

Isothermal Physical Aging of a Fully Cured Epoxy–Amine Thermosetting System

SHELLEE L. MADDOX, JOHN K. GILLHAM

Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08544

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ABSTRACT: The rate and effects of isothermal physical aging of a fully cured epoxy–amine/glass fiber composite specimen were studied for a wide range of isothermal aging temperatures (-180 to 200°C) using a freely oscillating torsion pendulum technique: torsional braid analysis (TBA). As assigned from the maxima in the mechanical loss vs. temperature, the glass transition temperature, T_g , was 182°C (0.9 Hz), and the principal glassy-state secondary transition temperature, T_{β} , was $\approx -30^{\circ}\text{C}$ (1.9 Hz). Plots of the increase in the isothermal modulus and of the decrease in the isothermal mechanical loss were linear vs. log aging time; their slopes provided aging rates. It was found that the isothermal aging rate varies with isothermal aging temperature (T_a) and that there are two maxima in the aging rate vs. T_a . A correlation presumably exists between the two maxima in the aging rate and the two transitions. This is not surprising since mechanical loss maxima (i.e., transitions) and aging rate maxima both correspond to specific, localized, and restricted submolecular motions. Effects after isothermal physical aging were investigated vs. temperature in terms of change of modulus of the specimen. The effect of isothermal aging existed primarily in a narrow temperature region localized about T_a . The majority of the isothermal aging effect can be eliminated by heating to temperatures above T_a but below T_g . Theoretical and practical implications of this observation are discussed. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 55–67, 1997

INTRODUCTION

This report furthers previous research in this laboratory which showed that spontaneous physical aging could be monitored, using the modulus and loss parameters of a freely oscillating torsion pendulum technique, to temperatures well below T_g . Epoxy–amine, polyimide, poly(methyl methacrylate), and polycyanurate systems have been examined.^{1–7} The purpose of the present report was to examine (1) the relationships between isothermal physical aging rate vs. temperature and the polymer transitions (T_g , T_{β}) and (2) the localization of the effects of isothermal physical aging about the aging temperature in temperature scans. The same chemical epoxy system as examined in some earlier reports¹ was used.

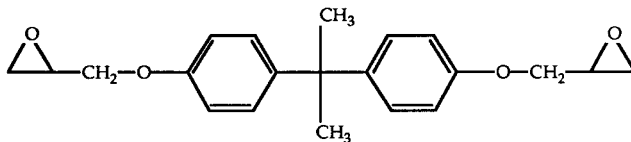
CHEMICAL SYSTEM

The thermosetting system used for the physical aging experiments was a miscible mixture of a difunctional aromatic epoxy and a tetrafunctional aromatic diamine in a balanced stoichiometric ratio (i.e., one epoxy group per one amine hydrogen). The epoxy monomer was a liquid diglycidyl ether of bisphenol A (DGEBA; DER 332 from Dow Chemical Co.) with an epoxide equivalent weight of 174 g. The amine curing agent was crystalline ($T_m = 125$ – 128°C) trimethylene glycol di-*p*-aminobenzoate (TMAB; formerly Polacure 740M from Polaroid Corp. but now Versalink from Air Products Co.), with an amine–hydrogen equivalent weight of 78.5 g. The chemical structures of the two reactants and the two principal chemical reactions involved in the cure are shown in Figure 1. A schematic representation of the fully cured network structure is shown in Figure 2.

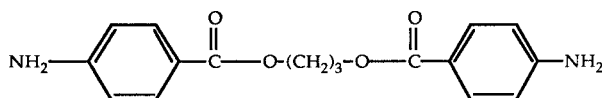
Correspondence to: J. K. Gillham.

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CHEMICAL REACTANTS



Diglycidyl ether of Bisphenol A

Trimethylene glycol di-*p*-aminobenzoate

CHEMICAL REACTIONS

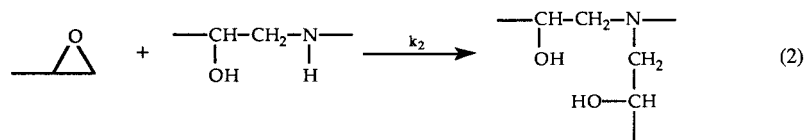
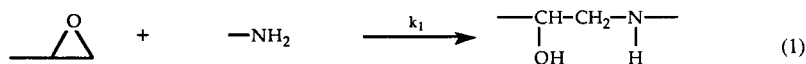


Figure 1 Difunctional aromatic epoxy and tetrafunctional aromatic diamine reactants; also, principal chemical reactions (k_1 and k_2 are the respective rate constants).

The crystalline amine was slowly added to the liquid epoxy at 100°C and then stirred vigorously for 30 min. Immediately after mixing, the warm liquid solution was degassed under a vacuum for 30 min at $\approx 75^\circ\text{C}$. The clear viscous liquid was then poured into small aluminum weighing pans, each of which was sealed in a plastic bag, kept in a desiccator, and stored in the freezer part of the refrigerator.

EXPERIMENTAL

All data were obtained using a single fully cured specimen using the freely oscillating (~ 1 Hz) TBA torsion pendulum technique.¹ The composite specimen (dimensions: ≈ 50 mm length and ≈ 0.5 mm radius) was made by first coating a heat-

cleaned, glass-fiber braid with the epoxy-amine liquid formulation in a fume hood and then, after insertion into the TBA unit, by fully curing at 220°C for 32 h in a flowing atmosphere of helium ($T_{g\infty} = 182^\circ\text{C}$). Data were then collected throughout a sequence of temperature scans and an isothermal (T_a) segment for a time $t_a = 600$ min ($\equiv 10$ h) as shown in Figure 3. This pattern was repeated for values of T_a ranging from -180 to 200°C . The specimen remained in the TBA unit throughout the experiments in a flowing atmosphere of dry helium. All cooling and heating rates were $2^\circ\text{C}/\text{min}$.

