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The effect of crystallization on the modulus of thermally conductive silicone adhesives

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Abstract

Low modulus, thermally conductive silicones were evaluated as soft mount adhesives for substrate attachment. It was determined that due to the existence of a crystalline phase, above the glassy transition temperature (T_g≈−125°C), the modulus of the adhesives can be orders of magnitude higher than at room temperature. Differential scanning calorimetry shows that at a cooling rate of 5°C/min the crystallization temperature, T_c, is −75°C, which shifts to −66°C under a slower ramp rate of 0.5°C/min. Correspondingly, a sharp increase in modulus also occurs at T_c when the adhesive undergoes the same thermal processes. When the temperature is held isothermally below the crystalline melting temperature (T_m=−42°C), the modulus increases simultaneously with the increase in the degree of crystallization. The growth rate of the modulus increases exponentially as the temperature approaches −75°C from T_m. Once the silicones are in the high modulus state, the temperature must be increased above T_m to melt the crystalline phase and recover the normal low modulus phase. If the heating rate is faster than about 0.5°C/min, the recovery temperature can pass over T_m to about −35°C.

Keywords: Crystallization; Silicone adhesive

1. Introduction

Low modulus thermally conductive adhesives (TCAs) are commonly used as soft mounts to join printed circuit (PC) boards to heatsinks in automotive electronic applications [1]. When a device undergoes thermal cycling, the thermal expansion mismatch of the metal substrate with the PC board can cause a bowing of the PC board, which leads to a delamination of the PC board from the baseplate. For example, the coefficient of thermal expansion (CTE) of a ceramic circuit board (e.g. alumina α_{CTE}=6.0 ppm/°C) with an Al or Cu baseplate (α_{CTE}=23.0 ppm/°C for Al, and α_{CTE}=17.0 ppm/°C for Cu) differs by a factor of 3–4. An efficient way to decrease the thermal stress is to add a low modulus adhesive between the substrate and baseplate as illustrated in Fig. 1.

A TCA with a low modulus can act as a buffer to take up the stress associated with the CTE mismatch without breaking the board. Typically, TCAs are dimethylsiloxane based silicones. After vulcanization they form rubbery materials having shear moduli of about 6.90×10^5 Pa (100 psi) at ambient temperature. Below their glass transition temperature, T_g∼−125°C, the materials are frozen and become extremely rigid. However, we found that at about −75°C, the moduli of some of these adhesives increase to over 100 times

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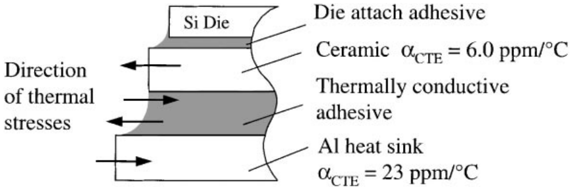

Fig. 1. Schematic drawing of a low modulus, thermally conductive adhesive between an aluminum heat sink and a ceramic substrate.

their room temperature value. The reason is that these materials become partially crystalline at about −75°C [2–4]. As the temperature is reduced, and the degree of crystallinity increases, the polymer chains in the network lose their flexibility, and the rigidity (moduli) of these materials increase dramatically. In order to design reliable products, a knowledge of the temperature dependence of the moduli of these adhesives at their crystallization temperature is critical.

2. Experimental procedure

2.1. Materials

Several commercially available TCAs have been studied. For simplicity, only one of these adhesives TCA-X is described in this paper. It is a vinyl terminated polydimethylsiloxane (PDMS) based silicone to which is added a PDMS polymer which contains silicon hydride functional groups, a Pt catalyst, an inhibitor (to prevent the polymer from reacting at room temperature), and about 30 to 40% of an alumina/ceramic filler. The filler increases the uncured polymer's viscosity, and improves the material's thermal conductivity and mechanical strength. After curing at 125°C for 45 min, the adhesive forms an elastic network with a shear modulus of about 80 psi at room temperature [5].

2.2. Sample preparation

Lap shear samples were prepared as illustrated in Fig. 2.

