Effect of crosslink density on physical ageing of epoxy networks

André Lee and Gregory B. McKenna*

Polymers Division, National Bureau of Standards, Gaithersburg, MD 20899, USA

Physical ageing of polypropylene oxide/DGEBA networks with different crosslink densities was investigated using the small-strain stress relaxation technique in simple extension. The effects of crosslink density on the glass transition temperature, T_g, and the change in specific heat ΔC_p at T_g were measured using a differential scanning calorimeter (d.s.c.) in heating. Although we observed an increase in T_g as crosslink density increased, contrary to other studies of crosslinked polymers, the ΔC_p did not change as the crosslink density changed. Ageing was studied at several temperatures below T_g after quenching from above T_g. It was possible to superimpose the stress relaxation curves at different ageing times, temperatures and crosslink densities to form a single master curve, demonstrating the applicability of a time–ageing time–temperature–crosslink density superposition principle to this type of network. Under all ageing conditions, the double logarithmic shift rate was found to decrease with increasing crosslink density while being independent of temperature for a given network. Furthermore, at temperatures of 10 and 5°C below T_g, we were able to age the network glasses into structural equilibrium, thus obtaining t^*, the time required to reach structural equilibrium. At a constant temperature ΔT below T_g, we observed increases in t^* as the crosslink density increased.

(Keywords: crosslink density; epoxy networks; glasses; heat capacity; physical ageing; superposition principle)

INTRODUCTION

Physical ageing is a result of the slow continuation below the glass transition temperature, T_g, of the glass formation process which begins at T_g[1-4]. After the (kinetic) transition from liquid-like to glass-like behaviour, the material is in a non-equilibrium state and its structure spontaneously evolves towards equilibrium. Accompanying the change in glassy structure are changes in the mechanical (viscoelastic) response of the glass[5]. It is these changes which have come to be known as physical ageing[6].

In many applications involving composites, the properties of the matrix strongly influence the behaviour of the composite material. In polymer based composites, the long term stability of the matrix is an important aspect of the performance of the composite itself. In this Paper, we are interested in studying the resistance of a series of network glasses, chosen as models of thermosetting matrices, to physical ageing. In particular, how does the degree of crosslinking affect the ageing behaviour of the glass?

One expects that the amplitude of the change in mechanical properties upon ageing into equilibrium depends on the magnitude of the initial departure, δ_i, from equilibrium. Hence, if one can reduce the magnitude of δ_i, the effects of physical ageing might be correspondingly reduced. Ellis *et al.*[7] showed that increased crosslinking of polystyrene decreases the mobility of the polymer chains in the liquid state, thus reducing the difference between the glassy and liquid

structures. As a result, when the crosslink density increases, not only does the glass transition temperature T_g increase, but the value of ΔC_p at T_g decreases[7]. Similar results have been reported as a function of degree of cure by Bair[8]. Therefore, upon cooling through the glass transition, the initial departure from equilibrium at a constant temperature below T_g should decrease and the tendency to age physically would be expected to decrease.

Below we describe work in which we studied model epoxy[9,10] systems of differing crosslink densities. We found that contrary to the results cited above, although T_g increased from -48 to 99°C as the molecular weight between crosslinks decreased from 2000 to 60 g mol^{-1}, the ΔC_p at T_g did not change. Analysis of data from the small-strain relaxation response in simple extension for different ageing times and temperatures showed that classical time–ageing time–temperature superposition principles could be used to describe the behaviour of the systems studied. Furthermore, the shape of the viscoelastic spectrum was found to be independent of crosslink density for the three crosslink densities for which mechanical measurements were made. Therefore, the master curves for different crosslink densities could be superimposed onto a single curve consistent with a time–ageing time–temperature–crosslink density superposition principle.

Interestingly, at temperatures close to T_g ($T_g - T = 10$ and 5°C), the system can be aged into structural equilibrium and the transition from ageing to non-ageing behaviour is quite abrupt. Values of t^*, the time required for these glasses to age into equilibrium, increased slightly with increasing crosslink density and decreased significantly with small increases in temperature.

