

Physical Aging in the Glassy State of a Thermosetting System vs. Extent of Cure

XIAORONG WANG and JOHN K. GILLHAM*

Polymer Materials Program, Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08544-5263

SYNOPSIS

The physical aging behavior of a high- T_g amine/epoxy thermosetting system has been investigated vs. change of chemical structure induced by cure and vs. aging temperature (T_a) using the Torsional Braid Analysis (TBA) technique. The chemical structure was changed systematically from monomer to highly crosslinked polymer by curing in the equilibrium state ($T > T_g$). The aging temperatures ranged from just below the glass transition temperature to deep in the glassy state ($T_a < T_g$). In the absence of chemical reaction, the physical aging rate at a given temperature, T_a , passes through a minimum with increasing chemical conversion (i.e., change of chemical structure). Analysis of this behavior is simplified by using T_g as an index of measurement of extent of cure. There is a superposition principle for normalizing the physical aging behavior of the thermosetting glasses, which involves a shift of $T_g - T_a$ and a shift of $C(T_a)$ (a function of aging temperature), regardless of chemical structure. Analysis reveals that: (1) this behavior is the consequence of the T_g and T_β transitions, (2) the segmental mobility ($1/\tau$) is a function of the deviation from equilibrium (as measured by $T_g - T_a$ and the aging time), (3) the segmental mobility, which is involved in the physical aging process in the glassy state, is insensitive to the extreme changes of chemical structure (from monomer, to sol/gel polymer, and to highly crosslinked polymer), and (4) physical aging deep in the glassy state affects both segmental mobility and cohesive energy density. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

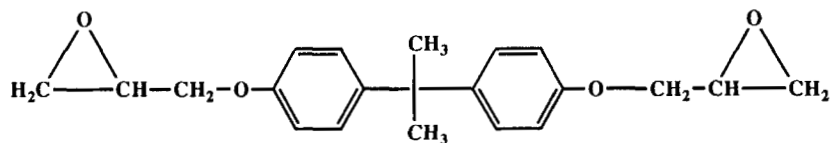
An amorphous glassy material can be regarded as a supercooled liquid with volume, enthalpy, and entropy greater than in the equilibrium state, which is a consequence of prior cooling through the glass transition region at a finite rate. The gradual approach to equilibrium of the material in the glassy state continuously affects material properties, and is termed physical aging. Early theoretical analysis of this phenomenon was in terms of free volume relaxation by using a modified Doolittle equation.¹⁻³ The Doolittle equation predicts that the relaxation time is totally determined by the structure parameter, that is, the free volume fraction. However, analysis of experimental results revealed that: (1)

submolecular mobility can be larger in densified glassy samples than in normal specimens,⁴⁻⁶ (2) submolecular mobility changes with temperature for iso-free volume specimens. In order to solve this paradox, some researchers considered that the physical aging process depends independently on both the structural variable and the temperature on the basis of a modified DiMarzio-Gibbs model⁷⁻⁹ or Tool equation.¹⁰⁻¹² However, there was insufficient experimental evidence for directly substantiating the proposition.

Experimental measuring probes used to monitor the physical aging process in polymeric materials, have included dilatometry, torsional creep, and tensile calorimetric, and dielectric properties.¹³⁻¹⁶ Recently, aging studies, using the dynamic mechanical freely oscillating torsional braid analysis (TBA) technique, have shown that it is a significant and sensitive method for monitoring the physical aging process over a wide temperature range.^{6,17-19} It is

* To whom correspondence should be addressed.

CHEMICAL REACTANTS



Diglycidyl Ether of Bis-phenol A

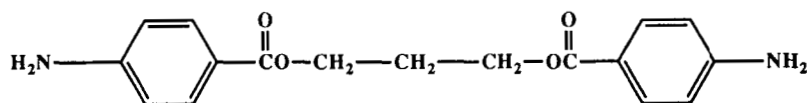
Trimethylene Glycol Di-*p*-aminobenzoate

Figure 1 Chemical structures of diglycidyl ether of bis-phenol A (DGEBA) and trimethylene glycol di-*p*-aminobenzoate (TMAB).

Physical Aging at 14°C vs. Time for Different Extents of Cure

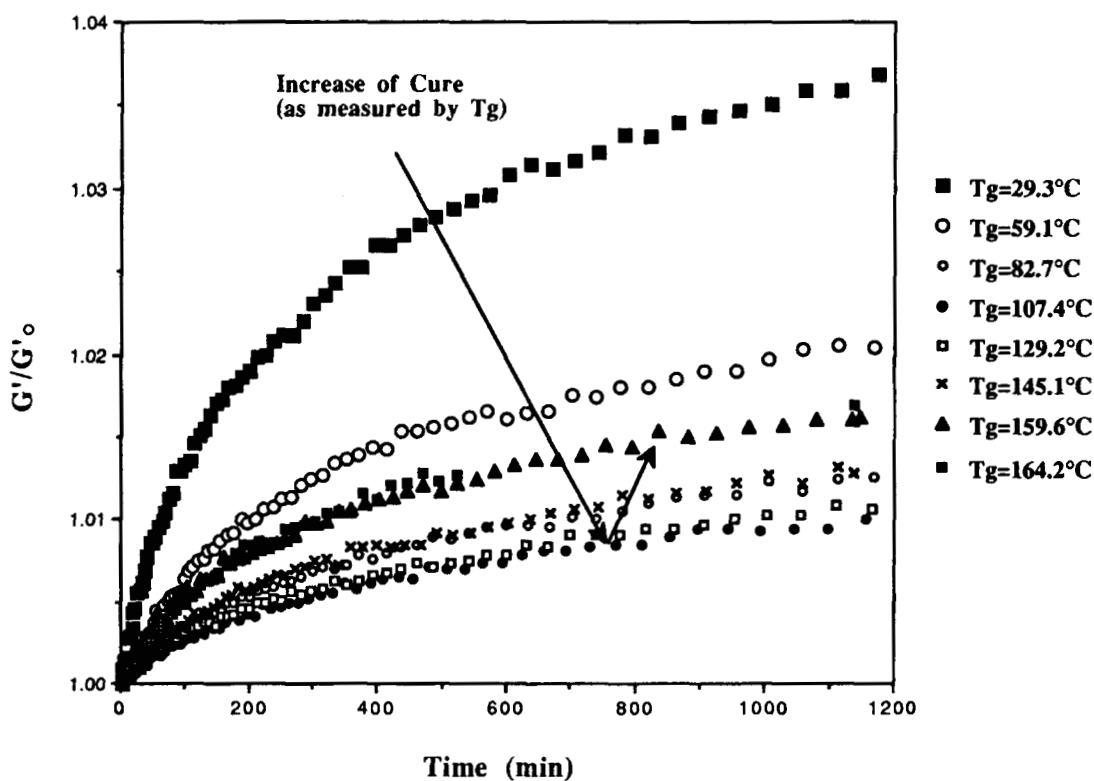


Figure 2 The modulus of the specimen increases with time during physical aging at a given aging temperature (i.e., $T_a = 14^\circ\text{C}$) for different of extents of cure (after cooling from above T_g at $5^\circ\text{C}/\text{min}$ to 14°C).

noteworthy that similar results have been obtained for both a composite TBA specimen and for a homogeneous film specimen.¹⁷