A review of the TBA torsion pendulum and its application to thermosetting systems has been published.¹ The output provides dynamic mechanical parameters: the relative rigidity (f^2 , where f is the frequency of oscillation of a damped wave)

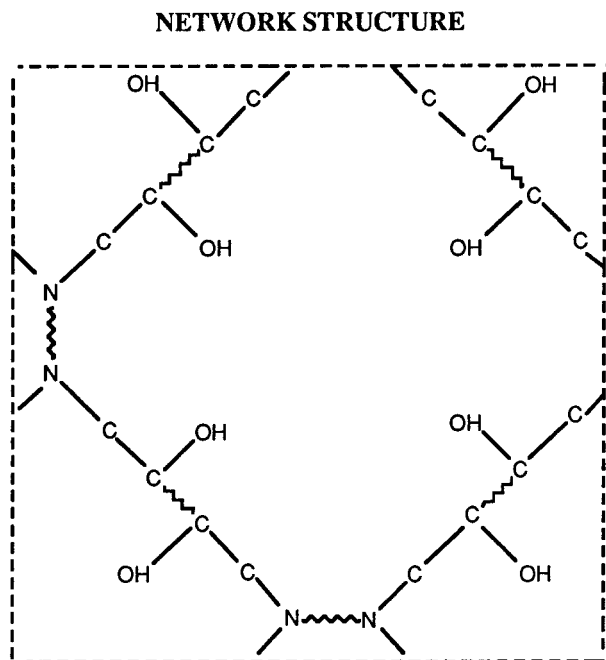


Figure 2 Schematic structure of fully cured epoxy-amine network. The ring size will vary throughout the network.

which is directly proportional to the elastic shear modulus (G') in the absence of dimensional changes and the logarithmic decrement which provides a measure of mechanical loss ($\approx \pi \tan \delta$, where δ is the phase angle between cyclic stress and strain). Transitions are assigned from the maxima in logarithmic decrement. Values of T_g in Table I present data for all aging experiments; values could be obtained to less than $\pm 0.1^\circ\text{C}$. Aging rates are obtained from the slopes of the modulus and mechanical loss vs. \log_{10} (time).

RESULTS AND DISCUSSION

Thermomechanical Properties of Fully Cured Specimen

TBA thermomechanical data for the unaged fully cured specimen are shown in Figure 4. The data were obtained from 220 to -180 to 220°C . $T_g = 182^\circ\text{C}$ (0.9 Hz), and $T_\beta \approx -30^\circ\text{C}$ (1.9 Hz). T_g and T_β were assigned from the maxima in the logarithmic decrement during the "up"-temperature scan: heating from -180 to 220°C .

Reversibility of Physical Aging

After each physical aging experiment at an isothermal aging temperature, T_a (see next sec-

tion), the specimen was cooled to -180°C and then heated to 200°C (a temperature above its glass transition temperature [$T_g = 182^\circ\text{C}$]) to erase the effects of previous aging. The dynamic mechanical properties of the base-line (unaged) specimen, obtained after deaging (by heating to 200°C), are shown from two separate, nonconsecutive experiments ($T_a = 50^\circ\text{C}$, $T_a = 130^\circ\text{C}$) in Figure 5. In each experiment, the thermomechanical spectrum was obtained by scanning from -180 to 200°C . The spectra from the two experiments are superimposable, illustrating that the effects of aging can be erased by heating to above T_g . Thus, a single specimen could be used to examine physical aging over a wide range of isothermal temperatures (-180 to 200°C). This was advantageous because it was then not required to know the relationship between the relative rigidity and the geometrical parameters of the specimen: Since the geometry was the same throughout the experiments (neglecting temperature effects), the relative rigidity was a relative modulus for comparative purposes. If more than one specimen had been used, it would have been difficult to obtain reproducible data due to the introduction of different geometries (since the pickup of resin onto the braid substrate could change from specimen to specimen), as well as changes associated with mounting and vertically aligning the specimens in the grips of the torsion pendulum. Use of a single specimen was also most efficient in

Temperature Profile of an Aging Experiment

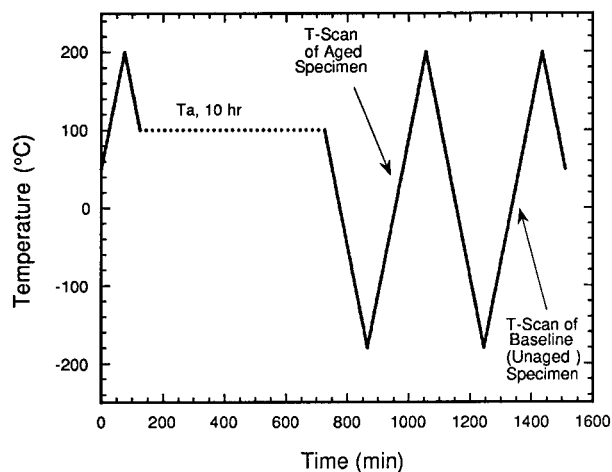


Figure 3 The time-temperature sequence of an aging experiment. All temperature scans were performed at $2^\circ\text{C}/\text{min}$.

Table I T_g of the Composite Specimen for the Aging Experiments (Experiments Listed Chronologically)

T_a (°C)	-180 → 200°C ^a	200 → -180°C ^b	-180 → 200°C ^b	200 → 50°C ^b
50	182.7	181.7	182.6	181.8
70	182.5	181.8	182.7	181.8
90	182.5	181.8	182.7	181.8
110	182.4	181.4	182.7	181.8
130	182.8	181.9	182.4	181.8
40	182.6	182.0	182.7	182.0
30	183.0	182.1	182.9	182.0
10	182.7	182.0	182.7	181.9
0	182.6	181.9	182.8	181.9
-20	182.8	182.0	182.5	181.9
-40	182.6	181.9	182.5	181.8
-60	182.7	181.8	182.9	181.7
-80	182.8	181.9	182.6	181.9
-100	182.5	181.9	182.8	182.0
-120	182.3	181.8	182.9	181.8
-140	182.6	181.9	182.5	181.8
-160	182.7	181.9	182.9	181.9
-180	182.6	181.9	182.8	182.0
140	182.8	182.0	182.8	182.0
150	182.7	182.0	182.6	182.0
160	183.4	181.9	182.9	181.8
50	183.0	181.7	182.9	182.1
165	183.5	182.0	182.9	182.1
170	183.2	181.9	182.7	181.8
172.5	183.1	182.1	183.0	182.0
167.5	182.6	182.1	182.8	182.1
10 (10 h)	183.1	182.3	183.0	182.1
10 (5 h)	183.1	182.0	183.0	182.3
10 (30 h)	183.1	182.1	183.2	181.9
10 ($T_{max} = 100$)	n/a	n/a	183.1	182.1
175	183.5	182.1	183.1	182.0
177.5	183.2	182.2	183.3	182.1
180	183.3	182.1	183.2	182.5
177.5	183.3	181.9	183.3	182.1
182.5	183.3	182.1	182.9	182.2
185	183.2	182.2	183.1	182.2
187.5	183.3	182.2	182.9	182.2
187.5	183.2	182.2	183.3	182.2
192.5	183.4	182.3	183.4	182.2
195	183.4	182.1	183.1	182.7
197.5	183.4	182.7	183.2	182.4
200	183.2	182.4	183.1	182.3
Average	182.9	182.0	182.9	182.0
Min/max	182.3/183.5	181.4/182.7	182.4/183.4	181.7/182.7

^a After aging.^b After deaging (see text).

terms of the number of experiments which could be performed and the quality of the data.