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*To whom correspondence should be addressed

Table 1 Chemical composition and molecular weight of Jeffamines

Name	Chemical composition	Approx. molecular weight
D230		230
D400	$H_2N-CH-CH_2(O-CH_2-CH)_xNH_2$ (with CH_3 groups)	400
D2000		2000
T403	(branched structure with CH_2, $O-CH_2-CH$, CH_3, NH_2 groups)	440
ED600	$H_2N-CH-CH_2(O-CH_2-CH)_x(O-CH_2-CH_2)_y(O-CH_2-CH)_zNH_2$ (with CH_3 groups)	600

EXPERIMENTAL PROCEDURES

Pure diglycidyl ether of bisphenol A (DGEBA, DER 332, Dow Chemical, USA*) epoxide monomer was used in this study and cured with amine terminated poly(propylene oxide) (Jeffamine, designation of Texaco Chemical Company*) of different molecular weights to form networks. The molecular weight between crosslink points was controlled by the molecular weight between amines. In *Table 1*, we list the molecular weights of the Jeffamines used.

The DGEBA epoxide monomer was preheated at 55°C for 2 h to melt any crystals present before hand mixing with the amines until the mixture was clear. The mole ratio of the DGEBA epoxide monomer and amine was that of the stoichiometric ratio. The mixture was degassed for 10 min at room temperature, 23°C, then cast into a mould with dimensions of $11 \times 9 \times 1/8$ in ($28 \times 23 \times 0.32$ cm) and cured at 100°C for 24 h. The sample was then allowed to cool slowly in the oven to 23°C overnight. Also, for one system we used ethylenediamine in place of the Jeffamine. This network was cured at 150°C for 24 h and cooled slowly in the oven to 23°C overnight. Strips of dimensions $3/4 \times 9 \times 1/8$ in ($1.9 \times 23 \times 0.32$ cm) were cut from the cast sheets, milled into dumb-bell shaped samples and kept in a sealed desiccator until the stress relaxation experiments were performed.

The glass transition temperature, T_g, and the changes in heat capacity ΔC_p at T_g for the glasses of different crosslink densities were determined in heating using a differential scanning calorimeter (d.s.c.; Perkin–Elmer DSC-2*) at 20°C min^{-1}. The heating scans were performed immediately after cooling (at 20°C min^{-1}) samples which had been held at 160°C for 30 min. The small-strain stress relaxation experiments in simple extension were performed on three of these glasses, chosen to have T_g values between 42 and 87°C.

The ageing behaviour was probed using the small-strain stress relaxation technique in simple extension. The mechanical experiments were performed using a computer controlled servo-hydraulic testing machine

(Instron Inc. model 132.25*) equipped with a temperature controlled oven. Measurements of the temperature between the top and bottom of the sample showed that the gradient was less than 0.5°C. Oven stability was better than ± 0.2°C for the duration of the experiment. The dumb-bell shaped samples were first annealed for 30 min at a temperature 22 ± 2°C above the T_g determined by the d.s.c., and then were placed in the Instron at the testing temperature ($T_g - T = 30, 25, 20, 15, 10$ and 5°C), where the glass began to age. Successive deformations were applied at ageing times, t_e, which approximately doubled with each test, i.e. $t_e \approx 30$ min, 60 min, 120 min etc. At each interval of deformation, the ratio of the deformation duration time, t_i, to ageing time was 0.056. The applied strain, ε, in these tests was 0.0025 and was measured with an Instron extensometer. The stress, $\sigma(t)$, was measured using a 1000 lb (450 kg) capacity load cell from Interface Inc. Thus the stress relaxation modulus was $E(t) = \sigma(t)/\varepsilon$.

RESULTS AND DISCUSSION

D.s.c. results

In *Table 2*, we list the values of T_g and change in heat capacity ΔC_p at T_g as determined by d.s.c. for all of the epoxy networks. One can see from the table that as the molecular weight of the amine decreased, T_g increased significantly. However, the ΔC_p at T_g changed by less than 10% as the molecular weight of the amine decreased. These results differ from the findings of Ellis et al.[7] with polystyrene/divinylbenzene networks, in which the ΔC_p at T_g decreased from 0.283 to 0.095 J g^{-1} K^{-1} as the molecular weight between crosslinks decreased from ∞ to 113 g mol^{-1}, while T_g changed from 385 to 445 K. In a future paper we will report results from a study of the relationship of ΔC_p and T_g to crosslink density in networks crosslinked with an epoxy of higher functionality. We further note that the observation that ΔC_p does not decrease as the crosslink density increases is similar to the results reported by Choy[11] of a study on DGEBA/DDS type epoxies where the molecular weights of the DGEBA were varied. In that study, dilatometric measurements of the change in volume expansivity, $\Delta \alpha$, at T_g were found to be independent of crosslink density.

