

Epoxy Network Structure Effect on Physical Aging Behavior

Y. G. LIN, H. SAUTEREAU, and J. P. PASCAULT, *Laboratoire des Matériaux Macromoléculaires—UA CNRS N° 507, Institut National des Sciences Appliquées de Lyon 20, Avenue Albert Einstein, 69621 Villeurbanne Cedex, France*

Synopsis

Using dicyandiamide as curing agent, several epoxy networks are formed with different formulations and curing cycles. Both sub- T_g isothermal enthalpy relaxation and dynamic enthalpy relaxation in transition zone have been studied using differential scanning calorimetry (DSC). The isothermal enthalpy relaxation rates of all epoxy networks are quite similar and in good agreement with Arrhenius' law. Nevertheless, dynamic relaxation behaviors in the transition zone are very different. These observations are discussed in connection with relaxation mechanism and chemical structure of the networks. Evolutions of mechanical properties during sub- T_g annealing are monitored by means of three-points bending tests. The ductility of unprecured epoxy networks decreases with time; otherwise, the precured and/or filled networks present a stability with regards to mechanical properties. Explanations for these phenomena take into account a possible competition between the relaxation of residual stresses and the network structural relaxation.

INTRODUCTION

The existence of volume relaxation enthalpy relaxation processes in amorphous polymers¹ has been known since 1958. These relaxation phenomena involve a structural recovery of polymers in the glassy state. Struik, who coined the term "physical aging,"² demonstrated that the chain mobility for macromolecules is not quite zero even when the material is stored in its glassy state.³ However, in an aging process, the chain mobility will be reduced nonlinearly with time as a result of a continuous decrease in free volume.⁴ The chain mobility is directly related to the relaxation times of the polymer, and thus aging may be studied using tests which are related to the relaxation spectrum. Volume relaxation,⁵ enthalpy relaxation,^{6,7} as well as primary creep³ and stress relaxation^{8,9} experiments have been used for this purpose.

Due to the easiness of monitoring enthalpic changes by differential scanning calorimetry (DSC), enthalpy relaxation is the most commonly studied parameter used to follow the aging process. As a polymer is cooled from the melt through the glass transition into the glassy state, a rapid decrease in molecular mobility occurs so that the molecules are essentially "frozen" into a nonequilibrium state with an excess of enthalpy and volume (Fig. 1). Therefore, a thermodynamic potential or driving force exists inducing them to approach to equilibrium by a sub- T_g structural recovery.⁴ Specifically, when the polymer is annealed at a temperature T_a below T_g , the enthalpy