Isothermal Aging

During isothermal aging, the relative rigidity appears to increase linearly with log aging time,

while the logarithmic decrement appears to decrease linearly with log aging time, as in Figure 6. The slopes of these curves are measures of the aging rate.

Neglecting the first 40 min of data, so as to allow temperature equilibration at T_a for which

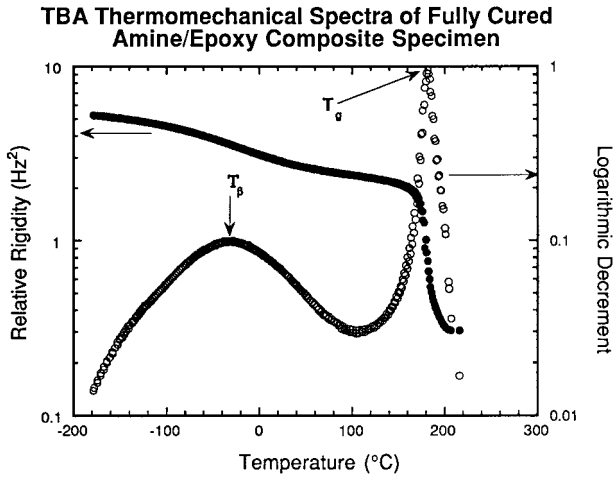


Figure 4 TBA dynamic mechanical properties (relative rigidity and logarithmic decrement) vs. temperature of the unaged fully cured amine-epoxy composite specimen. Data were obtained from 220 to -180 to 220°C , with both cooling and heating rates of $2^{\circ}\text{C}/\text{min}$. The glass transition temperature, $T_g = 182^{\circ}\text{C}$ (0.9 Hz), and a glassy-state secondary transition temperature, $T_{\beta}, \approx -30^{\circ}\text{C}$ (1.9 Hz), were defined by the temperature and frequency of the respective maxima in the logarithmic decrement curve. Both T_g and T_{β} were assigned from the maxima in the logarithmic decrement during the up-temperature scan: heating from -180 to 220°C . There is a suggestion of another transition at about -120°C .

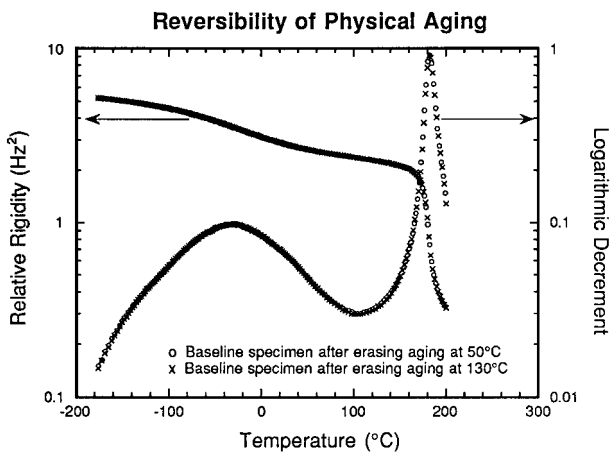


Figure 5 Dynamic mechanical spectra (from -180 to 200°C at $2^{\circ}\text{C}/\text{min}$) showing the reversibility of physical aging effects. The spectra shown, obtained after deaging in two separate experiments with $T_a = 50^{\circ}\text{C}$ and $T_a = 130^{\circ}\text{C}$, are superimposable. This indicates that aging effects have been erased by heating to 200°C (i.e., approximately 18°C above T_g). Therefore, one specimen could be used to examine physical aging for a wide range of isothermal temperatures.

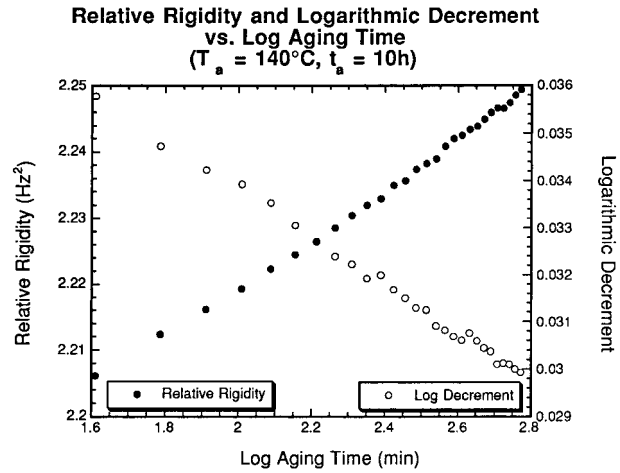


Figure 6 Relative rigidity and logarithmic decrement of the composite specimen vs. log aging time for an aging temperature, $T_a = 140^{\circ}\text{C}$. Isothermal aging time, t_a , was 10 h, with the relative rigidity and logarithmic decrement being measured every 20 min during this time. Neglecting the first 40 min of data (allowing T_a to equilibrate), the relative rigidity increases linearly while the logarithmic decrement decreases linearly with log aging time. The slopes of these curves are measures of aging rate.

$T_a = T_a \pm < 0.05^{\circ}\text{C}$, the modulus values during aging were normalized by assigning the value of 1 to the initial modulus at the isothermal temperature, as in Figure 7. The arrows indicate the changes in slope (i.e., changes in aging rate) that occur with changing aging temperature. The aging rate increases from $T_a = -100$ to 50°C , decreases from 50 to 90°C , increases from 90 to 165°C , and then decreases from 165 to 170°C . Thus, a local maximum in the aging rate occurs at 50°C and a global maximum corresponds to 165°C . This is shown similarly for mechanical loss data in Figure 8.

The aging rate was calculated from the slope of the relative rigidity and the slope of the logarithmic decrement vs. log aging time data (after 40 min) as $[dG'/d(\log t_a)]$ and $[-d\Delta/d(\log t_a)]$, respectively. The corresponding aging rates are plotted vs. isothermal aging temperature, T_a , in Figure 9. Some aging experiments were repeated (Fig. 9; "run 2" data are represented by filled and open triangles) at aging temperatures of 10, 30, 50, 177.5, and 187.5°C . The aging rate was reproducible at intermediate temperatures, but was less reproducible at higher temperatures near the T_g . Note that the shape of the aging rate vs. T_a data is similar to that of the thermomechanical spectrum as given by the logarithmic decrement vs. temperature (Fig. 4).

