

Physical Aging Deep in the Glassy State of a Fully Cured Polyimide

R. A. VENDITTI and J. K. GILLHAM*

Polymer Materials Program, Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08544

SYNOPSIS

Physical aging of a fully cured polyimide/glass fiber specimen has been investigated deep in the glassy state using a freely oscillating torsion pendulum (TBA). A single specimen, the physical aging effects of which could be erased by heating to above $T_g = 304^\circ\text{C}$ (0.8 Hz), could be used for all experiments. Data were obtained during isothermal aging at different aging temperatures, T_a , (from 10°C to T_g) and during subsequent temperature scans (T_a to 5 to 315°C). The aging rate depended upon the value of T_a relative to both T_g and the β -relaxation temperature, $T_\beta = 139^\circ\text{C}$ (1.3 Hz). Changes in thermomechanical behavior due to aging were localized about T_a . This suggests that only an intermediate portion of the relaxation spectrum participates in, and is affected by, isothermal physical aging. It follows, and is observed, that the intensity of the β -relaxation mechanical loss peak is perturbed most significantly by aging at T_a near T_β . The effect of isothermal aging deep in the glassy state could be essentially eliminated by heating to below T_g . © 1992 John Wiley & Sons, Inc.

INTRODUCTION

All glassy materials, well below their glass transition temperature, T_g , contain thermodynamic excesses of volume and enthalpy.¹ Glasses spontaneously densify in a slow approach toward equilibrium, a process termed physical aging. The physical aging process is self-retarding and, at temperatures well below T_g , does not result in the glass arriving at its equilibrium state in finite time. Physical aging at temperatures just below T_g lengthens the viscoelastic relaxation times and increases the experimentally observed T_g .²⁻⁵ All properties that depend upon the specific volume (or free volume) are altered during physical aging (e.g., mechanical, dielectric, diffusive) and thus physical aging is of practical importance to the engineering properties of glasses.

Most amorphous polymers have at least one secondary mechanical relaxation (transition) below T_g . Secondary relaxation mechanisms correspond to localized motions, including oscillations of a side group, torsional vibrations in the main chain, or

motions that involve a low-molecular-weight impurity (e.g., water).⁶ It is of interest to understand if physical aging has an effect on the secondary transitions, in particular, the β -transition, typically defined as the transition of highest temperature below T_g . To date, there seems to be no consensus among researchers pertaining to the effects, if any, that physical aging has on the β -transition. Some investigations report significant changes in the β -relaxation with physical aging,⁷⁻¹⁰ whereas others report negligible or no changes¹¹⁻¹⁴ and still others report different results for different polymers.^{15,16}

The main finding of this article is that changes in thermomechanical behavior due to isothermal physical aging deep in the glassy state of an amorphous semiladder polyimide are localized to the vicinity of the isothermal aging temperature, T_a . This behavior has also been reported for a fully cured network epoxy¹⁰ and a linear poly(methyl methacrylate).¹⁷ These findings aid in understanding the seemingly contradictory results in the literature concerning the effects of physical aging on the β -relaxation.⁷⁻¹⁶

It will also be demonstrated in this article that the effects of physical aging deep in the glassy state can be removed by heating to well below T_g .

* To whom correspondence should be addressed.

The article describes an investigation of the effects of physical aging performed isothermally at different aging temperatures between 10°C and T_g of a fully cured, glassy polyimide ($T_g = 304^\circ\text{C}$ at 0.8 Hz, $T_\beta = 139^\circ\text{C}$ at 1.3 Hz) using a freely oscillating torsional braid pendulum technique (TBA). Changes in modulus and mechanical loss were obtained during isothermal aging. Isothermal aging experiments were succeeded by measurements during temperature scans to determine the effect of isothermal aging on the thermomechanical behavior. A preliminary report has been published.¹⁸

EXPERIMENTAL

Materials

The polyamic acid solution, tradename Pyralin Polyimide Coating PI-2555, was obtained from Dupont and used as received.¹⁹ The cured polyimide has been shown using TBA dynamic mechanical measurements to correspond to a polyimide synthesized from benzophenone tetracarboxylic acid dianhydride (BTDA) and flexible aromatic diamine.²⁰ The aromatic diamines incorporated in this polymer are oxy-dianiline (ODA) and meta-phenylene-dianiline (MPDA). The structure and overall reaction of the BTDA-ODA type polyamic acid are shown in Figure 1. *N*-Methyl pyrrolidone (bp = 202°C) is the principal solvent in PI-2555; the percent solids is 18.2% and the viscosity is 14.5 poise at 25°C.¹⁹ The polyamic acid reacts in an intramolecular fashion upon thermal cure to form a polyimide and liberate water. Solvent is also eliminated during cure. A fully cured specimen was used for the aging studies (see later).

Aging Procedure

The TBA technique was used to measure the relative rigidity (proportional to the shear modulus) and logarithmic decrement (proportional to tan delta) of a polyimide/multifilamented glass braid composite specimen during isothermal aging and during temperature scans. The specimen is mounted in a torsional pendulum that is free to oscillate at the lower end. The pendulum is intermittently set into motion and each of the resulting damped waves generated is analyzed to determine the frequency of oscillation and the decay constant, which are used to calculate the relative rigidity (equal to the square of the frequency of oscillation) and the logarithmic

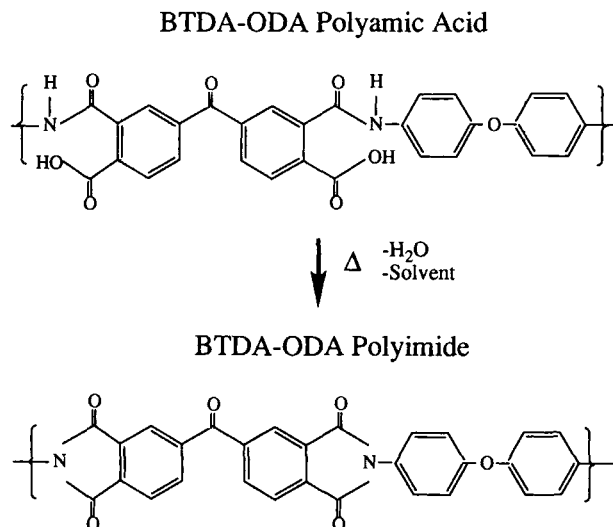


Figure 1 Thermal cure of BTDA-ODA polyamic acid to polyimide.

decrement, respectively. The frequency of oscillation in the experiment ranged between 0.6–1.4 Hz with a resolution of 0.0001 Hz below T_g . All experiments were performed under a slow, steady, dry helium purge. A review of the TBA technique has been published.²¹ The automated TBA torsion pendulum is manufactured by Plastics Analysis Instruments, Inc.

The TBA technique is especially convenient for experiments in which the specimen traverses T_g . This is due to the dimensional stability of the specimen, which is provided by the supporting substrate. The thermoreversible nature of physical aging allowed one specimen (except where noted) to be used for all the physical aging experiments; the effect of sub- T_g thermal histories of the polymer could be eliminated by heating to above T_g .