Table 2 D.s.c. results for the DGEBA/diamine networks

Sample	$M_c{}^a$	$M_c{}^b$	T_g (°C)	ΔC_p (J g^{-1} °C^{-1})
DGEBA/NH$_2$(CH$_2$)$_2$NH$_2$	60	247	99.5	0.405
DGEBA/D230	230	303	87.3	0.404
DGEBA/T403	–	243	72.3	0.404
DGEBA/D400	400	360	42.4	0.419
DGEBA/ED600	600	427	13.7	0.420
DGEBA/D2000	2000	893	−48.0	0.434

^{a} Based on assumption that DGEBA is a point crosslink and the molecular weight of the Jeffamine is the molecular weight between crosslinks, M_c

^{b} Calculated assuming a homogeneous network (this is supported by neutron scattering measurements on similar deuterated (DGEBA) networks[9]). Then M_c is calculated as $M_c = N_A V \rho / v$, where N_A is Avogadro's number, $V\rho$ is the number of grams of material and v is the total number of chains, $v = v_1 + v_2$, with v_1 the number of amine chains and v_2 the number of DGEBA chains. The functionality of the network here is assumed to be 3 and enters into the calculation of v_1 and v_2 from the stoichiometry of the network
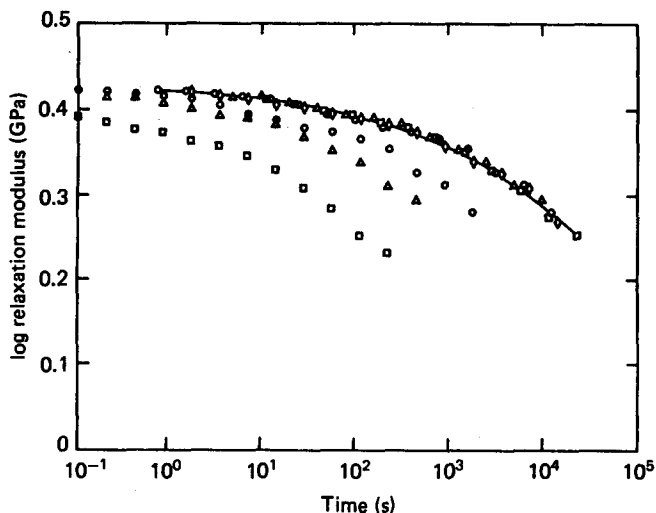

Figure 1 Small-strain stress relaxation modulus curves for DGEBA/ D230 quenched from 107°C (i.e. ≈ 20°C above T_g) to 62°C and kept at 62 ± 0.2°C for 3 d. Ageing time elapsed after quenching, t_e (min): $\square$, 28; $\triangle$, 126; $\bigcirc$, 503; $\diamond$, 4026. Solid line, master curve resulting from a superposition by shifting along the time axis

Ageing results

Figure 1 depicts a family of stress relaxation isotherms for the relaxation modulus, $E(t)$, at $T_g - T = 25$°C, obtained for the DGEBA/Jeffamine-D230 system ($T_g = 87$°C) at various ageing times, as indicated. Clearly, these relaxation curves can be superimposed by simple horizontal shifts along the time axis to form a master curve (we note that slight vertical shifts were needed to perform the individual superpositions).

Each stress relaxation curve at a given ageing time was curve-fitted with the Kohlrausch–Williams–Watts[12,13] stretched exponential function:

$$E(t) = E_0 \exp[-(t/\tau)^\beta] \qquad (1)$$

where E_0 is the modulus at $t = 0$, τ is a characteristic relaxation time and β describes the shape of the relaxation curve. To perform the superposition and form a master curve, the value of β at the various ageing times must be the same, i.e. the shape of the underlying relaxation spectrum must be invariant. Then the horizontal shifts, a_{t_e}, along the time axis were obtained as:

$$a_{t_e} = \tau(t_e)/\tau(t_e(\text{ref})) \qquad (2)$$

where the $\tau(t_e)$ is the value of τ at the relevant ageing time and $\tau(t_e(\text{ref}))$ is the τ at the reference ageing time. In *Table 3*, we present the parameters for the master curves fitted to equation (1) for each of the systems at different temperatures.

