Erasure Below Glass-Transition Temperature of Effect of Isothermal Physical Aging in Fully Cured Epoxy/Amine Thermosetting System

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Received 6 December 1999; accepted 28 August 2000

ABSTRACT: The erasure below the glass-transition temperature (T_g) of the effect of isothermal physical aging (at aging temperature T_a) in a fully cured epoxy/amine thermosetting system is investigated using the torsional braid analysis (TBA) dynamic mechanical analysis technique and the differential scanning calorimetry (DSC) technique. From the TBA temperature scans, the intensity of the localized perturbation of the moduli in the vicinity of the T_a (90°C), due to isothermal physical aging, is decreased by heating to below the T_g ($T_{g\infty}$ = 177°C), indicating that the physical aging effect can be eliminated by heating to below the T_g. The isothermal aging effect in the vicinity of the T_a is almost completely eliminated by heating to 50°C above the T_a (i.e., 140°C); however, a competing aging effect occurs above T_a at higher temperatures during the heating. Erasure below T_g of the isothermal physical aging effect is inferred from DSC experiments from the diminished relaxation enthalpy in the vicinity of the T_g, which is measured from the difference in areas between the aged (T_a = 150°C) and deaged thermograms. A comparison of the TBA and DSC results is made. Implications on the heterogeneous nature of the amorphous glassy state of polymers are discussed.
 J Appl Polym Sci 81: 396–404, 2001

Key words: glass-transition temperature; isothermal physical aging; epoxy/amine thermosetting system

INTRODUCTION

Physical aging occurs spontaneously below the glass-transition temperature (T_g) in amorphous polymer glasses and affects various properties related to density, which are of practical importance for engineering materials. There are contradictions in the literature on the temperature ranges for the occurrence of isothermal physical aging from well below[1–4] the glassy state relaxation T_β to T_g or only between T_β and T_g.[5–7] However, this report concerns the effect of isothermal physical aging on the modulus being localized to the vicinity of the aging temperature (T_a), which has been reported for both thermosetting (e.g., epoxy, polyimide)[8–10] and thermoplastic [e.g., poly(methyl methacrylate)][3,11,12] polymers.

Localization is theoretically and practically important. Theoretically, submolecular dynamics are involved in isothermal physical aging (discussed below). Practically, the localization shows that some changes of properties due to isothermal

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physical aging occur only within a limited range of temperatures about the T_a. It follows from the localization effect that the isothermal aging effect about the T_a can be diminished by heating to above the T_a but below the T_g. (Heating to above the T_g is considered to completely eliminate the effects of physical aging.)

Physical aging has been monitored at the T_a by changes in the elastic and loss moduli by means of the freely oscillating torsion pendulum in the torsional braid analysis (TBA) mode.[3,4,8–10] The moduli are measured intermittently at short time scales (ca. 1 s) compared with the time of aging (10 h = 36,000 s). In general, the intermittent isothermal elastic modulus increases while the loss modulus decreases on physical aging as a result of the decreasing mobility of submolecular segments.

On the basis of moduli measurements during a temperature scan-up after isothermal physical aging (at T_a), (partial) deaging of the effect of aging at the T_a occurs by about 50°C above the T_a, subsequent to which aging occurs prior to the T_g, and above the T_g deaging is completed.[10] During a temperature scan-down after isothermal aging, the physical aging effect resulting from aging at the T_a is retained: during a subsequent scan-up from below the T_a and through the T_a the effect of the isothermal physical aging perturbation remains localized to the vicinity of the T_a. If the isothermal T_a is reached after cooling (e.g., from above the T_g), physical aging progresses monotonically (i.e., the isothermal elastic modulus increases). If the isothermal T_a is reached after heating from a temperature below the T_a, isothermal deaging occurs before aging dominates (i.e., the isothermal elastic modulus initially decreases before increasing).[10]