The time-temperature sequence of the isothermal aging experiments was as follows (Fig. 2):

1. A glass braid impregnated with the polyamic acid solution was cured at 325°C (i.e., $>T_g = 304^\circ\text{C}$) for 3 h.
2. The specimen was then cooled to 5°C at 1°C/min and heated to 315°C at 1°C/min during which TBA data were taken. This provided the thermomechanical spectra (relative rigidity and logarithmic decrement) for the specimen before the first isothermal aging experiment.
3. The specimen was then cooled from 315°C at 1°C/min to an aging temperature, T_a .
4. The specimen was held isothermally ($T_a \pm 0.15^\circ\text{C}$) for an aging time, $t_a = 74$ h. TBA

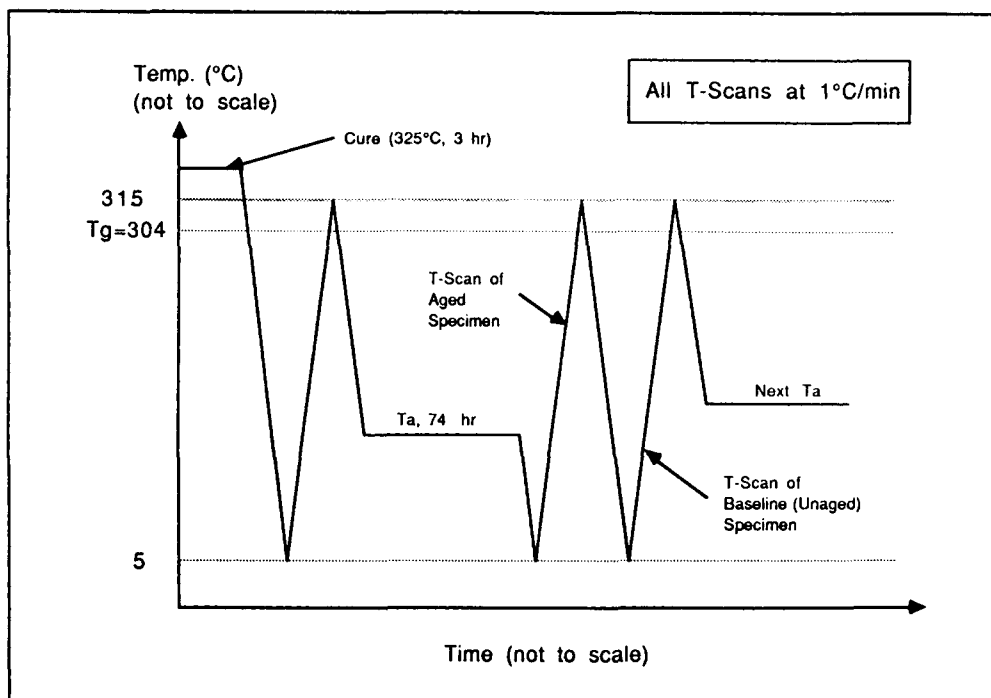


Figure 2 Time-temperature sequence of the cure and physical aging experiments (see text).

- data were obtained on a logarithmic time scale during isothermal aging (see later).
- The specimen was then cooled to 5°C at 1°C/min and heated to 315°C at 1°C/min. TBA data obtained upon heating provided the thermomechanical spectra of the aged specimen.
 - The specimen was again cooled to 5°C at 1°C/min and heated to 315°C at 1°C/min. TBA data obtained upon heating provided the thermomechanical spectra of the unaged specimen, which were compared with the behavior of the aged specimen (obtained in step 5).
 - Steps 3–6 (the aging cycle) were repeated for various values of T_a .

Comparison of the results of TBA measurements of the unaged specimen in step 6 over many cycles was used to detect changes in the unaged thermomechanical behavior of the specimen.

RESULTS AND DISCUSSION

Fully Cured Specimen

Obtaining full cure of a linear condensation-type polyamic acid is a nontrivial matter.²⁰ To achieve

full conversion, the polymer must be cured at a temperature close to its fully reacted T_g , designated $T_{g\infty}$. This is necessary to avoid the retardation of reaction due to vitrification ($T_g = T_{\text{cure}}$) during cure that immobilizes reactive groups (at $T_{\text{cure}} < T_{g\infty}$). However, even at higher curing temperatures a measurable fraction of the polyamic acid fails to imidize.²² Also, at temperatures near $T_{g\infty}$, typically between 250–700°C for linear polyimides, there is a competition between cure (which increases T_g) and thermal degradation (which decreases T_g).^{20,23,24} This presents a problem in determining a thermal cure schedule to obtain the pure polyimide.

The cure schedule used in this report (3 h at 325°C) was based upon previous research in this group on the same material in which it was shown that the time to isothermally vitrify increased with increasing T_{cure} in the temperature range from 290–305°C.²⁴ This phenomenon can be seen as the upper portion of the S-shaped vitrification curve in a time-temperature-transformation (TTT) isothermal cure diagram of the polyimide.²⁴ The time to vitrify increases with T_{cure} near $T_{g\infty}$ due to the decreasing concentration of reactive groups present at vitrification.

The TBA thermomechanical spectra of a fully cured specimen are shown in Figure 3. (A different specimen was used for these measurements than for

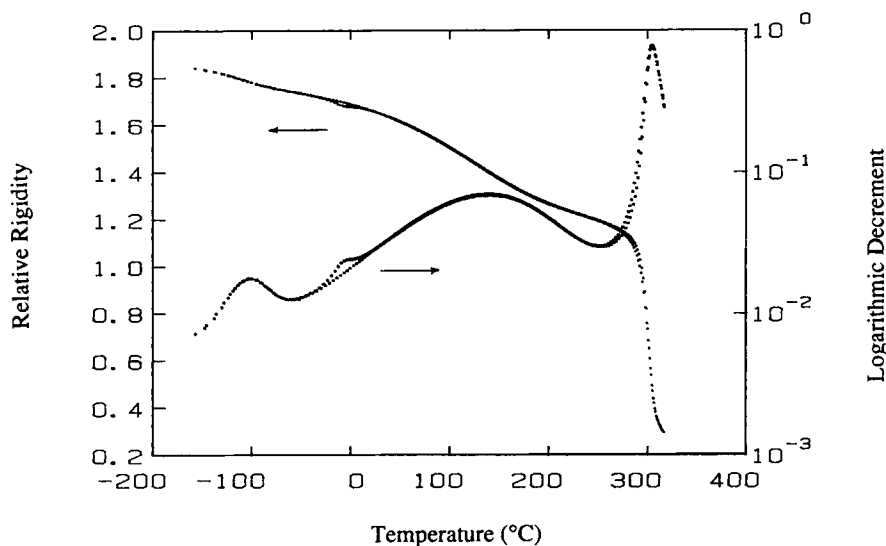


Figure 3 Thermomechanical TBA behavior of fully cured PI-2555 during cooling (315 to -170°C) at $1^{\circ}\text{C}/\text{min}$ and heating (-170 to 315°C) at $1^{\circ}\text{C}/\text{min}$. The principal transition temperatures are $T_g = 304^{\circ}\text{C}$ and $T_{\beta} = 139^{\circ}\text{C}$. The relaxation loss peak at $T_{\text{H}_2\text{O}} \approx -100^{\circ}\text{C}$ is due to small amounts of absorbed water. Transient water gives rise to hysteresis in the vicinity of 0°C ; the hysteresis is observed only on heating after cooling to low temperatures (see later text).

the aging experiments.) The T_g at 304°C , defined by the maximum in the logarithmic decrement, is accompanied by a large change in relative rigidity. T_{β} , defined by the maximum in logarithmic decrement of the relaxation of highest temperature below T_g , resides at $T_{\beta} = 139^{\circ}\text{C}$. The value of $T_{\beta}/T_g = 0.71$ (K) is typical for BTDA-based polyimides.²⁰ The relaxations at approximately 0 and -100°C are associated with small amounts of water (see later).