The thickness h is chosen to be 1.27×10^{-2} m (0.5 in.) and the other dimensions are: length $l=2.54\times10^{-2}$ m (1.0 in.) and width $w=2.54\times10^{-2}$ m. A detailed discussion of this test has been presented elsewhere [6,7]. The shear modulus can be calculated using the following equation:

$$G=\frac{Fh}{wld_{\text{total}}}\left(1+\frac{h^2}{3l^2}\right)=\frac{\tau}{\gamma}\left(1+\frac{h^2}{3l^2}\right) \tag{1}$$

where τ is the shear stress, γ is the shear strain, and $h^2/3l^2$ is a correction factor for bending deflection. The uncured polymer is first dispensed, at room temperature, into a mold which contained the Al lap bars. The mold is then deaired (under vacuum) to remove any trapped air bubbles. The adhesive is then cured at 125°C for 45 min. Shear measurements were performed under different temperatures using an Instron, with a crosshead speed of 1.0×10^{-3} m/min. The shear modulus was calculated at a strain of 1% (from the measured stress–strain curves).

2.3. DSC

A Mettler TC15 Differential Scanning Calorimeter was used to measure the crystalline transition temperature [8]. The crystalline/melting transition was measured by cooling the sample from room temperature to −100°C and then heating the sample back to room temperature at a fixed rate varying from 5 to 0.1°C/min. The peak temperatures from the exothermic and endothermic curves are defined as the crystalline temperature T_c and the melting temperature T_m, respectively.

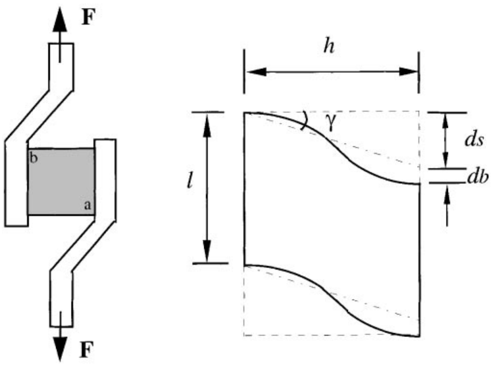

Fig. 2. Schematic sketch of the lap shear test. The sample has dimensions of $l=w=2.54\times10^{-2}$ m (1.0 in.) and thickness $h=1.27\times10^{-2}$ m (0.5 in.), where l and w are respectively the sample length and width. Total deformation is corrected for both from shear (ds) and from bending (db).

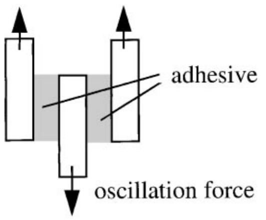

Fig. 3. Geometry of a shear sandwich specimen for modulus measurement in a Dynamic Mechanical Analyzer.

2.4. DMA

A TA Instruments Dynamic Mechanical Analyzer was used to study the variation of modulus with the temperature and time. Cured samples were cut into two symmetric specimens 3.0×10^{-3} m thick and 0.010 m×0.010 m square and put into a shear sandwich clamp as shown in Fig. 3. An oscillatory strain is applied to the material and the resulting stress is measured. The oscillatory frequency is set to 1 Hz and the shear strain is set to 1%.

3. Results and discussion

The sudden increase in shear modulus of TCA-X above its T_g was first observed in the lap shear measurement. The measured shear stress versus strain curves at 25 and −45°C (at a shear rate of 1.0×10^{-3}m/min) are plotted in Fig. 4. The shear modulus at 25°C is about 6.20×10^{5} Pa (90 psi) at a shear strain of 1%. When the sample was cooled to −45°C at 10°C/min and held at this temperature for 10 min, the modulus increased to about 1.24×10^{6} Pa (180 psi), whereas when the sample was cooled to −65°C at 10°C/min and held at this temperature for 10 min, the modulus increased to about 8.28×10^{6} Pa (1200 psi) as shown in curve (a) of Fig. 5. When the sample was cooled to −65°C at 10°C/min and held at this temperature for 20 min, the modulus increased to an even higher value of about 2.21×10^{7} Pa (3200 psi), as shown in curve (b) of Fig. 5. This high modulus value was maintained as the sample was warmed until about −40°C, at which point the modulus started to drop.

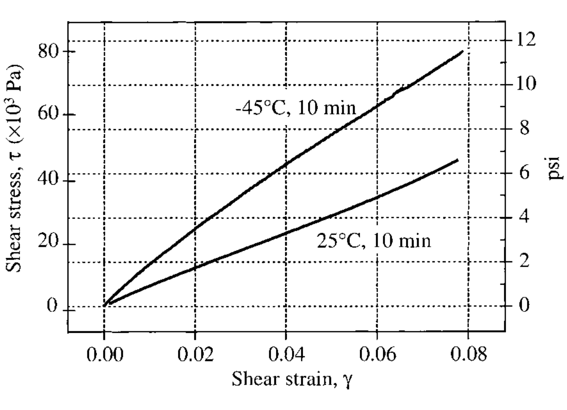

Fig. 4. Shear stress vs. shear strain at −45°C and 25°C for 10 min.