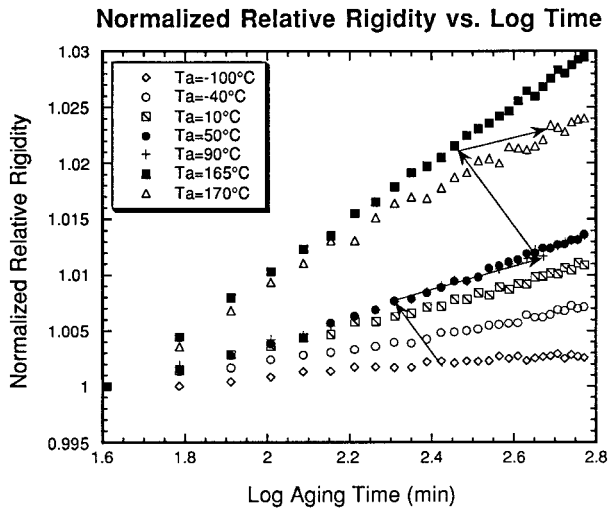


Figure 7 Normalized modulus of the composite specimen vs. log aging time for several aging temperatures, $T_a = -100, -40, 10, 50, 90, 165,$ and 170°C . Neglecting the first 40 min of data for each aging temperature, the modulus values during aging were normalized by assigning the value of 1 to the initial modulus at the isothermal temperature. The arrows indicate the changes in slope (i.e., changes in aging rate) that occur with changing aging temperature. It can be seen that the aging rate increases from $T_a = -100$ to 50°C , decreases from 50 to 90°C , increases from 90 to 165°C , and then decreases from 165 to 170°C . Thus, a local maximum in aging rate occurs at 50°C and a global maximum corresponds to 165°C .

Localization of Aging Effect on Thermomechanical Properties

Modulus and mechanical loss values for an aged ($T_a = 70^\circ\text{C}$) and unaged specimen are compared at different temperatures in Figures 10 and 11, respectively. Data are obtained from “up”-temperature scans, heating from -180 to 200°C after isothermal aging and cooling to -180°C , and after deaging by heating to 200°C and cooling, respectively.

Localization of the effects of isothermal physical aging is clearly illustrated by the percentage change of the modulus vs. temperature, found by using data such as those presented in Figure 10. The percent change of the modulus at a particular temperature due to physical aging is calculated by

$$\% \Delta G' = 100 \times [G'(a) - G'(u)] / G'(u) \quad (1)$$

where a and u represent the aged and unaged states, respectively. Percent change of the modulus vs. temperature is shown for $T_a = 70^\circ\text{C}$ in

Figure 12. The principal change in the modulus is localized about T_a . The percent change of the modulus due to aging is shown vs. temperature for different T_a 's in Figure 13. The largest percentage changes correspond to those aging temperatures at which the isothermal aging rate is highest. Localization of the aging effect is present in each case, but the widths of the difference peaks are broader at lower temperatures.

Intuitively, the localization of aging in the vicinity of T_a is initially unexpected. It would seem logical to anticipate that the aging effect (e.g., increased modulus) would be apparent over all temperatures below T_a rather than being localized about T_a . Localization of the aging effect suggests that specific “intermediate” relaxation elements are involved in the physical aging process at a particular T_a . At a particular T_a , elements of an intermediate length scale can move but are restricted by their environment. These elements are different from those of relatively long length scales that are immobilized in their environments such that they do not move during the aging process. They also differ from those elements with relatively short length scales that are free to move within their environment and are in a state of dynamic equilibrium. During isothermal physical aging, the intermediate length scale elements attempt to move from a state of nonequilibrium to one of equilibrium. While moving within their environment, they eventually become immobilized as the initial free volume decreases. The relaxation elements with relatively long and short

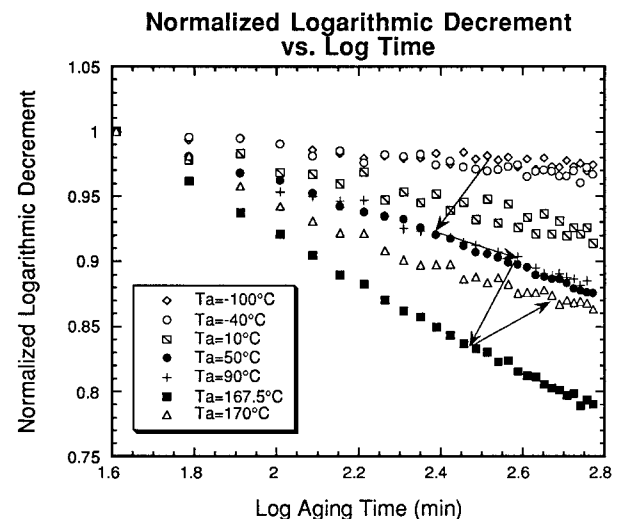


Figure 8 Normalized mechanical loss of the composite specimen vs. log aging time for $T_a = -100, -40, 10, 90, 167.5,$ and 170°C . See also caption for Figure 7. Data presented show a similar trend to that in Figure 7.

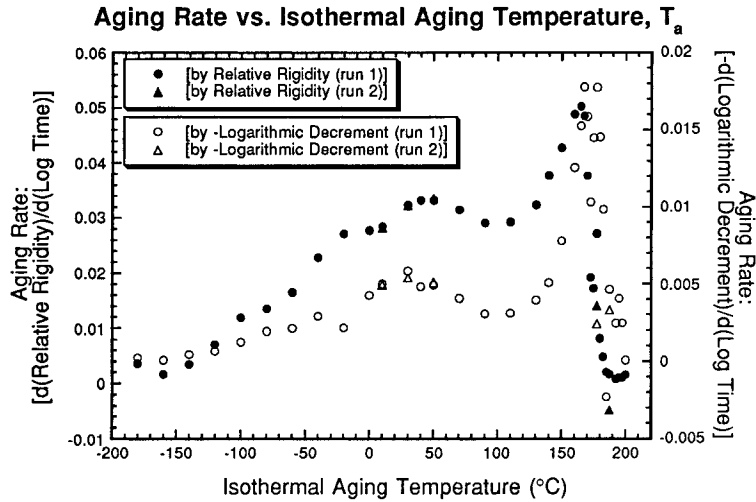


Figure 9 Aging rate vs. isothermal aging temperature. The aging rate was calculated from the slope of the relative rigidity and the logarithmic decrement vs. log aging time data (after 40 min). Aging experiments were repeated (“run 2” data are represented by filled and open triangles) at the following aging temperatures: 10, 30, 50, 177.5, and 187.5°C. The aging rate is reproducible at intermediate temperatures, but is less reproducible at higher temperatures near the glass transition temperature, T_g . Note that the shape of the aging rate vs. T_a data (as given by the relative rigidity and logarithmic decrement) is similar to that of the thermomechanical spectrum (as given by the logarithmic decrement) vs. temperature (see Fig. 4).