The temperature difference $T_g - T_{\beta} = 165^{\circ}\text{C}$ (Fig. 3) may be exploited to separate aging effects on the glass- and β -relaxation mechanisms. Similarly, $T_{\beta} - 25 = 114^{\circ}\text{C}$ provides a convenient temperature range for sub- T_{β} aging studies. Sub- T_{β} temperatures are common temperatures of use for polyimides. The effects of physical aging at temperatures below T_{β} are thus of practical importance for polyimides.

Isothermal Aging Behavior

Relative rigidity and logarithmic decrement data at different aging temperatures vs. log aging time are shown in Figures 4 and 5, respectively. Note that the scale in Figure 4 for the relative rigidity has been expanded 36 times that in Figure 3. The changes during isothermal aging are small compared

to those due to temperature changes. Disregarding the first 30 min of data (due to a systematic temperature overshoot originating from cooling at $1^{\circ}\text{C}/\text{min}$ to T_a), the relative rigidity increases and the logarithmic decrement decreases with log aging time. These changes in specimen behavior are considered to be a result of isothermal physical aging. Bulk volume contraction,²⁵ as well as the magnitude of endothermic enthalpy peaks,³ and shifts of creep relaxation curves to longer times²⁶ have been shown to be linearly proportional to log aging time. When the isothermal aging data in Figures 4 and 5 are presented at a lower magnification, the data appear to be linear with log aging time.²⁷

The rate of isothermal aging vs. T_a is shown in Figure 6. The slopes of the best-fit lines through the relative rigidity and the logarithmic decrement data vs. log aging time (after 100 min) were used as measures of the aging rate. (No attempt was made to compensate for the dependence of the initial density on T_a .) The results show that over a wide span of temperatures (between about 125 and 200°C) the rate of aging, as measured, is independent of temperature. This has previously been reported for a fully cured epoxy network¹⁰ and for several other amorphous polymers.²⁶ Also, note the measurable isothermal changes due to aging at temperatures well

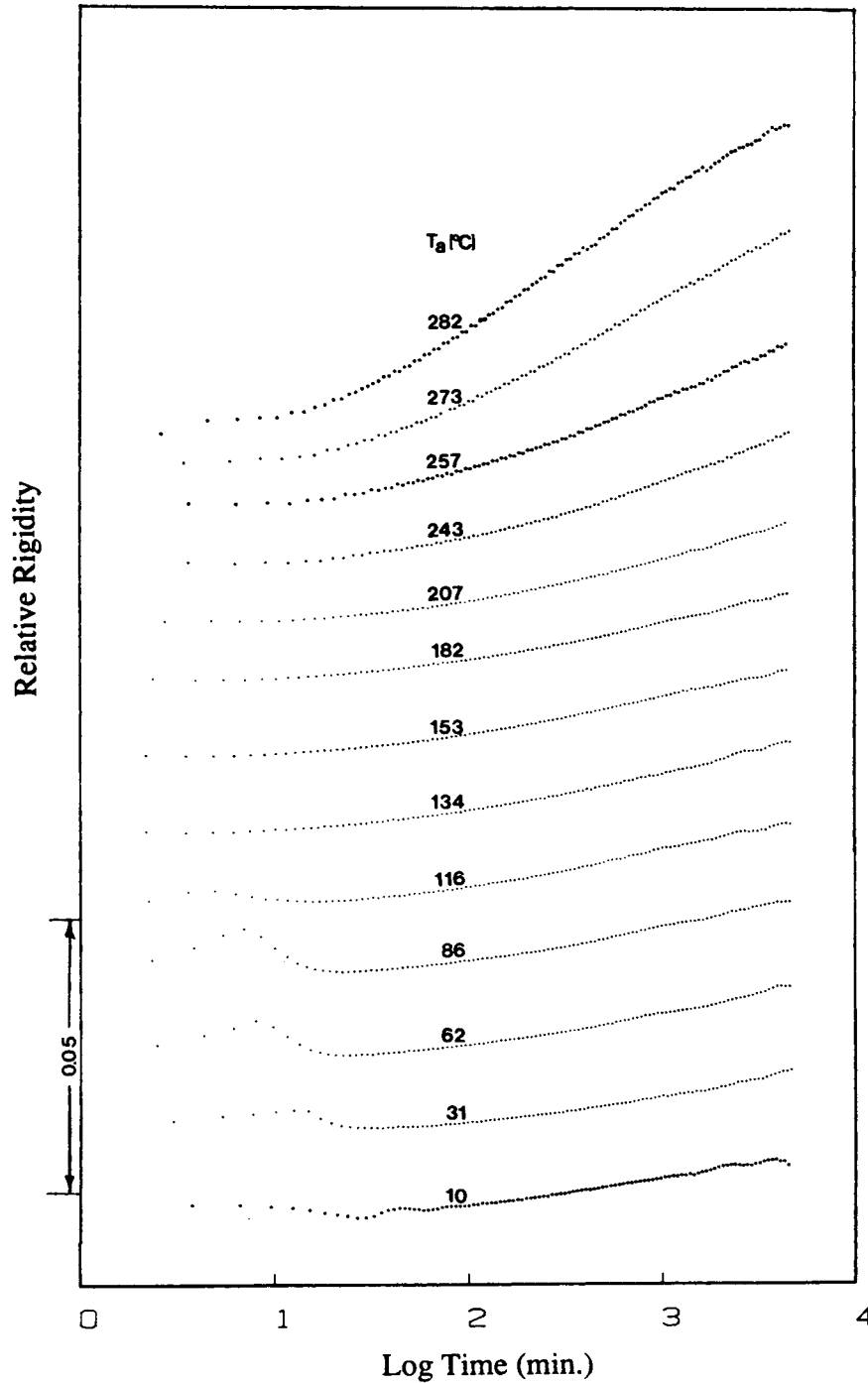


Figure 4 Relative rigidity vs. log aging time for different aging temperatures, T_a . Note the expanded scale vs. Figure 3. The corresponding logarithmic decrement data are shown in Figure 5.

below the designated T_β . To demonstrate the repeatability of the isothermal aging experiment, isothermal aging at 61°C was performed twice (the

second and eleventh aging cycles); the calculated aging rate is the same within experimental scatter for the two $T_a = 61^\circ\text{C}$ cycles (Fig. 6).