An explanation for these observations on the modulus stems from consideration of the length scales and the corresponding motions at the submolecular level that at the T_a are either free to move (short), or move slowly with time to a lower energy state (intermediate) and are responsible for the effects of physical aging (e.g., on the intermittent moduli), or are frozen in place (long).[4] The effects of aging at the T_a do not seem to be present when scanning to temperatures much above the region localized about the T_a because there is an expansion of the material upon heating to higher temperatures; thus, intermediate length scale elements at the T_a that are immobilized at the T_a by the process of physical aging (and cause an increase in the modulus at T_a) not only regain the mobility that they had before aging at the T_a but at higher temperatures they also acquire the same freedom to move freely as those elements of a short length scale. (Therefore, the intermittent moduli are unchanged from those of the unaged material during scanning to higher temperatures T_a.) In scanning down to temperatures well below the T_a the effect of aging at the T_a is absent because those intermediate elements that participate in the aging process at the T_a are long scale motions at the lower temperatures and are not involved in the measurement of the intermittent moduli at the lower temperatures. Different sets of short, intermediate, and long, length scales are involved at different (isothermal) T_a's and to different extents corresponding to the distribution of relaxation times in the glassy state. The rate of physical aging is highest in the vicinity of transitions (relaxations) such as the T_g and T_β because the intensity of submolecular motions involved in the process of physical aging also underlies the intensities of relaxations revealed by intermittent dynamic mechanical measurements.[4]

Although isothermal physical aging at the T_a produces localization of the increase in the elastic modulus about the T_a in subsequent temperature scans, the density increase accompanying isothermal physical aging is retained at temperatures below the T_a.

The above qualitative analysis on the submolecular dynamics of physical aging in polymers accounts for the inherently heterogeneous nature of the amorphous state of polymer glasses. Different time–temperature paths of cooling from above the T_g to (say) 25°C will lead to different distributions of localized density and therefore of free volume at 25°C. This could be useful for making glassy membranes for the selective transmission of gases.

The purpose of the present report was to investigate the (partial) elimination of the effects of isothermal physical aging by heating to above the T_a but below the T_g. A preliminary report has been published.[13] The techniques used were dynamic mechanical analysis and differential scanning calorimetry (DSC). Practical implications were discussed. A separate report[14] deals with the rate of isothermal physical aging versus conversion: in principle, a single specimen could have been used for that study by regenerating unaged material by eliminating the effect of isothermal aging by heating to below the T_g for a given conversion (without advancing conversion) and heating to above the T_g to advance conversion.

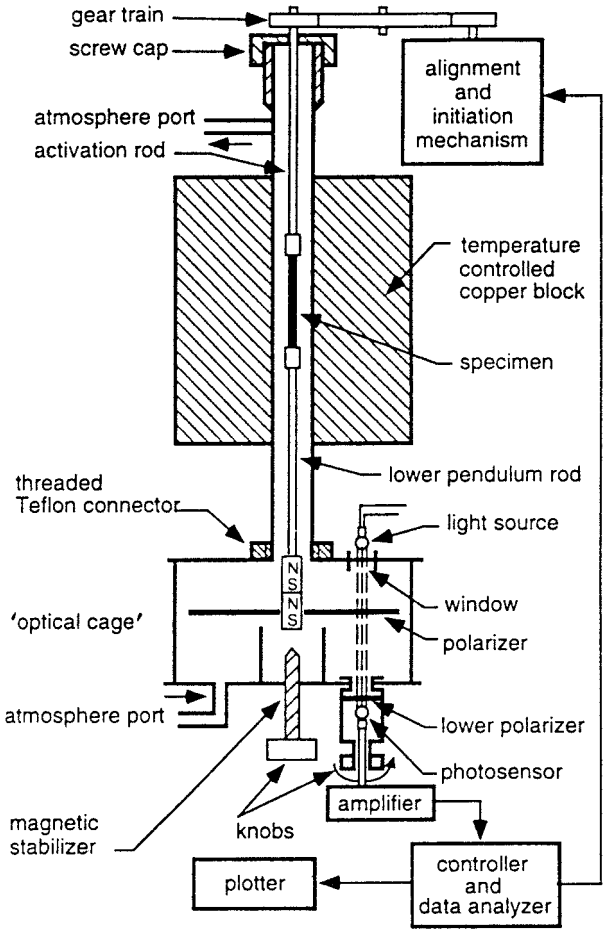


Figure 1 A schematic diagram of the TBA torsion pendulum.[15,16] Reproduced with the permission of Plastics Analysis Instruments, Inc. (Princeton, NJ).