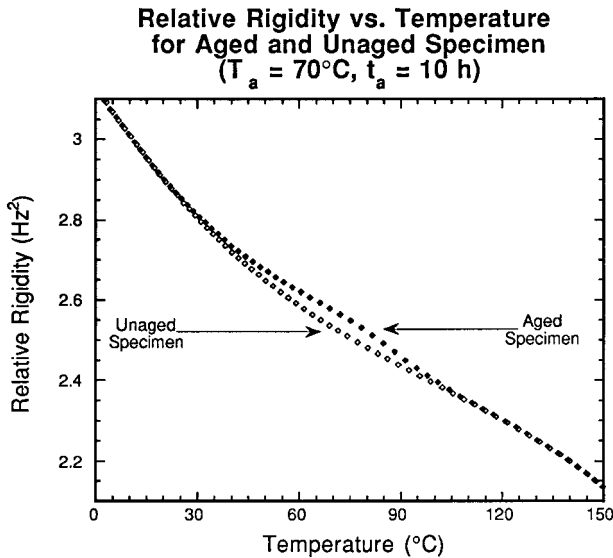


Figure 10 Relative rigidity vs. temperature of an aged composite specimen ($T_a = 70^\circ\text{C}$, $t_a = 10$ h) compared with that of the same specimen in the unaged state. Data are obtained from “up”-temperature scans, heating from -180 to 200°C after aging, and after deaging, respectively. Note that the temperature scale here has been expanded to emphasize the change in the vicinity of T_a due to aging at this particular temperature.

length scales remain largely the same during aging. The modulus measured at 1 Hz increases because of the decreased internal mobility of the intermediate elements which include those which move in the determination of the modulus at 1 Hz. It is important to note that these intermediate elements, which are in motion during isothermal physical aging, vary with T_a .

Effects of aging do not seem to be present at temperatures above the region localized about T_a because there is an expansion of the material upon heating to higher temperatures, and, thus, the intermediate elements which were immobilized not only regain the mobility that they had before the aging process but also acquire the same freedom to move as those elements with very short length scales. In temperature regions well below T_a , the effect of aging is absent because those intermediate elements which participated in the aging process at T_a are long scale motions and are not involved when the modulus is measured at the lower temperatures.

Localization of the aging effect suggests that it may not be necessary to heat an aged material to a temperature above its glass transition temperature to erase aging effects (this will be discussed

further later on). A practical application of this is the removal of stresses that develop during the physical aging of engineering materials without completely softening the material.

For aging temperatures at or near zero ($T_a = -20, 0, 10^\circ\text{C}$), in addition to the primary peak in $\% \Delta G'$ vs. temperature localized about T_a , a secondary peak in $\% \Delta G'$ occurs in a temperature region below that of T_a . Figure 14 shows this secondary difference peak which is localized about -60°C for $T_a = 10^\circ\text{C}$. This secondary peak may be due to trace amounts of water present in the flow of "dry" helium gas over the specimen during the isothermal period of aging.⁷⁻⁹

In Figure 15, the logarithmic decrement spectrum is shown vs. temperature for the aged at 10°C and unaged specimen. It is observed that the maximum change in the logarithmic decrement spectrum due to aging is in the vicinity of $T_a = 10^\circ\text{C}$ (the logarithmic decrement is lower for the aged specimen than for the unaged specimen). The increase in logarithmic decrement of the aged specimen in the vicinity of -40°C may be due to trace amounts of water present during aging at 10°C . Further investigation of this is warranted.

Effect of Aging Time

An attempt was made to determine the effect of aging time on two results: the measured aging

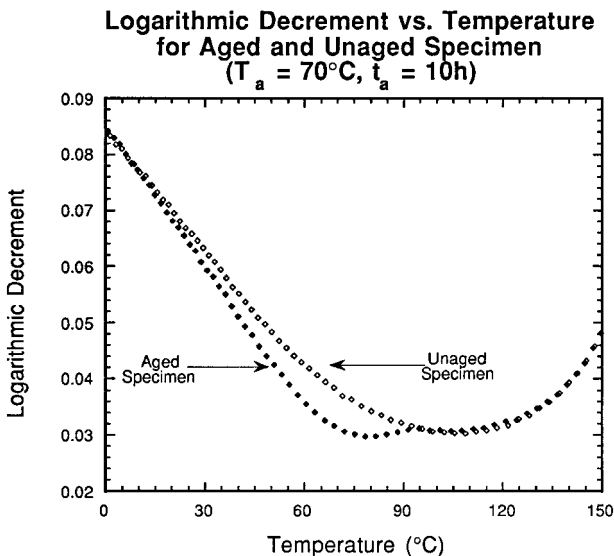


Figure 11 Logarithmic decrement vs. temperature of the composite specimen in its aged ($T_a = 70^\circ\text{C}$, $t_a = 10$ h) and unaged states. Similar to Figure 10, data are shown only for the temperature region which was affected most by aging (i.e., $\sim T_a = 70^\circ\text{C}$). The aging effect is localized about T_a .

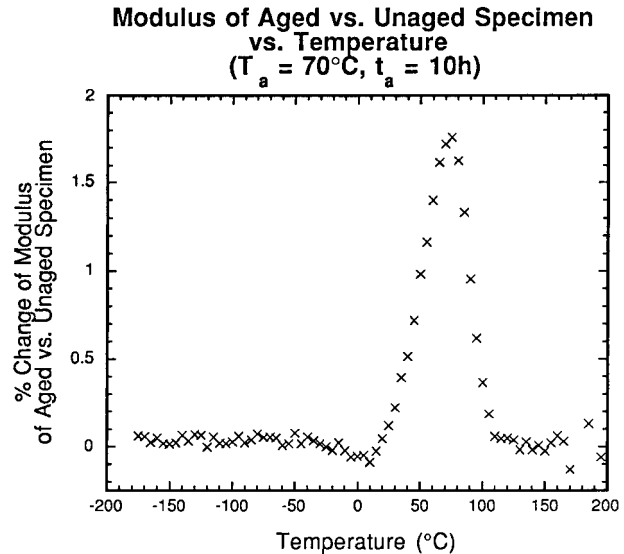


Figure 12 Percent change of the modulus of the aged specimen ($T_a = 70^\circ\text{C}$) with respect to the unaged specimen vs. temperature. There is a localization of the maximum percentage change in modulus about T_a . This localization of the aging effect in the vicinity of T_a suggests that the effects of aging may be erased by heating to above T_a but below T_g (182°C). (Note: At temperatures in the vicinity of T_g , data display more scatter because the mechanical properties at these temperatures are highly sensitive to small temperature fluctuations. This scatter is also seen in Figs. 14 and 16 but corresponding data have been omitted in Fig. 13 to maintain clarity in the presentation.)

rate and the relative intensities of the localized peaks in the $\% \Delta G'$ vs. temperature plots. To test the effect of different aging times on the measured aging rates, aging was monitored at $T_a = 10^\circ\text{C}$ in three separate experiments with aging times, $t_a = 10, 5,$ and 30 h, respectively. As opposed to performing one long isothermal aging experiment and examining the effects of aging over different time segments within that period, three separate experiments were conducted so as to also find out how t_a affects the relationship between $\% \Delta G'$ and temperature; 10°C was chosen as the temperature for which to examine the effect of aging time to ascertain if the intensities of the two peaks in the $\% \Delta G'$ vs. temperature plot changed proportionally with time. Results illustrating the effect of varying aging time are shown in Figure 16.