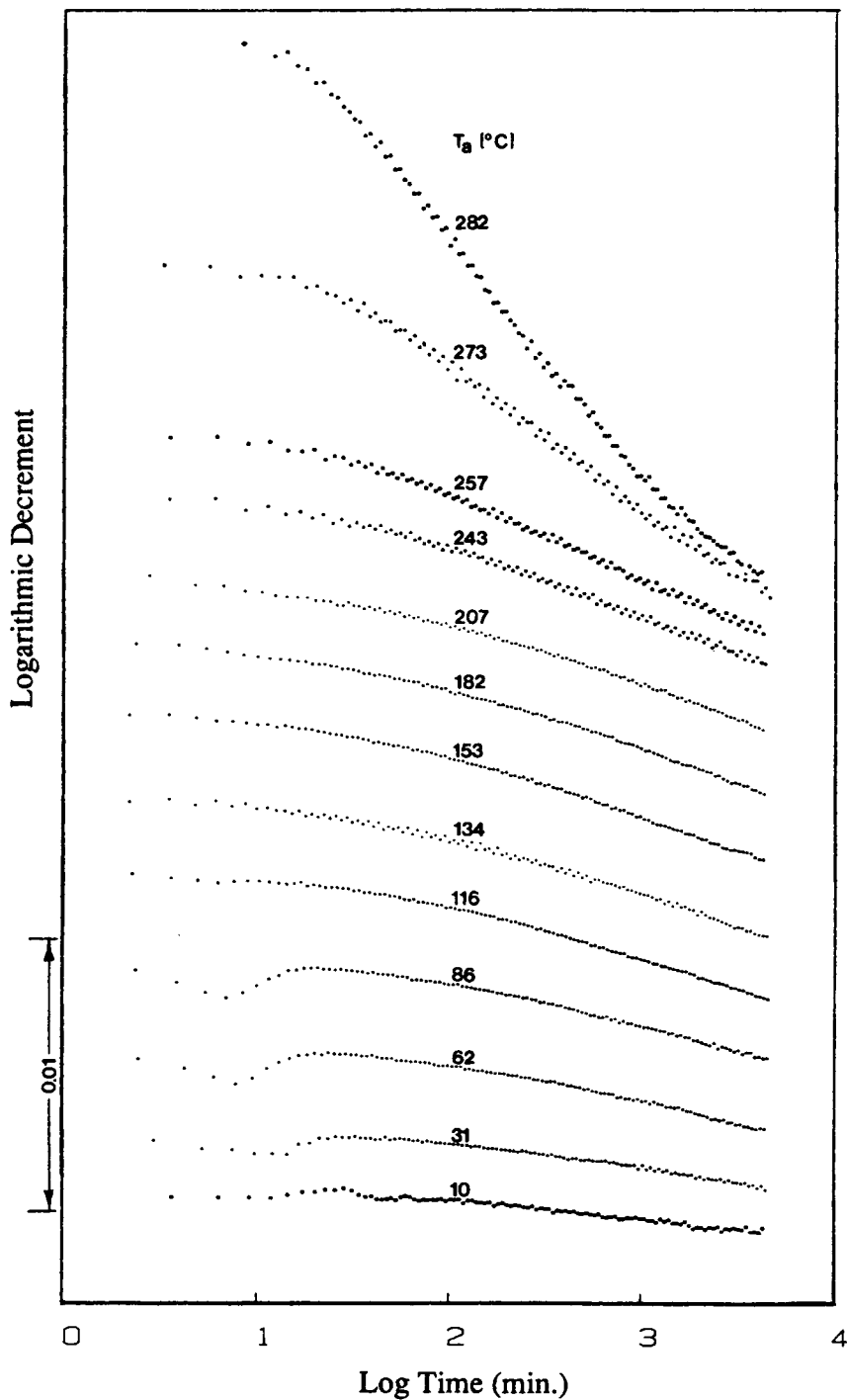


Figure 5 Logarithmic decrement vs. log aging time for different aging temperatures, T_a . The y-axis has a linear scale. The corresponding relative rigidity data are shown in Figure 4.

Note the decrease in aging rate with decreasing T_a for $T_a < T_\beta$ (Fig. 6). This decrease in aging rate below T_β should be compared with the much larger

decrease in aging rate with decreasing T_a below T_g . These decreases are in proportion to the intensity of their neighboring higher-temperature relaxations

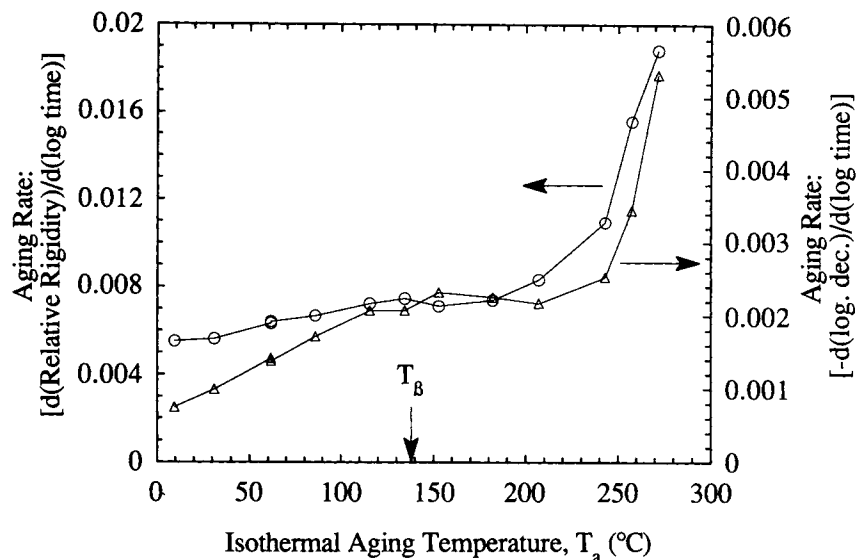


Figure 6 Aging rate, calculated from the slope of the best-fit line of the relative rigidity, and the logarithmic decrement vs. log (aging time) data (after 100 min) vs. T_a . The aging cycle for 61°C was performed twice (the second and eleventh aging cycles) to confirm that the aging properties of the specimen had not changed as a consequence of the aging cycles.

(transitions). This is offered as evidence that the difference $T_\beta - T_a$, not $T_g - T_a$, is the principal parameter affecting the aging rate for $T_a < T_\beta$. This suggests that the β -relaxation mechanisms play an integral role in the aging process at temperatures below T_β whereas the glass transition mechanisms dominate the aging process between T_β and T_g .

Thermomechanical Behavior vs. Aging Temperature

Using the experimental procedure defined in the experimental section, the effect of isothermal aging at different values of T_a on the thermomechanical behavior of the aged polyimide could be ascertained relative to the unaged specimen. The TBA behavior vs. temperature of the specimen aged at 134°C and also of the unaged specimen are shown in Figure 7. The principal differences are an increase in relative rigidity and a decrease in logarithmic decrement for the aged specimen in a temperature range about $T_a = 134^\circ\text{C}$. Similar results for a fully cured network epoxy system^{10,14} and linear poly(methyl methacrylate)¹⁷ have been reported.

Figures 8–11 are calculated from data such as those presented in Figure 7. The percent change of

the shear modulus of the aged vs. the unaged specimen

$$\%G' = 100[G'(a) - G'(u)]/G'(u)$$

where a and u designate the aged and unaged states, respectively, is plotted vs. temperature for different values of T_a . The changes in behavior are localized about T_a . It is noted that the peaks in $\%G'$ are slightly above T_a , are asymmetric, and decrease in magnitude with decreasing T_a . The results of two separate aging experiments at $T_a = 61^\circ\text{C}$ are essentially the same (Fig. 10), demonstrating the repeatability of the experiment.

The intermittent mechanical deformations imposed by the TBA experiments during isothermal physical aging do not affect the postaging results (Fig. 11). The thermomechanical perturbations due to isothermal aging at 140°C are shown to be quantitatively the same for aging when no measurements were performed, measurements were performed on a linear time scale (at 10-min intervals), and measurements were performed on a logarithmic time scale during isothermal aging.

