

Evolution of Properties with Increasing Cure of a Thermosetting Epoxy/Aromatic Amine System: Physical Ageing

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ABSTRACT: Isothermal physical ageing below the glass-transition temperature (T_g) of a high- T_g thermosetting difunctional epoxy/tetrafunctional aromatic amine system was investigated at different ageing temperatures (T_a) and chemical conversions (monitored by the T_g) using the torsional braid analysis freely oscillating torsion pendulum technique. In the absence of chemical reaction during an isothermal ageing process, the rate of isothermal physical ageing passes through a minimum with increasing conversion. The minimum is related to the minimum in mechanical loss between the secondary relaxation in the glassy state (T_β) and the glass-transition relaxation (T_g) (the temperatures of both of which increase with increasing conversion). If isothermal ageing rates for all conversions (beyond gelation) would have been measured directly from temperatures be-

low T_β to above T_g , it is concluded that two maxima in isothermal ageing rate would have been observed corresponding to the two relaxation processes. There exists a superposition in isothermal ageing rate versus $T_g - T_a$ [by shifting horizontally (and vertically)], which implies that the ageing rate is independent of the details of the changing chemical structure attributed to cure. Controlling mechanisms during physical ageing are segmental mobility associated with the T_g region and more localized motion associated with the glassy-state relaxation T_β . © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2665–2675, 2003

Key words: physical ageing; curing; glass-transition temperature; mechanical properties; thermosets

INTRODUCTION

In this laboratory, interesting “anomalous” interrelated phenomena have been investigated in studies on the evolution of isothermal physical properties with increasing conversion for different amorphous thermosetting systems. These studies stemmed from using a freely oscillating torsion pendulum technique—torsional braid analysis (TBA)—which in essence measures the elastic and loss moduli at about 1 Hz versus temperature and time. Properties such as the isothermal elastic modulus,^{1–4} room temperature density,^{1,5} water absorption,¹ and free volume^{6,7} showed anomalous behavior with increase of conversion. For example, well below the glass-transition temperature (T_g), the isothermal intermittent elastic modulus can increase, then decrease, and again increase with increasing conversion.² Understanding the evolution of properties with respect to conversion is especially significant in thermosetting systems where extreme changes take place during cure, not only molecularly from monomers to highly crosslinked polymer but also

macroscopically (viscoelastically) from the fluid state before gelation to the glassy state after vitrification. This evolution should be considered with respect to both the processing and end use of thermosetting materials. It is relevant that “optimum” properties do not necessarily correspond to full cure.

Physical ageing, defined as a gradual approach toward equilibrium by the loss of free volume, is known to occur always in a glassy polymer: the thermal history is an important determinant of its current and future physical properties.

Isothermal physical ageing has been investigated by means of TBA as one of the studies on evolution of properties versus conversion.^{8,9} Physical ageing has been examined by means of TBA in unreactive thermoplastics [e.g., poly(methyl methacrylate)¹⁰] and in fully reacted thermosets (e.g., polyimide¹¹ and an epoxy/amine system^{12,13}). The experiments demonstrated that, generally, the effects of isothermal physical ageing increased the elastic modulus and decreased the corresponding mechanical loss at the ageing temperature; however, the after-effect on the elastic and loss moduli versus temperature was restricted to a limited region centered around the ageing temperature (T_a), which presumably is a consequence of only a specific portion of the relaxation spectrum

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being effective under the imposed ageing conditions of temperature and time. This localized perturbation led to the concept of eliminating the effect of physical ageing at T_a by heating the specimen to an "erasure" temperature T_{er} above T_a but below T_g .

It has been shown also in the glassy state that with increasing conversion the isothermal modulus passes through a minimum value that corresponds to the principal glassy-state relaxation temperature (T_β) rising through the temperature of measurement,² which is evidence that the isothermal anomalies associated with increasing conversion depend on the relationship between the rising relaxation temperatures (e.g., T_β and T_g) and the temperature of measurement.

Evolution of isothermal physical ageing behavior for different conversions at different ageing temperatures is the subject of this report. Discussion centers on analysis of isothermal ageing rates, differences in moduli (storage and loss) versus temperature between aged and unaged behavior, and comparison of ageing rate versus temperature and thermomechanical spectra (especially mechanical loss versus temperature). The glass-transition temperature T_g , which has been shown to be uniquely related to conversion for this system,¹³ is used as a measure of conversion. A preliminary report has been published.¹⁴

EXPERIMENTAL

Technique

A freely oscillating dynamic mechanical technique, the TBA torsion pendulum, which operates at about 1 Hz, is shown in Figure 1.^{15,16} The relative rigidity ($\equiv f^2$) of the specimen, which is proportional to the elastic shear modulus (G'), was obtained from the natural frequency (f) in cycles/s of intermittently induced freely damped waves: in this report it is often referred to as the modulus. The corresponding loss shear modulus (G'') of the specimen, which can be expressed as the logarithmic decrement ($\cong \pi G''/G' = \pi \tan \delta$, where δ is the phase angle between the stress and strain in the oscillatory experiment), was computed from the corresponding decay of the oscillations in the intermittently induced freely damped waves: in this report it is often referred to as the mechanical loss.

A specimen was prepared as described later.

A key experimental procedure involved using a single specimen with different degrees of cure (i.e., T_g) for each ageing temperature (T_a) on the basis that the ageing effect at T_a could be removed for each degree of cure by heating to below the glass-transition temperature without changing conversion,^{11,17} and that the state of cure could be subsequently advanced by heating to above T_g . A fresh specimen (length ~ 2 in., diameter ~ 0.05 in.) was used for each isothermal ageing temperature. After inserting the uncured spec-

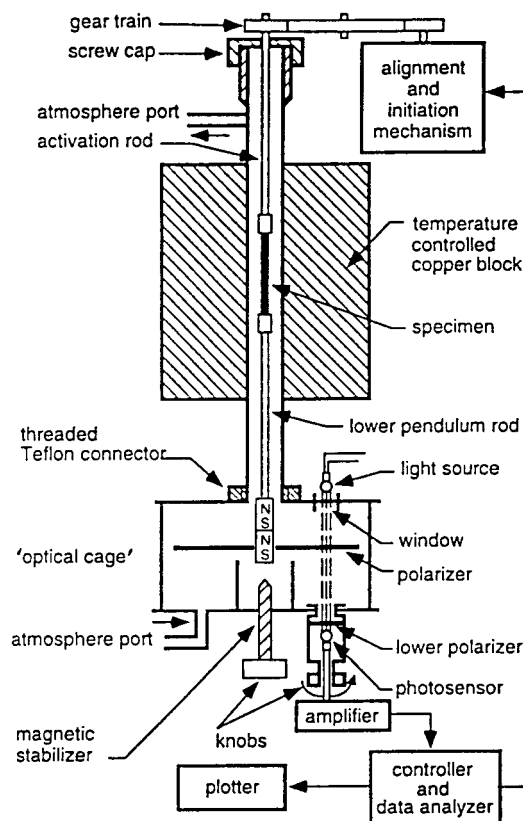


Figure 1 Schematic diagram of the TBA torsion pendulum system. [Reproduced courtesy of Plastics Analysis Instruments, Inc., Princeton, NJ.]

imen (see below) into the apparatus, the specimen remained in the apparatus throughout the experimental sequence for the particular value of T_a .