EXPERIMENTAL

Techniques

Reviews of the freely oscillating TBA dynamic mechanical technique, which is a torsion pendulum that operates at about 1 Hz, have been published.[15,16] (Note that a freely oscillating torsion pendulum is sensitive enough to measure the gravitational constant.[17]) Figure 1 shows a schematic diagram of the TBA torsion pendulum. The (relative) elastic shear modulus (G') of the specimen is termed the relative rigidity ($\equiv f^2$) and is obtained from the natural frequency (f) in cycles per second. (The relative rigidity is a true relative modulus in the absence of changes in the geometry of the specimen.) The loss shear modulus (G'') of the specimen is expressed as the logarithmic decrement ($\Delta \cong \pi G''/G' = \pi \tan \delta$, where δ is the phase angle between the stress and strain) and is computed from the decay of the oscillations in an induced damped wave. (Modern practice in dynamic mechanical experiments uses tan δ rather than the logarithmic decrement: the latter was used before the advent of computers by direct measurements of the peak amplitude, $\Delta = \ln(A_i/A_{i+1})$, where A_i is the peak amplitude of the ith oscillation in a freely damped wave.)

A single fully cured specimen (ca. 2-in. length, ca. 0.05-in. diameter) was used for the TBA experiments. After fully curing the initially unreacted liquid (T_{go} = 0°C)/glass braid composite specimen in the TBA unit at 220°C for 35 h, all subsequent scans were limited to 200°C. The T_g of the fully cured material ($T_{g\infty}$) was 177°C throughout the experiments (measured during cooling from above T_g). The heating and cooling rates were 2°C/min. The atmosphere was slow flowing helium.

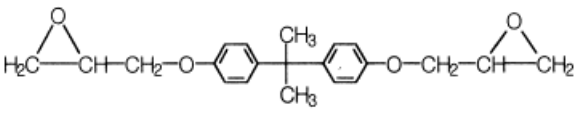
A single specimen was also used for the DSC (Dupont 910) experiments to examine the effect of isothermal physical aging. A hermetic pan containing about 10 mg of unreacted liquid mixture was sealed and placed in the DSC cell and then fully cured under the same conditions as the specimen for TBA (i.e., 220°C for 35 h). The T_g, which was measured by DSC during heating, was 179°C at the heating rate of 10°C/min. The atmosphere was slow flowing dry nitrogen.

Reactants

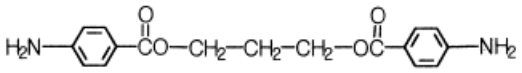
The chemical structures of diglycidyl ether of bisphenol A (DER 332, 174 g/eq, Dow Chemical Co.) and trimethylene glycol di-*p*-aminobenzoate (TMAB, 78.5 g/eq, Air Products Corp.) are represented in Figure 2. A stoichiometric mixture (epoxy/NH = 1/1) was formed by mixing (without solvent) at 100°C for 15 min.[4,8–10]

Temperature–Time Profiles

The temperature–time profiles are shown in Figure 3(A,B). Two different profiles (profiles I and II) for TBA [Fig. 3(A)] and one profile (profile III) for DSC [Fig. 3(B)] were used for this study. For profile I the specimen ($T_{g\infty}$ = 177°C from TBA) was isothermally aged at 90°C for an aging time (t_a) of 600 min, heated to an erasure temperature (T_{er}), and then immediately cycled twice between 0 and 200°C to enable the comparison of the residual aging effects versus the T_{er} (which varied from 90 to 160°C). For profile II the specimen was cycled between a low temperature of 50°C and a



Diglycidyl Ether of Bis-phenol A



Trimethylene Glycol Di-p-aminobenzoate

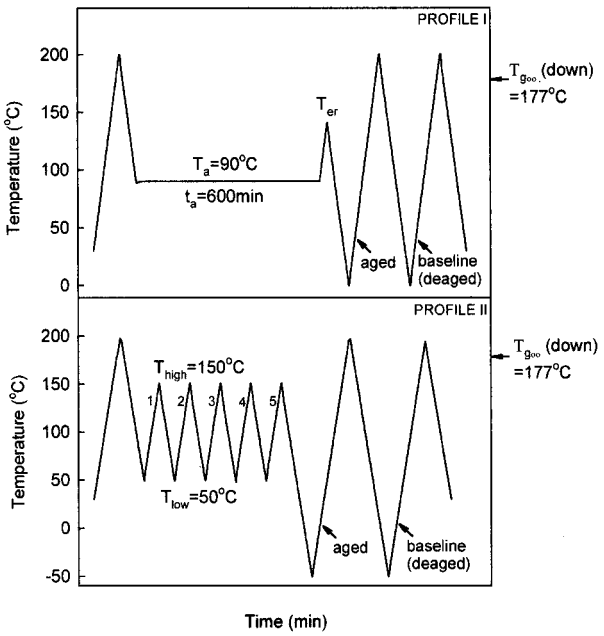
Figure 2 The chemical structures of the reactants: diglycidyl ether of bisphenol A epoxy resin and trimethylene glycol di-*p*-aminobenzoate curing agent.

high temperature of 150°C, and the net accumulation of the physical aging effects in this temperature range was ascertained by comparison of the up-temperature scans of the aged and deaged specimens from −50 to 200°C. Note that the specimen was heated to 200°C (i.e., above the T_g) to remove the previous thermal history.