The perturbations in thermomechanical behavior, measured at approximately 1 Hz, that are localized about T_a can be accounted for as follows. There is

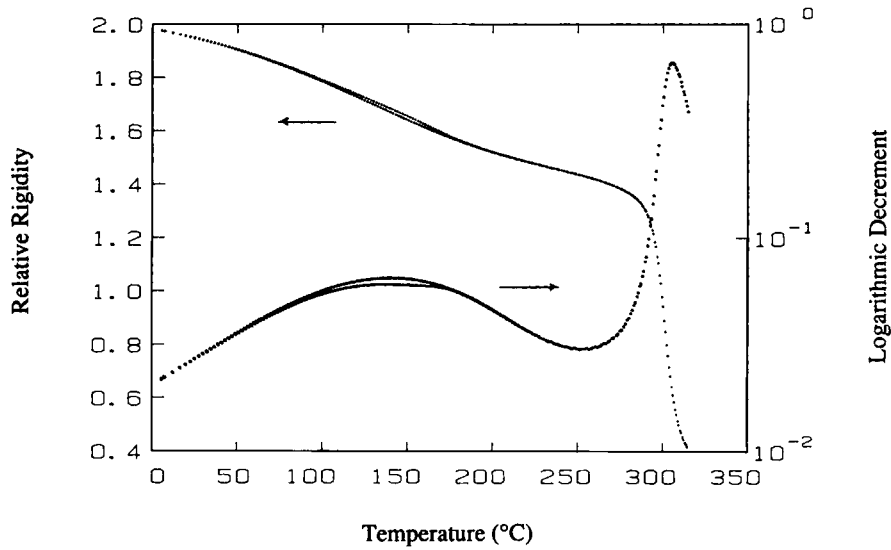


Figure 7 Relative rigidity and logarithmic decrement vs. temperature (5 to 315°C at 1°C/min.) of aged ($T_a = 134^\circ\text{C}$) and unaged specimen. The thermomechanical behavior of the specimen aged at T_a differs from that of the baseline specimen mainly in the vicinity of T_a . This is shown as an increase in relative rigidity and a decrease in logarithmic decrement of the aged specimen. The relative rigidity and the logarithmic decrement are on linear and logarithmic scales, respectively.

a spectrum of relaxation elements. Each relaxation mechanism can be associated with a certain length scale and temperature-dependent relaxation time. At a given T_a , each relaxation element can be cat-

egorized into one of the following three groups: (1) elements with relatively long length scales that are essentially “frozen” in place by their restrictive environment and do not participate in the aging pro-

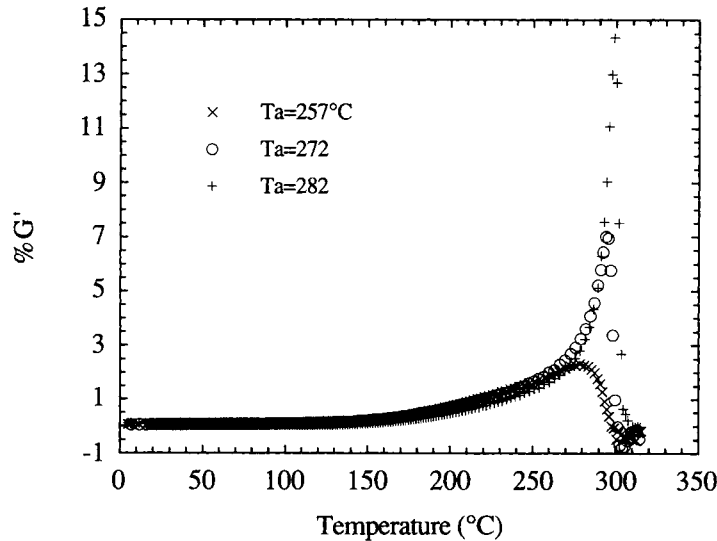


Figure 8 $\%G'$ vs. temperature for specimens aged at different isothermal aging temperatures, T_a . Note that the scales are different in Figures 8–11.

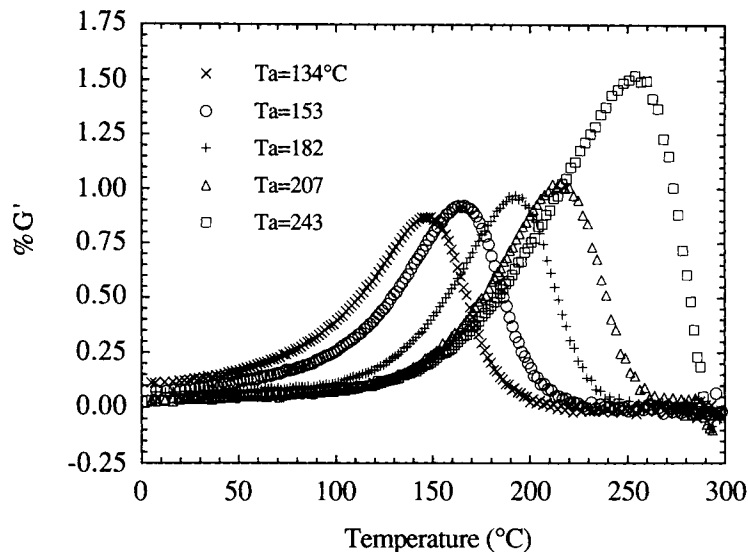


Figure 9 %G' vs. temperature for specimens aged at different isothermal aging temperatures, T_a . Note that the scales are different in Figures 8–11.

cess, (2) elements of intermediate length scale that are hindered by their environment at T_a but can still move (these take part in aging), and (3) elements of very small length scale that are able to move freely and are in a state of local equilibrium within their local environment. Elements in group 2 rearrange

during aging in the attempt to achieve an equilibrium state, and thus become hindered from motion themselves, whereas elements in groups 1 and 3 remain largely unchanged; this is the aging process.

Why the aging perturbations in thermomechanical behavior are not apparent above a certain tem-

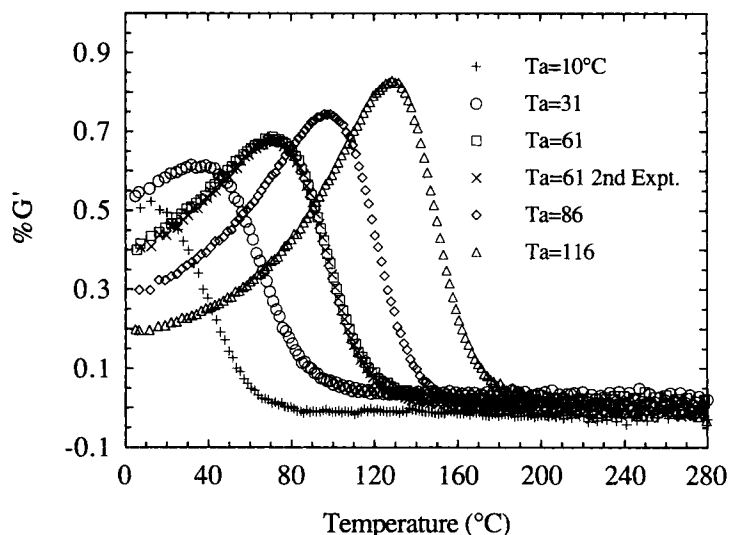


Figure 10 %G' vs. temperature for specimens aged at different isothermal aging temperatures, T_a . Note that the scales are different in Figures 8–11. The aging cycle for 61°C was performed twice (the second and eleventh aging cycles) to confirm that the aging properties of the specimen had not changed as a consequence of the aging cycles.