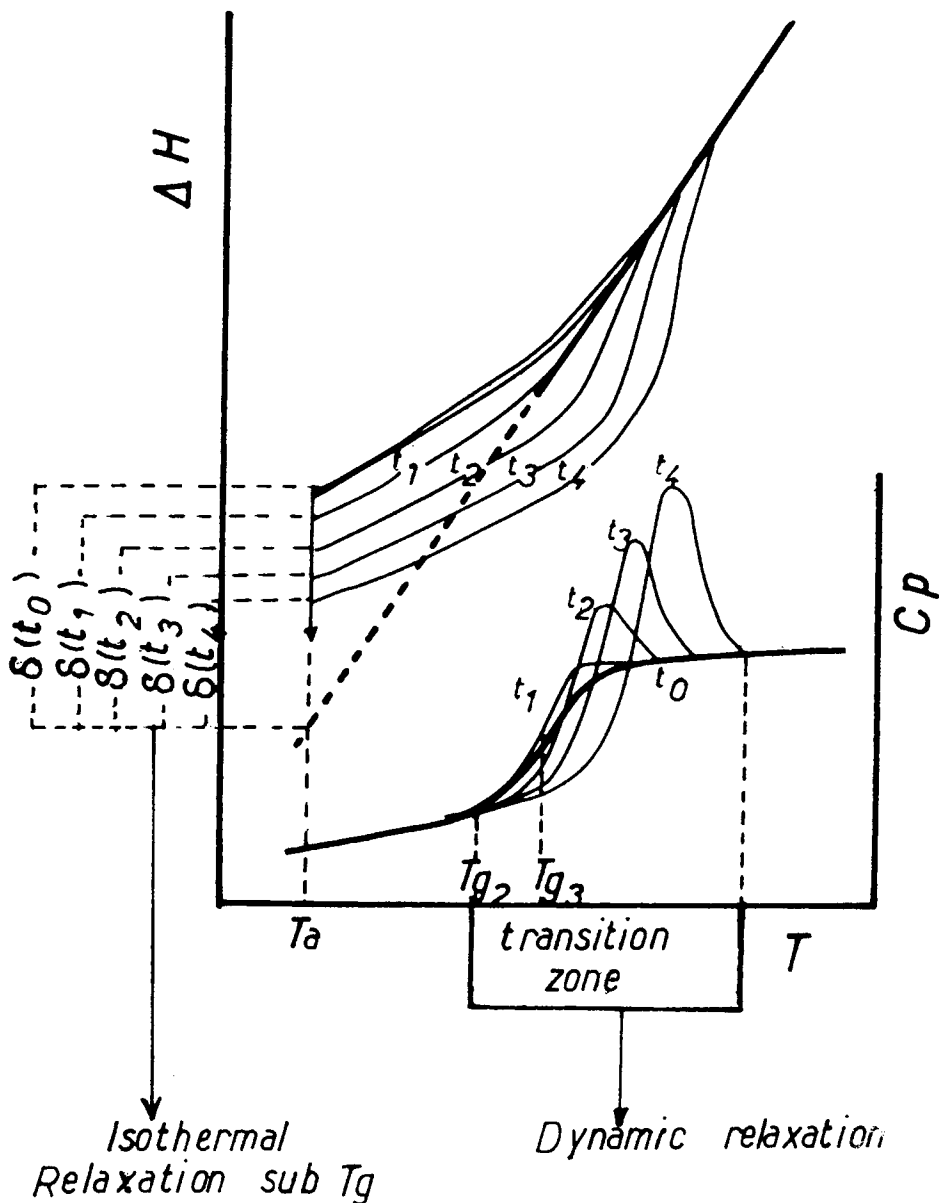


Fig. 1. Diagram of enthalpy relaxation.

excess decreases as a function of time. This process involves a shift of the relaxation times spectra to longer times, in other words, the relaxation rate becomes slower. In a DSC scan, the enthalpy relaxation cannot follow the heating rate, so that the system crosses the equilibrium line into another nonequilibrium state with a lack of enthalpy. Therefore, a new rapid structural recovery occurs with increasing temperature, and leads to an enthalpy relaxation peak in the transition zone. The position and amplitude of this peak vary with the heating rate,⁶ the annealing temperature and time.

Although it has been previously shown that epoxy networks undergo physical aging,³ it was ignored that epoxy network structures have a specific effect on the physical aging behavior. This paper is expected to demonstrate and elucidate this effect.

The structure of dicyandiamide (DDA)-cured epoxy networks is dependent on curing conditions, detailed investigations have been reported elsewhere^{10,11} and references cited. The results indicate that reaction pathways of the present system vary with curing temperature. The most important characteristics of the samples precured at 100°C (see Table I) are: (i) a lower mobility of the networks, due to an increase in the cross-link density and in the average functionality of the crosslinks; (ii) a poor homogeneity due to the presence of phase-separated residual DDA. Elsewhere a precure processing at 100°C increases the production of ether linkages and decreases the transformation of nitrile groups into imine groups.

In this work, we tried to connect the chemical structures of epoxy networks to (i) isothermal sub- T_g relaxation and (ii) dynamic relaxation in the transition zone, and finally we hoped to characterize the influence of physical aging on the mechanical properties.

EXPERIMENTAL

Materials

The prepolymer diglycidyl ether of bisphenol A (DGEBA, Bakelite 164), curing agent dicyandiamide (DDA, VE 2560) and accelerator benzyldimethylamine (BDMA) were commercial products, all were used without purification. The glass beads SOVITEC (4–44 μm) were used as filler, without surface treatment. The different formulations and curing cycles are described in Table I, where a/e indicates the amine-to-epoxy ratio.

The reagents were mixed by mechanical stirring under vacuum at 60°C for 1 hour, then the mixture was cast into a PTFE-coated aluminum mold and cured in an oven. It should be noted that a precure at 100°C for 3 hours makes the difference in curing cycles. After curing, the mold was taken out

TABLE I
Formulation and Curing Cycles of the Epoxy Networks: A, B, C, and D are Called "Unprecured Samples" and A', B', C', and D' "Precured" Ones

Formulation	A	A'	B	B'	C	C'	D	D'
a/e Amine-to-epoxy ratio			1.0				0.6	
Accelerator			1 mL (BDMA)/100 g (DGEBA)					
Filler vol fraction	0	0	0.2	0.2	0	0	0.2	0.2
Curing cycle $T(^{\circ}\text{C}) - t(\text{hour})$		100-3		100-3	160-1	100+3	160-1	100+3
		+		+	+	+	+	+
	160-1	160-1	160-1	160-1	180-1	180-1	180-1	180-1

of the oven and cooled in the air at room temperature. The samples for various tests were cut from the plates as prepared.