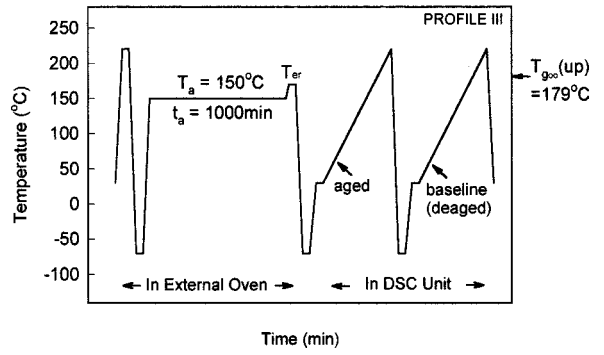
For profile III [Fig. 3(B)] for DSC a sealed DSC pan containing the fully cured specimen ($T_{g\infty}$ = 179°C from DSC) was heated in an external oven at 220°C (i.e., above the $T_{g\infty}$) for 15 min to eliminate the previous thermal history and then quenched by and held for 15 min in powdered dry ice maintained at −68°C. (A liquid such as acetone was not used for the cooling medium because the solvent might affect the specimen in the DSC pan.) The quenched DSC pan was immediately put into another external oven preheated at 150°C in order for the cured specimen to be isothermally aged at 150°C for a t_a of 1000 min. The aged specimen was then moved to an external oven preheated at an T_{er} for a time of erasure (t_{er}) of 10 min, followed by being quenched as before in powdered dry ice. The DSC pan was taken out of the dry ice after 15 min and was kept at room temperature for about 20 min to remove any condensed water vapor on the surface of the DSC pan. Then the DSC pan was placed into the DSC cell and scanned twice from 30 to 220°C to obtain the aged and deaged (baseline) DSC behavior. Between the scans the specimen was quenched as before. A comparison of the two up-temperature scans was made to examine the residual aging effects versus the T_{er} (which varied from 155 to 170°C). The segments in an external oven and in the DSC unit are shown in Figure 3(B).

A relatively high T_a (150°C) and a rapid cooling rate (dry ice quenching) were necessary for the DSC experiments because the effect of isothermal physical aging is so small or difficult to observe at low isothermal aging temperatures and at low rates of cooling. The rapid cooling was achieved by quenching into the dry ice from the external oven (because the cooling rate in the DSC unit equipped with a mechanical cooling system is limited).

In raising the T_a, a temperature gap between the T_a and T_g should be allowed for when heating to the T_{er}. The aging temperatures and time were determined from a series of preliminary DSC experiments. All specimens in the external oven were heated under an atmosphere of dry nitrogen.



(A)



(B)

Figure 3 Temperature–time profiles used for (A) TBA experiments (profiles I and II) and (B) DSC experiments (profile III).

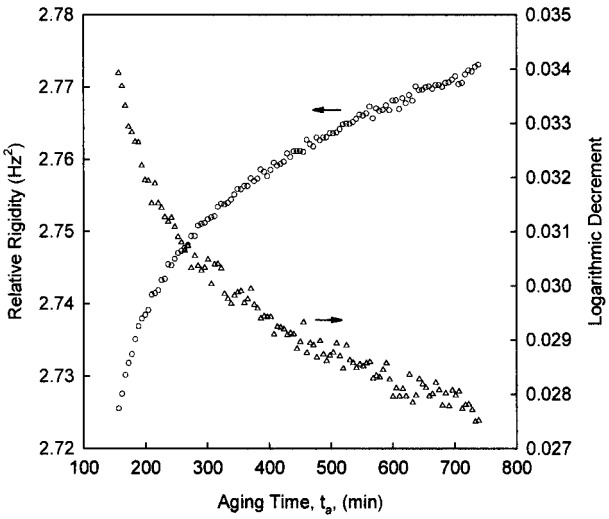


Figure 4 The relative rigidity and logarithmic decrement during isothermal physical aging at 90°C for 600 min.

The heating rate for the DSC up-temperature scans was 10°C/min with a slow dry external nitrogen flow.