Experimental evidence has shown that the effect of isothermal physical aging deep in the glassy state is different from that near the glass transition region.^{6,17-20} Recent results in this laboratory show that isothermal physical aging changes the dynamic mechanical moduli vs. temperature of a given material only at temperatures localized about the aging temperature.¹⁷⁻¹⁹ The degree of localization deep in the glassy state is a function of the aging time and the subsequent heating rate.¹⁸ Results also show that the isothermal physical aging rate usually decreases^{18,19} as the aging temperature (T_a) decreases ($T_a < T_g$). In other reports, the isothermal aging process rate deep in the glassy state has been found to pass through a minimum with decreasing T_a .^{5,17} An interesting result is that the volume relaxation rate deep in the glassy state shows a local

maximum in the vicinity of the β -transition.⁵ However, some polymer materials that display β -transitions in their glassy states do not show this phenomenon.^{6,17-19}

During a curing reaction a thermosetting material is in the physical aging regime when the glass transition temperature, T_g , of the material increases beyond the curing temperature (i.e., after vitrification).²¹⁻²³ The densification rate during reaction in the glass transition region is more efficient than that after full cure.²² A material may develop its highest density by cure in the glass transition region below its glass transition temperature.²¹ Since the physical properties of the material gradually change after vitrification, due to both chemical reaction and physical aging, it is important to analyze the physical aging process (or segmental mobility) in the absence of chemical reactions. Earlier research work in this laboratory investigated the physical aging phenomena in fully cured epoxy and polyimide materials,¹⁷⁻¹⁹

Glass Transition Temperature vs. Conversion

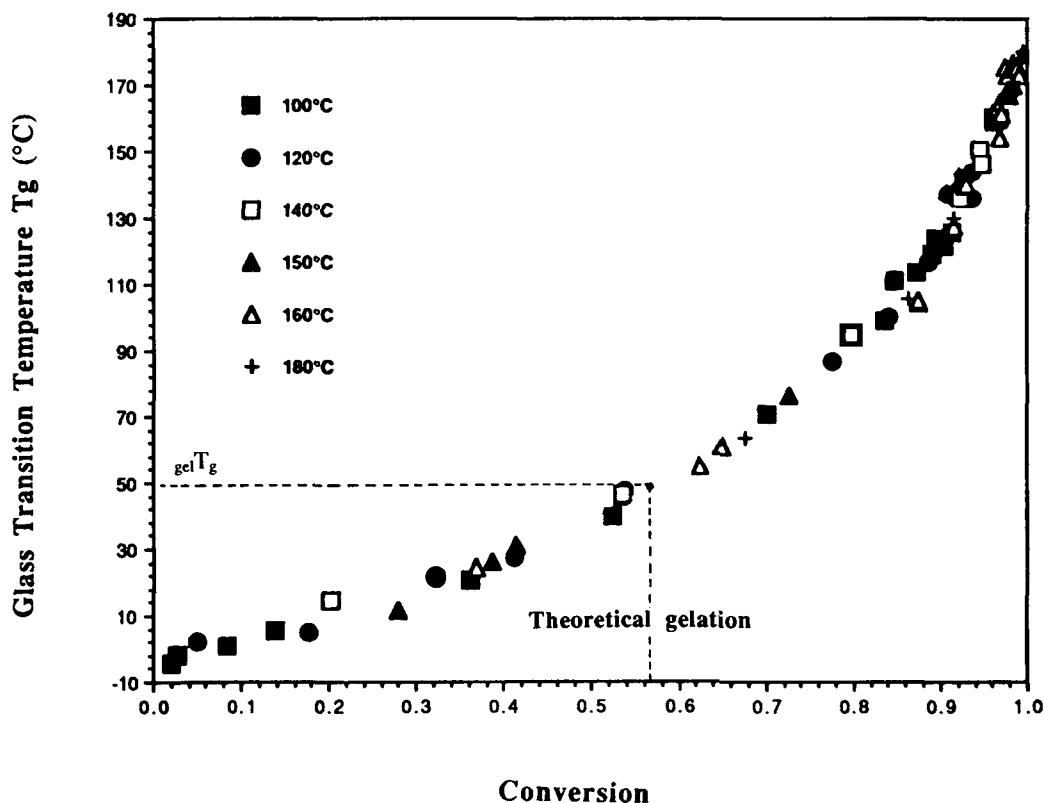


Figure 3 The unique relationship between T_g and conversion for a stoichiometrically equivalent DGEBA/TMAB system.²¹ The glass transition temperature of the initial mixture = 0°C; the glass transition temperature of the fully cured material = 180°C; the glass transition temperature at gelation \approx 50°C. The conversion at gelation is evaluated from Flory's theory.

and in an unreactive thermoplastic material, polymethylmethacrylate.²⁴

For the present communication, physical aging phenomena deep in the glassy state vs. change of chemical structure at different aging temperatures (T_a) were studied using a tetrafunctional aromatic diamine-cured difunctional epoxy system. The TBA technique was used to monitor the physical aging process. Effects of extreme changes in the chemical structure (from monomer, to sol/gel polymer, and to highly crosslinked polymer) on the physical aging process deep in the glassy state in the absence of chemical reaction are discussed. A further report will seek to combine physical aging with chemical reaction for understanding the diffusion controlled reaction in the glass transition region after vitrification. Another report will deal with the localization effect about the aging temperature vs. change of chemical structure (i.e., cure).

MATERIALS AND EXPERIMENTAL

Reactants

The chemical system used was a liquid difunctional epoxy (diglycidyl ether of bisphenol A, DER 332, Dow Chemical Corp., "DGEBA") with a tetrafunctional aromatic diamine (trimethylene glycol di-*p*-aminobenzoate, "TMAB", Polaroid Corp.) (Fig. 1). The epoxy monomer is a viscous liquid (at 25°C) with an epoxide equivalent weight (EEW) of 174 g/eq. The amine curing agent is a highly crystalline solid (melting point = 125°C) with an amine hydrogen equivalent weight of 78.5 g/eq. The chemicals were stoichiometrically mixed at 100°C for 15 min with vigorous stirring in order to dissolve the amine in the epoxy resin. Immediately after mixing, the warm liquid was degassed for 10 min in a vacuum oven held at room temperature. The resulting clear viscous liquid mixture was stored at -15°C. The