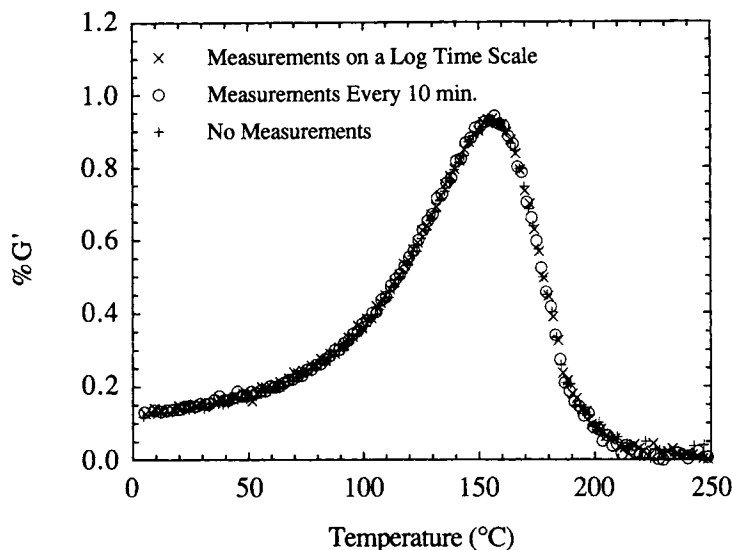


Figure 11 % G' vs. temperature for specimens aged at 140°C with TBA measurements obtained at different time intervals during isothermal aging. Note that the scales are different in Figures 8–11. The intermittent TBA measurements obtained during isothermal physical aging do not alter the subsequent thermomechanical behavior.

perature, termed the erasure temperature, T_{er} , above T_a , well within the glassy state, can be rationalized as follows. After aging, as the temperature is increased the specimen acquires thermal energy and expands, allowing submolecular motions that were frozen during aging (group 2 at T_a) to be released, thus returning the relative rigidity and the logarithmic decrement values of the aged specimen to those of the baseline specimen. Where the relative rigidity or logarithmic decrement curve has completely returned to the baseline curve, at T_{er} , the observed effect of physical aging has been eliminated, i.e., those group 2 relaxations (at T_a) have experienced a pseudo “glass transition temperature” above T_a for the defined experimental conditions. The motions that are initially group 2 at T_a are initially group 3 at T_{er} .

The values of T_{er} vs. T_a are plotted in Figure 12. Similar to the glass transition temperature, it is expected that T_{er} would increase with increasing heating rates, all other variables (T_a , t_a , prior cooling rate) being constant. For this reason, aging studies using relatively higher heating rates (in the order of 20°C/min), such as those used in differential scanning calorimetry (DSC), would be expected to show a higher T_{er} than those reported here. It follows that if the isothermally induced perturbations shown in the relative rigidity and the logarithmic decrement

correspond to a relative change in the volume of the aged specimen vs. the baseline specimen a weak endothermic relaxation peak should be observed by DSC at 20°C/min in the temperature range above T_{er} when comparing an aged and a baseline specimen. Sub- T_g endothermic peaks have been reported for specimens isothermally aged well below T_g .^{28–30}

The process of long-term isothermal physical aging at temperature $T_a < T_g$ leads to a freezing of certain motions (i.e., group 2, the length scale of which increases with T_a) that are only fully freed by subsequent heating to a higher temperature, T_{er} (Fig. 12). Similarly, the long-term chemical reaction of a (thermosetting) system at temperature, T_{cure} , leads through vitrification ($T_g = T_{cure}$) to a retardation of chemical reactions that are only fully unrestricted by subsequent heating to above the current glass transition temperature.²⁴ The length scale of motions involved in chemical vitrification correspond to those of the glass transition, which depends upon the temperature (of reaction). Similarly, again, the melting point, T_m , of a polymer crystallized isothermally at T_{cryst} ($< T_m$) is above and related to T_{cryst} .³¹ All three examples involve a progressively retarding molecular diffusion mechanism in which a length scale that depends upon temperature is progressively, physically immobilized.

The erasure of aging effects by heating to below

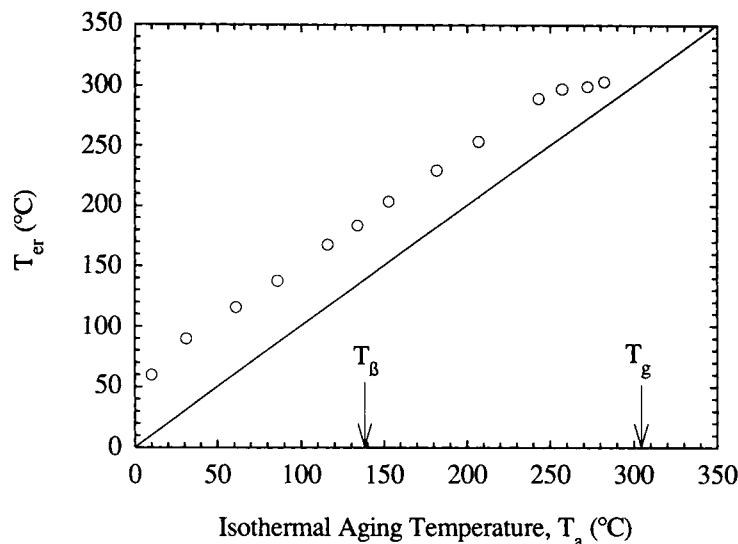


Figure 12 Temperature (T_{er}) necessary to heat the specimen at $1^{\circ}\text{C}/\text{min}$ to remove the effects of aging at T_a .

T_g may have important implications for glassy materials exposed to temperature cycling such as those used in encapsulated electronic devices that are at a higher temperature in the "on" than the "off" state, T_{on} and T_{off} , respectively. Glasses under these conditions may only accumulate modulus changes due to aging at T_{on} , the effects of aging at T_{off} being removed at T_{on} .

Consideration is given for $\%G'$ approaching zero at temperatures below T_a . Although different thermal histories may result in the same modulus at temperatures below T_a , i.e., $\%G' = 0$, the states differ since upon heating different thermomechanical behavior is displayed. The different states with the same modulus below T_a resulting from different thermal histories suggest that the motions that are responsible for aging at T_a are not involved in measuring the modulus at lower temperatures (where the 1-s modulus is unchanged before and after aging). That is, only an intermediate portion of the relaxation spectrum is involved in isothermal aging, the portion changing with T_a .

Effect of Aging on the β -Relaxation

The effects of aging are present and well outside measurement error at temperatures 100°C below T_{β} (Figs. 4, 5, and 10). As already noted, a decrease in the aging rate begins as T_a is decreased through T_{β}

(Fig. 6), suggesting that the β -relaxations play an integral part in the aging process below T_{β} .

The logarithmic decrement vs. temperature in the vicinity of T_{β} of aged and unaged specimen is shown for different values of T_a in Figure 13. The following observation is made: changes in the intensity of the β -transition peak are largest when T_a is near T_{β} . This is equivalent to stating that, by aging at a temperature near T_{β} , the relaxations associated with the β -relaxation are then members of the group 2 relaxation elements.

Aging at T_a slightly above T_{β} decreases the temperature location of the local maximum in logarithmic decrement used in defining T_{β} , whereas the converse is true for aging at T_a slightly less than T_{β} . For T_a much greater than T_{β} , as suggested in the literature,¹¹ the effect of aging on the low-temperature tail of the glass transition peak may persist down to temperatures as low as T_{β} . The observation that only by aging near T_{β} is the β -transition significantly affected clarifies some results in the literature. For example, in one report pertaining to the effect of physical aging on the shape and intensity of the β -transition for chlorinated poly(vinyl chloride)¹¹ aging was mainly performed at temperatures above T_{β} and for this reason would not have produced significant changes in the β -transition peak. Another investigation on the aging of chlorinated poly(vinyl chloride), where aging was performed in the T_{β} range, reported dramatic changes