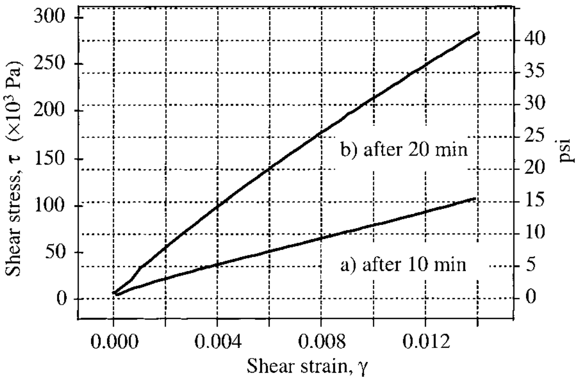

Fig. 5. Shear stress vs. shear strain at −65°C for 10 and 20 min.

Based on the results of the lap shear tests, the TCA appears to crystallize between −35 and −80°C. This transition is apparently related to both the temperature and the time at temperature. To understand this transition, we used DSC to study both the crystallization in the dynamic thermal process and also the crystallization kinetics in the isothermal process. The sample was first cooled to −100°C from 25°C and then heated back to 25°C using a constant ramp rate of 5°C/min. Fig. 6a and b show the measured DSC curves which display respectively the transitions in the cooling and heating processes. In cooling, the transition from the amorphous to the semicrystalline state occurs at the peak temperature $T_c\sim-75$°C. Upon heating, the transition from the crystalline to the amorphous state occurs at the peak temperature $T_m\sim-46$°C. The two transition temperatures T_c and T_m do not match each other under this thermal ramp rate.

Next the thermal ramp rate was decreased to 0.5°C/min. The DSC profiles corresponding to the cooling and heating processes are shown in Fig. 6c and d.

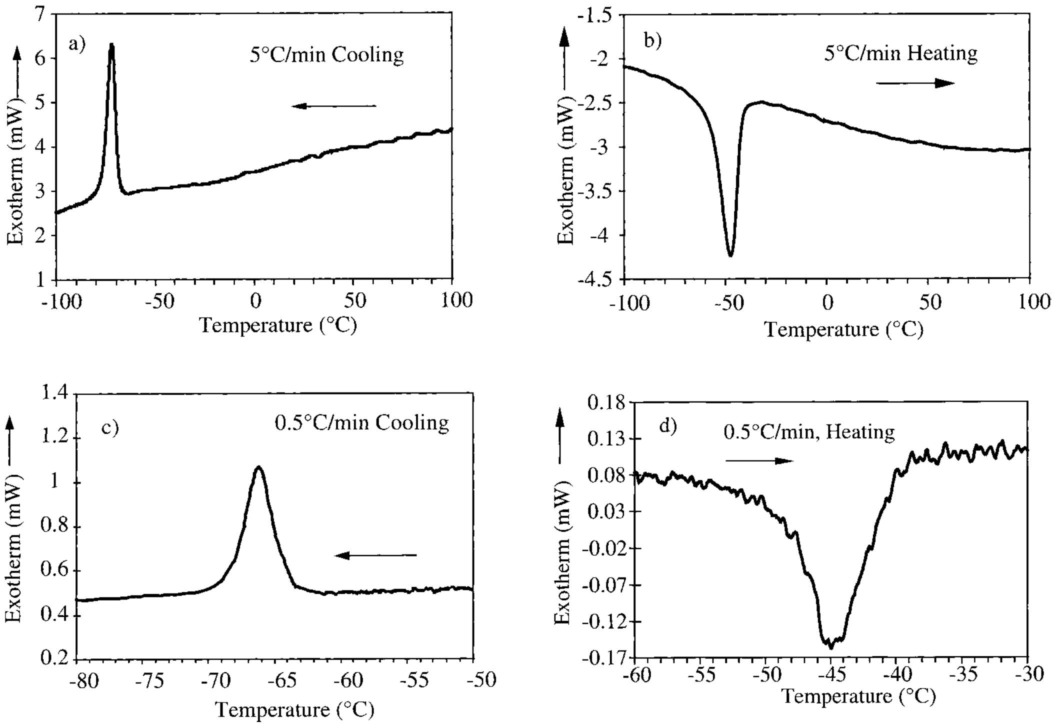

Fig. 6. DSCs showing the effect of thermal history on the crystallization and crystalline melt transitions. (a) Cooling at 5°C/min; (b) Heating at 5°C/min; (c) Cooling at 0.5°C/min; (d) Heating at 0.5°C/min.