Physical Aging at 14°C vs. Log Time for Different Extents of Cure

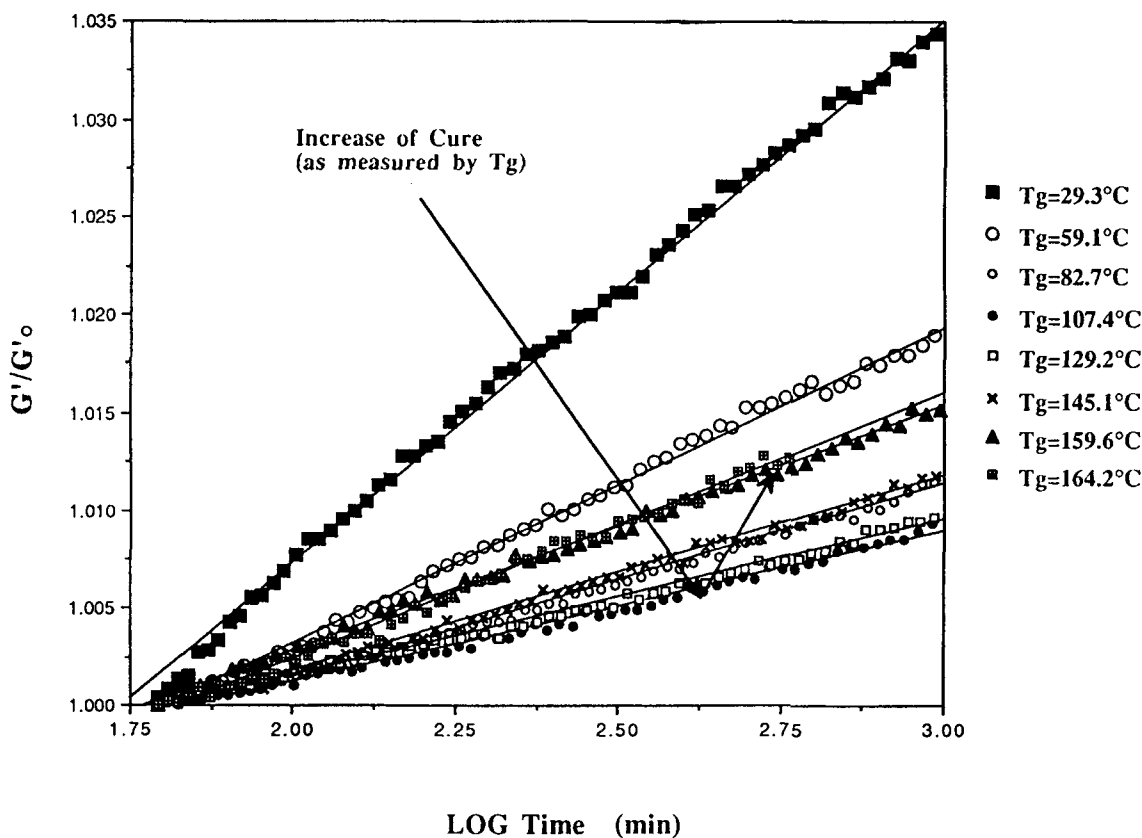


Figure 4 Physical aging at long times is linear with respect to log aging time for different extents of cure at $T_a = 14^\circ\text{C}$.

glass transition temperature of the initial mixture, $T_{g0} = 0^\circ\text{C}$; the glass transition temperature of the fully cured material, $T_{g\infty} = 180^\circ\text{C}$; the glass transition temperature of the undercured material at its theoretical gelation point, ${}_{\text{gel}}T_g \cong 50^\circ\text{C}$.²¹

Specimen Preparation

A typical TBA specimen was prepared by first dipping a heat-cleaned glass braid into the viscous reactive liquid at room temperature for 30 min; the impregnated glass braid was squeezed between aluminum foil to remove excess material and to insure good wetting of the glass filaments. The final amount of material on the substrate was approximately 15 mg. The specimen was mounted to form the TBA inner pendulum, which was inserted into the preheated chamber of the TBA instrument. All subsequent experiments were in an atmosphere of slowly flowing helium. Each of the four specimens was aged at one temperature for different extents of cure. Reviews of the TBA technique have been pub-

lished.²⁵ The frequency of the freely damped oscillations is from 1 to 2 Hz for glassy-state specimens, which corresponded to the temperature range investigated. The sensitivity of the technique is 0.01% of the property (i.e., modulus and mechanical damping) being measured (e.g., see Fig. 2). The automated TBA torsion pendulum system is available from Plastics Analysis Instruments, Inc., Princeton, NJ.

Experimental Procedure

A specimen was first heated to a temperature about 100°C higher than the initial glass transition temperature, T_{g0} , and was then quenched through the glass transition to the aging temperature ($T_a < T_g$, such as $T_a = T_g - 30^\circ\text{C}$, $T_g - 50^\circ\text{C}$, $T_g - 70^\circ\text{C} \dots$) at $5^\circ\text{C}/\text{min}$ cooling rate. Isothermal temperature (i.e., $T = T_a \pm 0.1^\circ\text{C}$) was obtained 30 min after reaching T_a . The specimen was then held at T_a for more than 1000 min to monitor the physical aging. After the isothermal aging, the specimen was heated

Physical Aging Rate at -15°C vs. Change of Chemical Structure

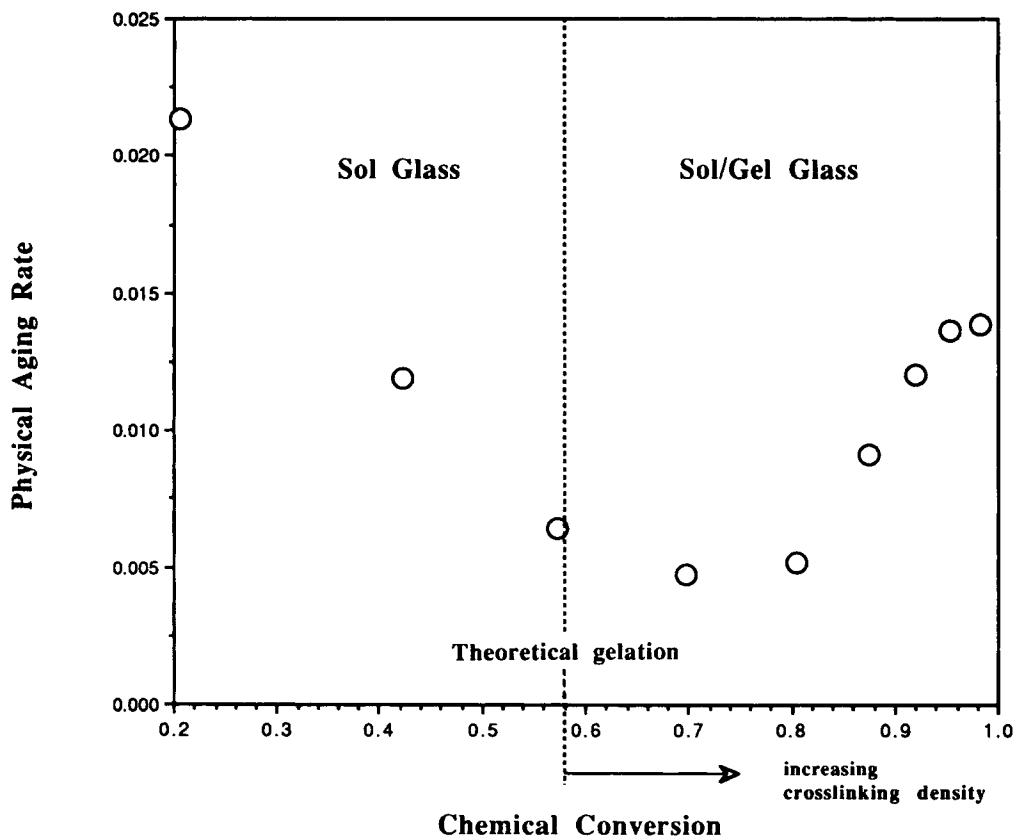


Figure 5 Physical aging rate at -15°C vs. change of chemical structure as measured by chemical conversion. The gelation line marks the change from sol glass to sol/gel glass.

at 1°C/min through the glass transition to about 50°C above T_g to eliminate the effects of physical aging prehistory, and also to allow further cure (i.e., higher conversion) in the equilibrium state. Dynamic mechanical measurements were taken throughout the time-temperature sequences (i.e., the repeated cooling, holding, and heating of the specimen). In particular, the preaged T_g values were obtained during cooling the specimen from the equilibrium state (i.e., $> T_g$) to the aging temperature (since physical aging below T_g can affect the value of T_g). This report analyzes the relationship between the physical aging rate at temperature T_a vs. T_g . The influence of isothermal aging on the subsequent modulus vs. temperature, and vs. conversion, will form the basis of a future report.