RESULTS AND DISCUSSION

TBA Measurements

The relative rigidity and logarithmic decrement versus time during isothermal physical aging at a T_a of 90°C and a t_a of 600 min are shown in Figure 4 (profile I). The relative rigidity increased and the logarithmic decrement decreased during isothermal aging. Isothermal data were obtained every 20 min (after deaging and after an initial period of 20 min to ensure stabilization of the temperature at $T_a = 90 \pm 0.05$°C).

The thermomechanical spectra for the aged (at 90°C for 600 min) and deaged (by heating to 200°C) specimens are shown in Figure 5. The differences in the relative rigidity and log decrement were mainly in the vicinity of the T_a (90°C).

The percentage of difference of the shear modulus between the aged and the deaged specimens ($\%\Delta G'$) at a temperature was calculated from the following equation:

$$\%\Delta G' = \frac{G'_{\text{aged}} - G'_{\text{deaged}}}{G'_{\text{deaged}}} \times 100$$

where G'_{aged} and G'_{deaged} are shear moduli for the aged and the deaged specimens, respectively. The effect of heating to different T_{er} values on the localized perturbation is shown as $\%\Delta G'$ versus temperature in Figure 6. The modulus difference was obtained after aging isothermally at 90°C, heating to various T_{er}'s (90–160°C), and immediately cooling to 0°C [Fig. 3(A), profile I]. The difference data for a T_{er} of 90°C, which corresponded to only isothermal aging, was included for comparison. Note that the perturbation due to the isothermal aging at a T_a of 90°C was localized between 30 and 130°C and the temperature of maximum perturbation (T_{max}) was about 90°C. The intensity of the peak in $\%\Delta G'$ and the T_{max} are influenced by the value of the T_{er} (Fig. 7).

Figure 7 displays the intensity in $\%\Delta G'$ at a T_a of 90°C ($\%\Delta G'_{90}$) and the intensity in $\%\Delta G'$ and T_{max} ($\%\Delta G'_{\text{max}}$) versus the T_{er}. The $\%\Delta G'_{90}$ was slightly decreased by heating to a T_{er} of 100°C but more so by heating to a T_{er} of 130°C, and it becomes almost zero for a T_{er} of 160°C. The $\%\Delta G'_{\text{max}}$ had a trend similar to $\%\Delta G'_{90}$ up to a T_{er} of 130°C, but it increased for T_{er} levels of 150 and 160°C. The increase in the intensity was due to the increase of the aging rate as the T_{er} approached the T_g.[4] The isothermal aging effect at a T_a of 90°C could be almost removed by heating above a T_{er} of 140°C (i.e., $> T_a + 50$°C), but residual aging by the heating process developed in the vicinity of the T_{er}. The T_{max} values for the specimen heated to between a T_{er} of 100 and 140°C

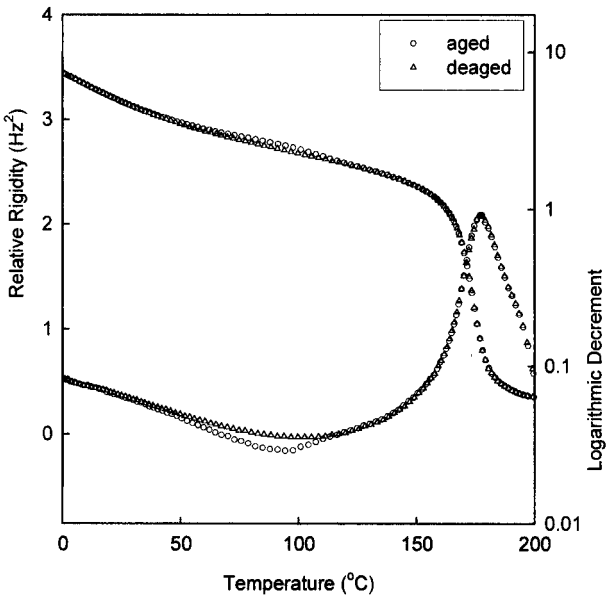


Figure 5 Thermomechanical spectra for aged (at 90°C for 600 min) and deaged (by heating to 200°C) specimens.