For a particular conversion, the rate of isothermal ageing was obtained directly from plots of the elastic and loss moduli versus log time. The subsequent effect of the isothermal ageing on the moduli versus temperature was obtained immediately after the isothermal ageing by comparison of two sequential temperature scans from below T_a to below T_g . Heating and cooling rates were $2^\circ\text{C}/\text{min}$. The atmosphere was slow-flowing helium.

Chemical reactants

The chemical system was a stoichiometric mixture (epoxy/NH = 1/1) of the difunctional diglycidyl ether of bisphenol-A and crystalline tetrafunctional trimethylene glycol di-*p*-aminobenzoate formed without solvent at 100°C for 15 min.¹⁸ Chemical structures of the reactants are represented in Figure 2.

Temperature-time sequence

A composite specimen,^{15,16} formed by impregnation of a heat-cleaned glass fiber braid with an uncured

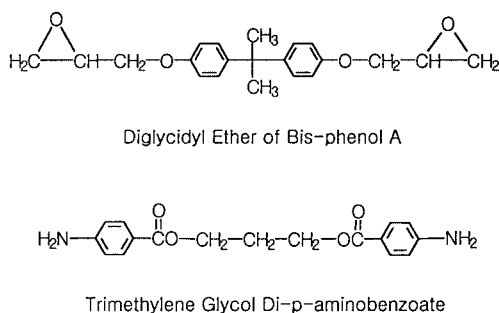


Figure 2 Chemical structures of the reactants.

mixture of reactants (no solvent), was prepared in the pendulum so as to provide a T_g of just above 70°C by temperature cycling (i.e., $30 \rightarrow -30 \rightarrow 140 \rightarrow 30 \rightarrow 140 \rightarrow 30 \rightarrow 140 \rightarrow 30^\circ\text{C}$). [T_g of the uncured specimen (measured during the first down-temperature scan from 30 to -30°C) was $T_{g0} = 0^\circ\text{C}$.] After the precure cycle, T_g was 72°C (measured during the last down-temperature scan from 140 to 30°C). [The precure was necessary because the moduli of the ungelled material ($_{\text{gel}}T_g \cong 70^\circ\text{C}^4$) may change as a consequence of microcracking during temperature scans and during isothermal physical ageing.⁴ Note that the glass-transition temperature of the material at its gel composition is $_{\text{gel}}T_g \cong 70^\circ\text{C}$.⁴]

The precured specimen then followed a temperature-time sequence shown in Figure 3. The specimen was first heated to a temperature (T_{max}) above $T_{g'}$, cooled to below a new T_g to an ageing temperature (T_a), and isothermally aged at T_a for a prespecified ageing time ($t_a = 600$ min) to provide an isothermal

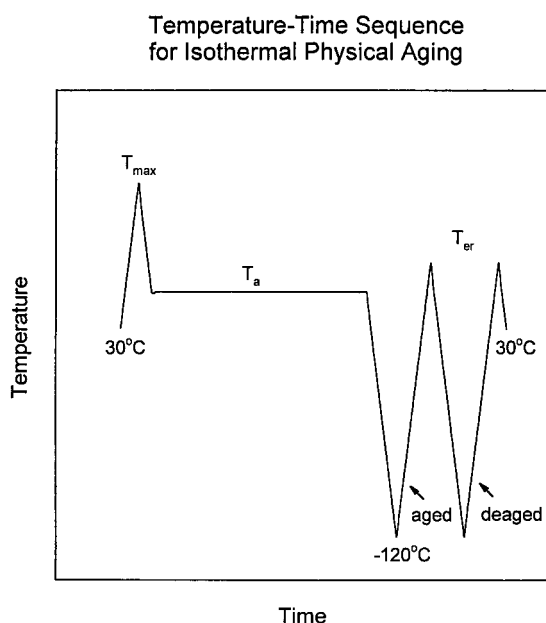


Figure 3 Temperature-time sequence for isothermal physical ageing experiments. [See text for definitions.]

TABLE I
Conversions (Measured by T_g) and Aging Temperatures (T_a) for All Seven Specimens

$T_{g,\text{pre}} (^\circ\text{C})$			$T_a (^\circ\text{C})$			
76	10	30	—	—	—	—
91	10	30	50	—	—	—
99	10	30	50	70	—	—
110	10	30	50	70	—	—
123	10	30	50	70	90	—
137	10	30	50	70	90	110
150	10	30	50	70	90	110
160	10	30	50	70	90	110
167	10	30	50	70	90	110
177	10	30	50	70	90	110

ageing rate at T_a for a particular value of T_g . Immediately after the isothermal physical ageing, two sequential up-temperature scans were compared from -120°C to an “erasure” temperature (T_{er}) less than T_g : the first up-scan included the isothermal ageing effect (“aged”) and the second was used as the baseline (“deaged”). The difference between the two temperature scans revealed the effect of the isothermal ageing for the particular conversion (T_g). Note that the conversion was essentially unchanged by heating twice to below T_g (see later). As discussed next, isothermal ageing at the same T_a was investigated sequentially for different conversions (T_g) using the same specimen.

In the sequence (Fig. 3) for a particular value of the isothermal ageing temperature (T_a), there are temperatures that should be selected carefully: T_{max} , T_{er} , and T_a . Heating to T_{max} ($>T_g$) is to cure further to a desired level (i.e., higher conversion) as well as to eliminate the effects of all previous physical ageing histories. From a series of preliminary experiments, T_{max} was selected to be 40°C above the previously determined glass-transition temperature ($T_{g,\text{pre}}$). The T_g in the last down-temperature scan of the temperature cycling for precure ($T_g = 72^\circ\text{C}$) was used to determine T_{max} in the temperature-time sequence for a specimen with the lowest conversion ($T_g = 76^\circ\text{C}$). More generally, the T_g (measured during cooling from T_{max} to T_a in the sequence) was the level of conversion for isothermal ageing, and was used also to obtain the value of T_{er} (see below) and for determining the next value of T_{max} . [The specimen after heating to $T_{\text{max}} = 112^\circ\text{C}$ (i.e., 40°C above the first $T_{g,\text{pre}}$) had a glass-transition temperature (on cooling) of 76°C .] The levels of conversion obtained by this procedure were $T_{g,\text{pre}} = 76, 91, 99, 110, 123, 137, 150, 160,$ and 167°C (see Table I). The specimen was finally cured by heating at 220°C for 20 h for “full” conversion and then (all subsequent scans being limited to 200°C) the temperature-time sequence was followed again. The T_g of the fully cured specimens was $T_{g^\infty} = 177^\circ\text{C}$.