It was found that aging rate increased with increased aging time. When comparing the aging rate (as measured by changes in the relative rigidity of the specimen with log time) for experiments with $t_a = 10$ (run 1), 5, and 30 h, it was found that the aging rate was $\approx 3.7\%$ lower and $\approx 17.55\%$

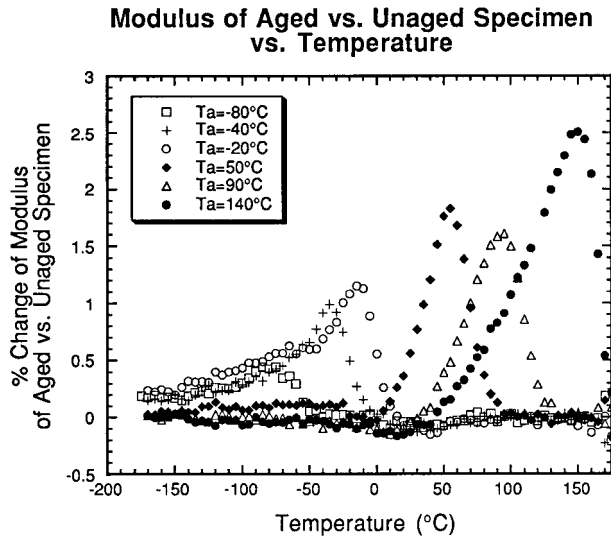


Figure 13 Percent change of the modulus of the composite specimen aged at different isothermal aging temperatures, $T_a = -80, -40, -20, 50, 90,$ and 140°C . (Note that the scales are different from those of Fig. 12.) The highest percentage changes correspond to those aging temperatures at which the aging rate is highest. Localization of the aging effect is present in each case, but the widths of the peaks are broader at lower temperatures.

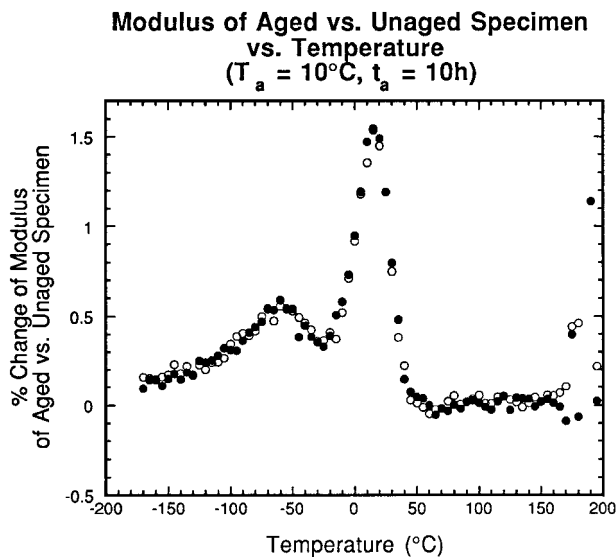


Figure 14 Percent change of the modulus of the composite specimen aged at $T_a = 10^\circ\text{C}$. The secondary peak may be due to trace amounts of water in the helium flowing over the specimen when aging in the vicinity of 0°C . Aging at 10°C was performed twice (the different symbols represent the two sets) to show that changes due to aging at a particular T_a are reproducible.

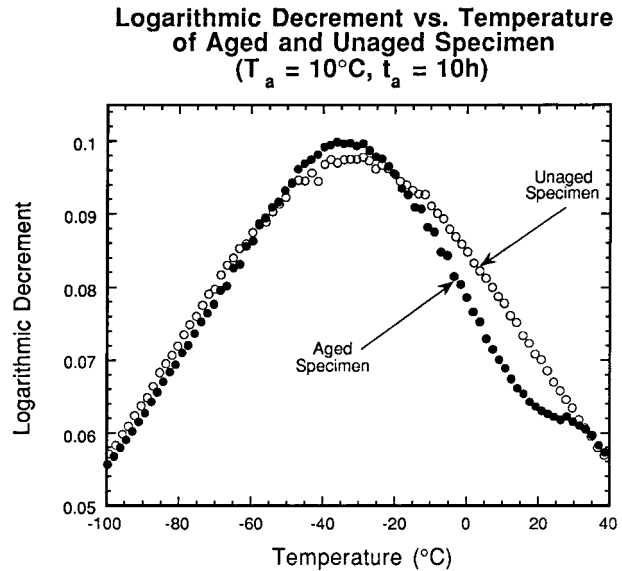


Figure 15 Logarithmic decrement vs. temperature of the aged composite specimen ($T_a = 10^\circ\text{C}$, $t_a = 10\text{ h}$) and that of the same specimen in its unaged state. Data are obtained from “up”-temperature scans, heating from -180 to 200°C after aging, and after deaging, respectively. The effect of aging is localized about T_a . Trace amounts of water present during aging at 10°C affect the mechanical loss in the vicinity of -40°C , which in this case corresponds to T_β .

higher, respectively, with respect to the first [$t_a = 10\text{ h}$ (run 1)]. Thus, it is important to use a fixed t_a in physical aging experiments so that aging rates are measured as a function of isothermal aging temperature only.

It can be seen from Figure 16 that both primary and secondary difference peaks remain localized with changes in isothermal aging time. Both primary and secondary localization peaks increased with increased aging time, but the changes were not proportional. The relative increase in magnitude of the secondary peak was greater than that of the primary localization peak. For example, upon increasing t_a from 10 h (run 1) to 30 h, the secondary peak in the $\% \Delta G'$ vs. temperature plot increased by $\approx 57\%$ while the primary localization peak increased by $\approx 36\%$. Further investigation of this is also warranted.