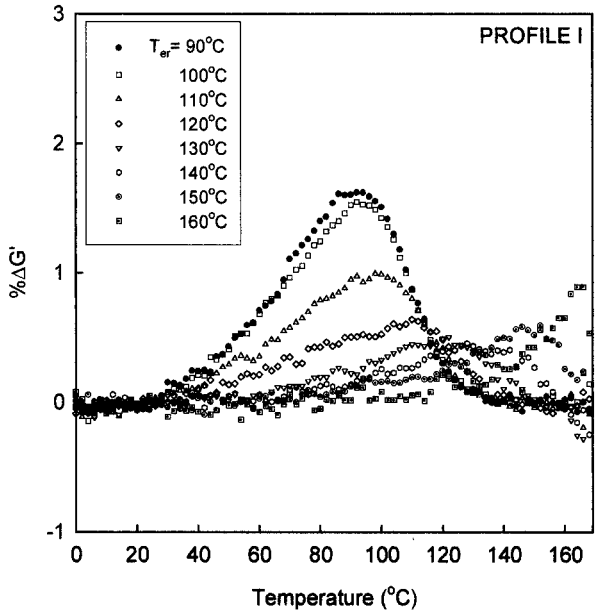


Figure 6 The modulus difference between the aged and deaged specimens (%$\Delta G'$) versus the temperature after aging isothermally at 90°C, heating to erasure temperatures (T_{er}) of 90–160°C, and cooling to 0°C (profile I).

were lower than their respective T_{er}'s, indicating that the effect of isothermal aging at 90°C remained and affected the T_{max}.

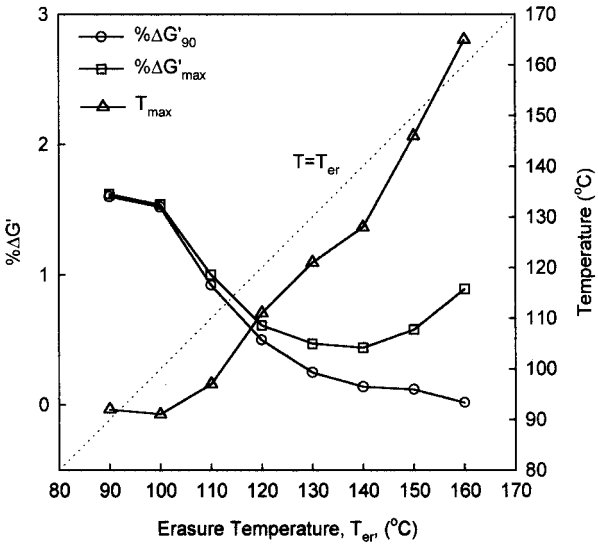


Figure 7 The intensity change (%$\Delta G'$) at an aging temperature of 90°C (%$\Delta G'_{90}$) versus the erasure temperature (T_{er}), and the %$\Delta G'$ at the temperature of maximum perturbation (%$\Delta G'_{max}$) and temperature at maximum perturbation (T_{max}) versus the T_{er}.

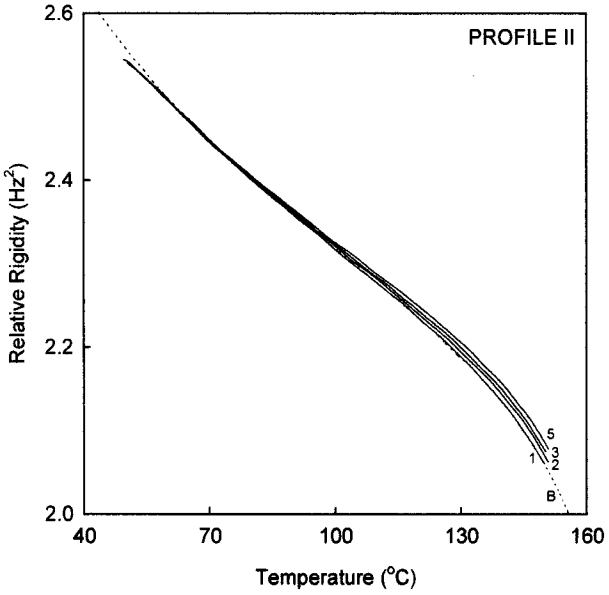


Figure 8 A comparison of the consecutive relative rigidity versus temperature plots (50–150°C) after consecutive thermal cycling between 50 and 150°C (profile II).