ANALYTICAL

The sub- T_g annealing process was performed under vacuum in order to prevent samples from thermal oxidization. The annealing temperatures were about 20°C and 10°C below T_{g2} , or occasionally near T_{g2} (Table II). After various annealing times, the enthalpy relaxation of the samples was measured with a microcalorimeter Mettler TA3000, and the mechanical properties were measured with three-points bending test on a tensile machine (DY 14 Adamel Lhomargy).

RESULTS AND DISCUSSION

Enthalpy Relaxation

The DSC results are discussed in terms of "dynamic relaxation" and "isothermal relaxation," respectively (see Fig. 1).

Dynamical Enthalpy Relaxation

The dynamic enthalpy relaxation behavior of unprecured samples (A, B, C, D) was less dependent on the temperature interval $T_{g2} - T_a$ than the precured one. In every case, an enthalpy relaxation peak appeared rapidly ($t_a \cong 3$ h), and the temperature and the amplitude of this peak increase with t_a [Fig. 2(a)].

On the opposite, the dynamic enthalpy relaxation behavior of precured samples (A', B', C', D') was sensitive to the temperature interval. When T_a was 20°C below T_{g2} [Fig. 2(b)], the annealing process led first to a narrowing of the transition zone, and then to the appearance of the relaxation peak; after a rather long time ($t_a \cong 100$ h), the peak form was less sharp. When the precured samples were annealed 10°C below T_{g2} [Fig. 2(c)], the relaxation peak appeared initially in the front part of the transition zone, and then shifted to higher temperatures, but remained less sharp. Only in the case

TABLE II
Isothermal Annealing Temperature T_a

Formulation	A	A'	B	B'	C	C'	D	D'
T_{g2} (°C)	119	129	119.5	120	127.5	128	128.5	133.5
T_{g3} (°C)	123	130.5	128	137	134.5	136.5	146	152.5
T_a (°C)					115	120	115	120
			100		125	130	125	130

T_{g2} indicates the beginning temperature of the glass transition and T_{g3} the midpoint of the transition zone (see Figure 1), measured on fresh samples by DSC with a heating rate of 10 K/min.