The preaged glass transition temperature, T_g , has been found to be a good index for monitoring the chemical conversion for this system.²¹ The fact that T_g increases nonlinearly with conversion in the

crosslinking system makes it more sensitive for monitoring the extent of cure at higher extents of reaction than chemical conversion (Fig. 3). It is noted, however, that a unique T_g does not necessarily imply a unique molecular structure, since T_g is an average property. The reported data of Figure 3 were obtained using the differential scanning calorimetry (DSC) technique.²¹ Both experimental and theoretical analyses²⁶ of this thermosetting system imply that the T_g vs. conversion relationship is unique, regardless of the time-temperature cure path. Consequently, in the experiments reported here, the preaged T_g has been chosen to monitor chemical conversion (it is designated T_g rather than "preaged T_g " hereafter). The experimental data of Figure 3 can be modeled by the DiBenedetto equation²⁷:

$$(T_g - T_{g0})/T_{g0} = [(E_x/E_m - F_x/F_m)\alpha] / [1 - (1 - F_x/F_m)\alpha] \quad (1)$$

Physical Aging Rate at Different T_a vs. Change of Chemical Structure

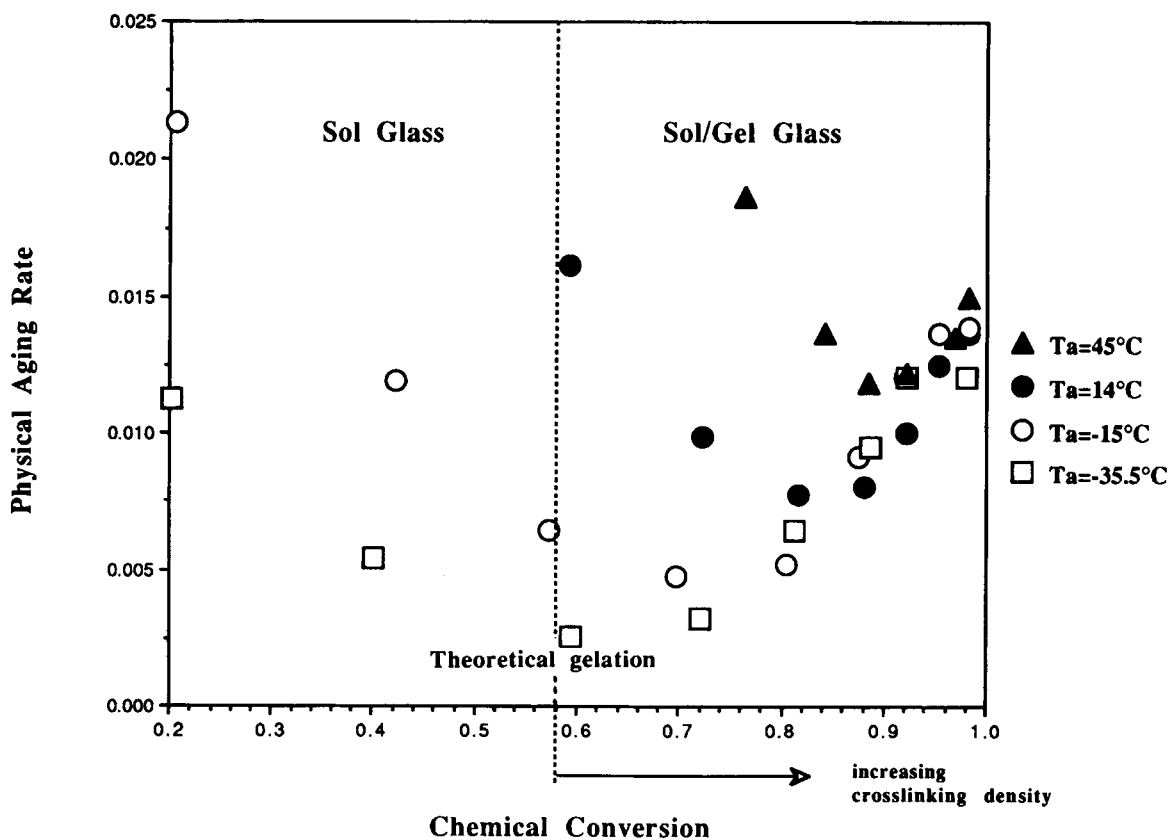


Figure 6 Physical aging rate vs. change of chemical structure as measured by chemical conversion for different aging temperatures (i.e., -35.5°C, -15°C, 14°C, and 45°C). The gelation line marks the change from sol glass to sol/gel glass.

where T_g is the glass transition temperature in K and α is the fractional chemical conversion. The best-fit value for the two ratios, E_x/E_m (the ratio of lattice energies for crosslinked and hypothetical uncrosslinked polymers) and F_x/F_m (the corresponding ratio of segmental mobilities), are determined to be 0.52 and 0.31, respectively.²¹ This equation provides a reasonable semiempirical relationship for relating T_g and conversion in the following text.

RESULTS AND DISCUSSION

The cure kinetics indicates that the rate of reaction is insignificant in the liquid material at 25°C and in the glassy state.²¹ Therefore, the material can be cured at a high temperature (i.e., $> 130^\circ\text{C} > T_g$) and be quenched to the aging temperature ($T_a < T_g$) to monitor the physical aging process in the virtual absence of chemical reaction. The modulus (G') of

the partially cured specimen, after cooling from above T_g at 5°C/min to a specific isothermal aging temperature (T_a), increases with aging time (t_a) at T_a , as presented in Figure 2. The increase of G' is related to the reduction in the volume of the epoxy material after the prior cooling has trapped excess volume in the glassy state. Many studies, including small strain creep, stress relaxation, enthalpy relaxation, volume relaxation, and dielectric relaxation experiments,¹³⁻¹⁶ have shown that physical aging at long times is linear with respect to log aging time. Figure 4 shows that the increase of the modulus of the undercured specimen deep in the glassy state is linear with the logarithm of t_a (after the initial period of about 60 min). The aging rate is defined as

$$R_a = [d(G'/G'_0)/d(\log t_a)] \quad (2)$$

where G'_0 is the modulus of the specimen at the beginning of the isothermal aging.