The ageing process at different temperatures is conveniently characterized by the double-logarithmic shift rate, μ, defined as[6]:

$$\mu = d \log a_{t_e}/d \log t_e \qquad (3)$$

In *Figures 2, 3* and *4*, we show double logarithmic plots of a_{t_e} versus t_e at different values of $T - T_g$ for each network. In all cases, the reference ageing time was chosen as 28 min. The slope, μ, was found to be independent of temperature in the range from 10 to 30°C below T_g and appears to decrease as the temperature approaches T_g. The last effect may be due to the limitation that measurements could not be carried out at ageing times shorter than 28 min, rather than a change in the intrinsic
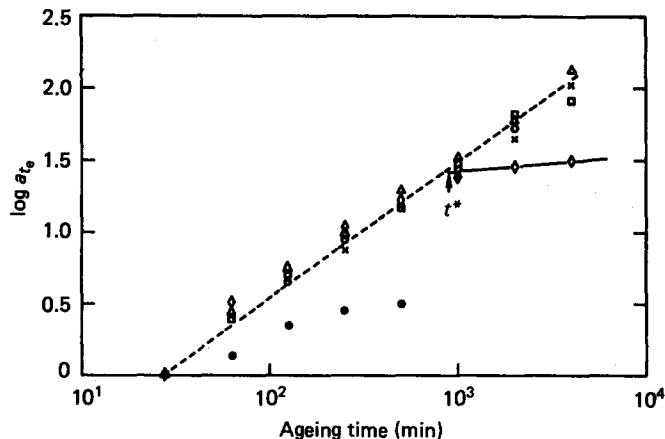

Figure 2 Double logarithmic plot of ageing time shift factor a_{t_e} versus ageing time for DGEBA/D230 sample at different temperatures (°C): $\bigcirc$, 57.6; $\times$, 61.9; $\square$, 66.9; $\triangle$, 71.5; $\diamond$, 77.0; $\bullet$, 81.8°C. Dashed line shows double logarithmic shift rate $\mu \approx 0.9$. Intersection of lines at 77.0°C in ageing and non-ageing regimes defines t^*
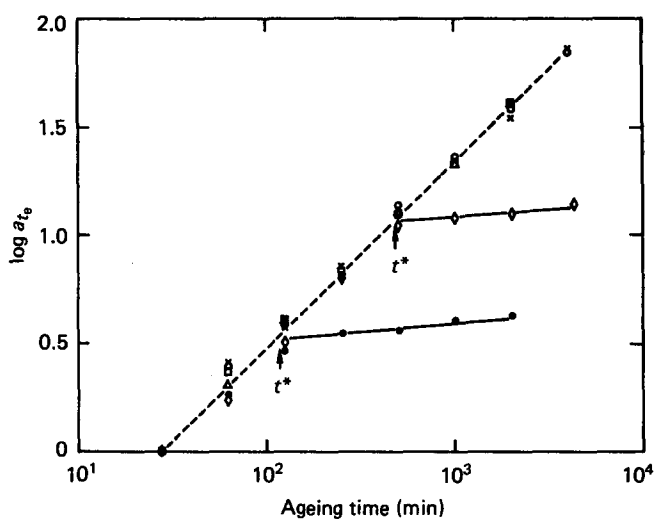

Figure 3 Double logarithmic plot of ageing time shift factor a_{t_e} versus ageing time for DGEBA/T403 sample at different temperatures (°C): $\bigcirc$, 42.2; $\times$, 48.3; $\square$, 51.5; $\triangle$, 57.2; $\diamond$, 62.0; $\bullet$, 66.0. Dashed line shows double logarithmic shift rate $\mu \approx 0.85$. Intersection of lines at 62.0 and 66.0°C in ageing and non-ageing regimes defines t^*

Table 3 Curve-fitting parameters[a] ($t_e(\text{ref}) = 28$ min)