Apparently, T_c shifts to −66°C, but T_m remains at about the same temperature as in the faster ramp rate case (shown in Fig. 6b). As the thermal cycling rate is reduced, the two transition temperatures move closer together. To see if these two points can be brought even closer together, the ramp rate was reduced even further to 0.1°C/min. It was found that T_c and T_m were −65 and −45°C, which is similar to the results obtained with a ramp rate of 0.5°C/min. Thermodynamically we would expect these two transitions to occur at the same temperature if the ramp rate were infinitesimally small. The reason that it does not, in our case, is that the crystallization transition is kinetically controlled. The highly crosslinked silicone network restricts the motion of the polymer chains from their completely disordered (high temperature) state to their partially ordered (low temperature) state.

The isothermal kinetics of the crystallization process were investigated by DSC. The sample was quickly cooled (~20°C/min) to below −45°C, held isothermally at this temperature for different periods of time and then heated up using a fairly fast rate of 5°C/min to room temperature. A typical DSC profile is shown in Fig. 7. The shadowed area is the melting peak of the crystalline phase that was formed in the previous isothermal process. From the area of the melting peak, the relative degree of crystallinity at different times can be determined. Fig. 8 shows the relative crystallinity versus isothermal time at −60, −65 and −70°C. The time needed for the crystallization process to approach equilibrium is about 120 min at −60°C, 9 min at −65°C, and 4 min at −70°C. As an approximation, the kinetics of the crystallization process can be simplified to include an initial nucleation stage followed by a crystalline growth stage. The initial delay period (induction time) is visible in Fig. 8, (e.g. 10 min induction period for crystallization to occur at −60°C) and corresponds to the nucleation process with approximately zero growth of the polymer crystal. Therefore, when the sample was cooled down to −60°C and then heated to room temperature at 0.5°C/min without an isothermal

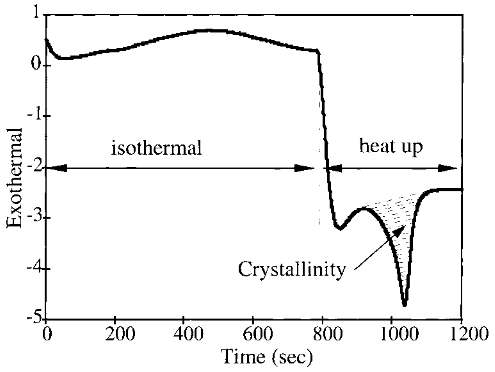

Fig. 7. DSC profile of the isothermal crystallization of a sample held at −65°C for 13 min, then heated at a ramp rate of 5°C/min.

hold at −60°C, no crystalline melting peak was observed in the thermal cycling process. This demonstrates that if the material is thermally cycled above T_c and then warmed, the polymer still keeps its amorphous state and the melting transition will not be observed.

It was found that the kinetics of the crystallization shown in Fig. 8 for the early stage (e.g. crystallinity less than about 70%) can be approximated by the Avrami Equation [9,10]:

$$P = 1 - \exp(-kt^n) \qquad (2)$$

where P is the relative crystallinity, n is found to be $\cong 2.5$ by a logarithm fitting of the equation to the measured data. From the slope of the plot of $\ln k$ versus $1/T$, the heat of crystallization was determined to be approximately 1010 KJ/mol, which is comparable to the 1250 KJ/mol reported in the literature [11] for the heat of fusion of a polydimethylsiloxane. The non-integral Avrami exponent reveals that the crystallite may be composed of a phase whose morphology is between that of a discoid and spherulite [9,12].