The erasure temperature (T_{er}) in the temperature-time sequence was chosen to be 15°C below the T_g value obtained on cooling from T_{max} to T_a in the temperature-time cycle so as to preclude chemical reaction during the subsequent scans to and from T_{er} . The first up-temperature scan to T_{er} was for aged and the second up-temperature scan was for deaged material. (The second up-temperature scan was used as the baseline because the isothermal ageing effect at T_a is removed by heating above T_a to T_{er} in the first up-scan.)

New specimens were used for the (seven) different isothermal ageing temperatures. For a particular value of T_a , there is a lower limit of conversion so as to prevent additional chemical reaction during isothermal ageing: in general, the upper temperature limit for isothermal physical ageing was adopted to be at least 30°C below the T_g value.

The ageing temperature range was from 10°C (below which the effect of small amounts of water may be involved; see later discussion) to 130°C (above which further reaction during isothermal ageing may occur for partially cured material); the conversion was systematically changed from above postgel ($T_g > \sim 70^\circ\text{C}$, below which microcracking occurs with change in temperature) to fully crosslinked ($T_g = 177^\circ\text{C}$). Table I contains all of the values of $T_{g,pre}$ and T_a .

All the $T_{g,up}$ (measured on heating to the next T_{max}) and $T_{g,down}$ values (measured on cooling from the previous T_{max}) were measured: $T_{g,up}$ is measured to be about 1 to 2.5°C higher than $T_{g,down}$. This is partly attributable to the difference in scanning mode (i.e., up- versus down-scan): at the heating rate of 2°C/min, $T_{g,up}$ is 0.9°C higher than $T_{g,down}$ for a fully cured epoxy specimen measured over 40 times and averaged.¹⁸ Therefore there may be slight reaction (up to 1.6°C increase in T_g) involved during the isothermal ageing and/or raising the temperature to T_{er} two times: this is presumed to occur on heating to T_{er} (see Figs. 5 and 6).

In principle, one single specimen could have been used for the total experiment; that is, for all conversions a range of T_a values would be investigated (before increasing conversion). However, problems arise because the deaged baseline would be complicated by incomplete removal of physical ageing effects for the different values of T_{er} (the residual ageing is greatest in the vicinity of T_{er} ¹⁷) and the limitations of the temperature programmer (currently to eight segments, which would result in extra ageing between sets of the eight segments).

RESULTS AND DISCUSSION

Isothermal physical ageing rates

The isothermal physical ageing process was characterized by measuring the rate of ageing, which changes

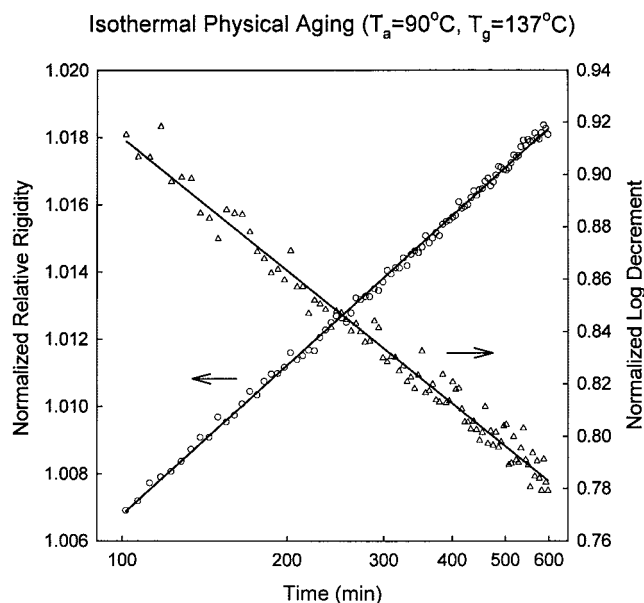


Figure 4 Normalized relative rigidity and logarithmic decrement versus log(aging time) at $T_a = 90^\circ\text{C}$, $T_g = 137^\circ\text{C}$.

linearly with $\log(\text{ageing time})$, from bulk volume contraction,¹⁹ magnitude of endothermic enthalpy peaks,²⁰ and shifts of creep relaxation response to longer times.²¹ Relative rigidity and logarithmic decrement from a TBA experiment during isothermal physical ageing are also reported to change linearly with $\log(\text{ageing time})$.^{8,10,11,13,18}

Figure 4 shows normalized relative rigidity and normalized logarithmic decrement ("log decrement") versus log time at an ageing temperature of 90°C for a partially cured specimen ($T_g = 137^\circ\text{C}$) in this work. Analysis of the relative rigidity data and logarithmic decrement (LD) data versus log time at different isothermal ageing temperatures shows that the relative rigidity increases and the LD decreases linearly with log time. Ageing rate (R_a), as defined below, was obtained from the increase of the normalized relative rigidity and the decrease of the normalized LD using the slopes of the linear regression lines (shown in the figure as solid lines):

$$R_a^{G'} = [d(G'/G_0)/d(\log t_a)]$$

$$R_a^{LD} = -[d(LD/LD_0)/d(\log t_a)] \quad (1)$$

In these equations, G_0 and LD_0 are the initial modulus and the initial logarithmic decrement [which were assigned as the first values after neglecting the initial 20 min of data during which the temperature stabilized; $t_a \equiv 0$ when the specimen first reached T_a on cooling]. The modulus (G') and logarithmic decrement (LD) at time t at T_a were normalized by the corresponding initial values at T_a . Note that data are presented from 100 min of ageing time (where linearity

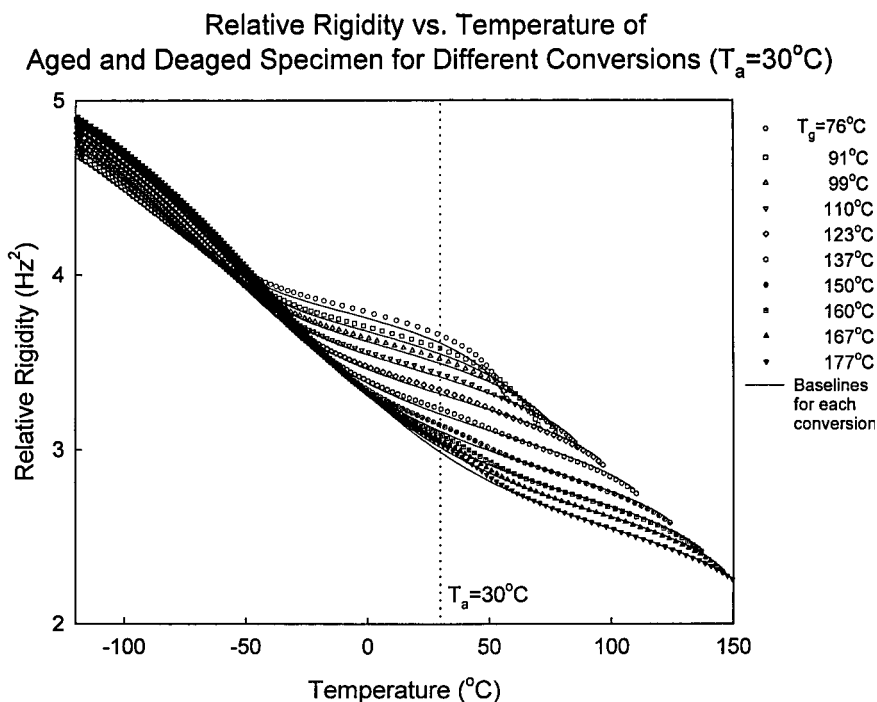


Figure 5 Relative rigidity versus temperature of aged (symbols) and deaged (solid curves) specimens for different conversions ($T_a = 30^\circ\text{C}$).