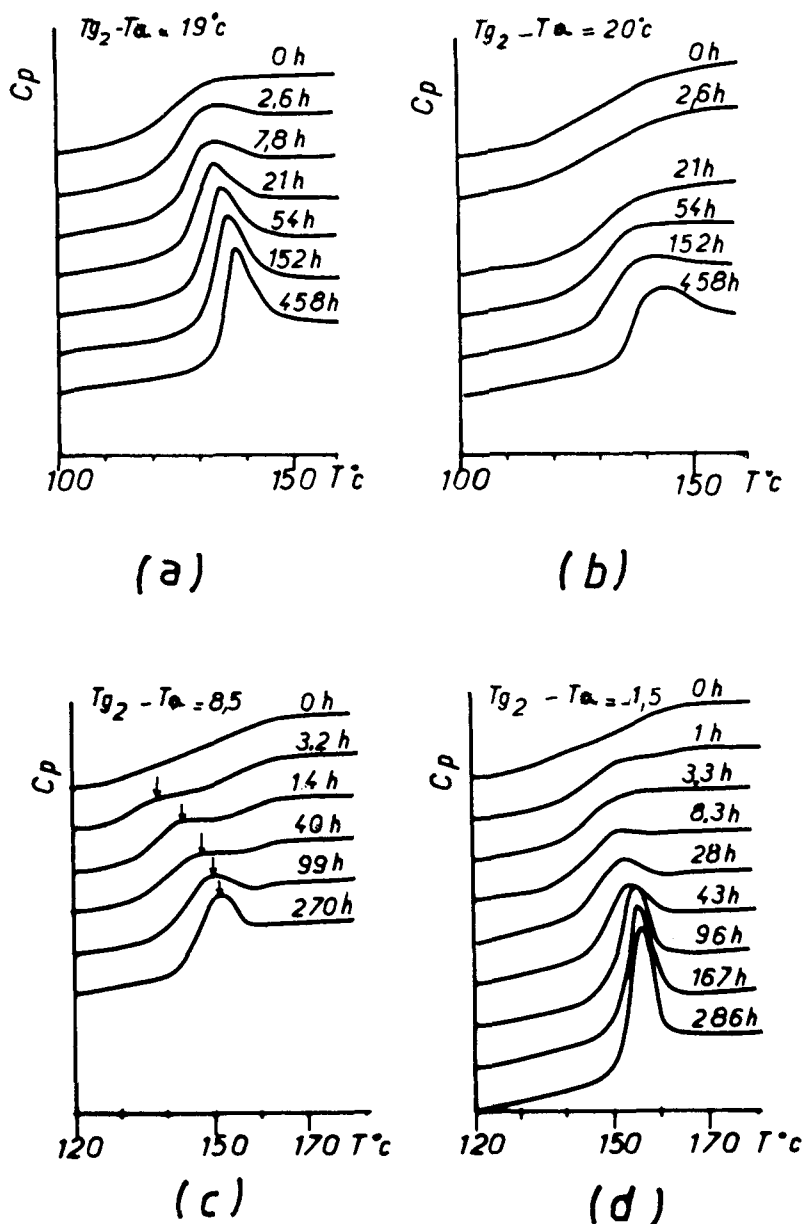


Fig. 2. Dynamic enthalpy relaxation in the transition zone. (a) A annealed at 100°C; (b) A' annealed at 100°C; (c) D' annealed at 120°C; (d) D' annealed at 130°C.

of an annealing at a T_a near T_{g2} [Fig. 2(d)], the precured samples had a similar behavior than the uncured samples.

Lachenal and Chauchard¹² have described the different appearances of enthalpy relaxation peaks as a function of T_a , t_a and the heating rate q . In this study, every annealed sample was measured with the same heating rate $q = 10^\circ\text{C}/\text{min}$. It is obvious that the precured samples and the uncured ones do not have the same function $\delta(T_a, t_a)$ describing their behavior

in the transition zone. So we had to characterize them in terms of relaxation times.

Hutchinson and Kovacs¹³ have proposed the following formula to describe the dynamic enthalpy relaxation process.

$$-d\delta_H/dT = \Delta C_p + \delta_H/\langle\tau\rangle q \quad (1)$$

where δ_H is the enthalpy distance from equilibrium, ΔC_p is the excess specific heat of the liquid with respect to the glass, and $\langle\tau\rangle$ is the average relaxation time, defined as:

$$\langle\tau\rangle = \sum_i^N \delta_i / \sum_i^N (\delta_i/\tau_i)$$

On the other hand, δ_H can be defined as:

$$\begin{aligned} \delta_H &= H - H_x \\ &= \{H_{(T_0)} - \int_T^{T_0} C_p dT\} - \{H_{(T_0)} - \int_T^{T_0} C_p(l) dT\} \\ &= \int_T^{T_0} C_p(l) - C_p dT \end{aligned} \quad (2)$$

where T_0 is a reference temperature at which the polymer reaches the equilibrium state ($T_0 = 180^\circ\text{C}$ is chosen in this study).

Therefore:

$$\frac{d\delta_H}{dT} = C_p - C_p(l) \quad (3)$$

and as

$$\Delta C_p = C_p(l) - C_p(g) \quad (4)$$

finally, we can rearrange the formula (1) in order to calculate the average relaxation time from the present results:

$$\langle\tau\rangle = \int_T^{T_0} C_p - C_p(l) dT / \{C_p - C_p(g)\}/q \quad (5)$$

Figure 3 gives an example of calculated results from the thermograms in Figures 2(a) and 2(b). It is noted that the annealing process shifted the relaxation times spectra to longer times, and that $\text{Log}\langle\tau\rangle$ presented a linear relaxation with temperature in the transition zone.