Sample	T (°C)	E_0 (GPa)	τ (s)	β
DGEBA/D230	57.6	2.518	7620.7	0.335
	61.9	2.532	3524.9	0.331
	66.9	2.479	1723.2	0.337
	71.5	2.517	1057.9	0.341
	77.0	2.401	102.9	0.344
	81.8	2.389	15.8	0.333
DGEBA/T403	42.2	2.547	7108.4	0.347
	48.3	2.633	3656.2	0.336
	51.5	2.501	933.5	0.342
	57.2	2.548	292.5	0.345
	62.0	2.545	60.5	0.339
	66.0	2.397	0.8	0.343
DGEBA/D400	24.5	2.559	1543.1	0.340
	32.4	2.391	101.9	0.344
	37.3	2.461	3.8	0.336

[a] Fit to equation (1) using a non-linear least squares regression analysis[16]

Table 4 Time needed for DGEBA/diamine glasses to reach structural equilibrium, t^*

Sample	T_g (°C)	$T_g - T$ (°C)	t^* (min)
DGEBA/D230		10.3	≈1000
	87.3	5.5	≈160
DGEBA/T403		10.3	≈500
	72.3	6.3	≈250
DGEBA/D400		10.0	≈500
	42.4	5.1	≈120
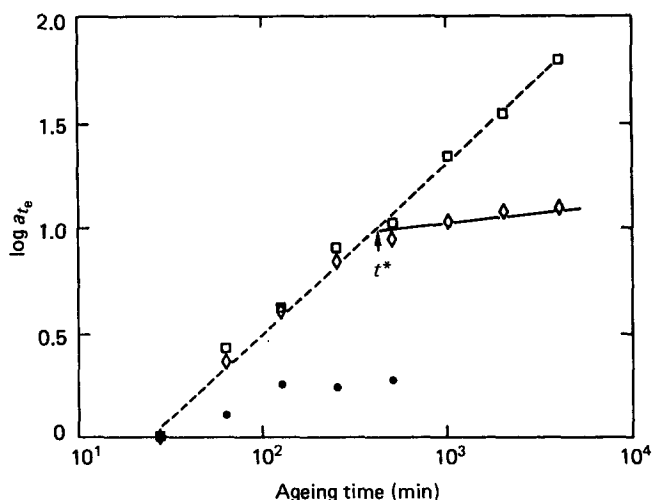
Figure 4 Double logarithmic plot of ageing time shift factor a_{t_e} versus ageing time for DGEBA/D400 sample at different temperatures (°C): □, 24.5; ◇, 32.4; ●, 37.3. Dashed line shows double logarithmic shift rate $\mu \approx 0.80$. Intersection of lines at 32.4°C in ageing and non-ageing regimes defines t^*

ageing behaviour near T_g. Furthermore, as the T_g of the network decreased (i.e. as crosslink density decreased), μ decreased slightly. Interestingly, at temperatures approximately 10 and 5°C below T_g, we were able to age the network glasses into structural equilibrium, i.e. the value of a_{t_e} became independent of ageing time. As shown in *Figures 2–4*, this transition from ageing to non-ageing behaviour is quite abrupt. Here, we define t^* as the intersection of the lines in the ageing and non-ageing regimes on a $\log a_{t_e}$ versus $\log t_e$ plot. At a constant temperature below T_g, the value of t^* increases as the T_g of the networks increases. Values of t^* for different values of $T_g - T$ are tabulated in *Table 4* for each of the three epoxy systems.

The time–temperature superposition principle was also investigated. *Figure 5* depicts a series of stress relaxation curves at a constant ageing time (≈ 8 h) as a function of temperature below T_g. As shown in *Figure 6*, a master curve can be obtained by simple horizontal shifting of the curves along the time axis combined with a small amount of vertical shifting. The temperature shift factor, $a_T(t_e)$, at a specific ageing time was obtained as:

$$a_T(t_e) = \tau(t_e, T)/\tau(t_e(\text{ref}), T(\text{ref})) \qquad (4)$$

where $\tau(t_e, T)$ is the value of τ at ageing time t_e and temperature T, and $\tau(t_e(\text{ref}), T(\text{ref}))$ is the value of τ at the reference ageing time and reference temperature.