holds). [It is noted that the rates of ageing as defined in eq. (1) are not true rates.]

Thermomechanical spectra of aged and deaged specimens for different conversions ($T_a = 30^\circ\text{C}$)

The effect of isothermal physical ageing on the subsequent thermomechanical properties (i.e., modulus and mechanical loss versus temperature) has been reported for different polymeric materials, illustrating the localized perturbation in the vicinity of ageing temperature on the modulus and loss spectra.^{10,11,13,18}

Figure 5 displays relative rigidity versus temperature of a specimen aged at $T_a = 30^\circ\text{C}$ and $t_a = 600$ min for different conversions (as measured by T_g varying from 76 to 177°C): also shown for each set of data is the corresponding relative rigidity versus temperature data after deageing. Comparison of aged (symbols) and deaged (baseline: solid curves) behavior was made for each conversion. All thermomechanical spectra after ageing show a perturbation mainly in the vicinity of the ageing temperature.

Note also that the modulus of the unaged specimen (i.e., deaged, or baseline) at a temperature changes differently in different temperature ranges with increase of conversion (see Fig. 5). The unaged isothermal modulus increases with increasing conversion below about -70°C , whereas the unaged isothermal modulus decreases with conversion above about 0°C . A transition in behavior exists between -70 and 0°C . The isothermal modulus versus conversion was inves-

tigated throughout a wide range of temperatures below T_g .^{2,3} The transition in behavior has been associated with the rise in the T_β relaxation with increased conversion.²

Figure 6 shows the logarithmic decrement versus temperature corresponding to the elastic modulus data of Figure 5. *LD* curves of the unaged (i.e., deaged, or baseline) specimen show that the beta transition temperature (T_β) and the logarithmic decrement value at T_β increase with increasing conversion. Above T_β , the logarithmic decrement of the deaged specimen decreases and shows a minimum for each conversion. The temperature at the minimum of the logarithmic decrement (T_{\min}) and the logarithmic decrement value at T_{\min} increase with conversion. Note that T_{\min} is located below the ageing temperature ($T_a = 30^\circ\text{C}$) at low conversions but passes through T_a as conversion increases.

Ageing rate versus conversion (T_g) for different ageing temperatures (T_a)

There is a similarity between the two major relaxations (i.e., T_β and T_g) corresponding to the two loss maxima in the *LD* curve of the deaged specimen versus temperature, and two maxima in isothermal physical ageing rate versus temperature in a fully cured epoxy.¹⁸ However, one maximum in the isothermal ageing rate occurs at a higher temperature ($\sim 170^\circ\text{C}$), below but close to the glass-transition temperature ($T_g = 182^\circ\text{C}$), whereas the other occurs at a lower temperature

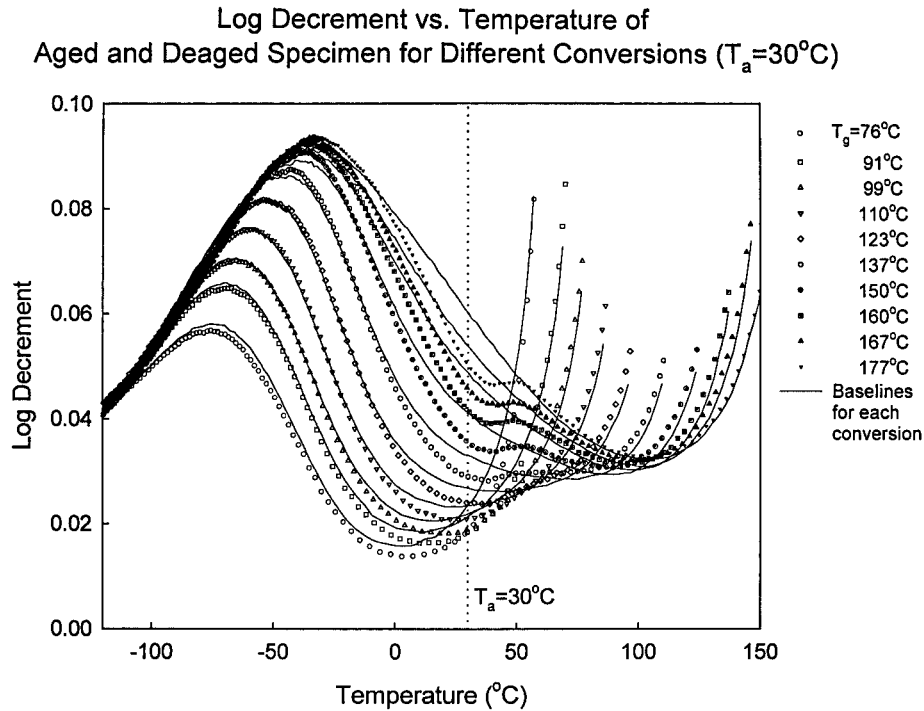


Figure 6 Logarithmic decrement versus temperature of aged (symbols) and deaged (solid curves) specimens for different conversions ($T_a = 30^\circ\text{C}$).