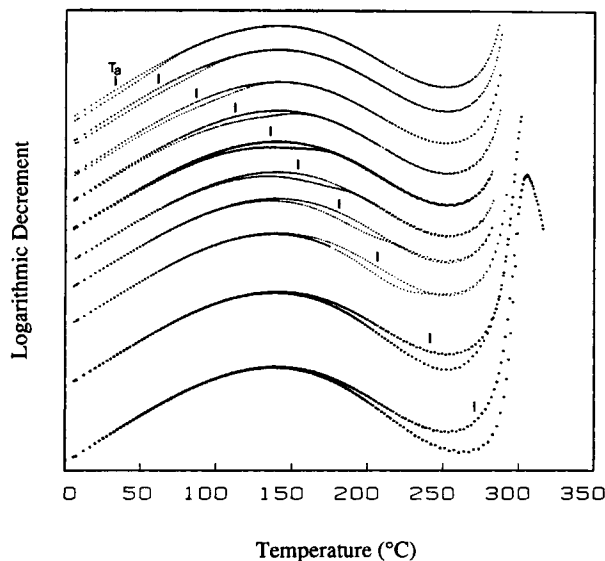


Figure 13 Logarithmic decrement vs. temperature of aged and unaged specimen for different T_a . Values of T_a are (from top to bottom): 31, 62, 86, 116, 134, 153, 182, 207, 243, and 273°C. The logarithmic decrement data on a logarithmic scale have been arbitrarily shifted vertically for clarity. The aged specimen displays a decrease in logarithmic decrement in the vicinity of T_a ; otherwise, the data of the aged and unaged specimen coincide.

in the β -transition in both intensity and temperature location.⁸

Memory Effects Below T_g and Below T_β

To further probe the phenomenon of erasing the aging effects at temperatures below T_g , and correspondingly below T_β , the following experiments were performed on a different, fully cured specimen (see Figs. 14 and 15). For Figure 14, a fully-cured polyimide specimen was first cooled at 1°C/min from above T_g (304°C) to a temperature T_{a1} (284°C) and aged for 1 day, and then heated (3°C/min) to a higher aging temperature, T_{a2} (294°C). The data in Figure 14 were taken at T_{a2} after attainment of thermal equilibrium, approximately 15 min. The relative rigidity of the specimen first decreases at T_{a2} and then increases. Correspondingly, the logarithmic decrement at T_{a2} first increases and then decreases. The initial decrease of the relative rigidity at T_{a2} is assumed to be a consequence of the removal of the effect of aging at T_{a1} (the unfreezing of relaxation mechanisms frozen at T_{a1}). Increases in the relative rigidity at longer times are due to isothermal physical aging at T_{a2} .

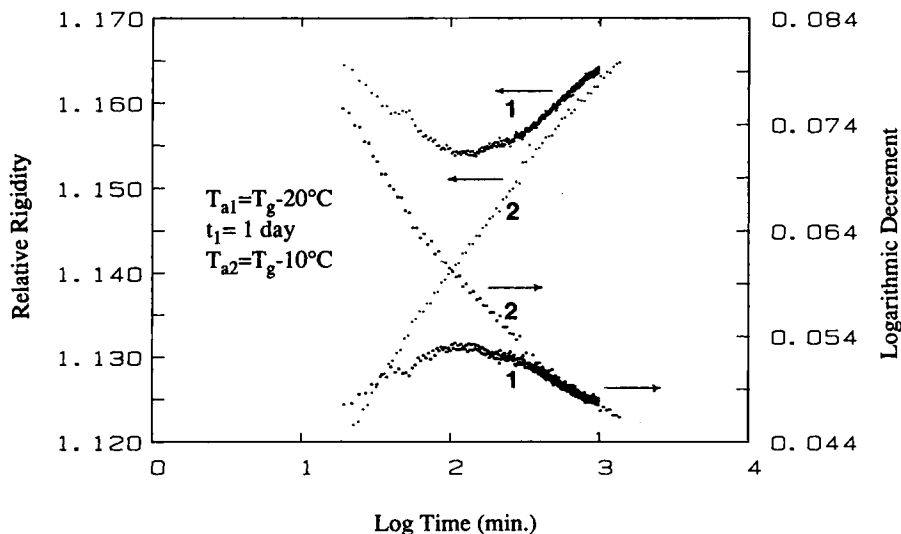


Figure 14 Isothermal memory effect in the temperature range between T_g and T_β . Isothermal behavior (relative rigidity and logarithmic decrement) at T_{a2} are shown for two different thermal histories: (1) after cooling from above T_g to T_{a1} at 1°C/min, aging at temperature T_{a1} for 1 day, and then heating to T_{a2} at 3°C/min; and (2) after directly cooling from above T_g to T_{a2} at 1°C/min (see text). Note that the scales are different for Figures 14 and 15.

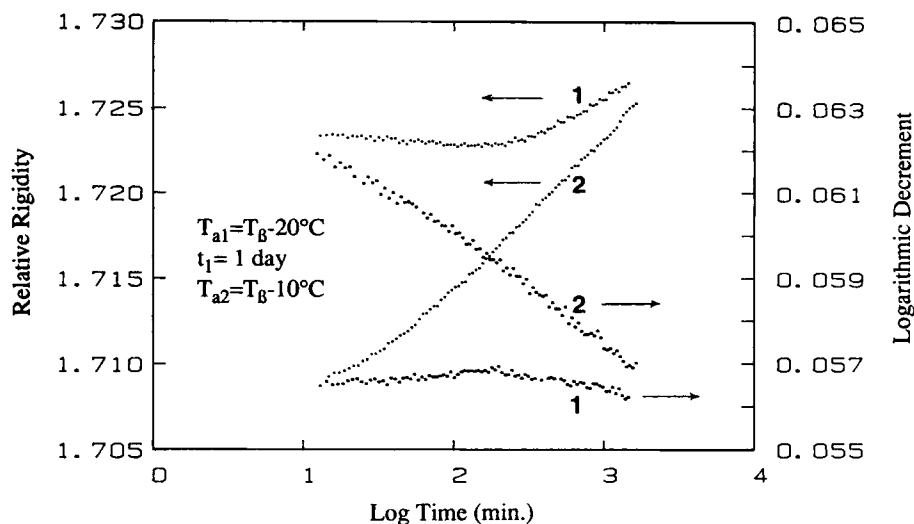


Figure 15 Isothermal memory effect below T_β . Isothermal behavior (relative rigidity and logarithmic decrement) at T_{a2} are shown for two different thermal histories: (1) after cooling from above T_g to T_{a1} at $1^\circ\text{C}/\text{min}$, aging at temperature T_{a1} for 1 day, and then heating to T_{a2} at $3^\circ\text{C}/\text{min}$; and (2) after directly cooling from above T_g to T_{a2} at $1^\circ\text{C}/\text{min}$ (see text). Note that the scales are different for Figures 14 and 15. The behavior is qualitatively similar in Figures 14 and 15; only the magnitude of changes and the times to maxima/minima are different. The existence of a “memory” effect proves that at least two relaxation mechanisms are in operation below T_β .

This behavior is a manifestation of the “volume-relaxation peak experiment,” a memory effect.^{1,26,32} An isothermal memory effect can only be observed if there is more than one relaxation mechanism (with different relaxation times) in operation.³² The observed behavior is consistent with the classification of relaxation mechanisms into three categories, as discussed earlier. Also shown in Figure 14 are TBA data obtained during aging at T_{a2} after cooling from above T_g directly to T_{a2} . Note that the locus of rigidity and logarithmic decrement for the two different thermal histories converge at long times, again reflecting the erasure of the effects of isothermal aging at T_{a1} during aging at T_{a2} .

The behavior is qualitatively the same, with a diminished magnitude, when T_{a1} (119°C) and T_{a2} (129°C) are below T_β (Fig. 15). This demonstrates that more than one relaxation mechanism (with different relaxation times) is in operation at a temperature below T_β .