Physical Aging Rate vs. T_g for Different Aging Temperatures

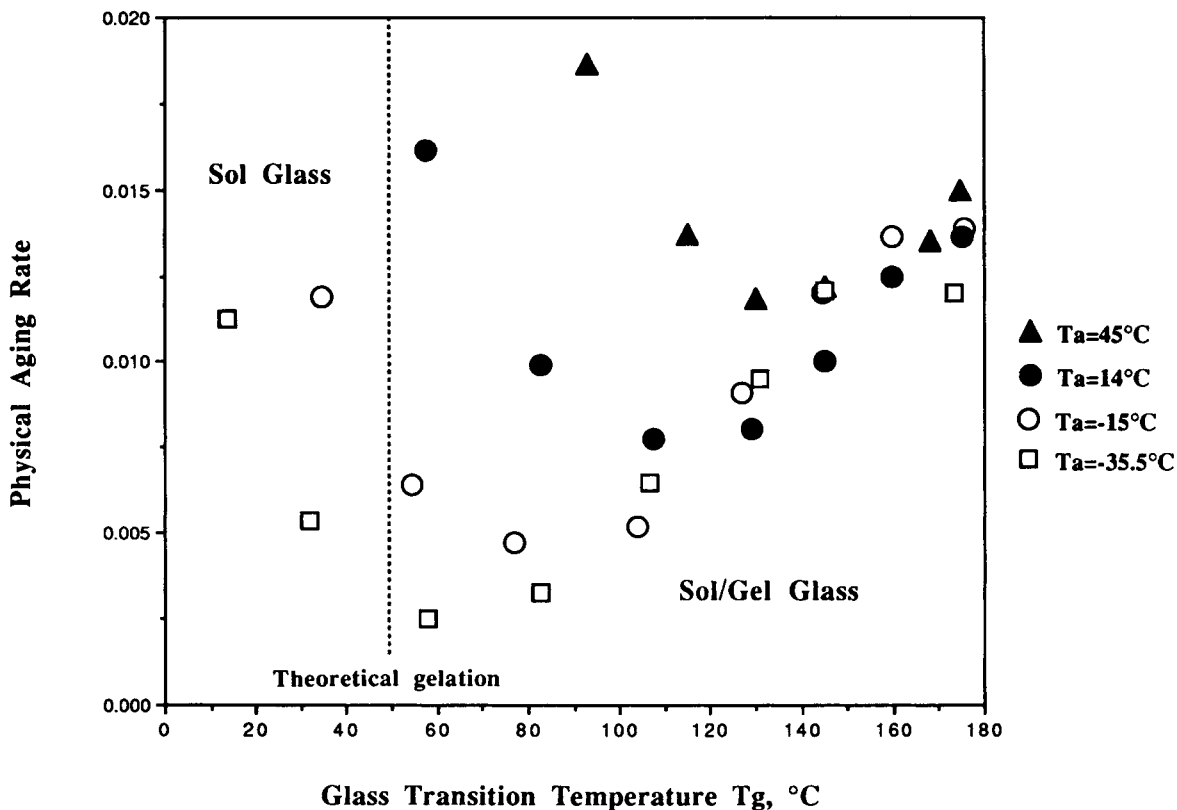


Figure 7 Physical aging rate vs. T_g at different aging temperatures. Experimental data of Figure 6 replotted using T_g as the X-axis. The glass transition temperature of the initial mixture = 0°C; the glass transition temperature of fully cured material = 180°C. The gelation line marks the change from sol glass to sol/gel glass.

The physical aging rate vs. fractional chemical conversion for a given aging temperature (T_a) is surprising; for example, at the temperature $T_a = -15^\circ\text{C}$ (Fig. 5), which is always in the glassy state, the physical aging rate decreases, reaching a minimum at the fractional conversion of epoxy = 0.72, then increases until the epoxy is fully cured. Similar results are obtained for different aging temperatures (Fig. 6). The aging temperature significantly affects the chemical conversion at the minimum and the radius of curvature of the concave-up curves. The higher the isothermal aging temperature, the higher the conversion and the lower the radius of curvature of the minimum for the aging rate vs. chemical conversion relationships.

The preaged glass transition temperature, T_g , has been found to be a good index for monitoring chemical conversion,^{21,26} since it is related to chemical conversion in a one-to-one manner (Fig. 3). Interestingly, when using T_g as the X-axis to replot the experimental data of Figure 6, the physical aging

rate, R_a , vs. T_g at different temperatures, T_a , show that the different curves have the same radius of curvature (Fig. 7). This characteristic indicates that T_g , rather than chemical conversion, is the principal parameter for understanding physical aging. The change of the curvature in presenting aging rate vs. T_g rather than vs. conversion arises from the non-linear one-to-one relationship of T_g and chemical conversion, for which the rate of change of T_g increases with increase of chemical conversion, especially at high chemical conversions. Note that the chemical structures at the minima are different (due to the different chemical conversions).

When using $T_g - T_a$ (a measurement of the departure from equilibrium) as the X-axis to replot the experimental data of Figure 7, the aging rate vs. $T_g - T_a$ data at different temperatures show (Fig. 8) the concave-up curves with the same radius of curvature and the same minimum at $T_g - T_a = ca. 100^\circ\text{C}$. As the distance from the equilibrium state increases, as measured by $T_g - T_a$, the physical aging rate ini-

Physical Aging Rate for Different Aging Temperatures vs. ($T_g - T_a$)

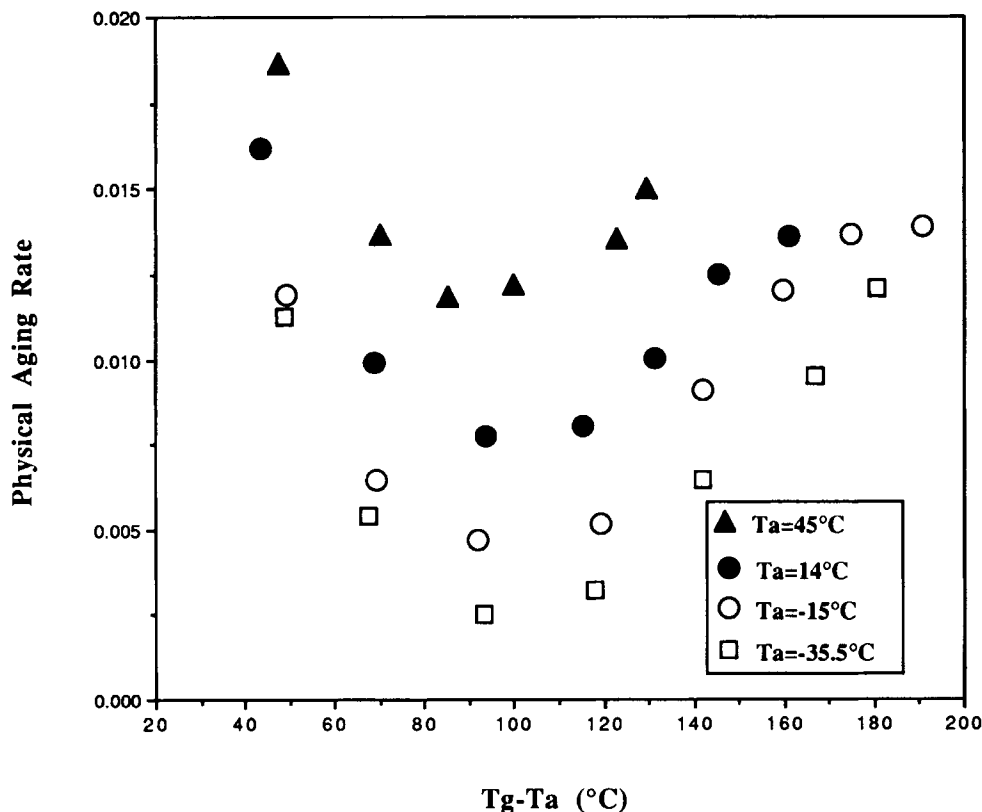


Figure 8 Physical aging rate vs. $T_g - T_a$ at different aging temperatures. Experimental data of Figure 7 replotted using $T_g - T_a$ as the X-axis. The glass transition temperature of the initial mixture = 0°C . The glass transition temperature of fully cured material = 180°C .

tially decreases, but then increases for $T_g - T_a > 100^\circ\text{C}$. Interestingly, all curves may then be simply shifted vertically together, as shown in Fig. 9. This double shift shows that physical aging is not affected by the change of chemical structure with increase of extent of cure (as measured by chemical conversion), i.e., from monomer to highly cross-linked polymer. The physical aging process of this material at a given temperature is governed mainly by the departure of the material from its equilibrium state (as measured by $T_g - T_a$) regardless of chemical structure. Furthermore, T_g is a better parameter than chemical conversion for understanding the physical aging properties of the material since the pattern of behavior is simplified by using T_g . Therefore, the physical aging rate of this material can be expressed using two terms:

$$R_a = F(T_g - T_a) + C(T_a) \quad (3)$$

$F(T_g - T_a)$ is a unique function of departure of the

material from the equilibrium state, as measured by $T_g - T_a$. $C(T_a)$ is only influenced by the aging temperature (T_a). The unique function $F(T_g - T_a)$ implies, for example, that the aging rate at a specific temperature T_a of a sample for different extents of cure (as measured by T_g) will be similar in form to the results for a sample with a given T_g , but at different aging temperatures (T_a).