All unprecured samples (A, B, C, D) presented a similar slope $d \text{Log}\langle\tau\rangle/dT$ as shown in Figure 3(a) independent of the temperature interval $T_{g2} - T_a$. On the opposite, this slope varied obviously with the temperature interval for precured samples (A', B', C', D') it was small when T_a was 20°C below

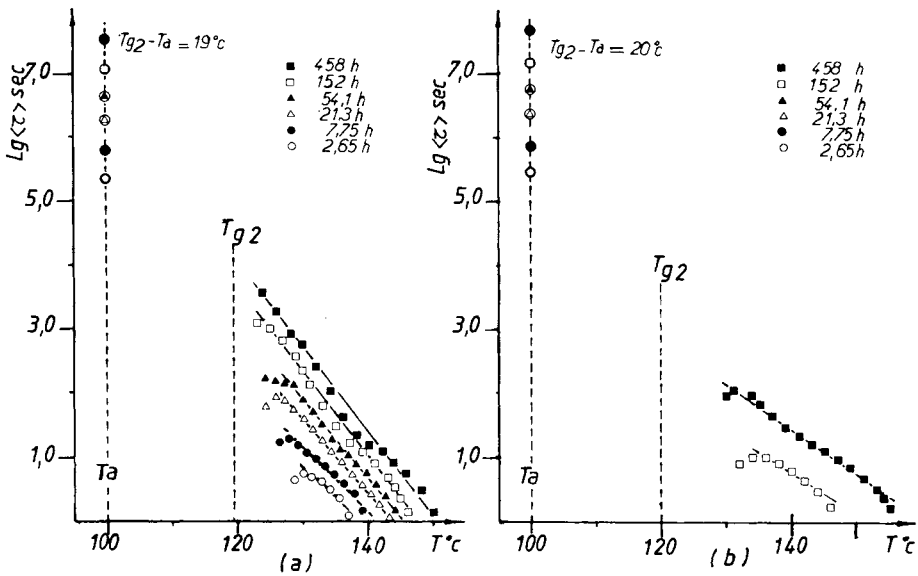


Fig. 3. Average relaxation times $\langle \tau \rangle$ in the transition zone and those at annealing temperature T_a (for a) A; b) A', annealed at 100°C for various times.

T_{g2} [Fig. 3(b)], but became as important as the one for unprecured samples when T_a was near T_{g2} .

Isothermal Enthalpy Relaxation

When the samples were annealed at T_a , their enthalpy distance decreases linearly with $\ln t_a$. With $\beta = -d\delta_H/d \ln t_a$, an Arrhenius plot $\beta = A \exp(-E/RT_a)$ can be made (Fig. 4), indicating that all samples, regardless of different curing cycles, have a similar rate of isothermal enthalpy relaxation at a same temperature, although their dynamic relaxation behaviors in the transition zone were quite different.

In order to calculate the average relaxation time $\langle \tau \rangle$ in the isothermal case, we have developed the following formula:

$$\begin{aligned} \langle \tau \rangle &= -dt_a/d\ln \delta_H \\ &= -t_a \cdot \frac{dt_a}{t_a} \bigg/ \frac{d\delta_H}{\delta_H} \\ &= -t_a \cdot \delta_H \cdot \{d\ln t_a/d\delta_H\} \end{aligned}$$