Effect of Physical Aging on T_g

Table I shows values of the T_g of the composite specimen, obtained during temperature scans for all of the scans associated with each and every T_a . The experiments are listed chronologically to ascertain if there were systematic changes in the

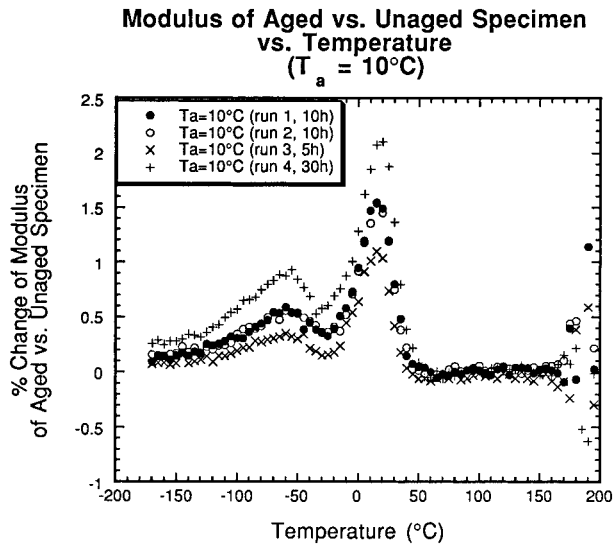


Figure 16 Percent change of the modulus of the composite specimen aged at $T_a = 10^\circ\text{C}$ for different aging times, $t_a = 5, 10,$ and 30 h. Aging at 10°C for 10 h was performed twice (in two nonconsecutive experiments) to show that changes due to aging at a particular T_a are reproducible. The secondary peak in each curve may be due to traces of water; it arises when aging at temperatures near 0°C (see text). Both the primary and secondary maxima peaks increase in intensity with increased aging time; however, they do not increase proportionally.

course of all of the experiments due to multiple heatings of the specimen to 200°C . Values of T_g were determined from the logarithmic decrement spectrum obtained during temperature scans after each physical aging experiment at T_a . Each T_g value was obtained by curve fitting the T_g peak (taken as seven data points) in the logarithmic decrement spectrum to a second-order polynomial that is used to calculate the maximum (defined as T_g).

The values in the second column of Table I represent the T_g of the aged specimen obtained during an “up”-temperature scan from -180 to 200°C directly after the specimen had been cooled from T_a to -180°C . T_g values in the third, fourth, and fifth columns correspond to the unaged specimen and were measured during the following temperature scans, respectively: 200 to -180°C , -180 to 200°C , and 200 to 50°C . After deaging, the value of T_g obtained during an “up”-temperature scan (column 4) was $\approx 0.9^\circ\text{C}$ higher than that obtained during a “down”-temperature scan (columns 3 and 5). This is due to a temperature lag between the specimen and the measured temperature. During cooling, the temperature of the specimen is higher than that of the measuring thermocou-

ple (which is in the copper block of the TBA oven), whereas during heating the specimen is at a lower temperature than is the thermocouple. Thus, properties measured during temperature scans are compared from scans in the same direction. Data collected from aging experiments are compared for “up”-temperature scans.

Values of T_g , obtained from heating the specimen from -180 to 200°C after aging (column 2), do not appear to be affected by aging for most values of T_a . However, T_g values do appear to be affected for isothermal aging at temperatures near T_g . For $175 \leq T_a \leq 200^\circ\text{C}$, T_g values obtained upon heating the aged specimen from -180 to 200°C are $\approx 0.5^\circ\text{C}$ higher on average than are the T_g values measured for lower values of T_a . For the latter, T_g values should be the same on cooling the specimen from 200 to -180°C and from 200 to 50°C in the absence of any drift of T_g with repetitive heating to and cooling from 200°C : For most experiments, the difference between T_g values listed in columns 3 and 5 of Table I is not greater than 0.1°C .

Erasing Aging Effect by Heating to Below T_g

As part of the procedure for these physical aging experiments, effects of aging are removed by heating the aged specimen to a temperature, $T_{\max} = 200^\circ\text{C}$, which is above the glass transition temperature (182°C). After this, the specimen is “rejuvenated,” and “down”- and “up”-temperature scans are performed to obtain the thermomechanical spectra of the unaged specimen.

As was discussed earlier, the difference of modulus and the difference of mechanical loss for the aged and unaged specimen vs. temperature due to isothermal physical aging at a particular T_a were localized about T_a . This suggested that the aging effect could be erased by heating to a temperature above T_a but below T_g (182°C). To test the validity of this hypothesis, two separate, consecutive experiments were run in which experimental variables were kept constant (i.e., T_a, t_a) except for the erasure temperature (T_{\max}). Two experiments were performed in which the specimen was held isothermally at $T_a = 10^\circ\text{C}$ for 10 h; in the one, T_{\max} was chosen to be 200°C (as it usually was), and in the other, T_{\max} was selected as 100°C . Figure 17 shows relative rigidity data vs. temperature from each experiment obtained during the “up”-temperature scan after heating the specimen to T_{\max} .

Data from the two experiments appeared to be superimposable when examining the modulus

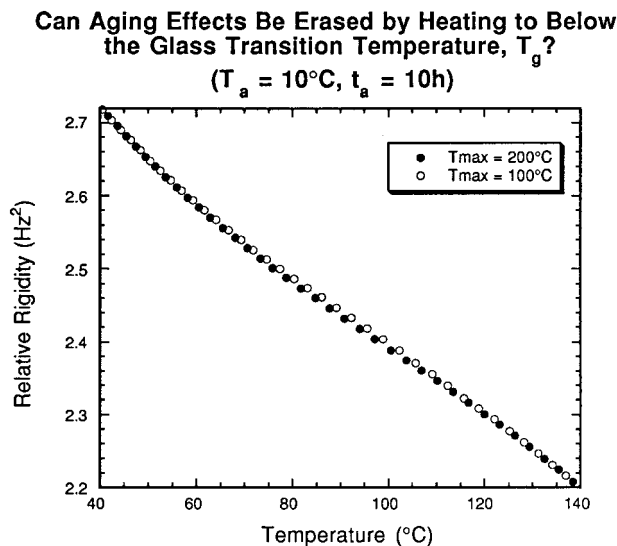


Figure 17 “De-aged” base-line temperature scans are shown from two separate aging experiments, both with $T_a = 10^\circ\text{C}$ and $t_a = 10\text{h}$. T_{max} , the temperature to which the specimen was heated to erase the aging effect, was chosen above T_g (200°C , as usual) in the one experiment and below T_g (100°C) in the other to test if the effects of aging can be removed by heating the specimen to below T_g . Notice that when the temperature scale is expanded, as it is here, there is a slight difference between the two base lines. This suggests that although most of the aging effect is removed by heating to below T_g , some residual aging effects still exist, especially in the vicinity of the lower T_{max} temperature.

data over the complete range of temperatures (-180 to 200°C). However, when the temperature scale is expanded (as it is in Fig. 17) to focus on a particular temperature region, a slight difference is noticed between data obtained from the two experiments, indicating that aging effects have not been completely removed by heating to 100°C , which is below T_g . Residual aging effects are present, particularly in the vicinity of the second T_{max} (100°C). Thus, it seems that heating to a temperature well above T_a (T_{max} is 90°C above T_a) but below T_g is not sufficient for the complete removal of aging effects. Further investigation of this could be an interesting research project.