The dynamic mechanical properties (i.e., modulus and mechanical damping) have been found to be sensitive parameters for monitoring the physical aging process through a wide range of temperature using the TBA technique.¹⁷⁻¹⁹ Considering that physical properties are related to one another, and using the linear viscoelastic theory, the physical aging rate as monitored by dynamic mechanical techniques, $R_a = d(G'/G'_0)/d\log(t_a)$, should be:

$$R_a \cong 2.303 [\mu(2/\pi)\tan\delta + \xi] \quad (4)$$

where μ is the sensitivity of the segmental mobility

Unique Physical Aging Behavior

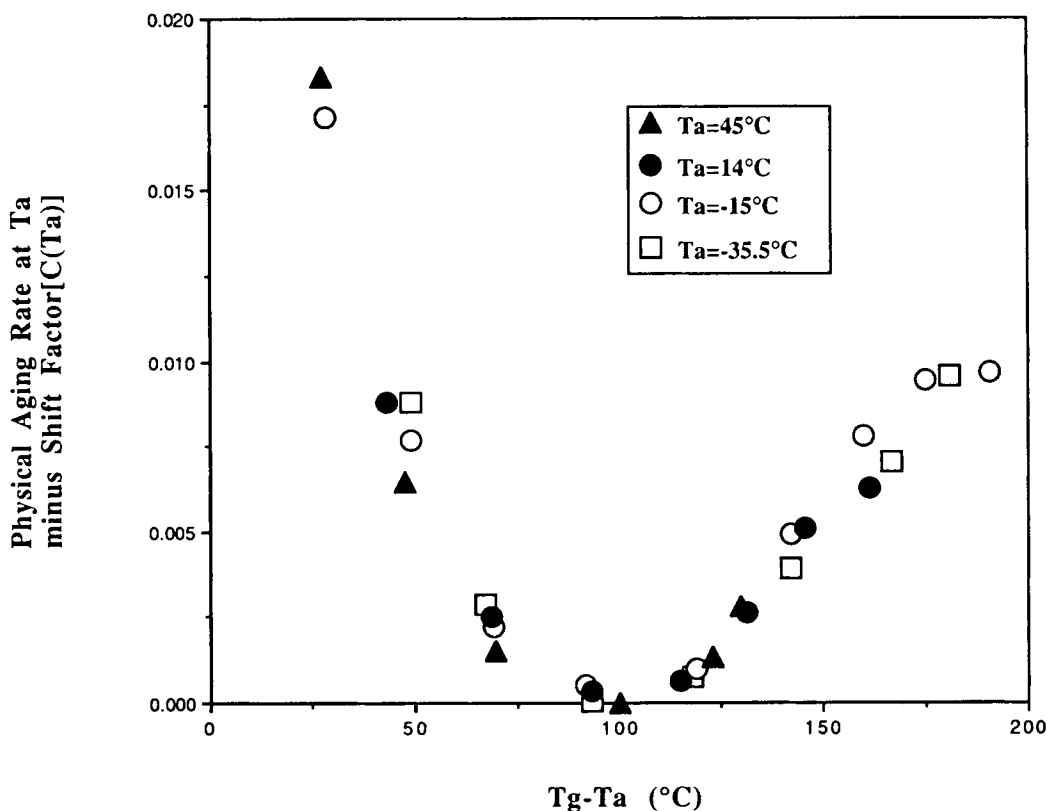


Figure 9 Physical aging rate vs. $T_g - T_a$ at different aging temperatures after vertical shifting of the experimental data of Figure 8. The shifts were made to the level where the minimum aging rate would be zero.

to the physical aging time⁴ and ξ is the sensitivity of the cohesive energy density to the aging time (see Appendix). ξ is usually smaller than μ , and $0 < \mu \leq 1$. $\tan\delta = G''/G'$, where $G'' \equiv$ loss modulus.

Experimental results show that the initial value of $\tan\delta$ of the material at a given temperature T_a changes with change of T_g (Fig. 10), and that the $\tan\delta$ data for different values of T_a may be horizontally shifted together using $T_g - T_a$ as the X-axis (Fig. 11), which indicates that $\tan\delta$ is also a function of $T_g - T_a$ for the present system in the range of temperatures investigated. Therefore, the concave-up curve (Fig. 9) determined by the first term $F(T_g - T_a)$ of eq. (3) is considered to be related to the $\tan\delta$ term of eq. (4). Comparison of eq. (3) with eq. (4) yields:

$$F(T_g - T_a) \cong 2.303\mu(2/\pi)\tan\delta \quad (5)$$

and

$$C(T_a) \cong 2.303 \xi \quad (6)$$

Since both $F(T_g - T_a)$ and $\tan\delta$ are functions of $T_g - T_a$, regardless of the extreme changes of chemical structure, and since the sensitivity of the segmental mobility to the aging time is

$$\begin{aligned} \mu &= -d\log(1/\tau)/d\log(t_a) \\ &\cong F(T_g - T_a)/[2.303(2/\pi)\tan\delta] \quad (7) \end{aligned}$$

the segmental mobility, $1/\tau$, which is involved in the physical aging process in the glassy state, is not a function of chemical structure, but is a function of the deviation from equilibrium ($T_g - T_a$) and aging time.

Interestingly, the change of the cohesive energy density during aging is also insensitive to the change of chemical structure, since the concave-up curves can be simply vertically shifted together. The shift for each set of data was made to a level where the minimum aging rate equals zero. The limited data show that the shift, as defined, could be expressed