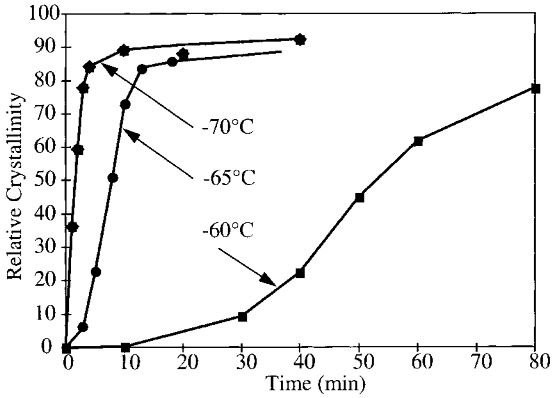

Fig. 8. Relative crystallinity at −70, −65, and −60°C as a function of time.

The appearance of the crystalline phase is directly responsible for the behavior of the modulus, i.e. the increase of modulus with isothermal holding time at −65°C shown in Fig. 5. To better understand the dependence of the modulus on thermal history and crystallization, a shear sandwich of the adhesive was made and evaluated using DMA. Fig. 9a shows the cooling of the sample from room temperature to −80°C followed by heating to room temperature at a rate of 5°C/min. The modulus increasing sharply at −85°C (at a ramp rate of 5°C/min) in a thermal cooling process and then dropping to its normal value

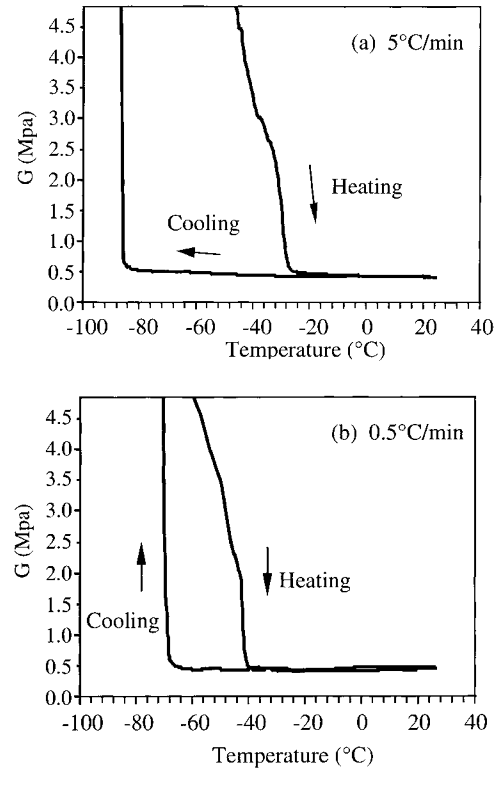

Fig. 9. Thermal history relating shear modulus vs. temperature, measured from DMA shear sandwich. (a) Ramp rate=5°C/min; (b) Ramp rate=0.5°C/min.

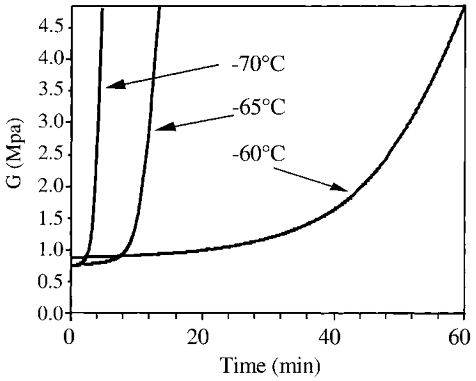

Fig. 10. Increase in shear modulus as a function of time at constant temperatures, measured using a DMA shear sandwich.

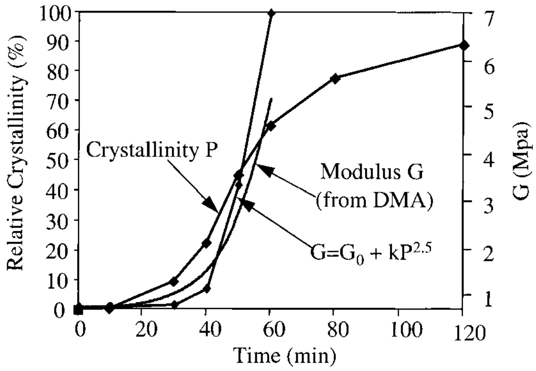

Fig. 11. Empirical relationship of modulus with relative crystallinity. The calculated curve is obtained using the equation $G=G_0+kP^{\alpha}$ using measured values of relative crystallinity P obtained by DSC.

of ~6.90×10^5 Pa (100 psi) at −32°C during the heating process. This transition temperature matches reasonably well with the T_c (−75°C) and T_m (−46°C) measured by the DSC at the same ramp rate. Similarly, as shown in Fig. 9b, the temperature corresponding to the sharp change of modulus shifts to −65 and −43°C when the thermal cycling rate decreases to 0.5°C/min which also matches with the DSC result shown in Fig. 6c and d. Further, when the sample was cooled down to −65°C and heated back to room temperature at 5 or 0.5°C/min, there was no significant modulus change observed either in cooling process or in heating process.