Relationship Between Aging Rate vs. Temperature and Mechanical Loss vs. Temperature

The isothermal aging rate, as measured by the change in modulus, and the logarithmic decrement spectrum of the unaged specimen vs. temperature are shown together in Figure 18 to emphasize the similarity between these two sets of

data. There is a relationship between the temperatures at which there are maxima in the aging rate and the transition temperatures (T_β and T_g) corresponding to the maxima in the logarithmic decrement. The isothermal aging rate as measured by the change in the logarithmic decrement and the logarithmic decrement spectrum vs. temperature are shown in Figure 19 to further emphasize the similarity.

When considering this similarity, it is pointed out that the mechanical loss is not just a measure of the loss of energy of the specimen upon deformation, but it is also a measure of submolecular motions which are responsible for the transitions (relaxations). Likewise, the isothermal aging rate is a measure of submolecular motions.

To date, ideas about this similarity are summarized as follows¹⁰:

- Isothermal physical aging rate and logarithmic decrement are both measures of submolecular motions.
- There are two types of specific and localized motion occurring with both logarithmic decrement vs. temperature and with isothermal aging rate vs. temperature as indicated by the two maxima in each plot.
- Do the maxima for the two ways of detecting submolecular mobility correspond?
- If they correspond, why is one from the isothermal aging rate data higher than T_β and the other lower than T_g ? Transitions (e.g., T_g and T_β) move to higher temperatures with higher frequency (e.g., T_g increases $\approx 7^\circ\text{C}/$ decade increase of frequency). The lower isothermal aging rate maximum is at a higher temperature than T_β . However, the primary maximum in isothermal aging rate occurs at a lower temperature than T_g .
- What is the time scale of the measurements? The aging rate as measured is a rate obtained over a logarithmic time period of 9 h and 20 min. The instantaneous aging rate therefore decreases with linear time. Logarithmic decrement (or loss modulus) is a 1 s measurement (i.e., the relationship between stress and strain is obtained at 1 second).
- The primary maximum in aging rate must occur at a temperature below T_g because the rate of aging at temperatures above T_g is considered to be zero.
- Is there theoretically a maximum in the aging rate just below the T_g ? The aging rate increases as the temperature increases to

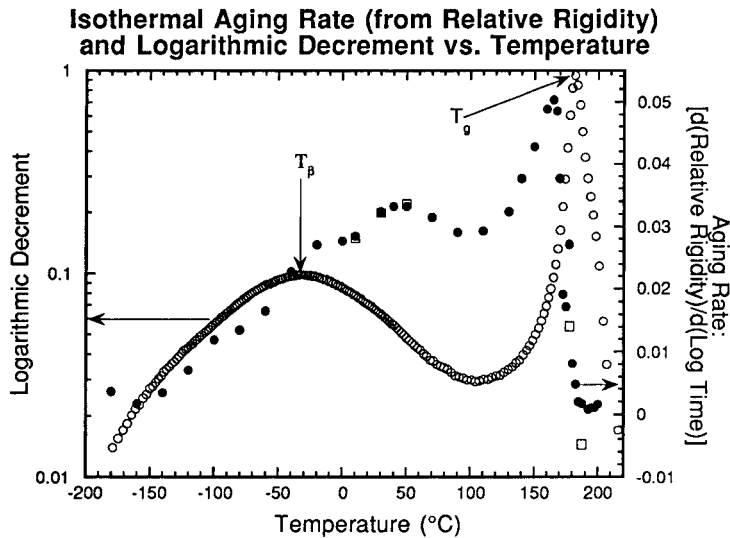


Figure 18 Isothermal aging rate (measured by modulus) and the logarithmic decrement (mechanical loss) spectrum (obtained during a temperature scan “up” of the unaged, fully cured specimen) vs. temperature. There is a relationship between the transition temperatures (T_β and T_g) corresponding to the maxima in the logarithmic decrement curve and the temperatures at which there are maxima in the isothermal physical aging rate.

ward T_g and is zero above T_g . Therefore, the rate of physical aging could pass through a maximum (as measured) or through a discontinuity (with an infinite rate as T rises through T_g).

As discussed in connection with the origin of the localized effect of physical aging about T_a in the thermomechanical behavior, restricted mo-

tions of intermediate length scale are considered to be involved in the physical aging process. Similarly, the origin of a loss maximum in the TBA dynamic mechanical behavior vs. temperature of the unaged material is also a consequence of restricted motions of specific entities (in the time scale of about 1 sec): no mechanical loss occurs at temperatures well below (the entities are frozen) or well above (the entities are in dynamic equili-

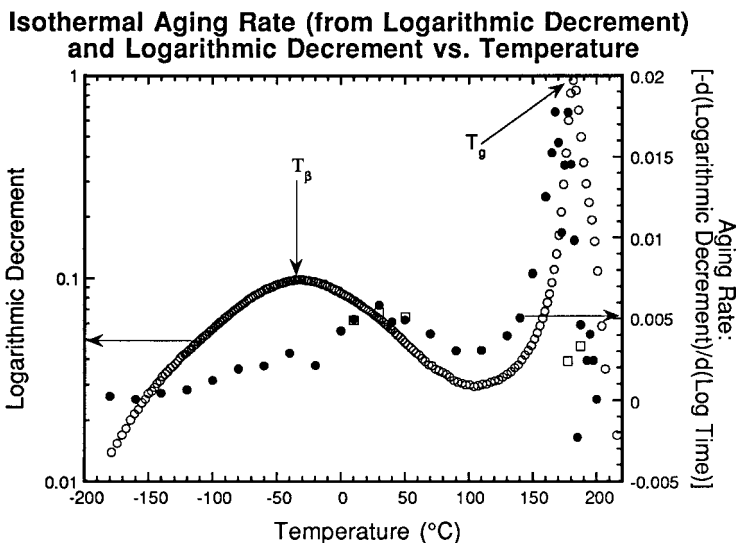


Figure 19 Isothermal aging rate (measured by logarithmic decrement) and the logarithmic decrement spectrum vs. temperature. See also caption for Figure 18.

brium) the temperature of the maximum in mechanical loss.

CONCLUSIONS

Two maxima in the isothermal physical aging rate were observed for a fully cured diepoxy/tetrafunctional aromatic diamine system at 50 and 165°C, respectively. They appear to correlate with the $T_{g\infty}$ (182°C) and T_{β} (30°C) transitions (relaxations): This is not surprising since both types of experiments respond to specific, localized, and restricted submolecular motions. The effect of isothermal aging is localized in a subsequent temperature scan to the vicinity of the aging temperature (T_a). Aging effects could be almost completely eliminated by heating to temperatures below $T_{g\infty}$. This has practical implications as in the removal of stresses in physically aged polymers.

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