($\sim 40^\circ\text{C}$), which is much higher than the secondary glassy-state transition temperature ($T_\beta = -50^\circ\text{C}$). Understanding the relationship between ageing rate and the relaxational transitions is explained elsewhere in terms of (sub)molecular motions.^{17,18}

Figure 7(a) shows the ageing rate ($R_a^{G'}$) from mod-

ulus versus log time data for different conversions (T_g) for specimens aged at $T_a = 10, 30, 50, 70, 90, 110,$ and 130°C . At $T_a = 10, 30, 50, 70,$ and 90°C , the ageing rate initially decreases and then increases with increasing conversion. The minimum in ageing rate shifts to higher conversions with increasing ageing tempera-

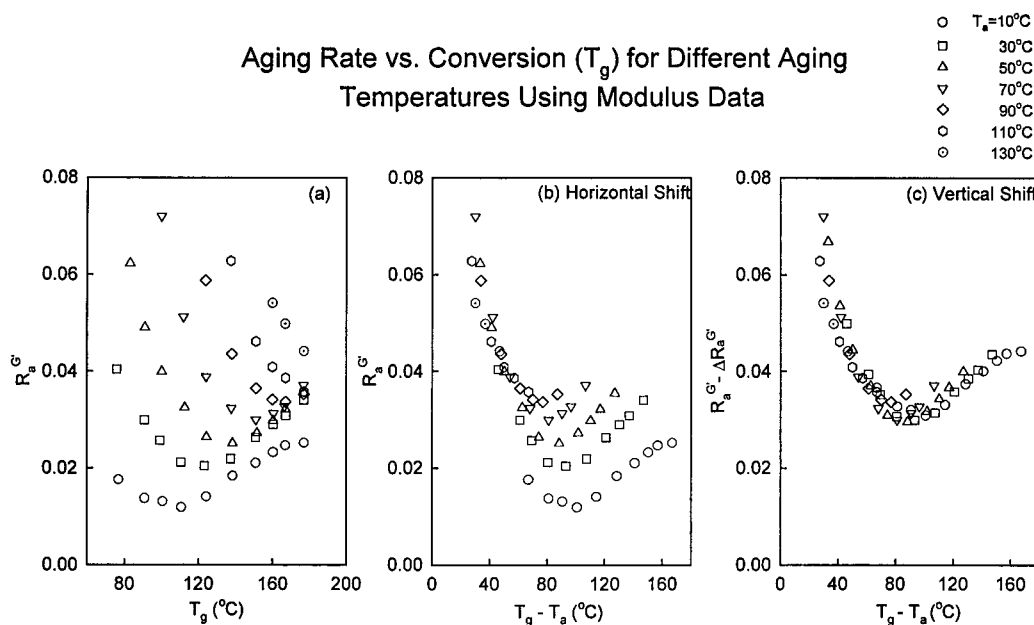


Figure 7 Ageing rate versus conversion (T_g) for different ageing temperatures using modulus data: (a) $R_a^{G'}$ versus conversion (T_g) for different ageing temperatures; (b) $R_a^{G'}$ versus $(T_g - T_a)$ [horizontal shift]; (c) $(R_a^{G'} - \Delta R_a^{G'})$ versus $(T_g - T_a)$ [horizontal + vertical shift].

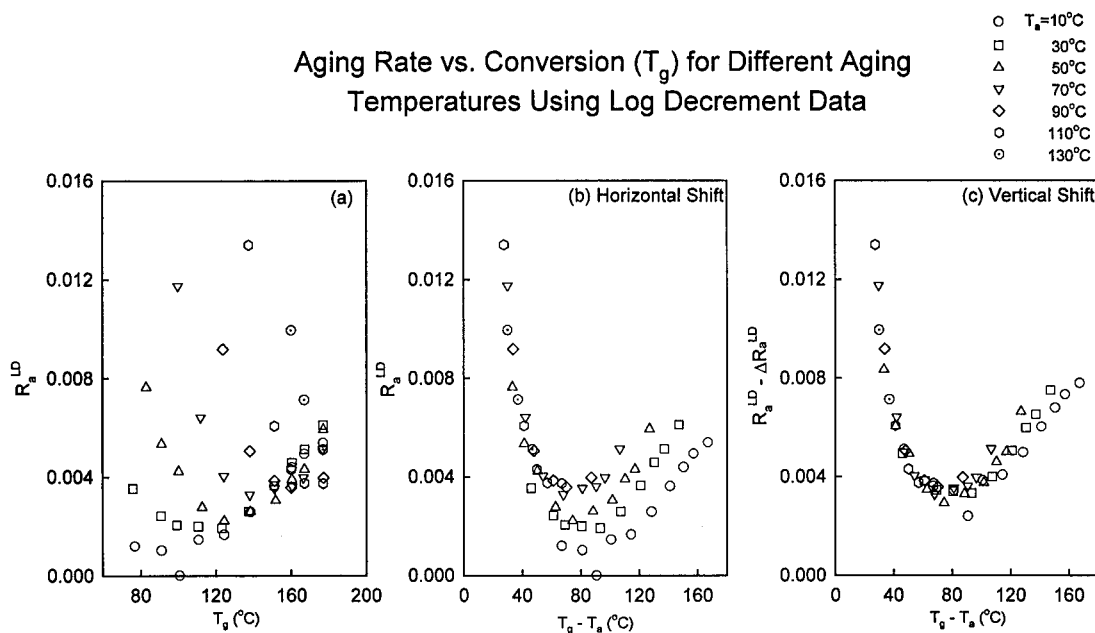


Figure 8 Ageing rate versus conversion (T_g) for different ageing temperatures using log decrement data: (a) R_a^{LD} versus conversion (T_g) for different ageing temperatures; (b) R_a^{LD} versus ($T_g - T_a$) [horizontal shift]; (c) ($R_a^{LD} - \Delta R_a^{LD}$) versus ($T_g - T_a$) [horizontal + vertical shift].

ture. However, the ageing rate simply decreases with increase of conversion for $T_a = 110$ and 130°C .

The ageing rate from the modulus data in Figure 7(a) was replotted by shifting horizontally, and the result is shown in Figure 7(b) as the ageing rate versus $T_g - T_a$ for specimens aged at $T_a = 10, 30, 50, 70, 90, 110,$ and 130°C . $T_g - T_a$ is a measure of the departure from the equilibrium rubbery state to the nonequilibrium glassy state. As a result of the horizontal shifting, the ageing rate data seem to fall on a single curve at higher ageing temperatures, that is, $T_a = 70, 90, 110,$ and 130°C (where $T_g - T_a < 50^\circ\text{C}$), but not at lower ageing temperatures, that is, $T_a = 10, 30,$ and 50°C . For greater differences in $T_g - T_a$ (i.e., $T_g - T_a > 50^\circ\text{C}$), the level of the ageing rate decreases as the ageing temperature decreases. Lowering of the ageing rate at $T_a = 10, 30,$ and 50°C after the horizontal shift may be attributed to the absorption of adventitious water during the isothermal physical ageing (which is discussed later).

Figure 7(c) shows the ageing rate versus $T_g - T_a$ data but with data for $T_a = 10, 30,$ and 50°C shifted up by the amounts of a vertical shift value (ΔR_a^{LD}) = 0.019, 0.0095, and 0.0045, respectively. $T_g - T_a$ data for all ageing temperatures for the entire conversion range tested in this experiment then form a single curve after the vertical shift for the three sets of data. The single curve obtained after the additional vertical shift implies that the fundamental mechanism of the physical ageing process is independent of conversion (i.e., change of chemical structure) but is affected by another factor for high values of $T_g - T_a$.