When the sample was held isothermally at −65°C, the modulus was found to increase exponentially after about 15 min, as shown in Fig. 10. Also shown in Fig. 10 are the changes in modulus versus isothermal hold time at −70 and −60°C. Comparing the crystallization kinetics shown in Fig. 8, with the change in modulus, it was found that the increase in modulus follows the increase in the degree of crystallization. For instance, the relative crystallinity approaches 90% in about 4, 19 and 130 min at −70, −65, and −60°C, respectively. The shear modulus also approaches a value of about 9.66×10^6 Pa (1400 psi) at about the same times, if held isothermally at −70, −65, and −60°C. The relationship between the increase in modulus with the increase in the degree of crystallinity for the early stages of crystal growth ($P<70\%$) may be described using an empirical equation of

$$G = G_0 + kP^a \qquad (3)$$

(when $T<T_m$), where $G_0=7.59\times10^5$ Pa (110 psi) is the modulus at T_m without any crystallization, P is the relative degree of crystallization, and α and k are constants, α is taken to be around ~2.5 and the coefficient $k=2.28\times10^7$ Pa (3300 psi). Shown in Fig. 11 is a plot of this empirical relationship at −60°C using values of P obtained from DSC measurements. This result indicates that the increase in modulus and crystallinity are not linearly related to one another, for the adhesive studied.

Considering that it takes a slightly longer time to heat the sample in the DMA (a DMA sample has a significantly larger mass than a DSC sample), the kinetics of the growth of the shear modulus agrees reasonably well with the kinetics of crystallization. As a simple comparison, we compared the time necessary to achieve 50% relative crystallinity (as measured by DSC) with the time necessary for the modulus to increase to 4.83×10^6 Pa (700 psi) (as measured by DMA). Fig. 12 shows this comparison, which demonstrates a reasonable match in the temperature range from −75 to −60°C. Based on DSC measurements (Fig. 12), at temperatures below −80°C the isothermal crystallization rate slows down. This slow down is the result of a reduction in the nucleation rate at very low temperatures [8,10]. The maximum rate of crystallization was found to occur at a temperature of about −75°C. When the temperature cools to −75°C, both the crystallization rate and the modulus growth rate increases exponentially. Once the adhesive is heated

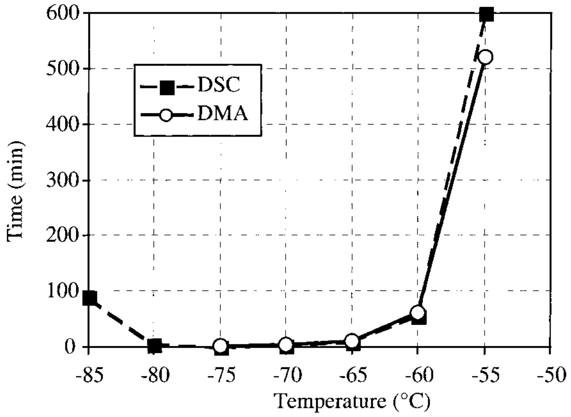

Fig. 12. Comparison of the time needed to achieve 50% crystallization with the time needed for the shear modulus to approach 4.83×10^6 Pa (700 psi).

above T_m (to melt the crystalline phase), the modulus returns to its normal value.

4. Conclusions

The rapid increase in the modulus of the thermally conductive adhesives, above their glassy transition temperature, was found to be caused by an amorphous to crystalline transition. The crystallization starts well below room temperature and is strongly time and temperature dependent. The crystallization temperature, T_c, shifts from -75°C at a ramp rate of 5°C/min to -68°C at 0.5°C/min. The crystalline melting temperature T_m is constant at about -42°C. The increase in modulus was found to follow the crystallization kinetics. The crystallization kinetics increase as the temperature approaches -75°C and rapidly drop as the temperature departs from -75°C. Once the adhesive becomes partially crystallized (and develops a high modulus), the modulus can only recover to its normal low value if the temperature is raised above the T_m. If the ramp rate is greater than 0.5°C/min, the recovery temperature is greater than -42°C. At a ramp rate of 5°C/min the recovery temperature is about -35°C.

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