Figures 7, 8 and *9* show $\log a_T$ versus $T - T_g$, at different ageing times for the networks investigated. The reference was chosen at a temperature approximately 10°C below T_g and an ageing time of 503 min. In *Figures 7* and *8*, there

are two regions of behaviour. At lower values of $T - T_g$ there is a linear temperature dependence. For $T - T_g = -10$ to -15°C there is a rapid decrease in shift factor; this is apparently a transition region from the linear dependence to a WLF[14] type dependence on temperature. This transition region appears more abrupt in character than that reported in the literature, possibly due to the fact that here we carried out experiments at 5°C intervals, while the tests of Hunston *et al.*[15] were performed at intervals of approximately 20°C. Insufficient data were obtained for the DGEBA/D400 sample depicted in *Figure 9* to comment on its low temperature behaviour, although the transition region appears smoother for this network than for the D230 and T402 networks depicted in *Figures 7* and *8*.

We also examined the suitability of a time–crosslink density superposition principle for our relaxation data. We chose to compare the DGEBA/D230 with the DGEBA/D400, since the crosslink point has the same chemical components for these two systems (i.e. all DGEBA–amine, while the T403 has the aliphatic crosslink joining the three PPO chains, see *Table 1*).
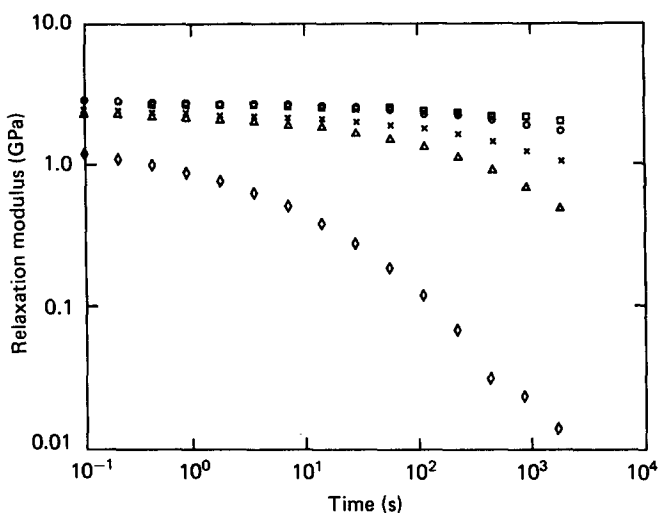
Figure 5 Small-strain stress relaxation modulus curves for DGEBA/T403 quenched from 94°C to various temperatures. Temperature (°C): □, 42.2; ○, 51.5; ×, 57.2; △, 62; ◇, 66. Ageing time after quenching: 503 min
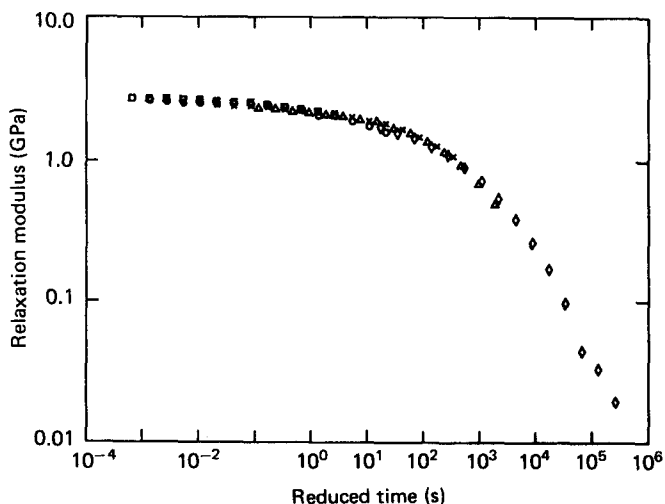
Figure 6 Master curve resulting from a superposition of data presented in *Figure 5*, obtained by shifting the data along the time axis
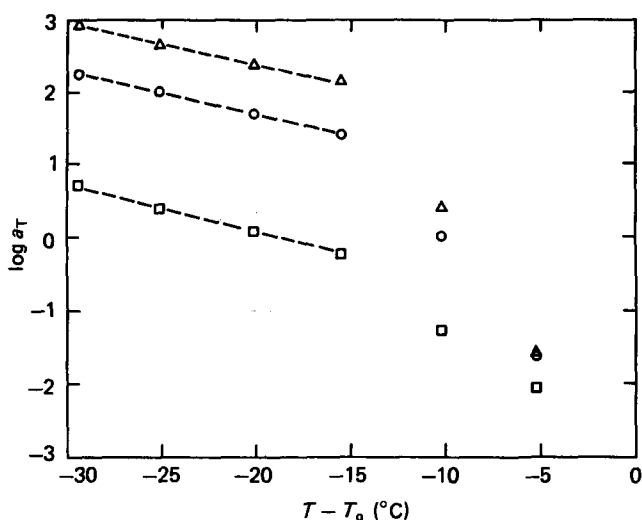
Figure 7 Log of temperature shift factor a_T versus temperature difference $T - T_g$ for DGEBA/D230 at various values of ageing time (min): $\square$, 28; $\bigcirc$, 503; $\triangle$, 2013. For $T - T_g = -10$ to $-15°C$ a_T decreases rapidly; this is apparently a transition region from linear dependence to a WLF type dependence on temperature
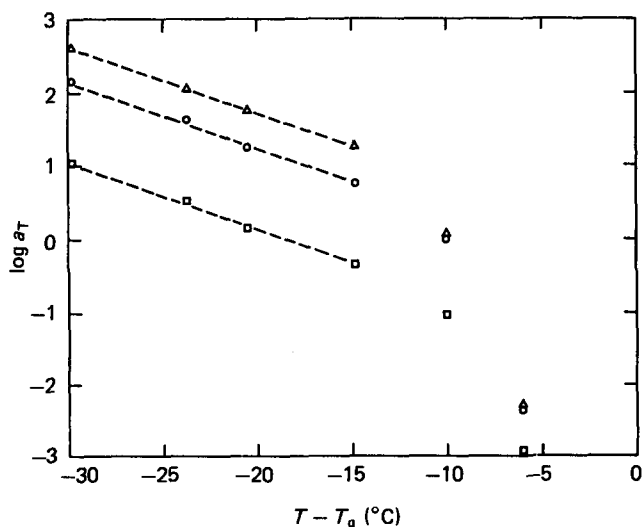