It seems that the change in crosslinking density from that of initially gelled material ($g_{\text{gel}}T_g \cong 70^\circ\text{C}$) to full cure ($T_{g\infty} = 177^\circ\text{C}$) is not sufficient to affect the mechanism of physical ageing in the glassy state.

Figure 8 displays corresponding plots of ageing rate data obtained from logarithmic decrement data versus conversion. All trends on ageing rate are similar to those in Figure 7. Figure 8(a) displays ageing rate (from logarithmic decrement) versus conversion (T_g) for specimens aged at $T_a = 10, 30, 50, 70, 90, 110,$ and 130°C . Note that the minimum in ageing rate also shifts to higher conversions with increasing ageing temperature. The horizontally shifted data of Figure 8(b), ageing rate versus $T_g - T_a$ for specimens aged at $T_a = 10, 30, 50, 70, 90, 110,$ and 130°C , shows that the ageing rate data fall on a single curve at $T_a = 70, 90, 110,$ and 130°C but fall below the curve at lower ageing temperatures of $T_a = 10, 30,$ and 50°C . After the vertical upward shift of the lowered data of Figure 8(b), a single curve was obtained for all ageing temperatures and the entire conversion range, as shown in Figure 8(c). The amounts of a shift value (ΔR_{azbeLD}) were 0.0024, 0.0014, and 0.0007 for $T_a = 10, 30,$ and 50°C , respectively.

Absorption of water

The localized perturbation in the modulus versus temperature behavior attributed to the isothermal physical ageing for different conversions in Figure 5 can be more clearly illustrated by the modulus difference between that of the aged and deaged specimen versus

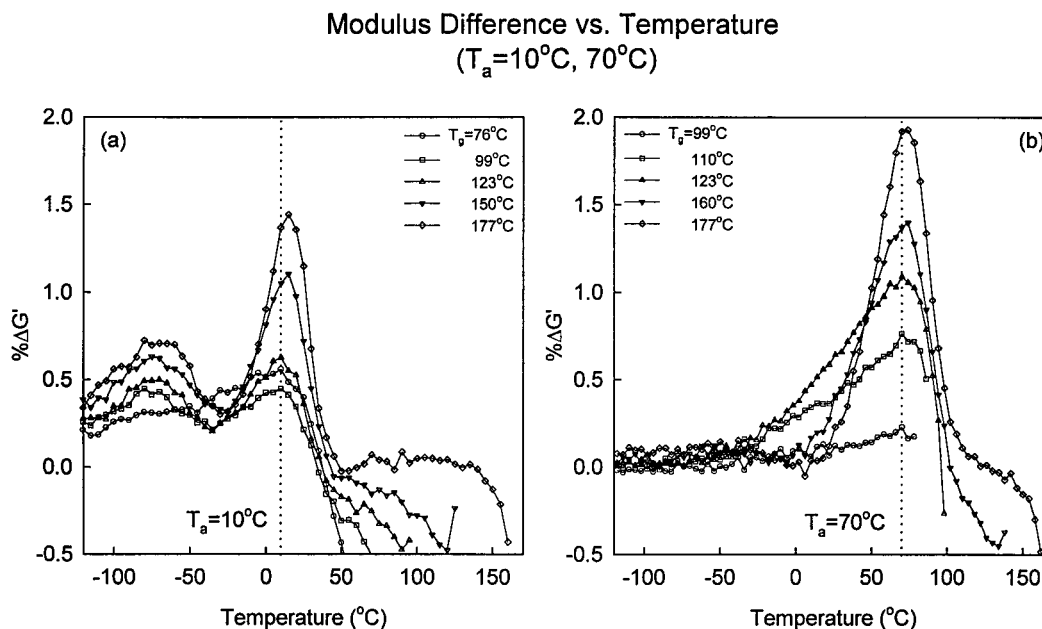


Figure 9 Modulus difference between aged and deaged specimens versus temperature: (a) $T_a = 10^\circ\text{C}$; (b) $T_a = 70^\circ\text{C}$.

temperature. The modulus difference at a particular ageing temperature is calculated by

$$\% \Delta G' = \frac{G_{\text{aged}} - G_{\text{deaged}}}{G_{\text{deaged}}} \times 100 \quad (2)$$

where G_{aged} and G_{deaged} are the moduli of the aged and the deaged specimen at the same temperature, respectively. Figure 9 shows the modulus difference ($\% \Delta G'$) between the aged and deaged specimens versus temperature of specimens aged at $T_a = 10$ and 70°C for 600 min for various conversions (T_g).

A localized perturbation attributed to the isothermal ageing is apparent in the vicinity of each ageing temperature for $T_a = 10$ and 70°C . The magnitude of the perturbation at $T_a = 10^\circ\text{C}$ decreased and then increased with increase of T_g as in the ageing rate versus T_g (see Fig. 7). However, variation of the peak magnitude does not match with ageing rate versus T_g at $T_a = 70^\circ\text{C}$ for low conversions ($T_{g,\text{pre}} = 99, 110, 123^\circ\text{C}$). This is because $T_a (=70^\circ\text{C})$ and $T_{\text{er}} (=T_{g,\text{pre}} - 15^\circ\text{C})$ were too close for the ageing effect to be removed effectively for the low conversions. [It is also noted that the density at T_a can decrease with increasing conversion (T_g)⁵⁻⁷ and therefore, on that basis because of the increased free volume, the physical ageing rate could increase with increasing T_g .]

Another perturbation peak is apparent in the vicinity of -70°C only for the specimen aged at $T_a = 10^\circ\text{C}$. Perturbation peaks in the vicinity of -70°C with lower intensities were also observed for ageing temperatures of $T_a = 30$ and 50°C (not shown). However, a perturbation peak at -70°C was not apparent for $T_a = 70^\circ\text{C}$.

This phenomenon has been observed for the fully cured epoxy/amine system¹⁸ and other systems^{22,23} and is considered to be attributable to adventitious water that is absorbed during isothermal ageing at the ageing temperatures. [For a fixed ppm $\text{H}_2\text{O}/\text{atm}$ above 0°C , the relative humidity will increase with decreasing temperature; therefore for a fixed time more water may be absorbed at lower temperatures.] The present results indicate that water is absorbed below the ageing temperature of 70°C during isothermal physical ageing and lowers the apparent ageing rate at temperatures less than about 70°C (i.e., see data for ageing rate at 10, 30, and 50°C in Figs. 7 and 8). It has been reported that absorbed water molecules form strong polar interactions with network chain segments,²⁴⁻²⁶ the segmental mobility of which may be thereby reduced during the physical ageing. That the peak intensity at -70°C increases with conversion may be attributed to the increase of hydroxyl groups in the molecular network as the cure proceeds.