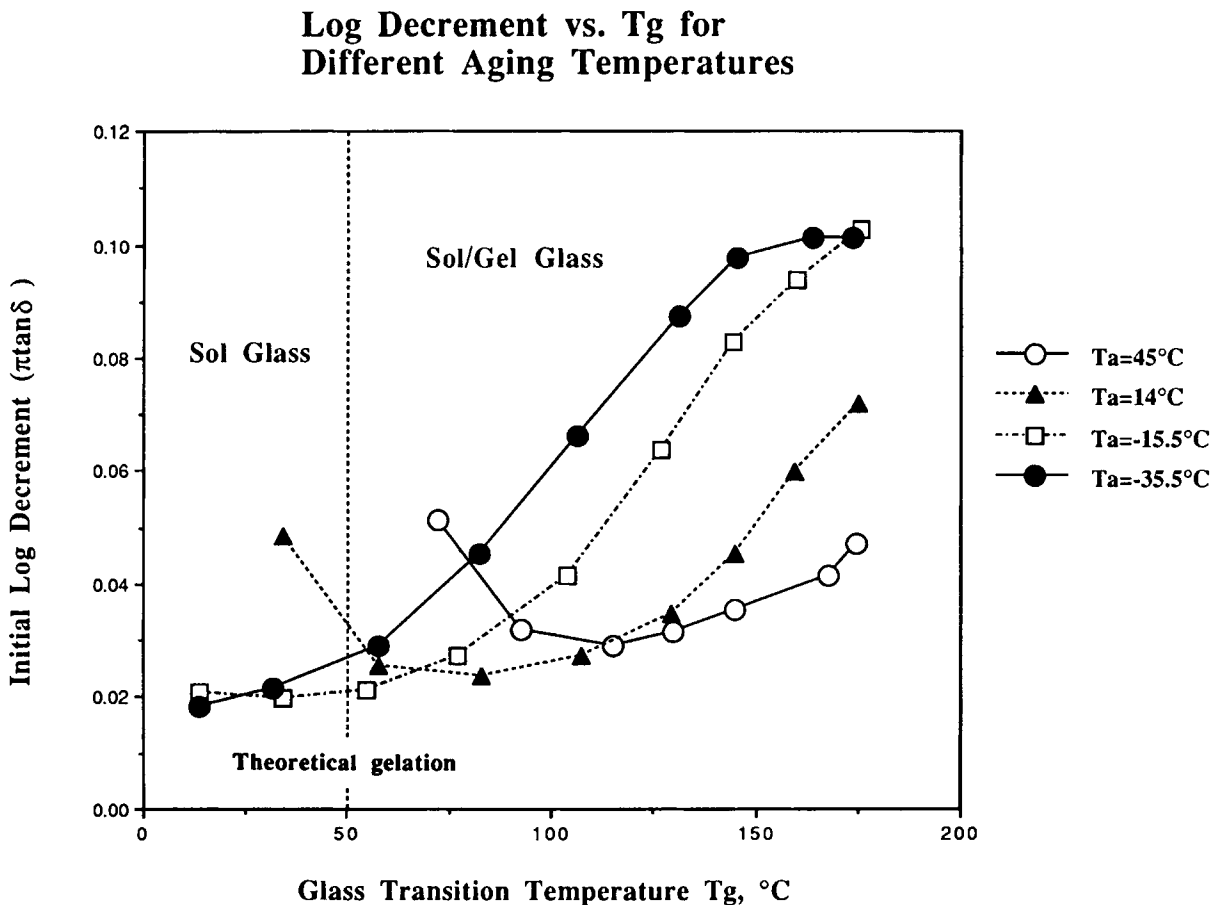


Figure 10 Initial logarithmic decrement ($\cong \pi \tan\delta$) vs. T_g at different aging temperatures. The gelation line marks the change from sol glass to sol/gel glass.

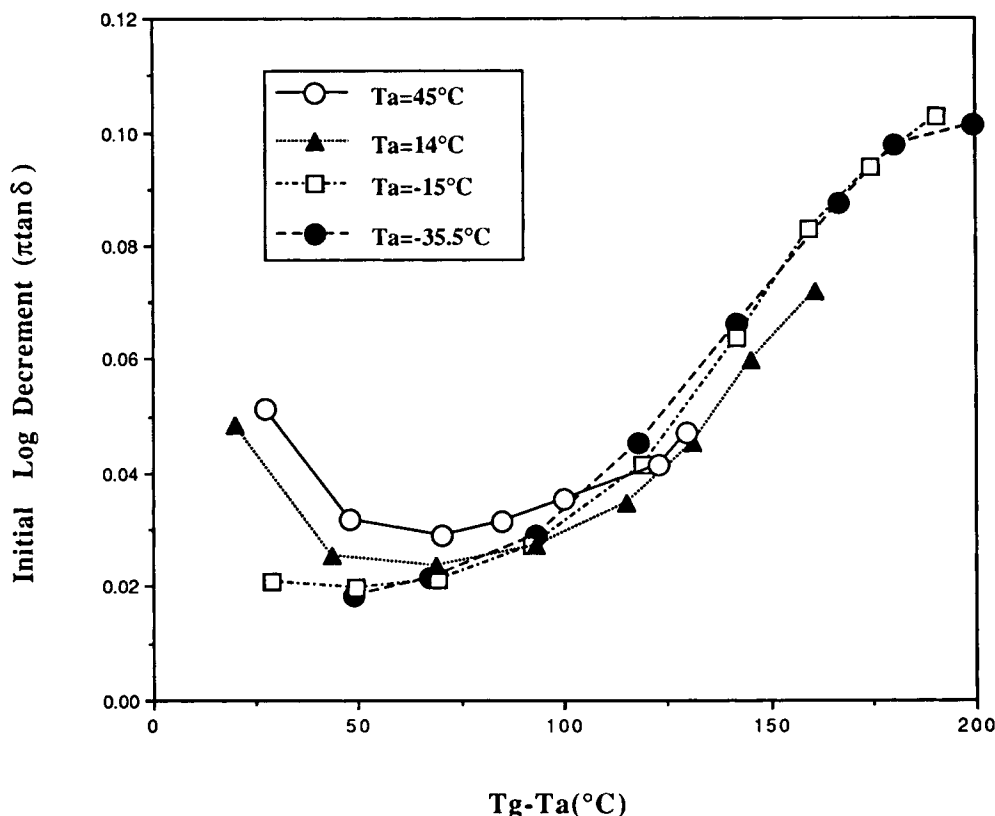
Log Decrement vs. $T_g - T_a$ 

Figure 11 Initial $\pi \tan \delta$ vs. $T_g - T_a$. Experimental data of Figure 10 replotted using $T_g - T_a$ as X-axis.

in a restricted Arrhenius form with "activation energy" = 3 kcal/mole (Fig. 12).

Equation (3), describing the physical aging behavior, has two limiting cases. If the physical aging rate is primarily influenced by the term $F(T_g - T_a)$ (when the term $C(T_a)$ is relatively small), the relationship between $R(T_a)$ and T_a will follow the changes of $\tan \delta$; that is, the physical aging process rate at different temperatures (T_a) will be related to the different transition loss peaks deep in the glassy state (such as the β and γ transitions).^{5,17,18} However, if the material has a relatively larger $C(T_a)$ term, the behavior of the physical aging process will be dominated by the aging temperature, T_a .

Researchers in this field have considered that the rate of physical aging approaches zero when T_a is below T_β (which does not imply that segmental motion ceases). This conclusion originates from the experimental evidence that the sensitivity of segmental mobility to the physical aging time, $\mu = -[\text{dlog}(1/\tau)/\text{dlog}(t_a)]$, approaches zero when

T_a is below T_β .⁴ Recent experimental results in this laboratory (not shown here) show that the effect of physical aging for $T_a < T_\beta$ is still measurable mechanically by the TBA technique for three typical polymer materials, i.e., linear polymer,²⁴ semi-ladder polymer,¹⁸ and crosslinked polymer.^{17,19} Generally, the lower the temperature, the lower the specific volume of a material, and the shorter the distance between adjacent segments, the larger the intersegmental forces and the greater the sensitivity of the cohesive energy density to the change of specific volume. Therefore, the effect of physical aging on the cohesive energy density becomes important below T_β , despite the insignificant changes of the specimen's dimensions (because the aging rate is low when the specimen is aged below T_β). A reason that use of dynamic mechanical techniques to monitor physical aging processes shows higher sensitivity than many other techniques is that the physical aging process, measured by dynamic mechanical properties, primarily involves two important factors [eqs. (4) and (A12)], i.e., changes of segmental mobility