as

$$\beta = -d\delta_H/d\ln t_a$$

hence

$$\langle \tau \rangle = t_a \cdot \delta_H \cdot \beta^{-1} \tag{6}$$

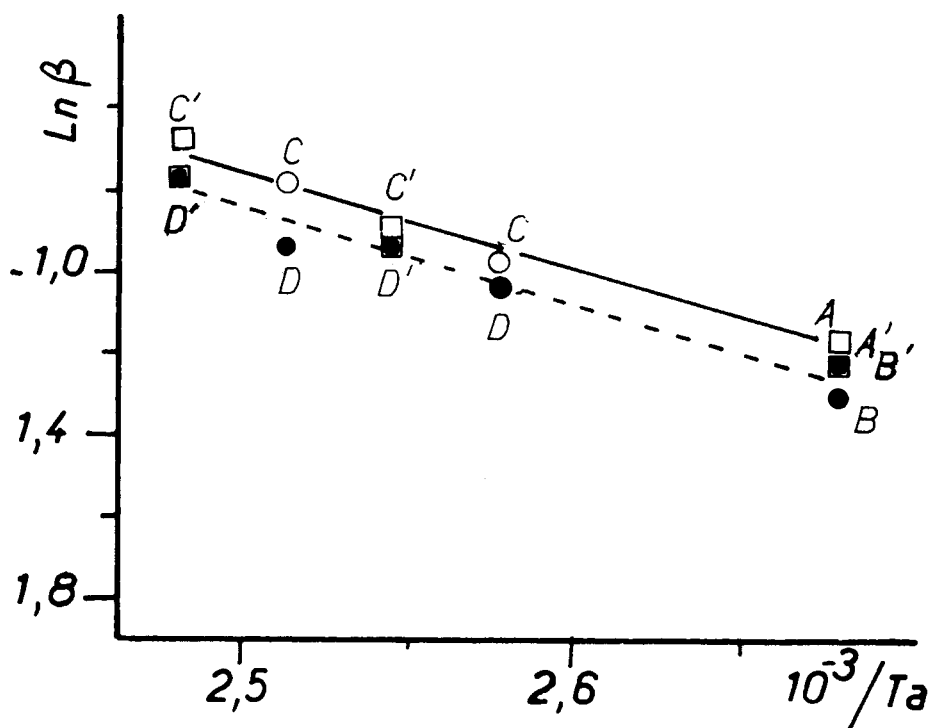


Fig. 4. Arrhenius plot $\ln \beta$ vs. $1/T_a$. T_a is annealing temperature. Letters indicate the formulation.

where the enthalpy distance δ_H as a function of t_a , can be measured by means of DSC.

As stated previously, the sub- T_g annealing process involves a shift of relaxation times spectra to longer times, the results on Figure 5 show that the precured and uncured samples (A, A') had a similar relaxation time and a parallel increase in their relaxation time at a same temperature.

The enthalpy relaxation, as a consequence of structural recovery, is related to the mobility of network structures, it can include the motion of chain segments as well as the crosslinks. In the glassy state, the relaxation is essentially related to the localized movements of the chain segments. In all networks, the chains were made up with the same DGEBA prepolymers, which can explain why all networks had similar relaxation times (τ) at a sub- T_g temperature, and why the isothermal enthalpy relaxation rates of all networks followed a same Arrhenius law. Otherwise, in the transition zone, the movements involve longer chain segments, and could even drag the crosslinks, so that the dynamic enthalpy relaxation behavior in the transition zone also depends on the shifts to crosslinks which have taken place during the annealing process. As previously shown, the dynamic enthalpy relaxation behavior of the precured networks was sensitive to temperature interval $T_{g2} - T_a$, which may indicate that their crosslinks were more difficult to move, having a greater energy of activation, because of a higher cross-link density and a higher functionality of the crosslinks.¹¹

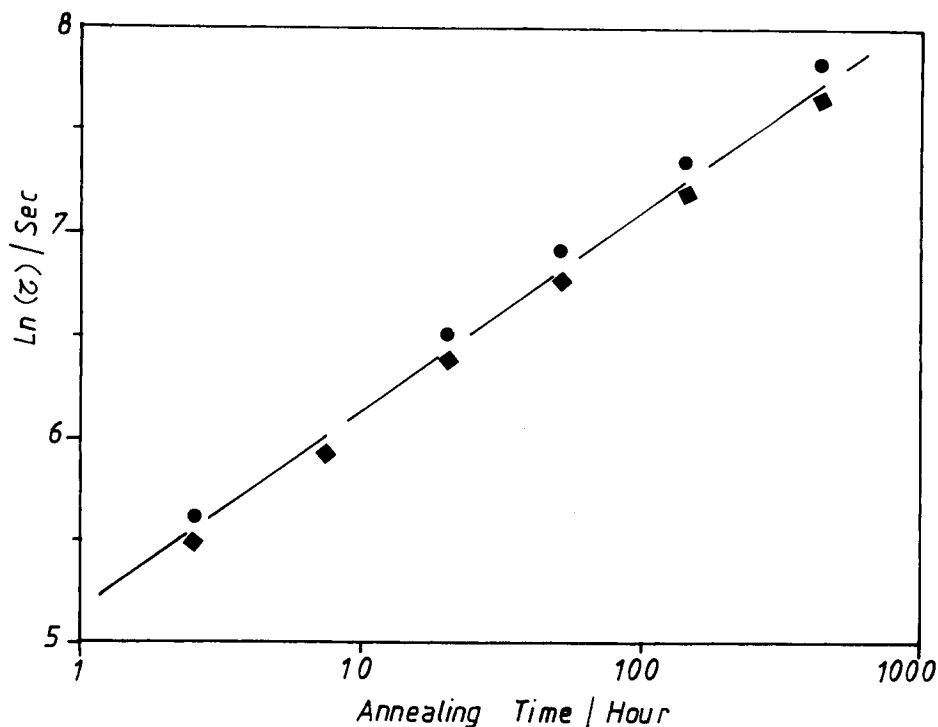


Fig. 5. Average relaxation increases with annealing time (■) A, (●) A' annealed at 100°C under vacuum.