Figure 8 Log of temperature shift factor a_T versus temperature difference $T - T_g$ for DGEBA/T403 at various values of ageing time (min): $\square$, 28; $\bigcirc$, 503; $\triangle$, 2013. For $T - T_g = -10$ to $-15°C$ a_T decreases rapidly; this is apparently a transition region from linear dependence to a WLF type dependence on temperature

Figure 10 shows the stress relaxation modulus curves for the D400 and D230 systems at the same temperature relative to their T_g values ($T_g - T = 10°C$) and ageing times (≈ 60 min and 2000 min). There are several things to notice in *Figure 10*. First, each sample at the two different ageing times can be superimposed by a horizontal shift a_{t_e}. Again a small vertical shift is required for this superposition. The curves for D230 are shifted to longer times than for D400, which has a lower crosslink density. Second, the curves for the same ageing times but different crosslink densities are shifted relative to each other, by a factor a_x. Again, a small vertical shift was required to obtain superposition. Interestingly, the value of a_x is a function of the ageing time. This can be attributed to two factors, best seen by reference to *Figure 11*, which shows log a_{t_e} versus log t_e for the D230 and D400 systems at

$T_g - T = 10°C$. Here we chose the reference point as DGEBA/D400 at $t_e \approx 28$ min. The vertical difference between the two curves in *Figure 11* at the same ageing time is a_x. The first factor is that the slope of these curves for the two systems in the ageing regime are different. The second is that the time, t^*, required to reach structural equilibrium for the two systems is also different (see *Figures 2* and *4* and *Table 4*). Thus a_x varies with ageing time, but when each system has reached its respective equilibrium, the value of a_x becomes constant and independent of the ageing time.