Ageing rate versus ageing temperature (T_a) for different conversions (T_g)

Figure 10(a) displays the ageing rate ($R_a^{G'}$) versus T_a for different conversions (T_g) in the temperature range of 10 to 130°C [obtained from crossplotting interpolated ageing rate versus T_g data in Fig. 7(a) at every 10°C increment of T_g starting from 80 to 170°C , and including data for $T_{g,\infty} = 177^\circ\text{C}$]. The ageing rate ($R_a^{G'}$) versus T_a passes through a weak broad maximum (or shoulder) for higher values of T_g before increasing. For low values of T_g only the increase is observed.

Ageing Rate from Modulus vs. T_a for Different Conversions (T_g)

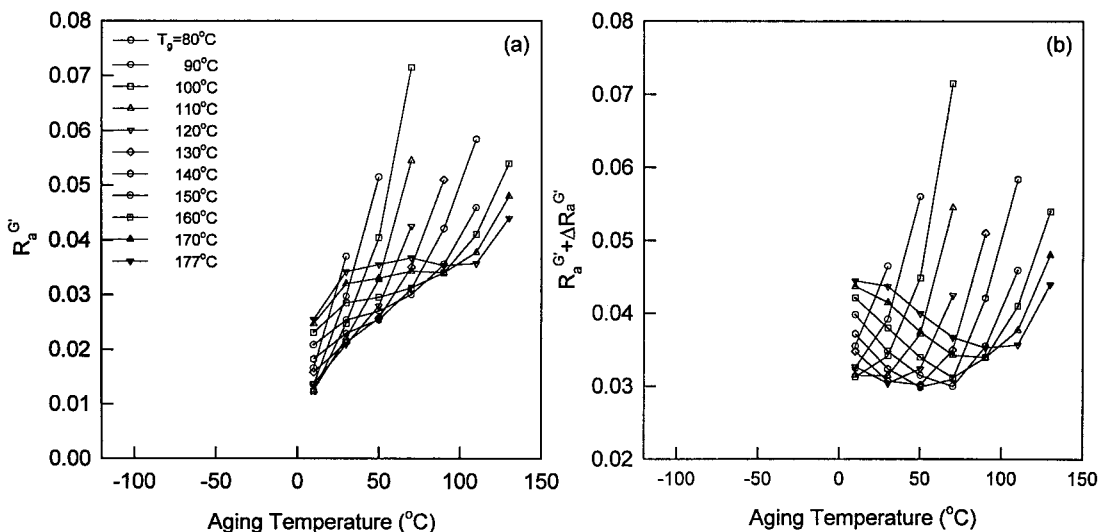


Figure 10 Ageing rate from modulus versus T_a for different conversions (T_g): (a) before vertical shift, (b) after vertical shift.

In Figure 10(b), data in Figure 10(a) are replotted after taking into account the vertical shift values for specimens at $T_a = 10, 30,$ and 50°C [see Fig. 7(c)]. Because the ageing rate is considered to decrease as a consequence of water absorption at $T_a = 10, 30,$ and 50°C , this plot shows the ageing rate versus ageing temperature in which the effect of water has been eliminated by the vertical shift. The shape of the curves for each conversion is similar to LD curves of unaged specimens (see Fig. 6) in the same temperature

range (i.e., from 10 to 130°C). This provides support that the ageing rate is closely related to the mechanical loss.

Examination of the ageing rate data from LD versus T_a for different conversions (T_g) using the above procedure for modulus data leads to the same results as obtained using modulus data.

Figure 11(a) and (b) show ageing rate (R_a^{LD}) from LD versus T_a for different conversions (T_g) in the temperature range of 10 to 130°C before and after the vertical

Ageing Rate from Log Decrement vs. T_a for Different Conversions (T_g)

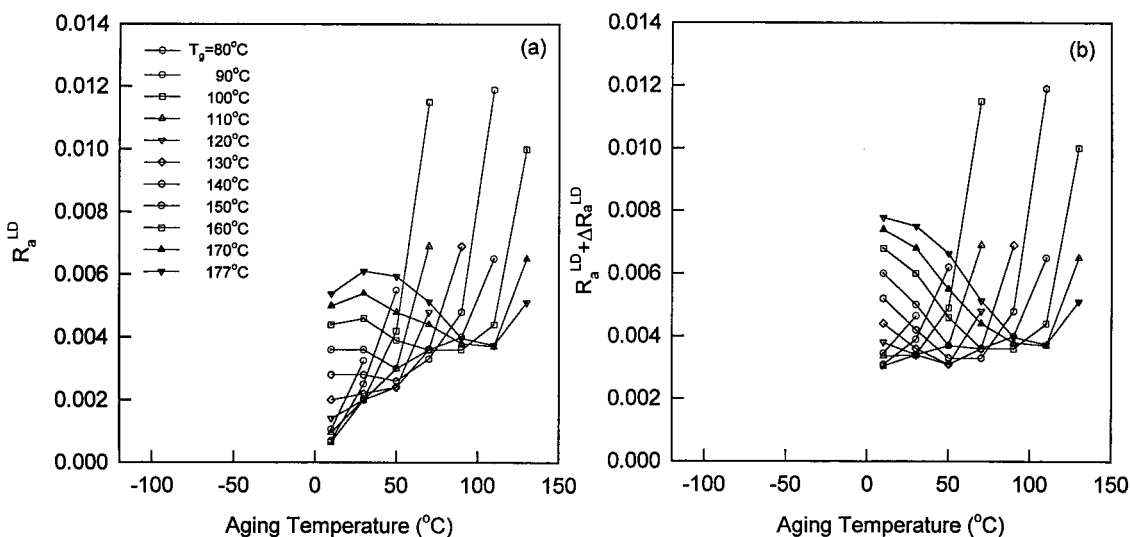


Figure 11 Ageing rate from logarithmic decrement versus T_a for different conversions (T_g): (a) before vertical shift, (b) after vertical shift.

shifts, respectively. R_a^{LD} increases at lower conversions with increase of ageing temperature but at the highest conversions shows a maximum. The maximum temperature for the fully cured specimen ($T_g = 177^\circ\text{C}$) occurs from 30 to 40°C in the plot of Figure 11(a). After the vertical shifts for $T_a = 10, 30,$ and 50°C , the shape of the curves in Figure 11(b) is again very similar to LD curves of deaged specimens (see Fig. 6) in the same temperature range (i.e., from 10 to 130°C). It seems, by extrapolation, that the maximum in the rate of ageing appears to be below 0°C for all conversions.

Control mechanism for physical ageing

It is well known that the rate of physical ageing depends on segmental mobility, which decreases as ageing proceeds.²⁷ As discussed earlier, the effect versus temperature of isothermal physical ageing is localized to a temperature range in the vicinity of ageing temperature, which implies^{17,18} that localized and specific submolecular motion is involved in the ageing process at a particular ageing temperature. In this present work, it has been shown that for a wide range of conversion the isothermal physical ageing rate is closely related to the logarithmic decrement value from the similarity between maxima in the ageing rate versus temperature, and the mechanical loss maxima of the transitions (relaxations) in the logarithmic decrement versus temperature.