In composites, the matrix exhibited slightly smaller β values than the matrix of unfilled samples (Fig. 4), implying that the presence of glass filler may delay the enthalpy relaxation of the matrix in a sub- T_g annealing process.

Evolution of Mechanical Properties

It has been reported that below the glass transition temperature, the cured epoxies display time-dependent changes in their mechanical properties, especially the ultimate elongation decreases with annealing time.⁹ In this study, the variation of mechanical properties during the annealing process were monitored by three-points bending tests.

At the outset, the unprecured epoxy networks (A, C) were more ductile, but became brittle in the course of annealing (Figs. 6 and 7). On the contrary, the precured or filled networks (A', B, B', C', D, D') were initially less ductile, but there was no longer an obvious change in deflection to break during sub- T_g annealing (Figs. 6 and 7). This difference is probably due to the relaxation of thermic stresses.

The precured networks have less mobility and lower homogeneity, which would produce important thermic stresses during the transition from liquid state to glassy state; the presence of glass filler and/or residual DDA grains in precured samples¹⁰ have the same effect due to the excess shrinking of the polymer matrix. At room temperature, these residual thermic stresses

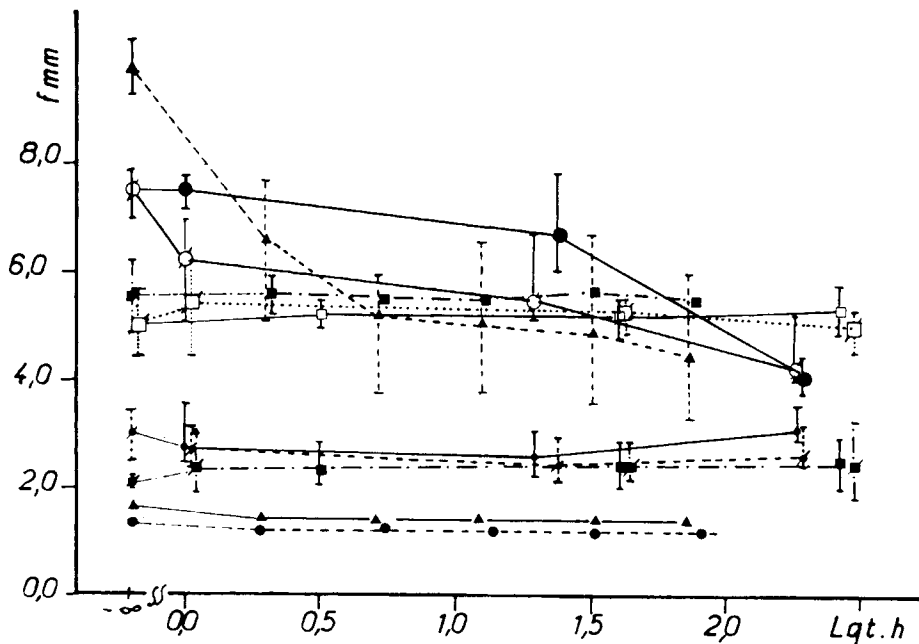


Fig. 6. Deflection to break of all samples vary as a function of logarithmic annealing time (---▲---) A, (-.-.■-.-.) A', (—▲—) B, (-.-●-.-.) B', annealed at 100°C, (—●—) C, (—●—) D annealed at 115°C; (—○—) C, (—●—) D annealed at 125°C, (—□—) C', (—■—) D' annealed at 120°C, (...□...) C', (...■...) D' annealed at 130°C.

decrease the degree of ductile behavior of the materials. During the annealing process, there would be a competition between two effects: (i) the relaxation of thermic stresses enhances the materials properties and (ii) the structural relaxation embrittles the materials. In the case of the precured and/or filled networks, the competition between these two effects can lead to a unchanged ductile behavior. On the other hand, the epoxy networks neither precured nor filled (A, C) have a relatively greater mobility and a good homogeneity,¹¹ hence the cooling induces less thermic stresses, this can explain their ductile character. During a sub- T_g annealing process, the structural relaxation played the major role, so that the network became brittle as the annealing was taking place.

In all cases, no significant changes in flexural modulus were observed.