Effect of Heating and Cooling Rates on Thermomechanical Behavior

To isolate the effect of isothermal aging when comparing aged and unaged material, the thermal history

of the aged and unaged material should be identical except for the isothermal aging. For this reason, in the isothermal aging experiments reported herein all heating and cooling rates ($1^\circ\text{C}/\text{min}$) and end points (5 and 315°C) were the same for the aged and unaged material (Fig. 2). Differences in cooling and heating rates for an aged and unaged specimen can result in more complex thermomechanical behavior. As an example, $\%G'$ vs. temperature is shown in Figure 16 for an isothermally aged ($T_a = 170^\circ\text{C}$) versus the unaged specimen with thermal histories as prescribed previously herein with the following single exception: the aged specimen was cooled from above T_g to T_a at $5^\circ\text{C}/\text{min}$ instead of $1^\circ\text{C}/\text{min}$ (step 3 in the aging cycle). The results show that $\%G'$ is positive and experiences a maximum in the vicinity of T_a due to the effect of physical aging at T_a (as before). However, at higher temperatures $\%G'$ is negative and passes through a minimum. This is a consequence of the decreased aging experienced by the “aged” specimen upon cooling at a higher rate ($5^\circ\text{C}/\text{min}$ from $> T_g$ to T_a) relative to that of the baseline specimen ($1^\circ\text{C}/\text{min}$ from $> T_g$ to T_a of the aged specimen).

Thus, the thermomechanical spectra of a single specimen can exhibit both aged ($\%G' > 0$) and un-

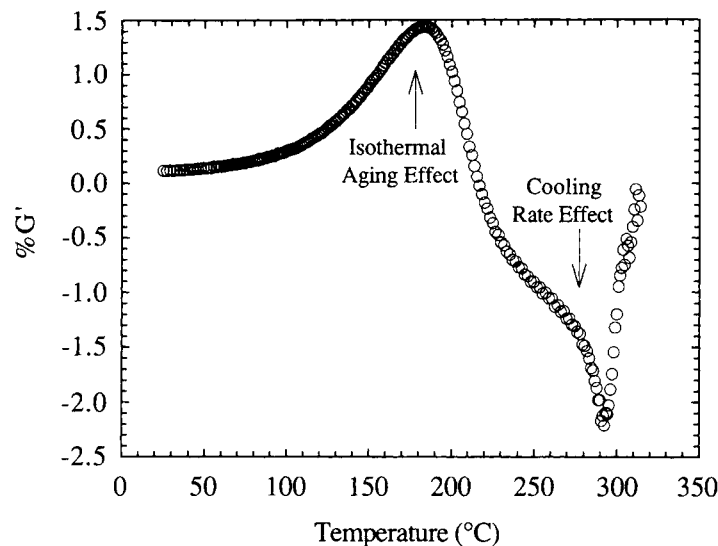


Figure 16 Effect of preaging cooling rate on % G' vs. temperature (see text). The aged specimen displays aged (% $G' > 0$) and “unaged” (% $G' < 0$) behavior relative to the unaged specimen in different temperature regions due to different cooling rates (from $>T_g$ to T_a) between the aged specimen (5°C/min) and unaged (baseline) specimen (1°C/min).

aged (% $G' < 0$) behavior relative to another specimen in different temperature regions. This effect can be seen in the aging data of an epoxy in a previous report (i.e., Fig. 12 of ref. 10). These observations demonstrate that the mechanical behavior at a given temperature below T_g mainly depends upon the (aging) time spent at that temperature. This is consistent with the classification of mechanical relaxation elements into three groups as discussed before.

Reversibility of Aging

Changes in the polymer-braid composite specimen over the many aging cycles were followed by monitoring the numerical values of T_g and T_β of the specimen during each temperature scan. T_g increased approximately 0.03°C for each heating ramp to above T_g , whereas T_β remained essentially constant (within detection) throughout the entire experiment. To show that the aging behavior of the specimen had not changed during the course of the aging cycles, the isothermal aging cycle for $T_a = 61^\circ\text{C}$ was performed twice (the second and the eleventh isothermal aging experiment). Figure 6 shows the rate of aging to be equal, within the scatter of the data, for the two cycles. Also, the perturbations in % G' for the two cycles coincide (Fig. 10).

The results of this article show that after aging, when heating to a higher temperature, T , it is not the value of $T - T_g$ that is most significant for the elimination of aging effects but $T - T_{er}$. Thus, for aging studies of glasses that degrade or react at temperatures near T_g heating only to above T_{er} and not to above T_g may be used as a nondestructive method to reestablish the properties of the nonaged specimen.

Humidity Effects on Thermomechanical Behavior

It has been shown for polyimides that a water-sensitive relaxation may be induced at temperatures below T_β .^{22,33} Figure 3 shows the effect of small amounts of water on the dynamic mechanical spectrum of a fully cured PI-2555 specimen. (A different specimen was used for this experiment.) The maximum of a water-sensitive mechanical loss peak, the intensity of which increases with the amount of water in the specimen, centered at about -100°C is termed T_{H_2O} . The temperature location of this peak is a function of the structure of the polymer, e.g., an epoxy has a different numerical value of T_{H_2O} than does this polyimide.^{33,34} This relaxation is reversible with respect to cooling and heating.

The less intense mechanical loss peak centered

at 0°C is also due to water but is only observed upon heating after excursions to low temperatures.^{33,34} Water vapor is adsorbed on the inner wall of the TBA chamber upon cooling to -170°C (during which the polymer experiences a dry atmosphere) and subsequently is released in the vicinity of 0°C from the chamber wall surface upon heating (thereby plasticizing the polymer). The hysteresis observed around 0°C shows a decreased relative rigidity and increased logarithmic decrement upon heating.

The lower limit for temperature scanning was set at 5°C in the aging experiments reported in this work to avoid complications brought about by adventitious water. The thermomechanical data collected during cooling and heating near 5°C do not show hysteresis²⁷; thus, the thermomechanical spectra at temperatures above 5°C are not affected by transient water. Also, by heating to 315°C (i.e., slightly above T_g) immediately before each isothermal aging experiment a constant drying procedure for all aging cycles was provided.

TBA as a Technique for Investigating Physical Aging

1. The freely oscillating nature of the pendulum is a factor in the sensitivity of the TBA technique. In this report, for example, the difference between the highest oscillation frequency (at 5°C) and lowest oscillation frequency (at 315°C) was 0.8 Hz whereas the TBA data showed a precision of about 0.0001 Hz in oscillation frequency for $T \ll T_g$. The sensitivity increases below T_g with decreasing temperature (e.g., see Fig. 4).
2. The specimen examined in this study was a polyimide/glass fiber composite. In a previous study,¹⁰ the aging rate of a fully cured epoxy/braid composite specimen was shown by the TBA technique to be directly proportional to that of the same epoxy material as an unfilled self-supporting film for all temperatures investigated. The relative rigidity of the epoxy/braid composite specimen below T_g was also directly proportional to the shear modulus, G' , of the unfilled epoxy film.¹⁰
3. The TBA measurements during isothermal aging show no measurable effect on the aging rate or subsequent thermomechanical behavior (Fig. 11).

CONCLUSIONS

1. The isothermal physical aging process has been investigated for a polyimide at temperatures between T_β and T_g and also below T_β .
2. The mechanisms associated with the β -transition contribute to the aging process below T_β . This is reflected in the decreasing aging rate with decreasing aging temperature below T_β .
3. Physical aging changes the low strain modulus of the polyimide only at temperatures localized about the aging temperature. This implies that physical aging at a given T_a involves an intermediate portion of the relaxation spectrum, not all relaxations equally.
4. The effects of physical aging can be essentially eliminated deep in the glassy state by heating to above the aging temperature but to still well below T_g .
6. Significant changes in the temperature region of the β -transition occur only by aging at a temperature near T_β .
7. An isothermal memory effect is observed at temperatures below T_β , as well as between T_g and T_β .

Financial support was provided by IBM Corporation.

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Received August 8, 1990

Accepted March 27, 1991