Conversions (expressed by T_g) at the minimum in ageing rate at five ageing temperatures ($T_a = 10, 30, 50, 70,$ and 90°C) in Figures 7(a) and 8(a) were determined. Similarly, the temperatures at the minimum of log decrement versus temperature in Figure 6 between T_β and T_g were determined. Figure 12 displays temperatures at the minimum ageing rates for different conversions [$T_{g,\min}(R_a^{G'})$ from Fig. 7(a) and $T_{g,\min}(R_a^{LD})$ from Fig. 8(a)] marked as solid symbols, and temperatures at the minimum log decrement [$T_{\min}(LD)$] from the deaged data of Fig. 6] as open symbols versus conversion (T_g). Note that the change of the minimum ageing rate is close and similar to the change of the minimum in the logarithmic decrement (unaged) with conversion.⁸ This indicates that physical ageing is related to the segmental mobility, which in turn is related to the LD value. Therefore, the glass-transition relaxation controls physical ageing above $T_{\min}(LD)$ and the secondary beta transition relaxation controls physical ageing below $T_{\min}(LD)$. A comparison of isothermal ageing rate and logarithmic decrement (no ageing) versus temperature for a fully cured specimen was previously discussed.¹⁸

From the experimental results on the change of physical ageing rate with respect to T_g (rather than conversion) at different ageing temperatures in this material, the physical ageing process is considered to be a function of the departure from the equilibrium

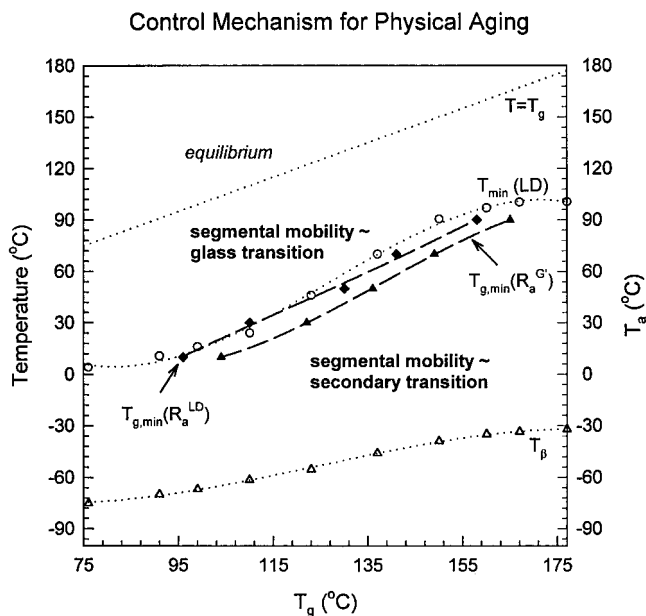


Figure 12 Control mechanism for physical ageing. [See text for definitions of $T_{\min}(LD)$, $T_{g,\min}(R_a^{LD})$, and $T_{g,\min}(R_a^{G'})$].

state ($T_g - T_a$) and of the ageing temperature (T_a).⁸ A relationship between the physical ageing rate, segmental mobility, and cohesive energy density has been derived on the basis of the Kohlrausch–Williams–Watts (KWW) equation,^{28,29} as shown in the following equation⁸:

$$R_a^{G'} = R^{G'}(T_g - T_a) + R^{G'}(T_a) = 2.303[\mu(2/\pi^2)(LD) + \phi] \quad (3)$$

where μ and ϕ are the sensitivity of the segmental mobility and the cohesive energy density to the physical ageing time, respectively, and LD is a logarithmic decrement value. In eq. (3), $R^{G'}(T_g - T_a)$ is a function of μ and LD , and $R^{G'}(T_a)$ is a function of ϕ . The procedure used in Figure 7 showed that vertical shifts were necessary for ageing rate versus $T_g - T_a$ data obtained after shifting horizontally to be on a single curve for all ageing temperatures. The vertical shift implies that the ageing rate is affected by the cohesive energy density. According to the results in this report, the change of the cohesive energy density is attributed to the water absorbed during isothermal physical ageing. The ageing rate was reduced by the presence of water. Thus the effect of water can be eliminated from the ageing rate by considering the amount of vertical shift (shift value). If there is no water, then the ageing rate should form a single curve after a horizontal shift. In other words, the ageing process is primarily governed by the term $R^{G'}(T_g - T_a)$ or the segmental mobility; that is, the transition loss peaks in the glassy state will influence the physical ageing rate. Similarity in shapes of the curves in Figures 10(b) and 11(b) and

those in Figure 6 in the temperature range tested confirms the dependency of the ageing process on the loss peaks.

CONCLUSIONS

As an example of the evolution of properties with increasing cure, isothermal physical ageing and its effects have been studied at different temperatures (i.e., $10 \leq T_a \leq 130^\circ\text{C}$) and at different chemical conversions (i.e., $70 < T_g \leq 177^\circ\text{C}$) for an epoxy/aromatic amine system ($T_{g\infty} = 177^\circ\text{C}$). The ageing temperature was from 10°C (below which the effect of small amounts of adventitious water may be involved) to 130°C (above which further cure reactions may occur during the isothermal ageing of incompletely cured material).

The rate of the isothermal physical ageing versus conversion (i.e., T_g) at a given ageing temperature passes through a minimum.

The ageing rate versus conversion (i.e., T_g) data fall on a single curve after shifting horizontally and replotting the ageing rate versus $T_g - T_a$, except for lower ageing temperatures (i.e., $T_a = 10, 30,$ and 50°C) at which the ageing rate becomes lower. The ageing rate versus $T_g - T_a$ data could be superposed for all ageing temperatures tested by shifting the data at the lowest temperatures vertically. The superposition methodology indicates that the mechanism involved in the physical ageing process is identical regardless of the change of the chemical structure.

The modulus difference between aged (at T_a) and deaged specimens versus temperature showed a principal peak in the vicinity of T_a , attributed to the localized effects of isothermal physical ageing, which appeared for all ageing temperatures, and an additional peak at about -70°C after ageing below $T_a = 70^\circ\text{C}$. The additional peak is considered to be a consequence of the water adventitiously absorbed during ageing. The absorbed water was found to retard the ageing process presumably because water molecules interact with hydroxyl groups in the epoxy network.

Comparison of the ageing rate versus T_a and the logarithmic decrement versus temperature shows that there is a similarity between the ageing rate and logarithmic decrement. The minimum in the ageing rate is closely related to the minimum in logarithmic decrement between the glass transition (T_g) and the sec-

ondary glassy-state relaxation (T_β). The rate of ageing is correlated with the logarithmic decrement values of the two relaxations at T_a . Controlling mechanisms during physical ageing are segmental mobility associated with the T_g region and the more localized mobility associated with the glassy-state relaxation, T_β .

The research follows up the undergraduate thesis of Brock M. Harvey.⁹

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