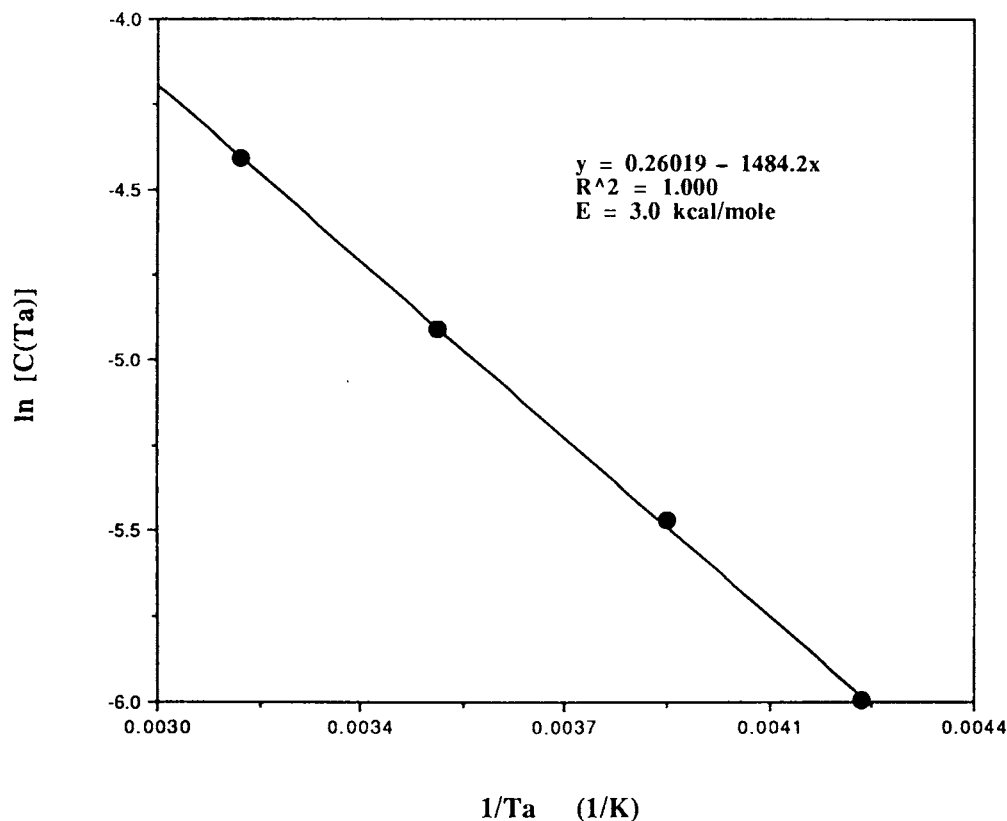
Ln [C(T_a)] vs. 1/T_a

Figure 12 Plot of $\ln C(T_a)$ vs. $1/T(K)$. The “activation energy” for the best fit is 3 kcal/mole.

and changes of the cohesive energy density, both due to physical aging.

CONCLUSIONS

1. In the absence of chemical reaction, the physical aging rate at a given temperature, T_a , below the glass transition passes through a minimum with increasing chemical conversion. This behavior is the consequence of the T_g and T_β transitions.
2. There is a superposition principle for normalizing the physical aging behavior, which involves a shift of $T_g - T_a$ and a shift of $C(T_a)$, regardless of the change of chemical structure.
3. Physical aging deep in the glassy state affects the segmental mobility and the cohesive energy density. The effect of the cohesive energy density on the physical aging rate becomes more important at low values of T_a .

APPENDIX

Relationship between Physical Aging Rate, Segmental Mobility, and Cohesive Energy Density

A semi-quantitative theoretical analysis follows.

Experimental studies of the dielectric, mechanical, and NMR properties of glass-forming materials show that relaxations appear to obey an empirical function, known as the Kohlrausch–Williams–Watts (KWW) equation.^{28–31} For isothermal creep compliance, it yields

$$J(t) = J_0 \exp[-(t/\tau)^m] \quad (\text{A1})$$

where $J(t)$ is the creep compliance, J_0 is for $t = 0$, τ is the equivalent relaxation time, and $0 < m \leq 1$. This equation gives a good fit for a wide variety of polymer systems under isothermal conditions. Theoretical studies have attempted to provide a mechanistic and molecular basis for the KWW function.³¹ The creep compliance of a glassy material

for a given time is influenced by prior physical aging since glassy materials are inherently not in equilibrium and are far from it. Struik found that isothermal creep curves after different aging times may be shifted together along the logarithmic time scale⁴ using a horizontal shift factor $a = 1/\tau$, and a vertical shift factor J_0 when the time scale for creep is much less than the time scale of physical aging (i.e., $t \ll t_a$). Therefore, the parameters τ and J_0 are considered to be functions of prior physical aging time:

$$\tau = \tau(t_a) = 1/a \quad (\text{A2})$$

$$J_0 = J_0(t_a) \quad (\text{A3})$$

From linear viscoelastic theory and to a first approximation³²:

$$G' \cong 1/J(t) = (1/J_0)\exp[-(t/\tau)^m] \quad (\text{A4})$$

and

$$\begin{aligned} \tan\delta &\cong (\pi/2) [d \ln J(t)/d \ln (t)] \\ &= (\pi/2) m(t/\tau)^m \quad \text{when } \omega = 1/t \quad (\text{A5}) \end{aligned}$$

Taking the derivative of eq. (A4):

$$\begin{aligned} dG'/d\log(t_a) &\cong 2.303G' \{ - [d\log(J_0)/d\log(t_a)] \\ &\quad - m(t/\tau)^m [d\log(1/\tau)/d\log(t_a)] \} \quad (\text{A6}) \end{aligned}$$

where the factor 2.303 originates from the change of $\log(\)$ to $\ln(\)$. Let the double-logarithmic horizontal shift rate

$$\mu \equiv - [d\log(1/\tau)/d\log(t_a)] \quad (\text{A7})$$

which is the sensitivity of the segmental mobility to the physical aging time.⁴ Let the double-logarithmic vertical shift rate

$$\begin{aligned} \xi &\equiv - [d\log(J_0)/d\log(t_a)] \\ &= d\log(1/J_0)/d\log(t_a) \quad (\text{A8}) \end{aligned}$$

which is the sensitivity of the cohesive energy density to the physical aging time, since the modulus at infinite frequency [$= 1/J_0(t \rightarrow 0^+)$] is principally related to the cohesive energy density. Rearranging eq. (A5) yields:

$$m(t/\tau)^m \cong (2/\pi) \tan\delta \quad (\text{A9})$$

Substituting the expressions for $[d\log(1/\tau)/d\log(t_a)]$, $[d\log(1/J_0)/d\log(t_a)]$ and $m(t/\tau)^m$ of eqs. (A7), (A8), and (A9) into eq. (A6):

$$dG'/d\log(t_a) \cong 2.303G' [\xi + \mu(2/\pi) \tan\delta] \quad (\text{A10})$$

Combining eqs. (A10) and (2) yields:

$$\begin{aligned} R_a &= d(G'/G'_0)/d\log(t_a) \\ &\cong 2.303(G'/G'_0) [\xi + \mu(2/\pi) \tan\delta] \quad (\text{A11}) \end{aligned}$$

Considering that physical aging deep in the glassy state is slow and that the experimental results show $G'/G'_0 \cong 1$, the physical aging rate:

$$R_a \cong 2.303 [\xi + \mu(2/\pi) \tan\delta] \quad (\text{A12}) \equiv (4)$$

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