It was suggested earlier[3] that when glassy materials are exposed to temperature cycling between a high temperature (T_{on}) and a lower temperature (T_{off}), such as in epoxy-encapsulated electronic devices, changes due to aging at T_{on} accumulate and those at T_{off} are removed at T_{on}. The present study supports this statement. The relative rigidity versus temperature plots after consecutive thermal cycling between 50 and 150°C [Fig. 3(A), profile II] are compared in Figure 8. Note that the numbers (1, 2, 3, and 5) in the figure correspond to the numbers shown in profile II (up-data). For comparison, the up-baseline (dotted curve B) is also shown. The data showed that the residual aging effect was zero at the lower temperatures but continuously increased at the higher temperatures of the cycles. Cycling in the glassy state between low and high temperatures resulted in accumulation of aging effects only at the higher temperatures. At lower temperatures, where all cycling scans were on the same curve, aging and deaging occurred successively during cycling. Therefore, the specific volume of the specimen decreased with time at T_{on} whereas the specific volume consecutively decreased and increased at T_{off}. (All cycling scans on the same curve at lower temperatures were slightly off from the baseline. This may have been due to the baseline having been obtained in the

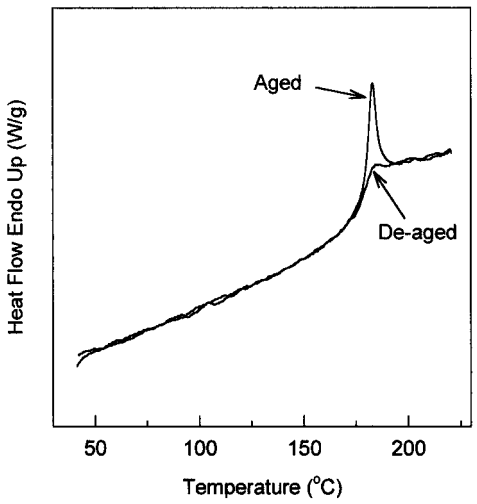


Figure 9 DSC thermograms of aged (at 150°C for 1000 min) and deaged specimens.

up-temperature scan from −50°C rather than from +50°C. Extra aging effects at 50°C could have arisen in the baseline scan during heating from about 0 to +50°C.)

DSC Analysis

Localization of the effect of isothermal physical aging and erasure of the localized aging effect below the T_g were directly shown using TBA. The present DSC results revealed the erasure below the T_g of the isothermal physical aging effect and implied the localization of the aging effect. The DSC technique was used to study the isothermal physical aging of epoxy thermosets.[1,18–20] An effect of physical aging for a specimen isothermally aged near the T_g normally appears in a DSC scan-up as an endothermic peak in the glass-transition region. However, for aging temperatures well below the T_g only a small endothermic peak appeared below the glass transition in subsequent temperature scans.[1,12,20]

Up-temperature DSC scans of aged and deaged specimens are shown in Figure 9. An endothermic peak appeared in the glass-transition region for the aged specimen (T_a = 150°C, t_a = 1000 min), and it was much less apparent after deaging by heating to 220°C for 15 min. A relaxation enthalpy was obtained from the area difference between the aged and deaged specimens of the DSC curves, which was related to the amount of isothermal physical aging. It is known that the endothermic peak intensity and peak temperature (T_p) both increase with aging temperature and time.[18–20]

Up-temperature DSC scans for the specimen isothermally aged at 150°C for 1000 min followed by heating to different T_{er}'s (155, 160, 165, and 170°C) for a t_{er} of 10 min are shown in Figure 10 using profile III, together with that of the aged specimen without the heating (dashed curve). The figure shows that the endothermic peak intensity varied with the T_{er}. The relaxation enthalpy from the area difference between the aged and deaged specimens versus the T_{er} is shown in Figure 11. The relaxation enthalpy value increased slightly upon heating at a T_{er} of 155°C for a t_{er} of 10 min. This may have been due to the additional aging during the heating because the T_{er} was close to the T_a. However, the relaxation enthalpy decreased rapidly as the T_{er} approached the T_g of 179°C. The decrease of the enthalpy value with the increase of the T_{er} implied that the effect of isothermal physical aging was greatly diminished by heating above the T_a but below the T_g. Therefore, the DSC data supported the localization and erasure of the effect of isothermal physical aging by heating to below the T_g.