CONCLUSION

This paper is expected to indicate the influence of network structures in DDA cured epoxy on their physical aging behavior. It was shown that the structural relaxation is related to the molecular mobility of chain segments and crosslinks. Though the apparent rates of enthalpy relaxation during an isothermal sub- T_g annealing were quite similar for all epoxy networks, the consequences of the relaxation were very different, which can be demonstrated by the dynamic enthalpy relaxation in the transition zone. In this way, the precured epoxy networks display a lower molecular mobility owing

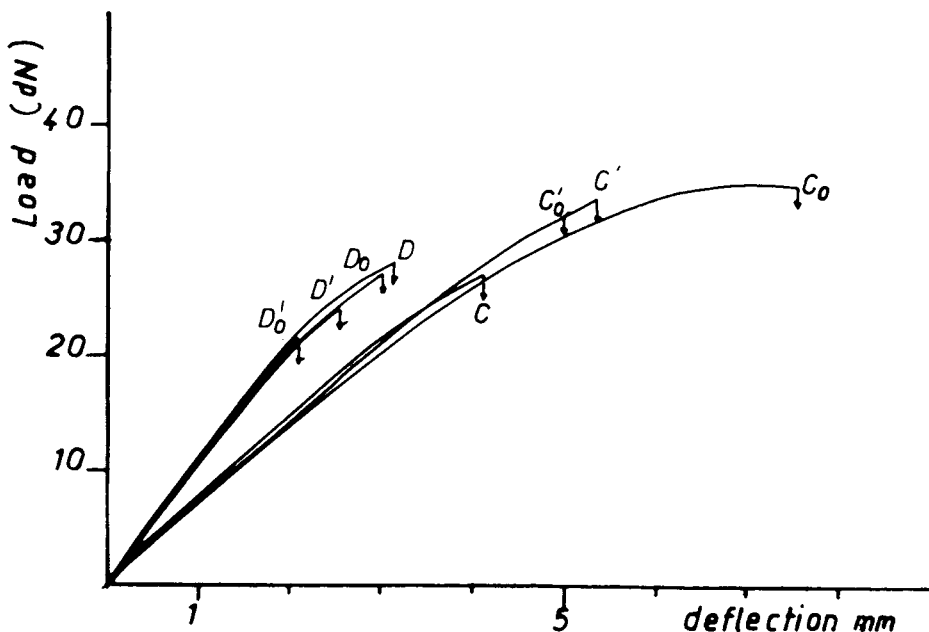


Fig. 7. Three-points bending test curves. C_0 , C'_0 , D_0 , D'_0 before annealing; C and D after 195 h annealed at 115°C; C' and D' after 270 h annealed at 120°C.

to the fact that their structural relaxation are sensitive to the temperature interval $T_{g2} - T_a$.

The structural relaxation can be in competition with a relaxation of thermic stresses, which explains the stability of mechanical properties of precured and/or filled epoxy networks during sub- T_g annealing process.

References

1. A. J. Kovacs, *J. Polym. Sci.*, **30**, 131 (1958).
2. L. C. E. Struik, *Physical Aging in Amorphous Polymers and other Materials*, Elsevier Publishing Company, New York, 1978.
3. L. C. E. Struik, Physical aging in amorphous glassy polymers, *Ann. N. Y. Acad. Sci.*, **279**, 78-85 (1976).
4. M. R. Tant and G. L. Wilkes, *Polym. Eng. Sci.*, **21**(14), 874-895 (1981).
5. A. J. Kovacs, *Fortscher. Hochpolym. Forsch.*, **3**, 394 (1963).
6. S. E. B. Petrie, *J. Polym. Sci.*, **17**(A-2), 1255 (1972).
7. A. R. Berens and I. M. Hodge, *Macromolecules*, **15**, 756-770 (1982).
8. S. Matsuoka, H. E. Bair, S. S. Bearder, H. E. Kern, and J. T. Ryan, *Polym. Eng. Sci.*, **18**, 1073 (1978).
9. Z. H. Ophir, J. A. Emerson, and G. L. Wilkes, *J. Appl. Phys.*, **49**(10), 5032 (1978).
10. Y. G. Lin, H. Sautereau, and J. P. Pascault, *J. Polym. Sci. Chem.* (in press).
11. Y. G. Lin, H. Sautereau, and J. P. Pascault, *J. Appl. Polym. Sci.* (in press).
12. G. Lachenal and J. Chauchard, *Die Makromol. Chem.*, **185**, 601-613 (1984).
13. J. M. Hutchinson and A. J. Kovacs, *J. Polym. Sci. Phys.*, **14**, 1575 (1976).

Received November 12, 1985

Accepted January 2, 1986