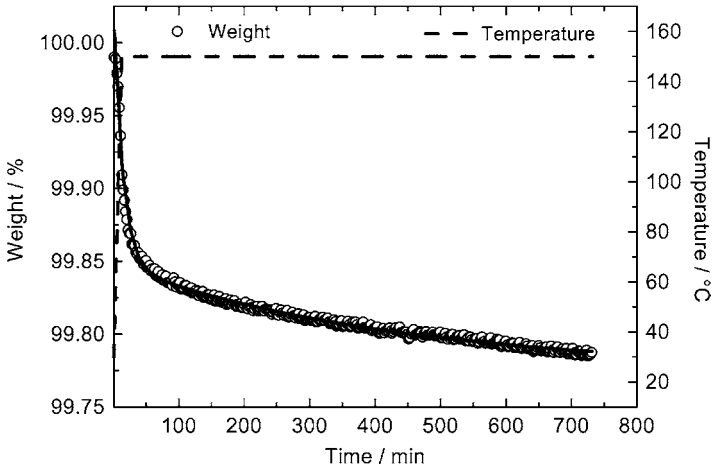

Fig. 12. Isothermal TGA curve of the thermal interface material at 150 °C. Dashed line is the temperature profile, open symbols are measured relative weight, and solid line is the fitted weight loss profile based on the experimental data.

well described by a second order exponential decay function:

$$W(\%) = 99.775 + 0.18182\,e^{-t/13.95} + 0.07315\,e^{-t/424.2}$$

where t is the isothermal time in minute. As t approaches infinity, the sample weight will reach a plateau of 99.775%, which means the maximum weight loss will be 0.225% at 150 °C. Furthermore, the weight loss behavior of a cured specimen was monitored at 110 °C for 72 h. At the end of the 72 h, the total weight loss was approximately 0.1%. These results indicated that this TIM is very stable at its operational temperatures.

4. Conclusions

Curing behavior of a thermal interface material has been studied using DSC. During continuous heating, this material showed an exothermic peak near 105 °C, and the total heat of reaction is about 1.2 J/g, which is quite small. Based on isothermal DSC results, the activation energy for the curing reaction is estimated to be 129 kJ/mol. Although DSC results indicated that when $T \geq 80$ °C, the curing reaction should be nearly completed after 30 min, DMTA results indicated that further increase in modulus is still taking place at temperatures near or above the curing temperature.

On heating of the cured material, DSC results showed an endothermic peak near −43 °C. This peak corresponds to the melting of silicone oils in the cured TIM. Below and above this melting point, thermo-mechanical properties of the TIM change drastically. Below this temperature, the material has a relatively high modulus, and the ultimate elongation before fracture is limited to only about 2%. Above this melting temperature, the tensile modulus of this material decreases sharply, and the ultimate elongation increases to ∼20%. Therefore, it is suggested that the lowest end-use temperature the microelectronic package should experience is limited to −40 °C or above to reduce the risk of thermal stress induced cracking or delamination in the thermal interface material.

TGA studies showed that this material has a relatively high thermal stability with an onset of degradation of ∼353 °C. When held isothermally at 150 °C, the maximum weight loss of this material is expected to be ∼0.23%. These results suggest that the degradation of this TIM near the maximum operational temperature (∼100 °C) is negligible.

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