Comparison of TBA and DSC Results

The important temperatures in the TBA and DSC experiments (T_a, T_{er}, T_{max}, T_p, and T_g) are marked on the horizontal lines in Figure 12. The T_{max} due to the isothermal physical aging was determined from the $\%\Delta G'$ for TBA (Fig. 7) whereas the endothermic peak (Fig. 10) was de-

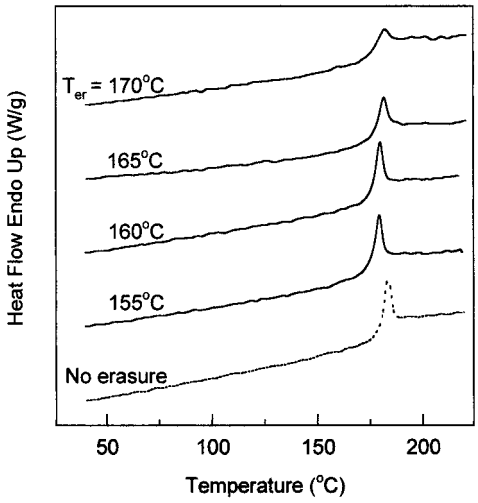


Figure 10 DSC thermograms of aged specimens after heating to different erasure temperatures (T_{er} = 155, 160, 165, and 170°C) and of an aged specimen without erasure.

termined from the DSC (designated T_p): note that the two maxima arose for different reasons. As shown in this comparison, the T_{max} from the TBA was located near the T_a whereas the T_p from the DSC was near the T_g (~30°C above T_a). Note that the T_{er} for the TBA was above the T_{max} but that for the DSC was below the T_p. In the DSC the peak intensity at the T_p became less when heating to the T_{er}, although the T_{er} was lower than the T_p. This indicated that aging did occur in the vicinity of the T_a in the DSC as in the TBA experiments, but the effect due to aging was revealed at a higher temperature as an endothermic peak in a DSC thermogram.

CONCLUSIONS

Isothermal physical aging occurred mainly in the vicinity of the T_a, and the effect of the physical aging on the modulus was localized in a limited temperature range in the vicinity of the T_a. The localized effect could be eliminated by heating above the T_a. In this study, a fully cured epoxy/amine specimen was isothermally aged below the T_g, and the erasure below the T_g of the effect of isothermal physical aging was investigated through TBA and DSC experiments. The erasure from the TBA experiments was examined by the decrease of the intensity of localized perturbation at the T_a by heating above the T_a but below the T_g. The TBA results showed that the isothermal aging effect in the vicinity of the T_a was almost completely erased by heating to 50°C above the T_a, but new aging developed during the heating process. The relaxation enthalpy obtained from the aged and deaged specimens using DSC confirmed the erasure of the isothermal physical aging effect by heating above the T_a but below the T_g. There is always competition between aging and deaging in the glassy state with a change of temperature and time.

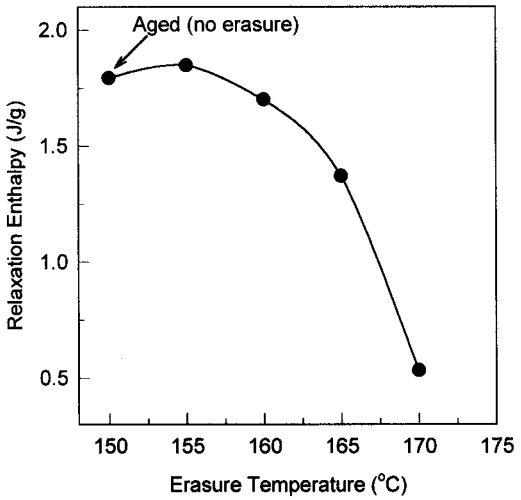


Figure 11 Relaxation enthalpy for all erasure temperatures obtained from the difference in areas between the aged and deaged DSC thermograms.

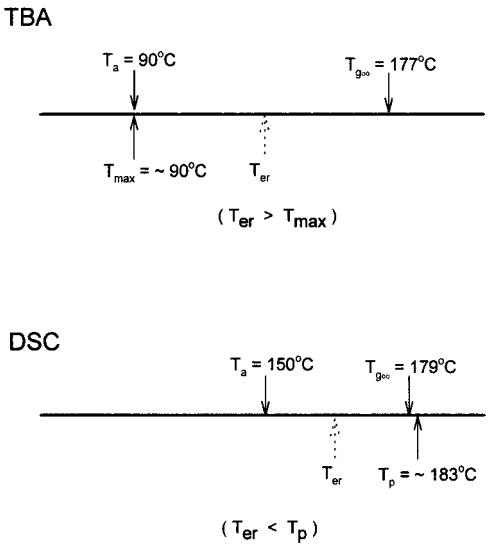


Figure 12 A comparison of the temperatures of aging (T_a), erasure (T_{er}), maximum perturbation (T_{max}), peak (T_p), and glass transition (T_g) from the TBA and DSC.

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