SUMMARY AND CONCLUSIONS

We have described a study of the relationship between physical ageing and crosslink density in DGEBA/diamine model networks. Our original hypothesis, that ageing would be reduced upon changing the value of the ΔC_p at the glass transition could not be tested because we found that, contrary to reports in the literature for
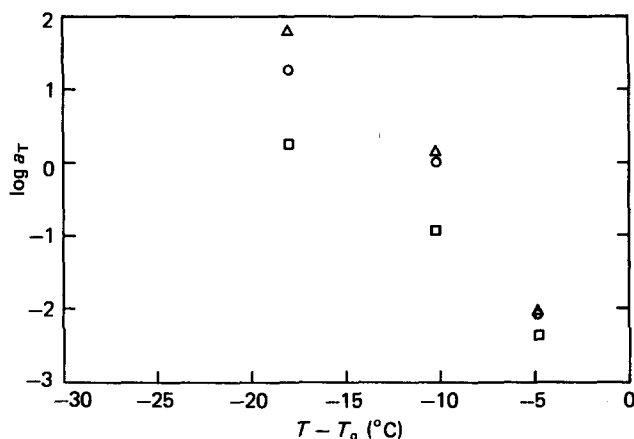

Figure 9 Log of temperature shift factor a_T versus temperature difference $T - T_g$ for DGEBA/D400 at various values of ageing time (min): $\square$, 28; $\bigcirc$, 503; $\triangle$, 2013
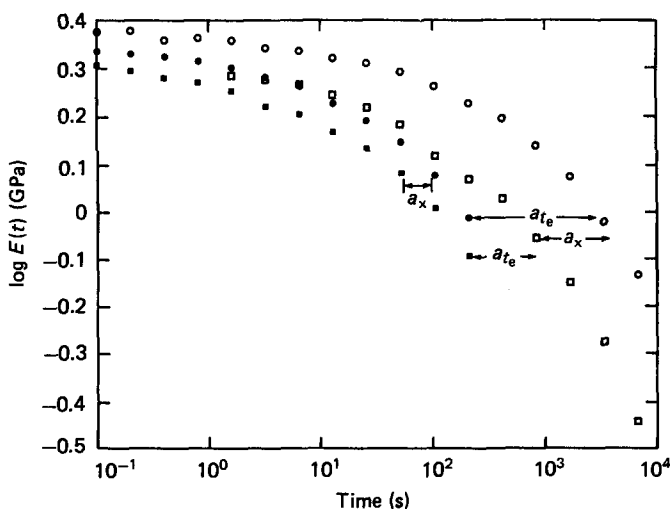

Figure 10 Small-strain stress relaxation modulus $E(t)$ curves for DGEBA/D230 ($\bullet$, $\bigcirc$) and DGEBA/D400 samples ($\blacksquare$, $\square$) quenched from $T_g + 22°C$ to similar constant temperatures below T_g ($T_g - T(D400) = 10.3°C$ and $T_g - T(D230) = 10.0°C$). Ageing time (min): $\blacksquare$, $\bullet$, 63; $\square$, $\bigcirc$, 2013. a_x shows the amount of shift required to superimpose curves for two samples of different crosslink density. a_{t_e} shows the amount of shift needed to superimpose curves for the same sample but different ageing times
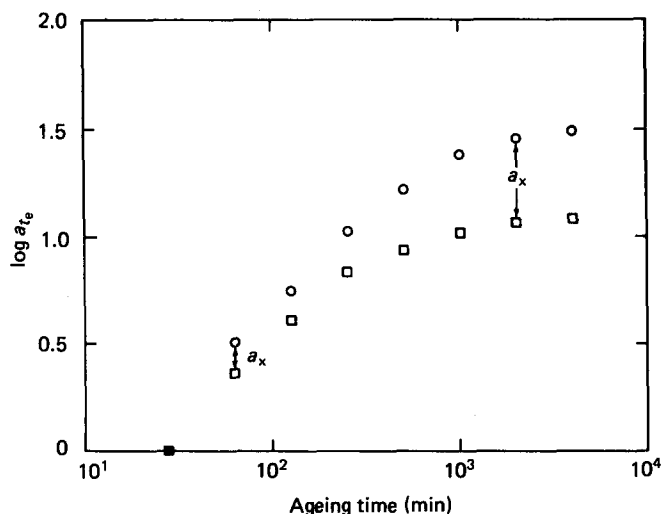
Figure 11 Log of shift factor a_{t_e} *versus* ageing time for DGEBA/D400 and DGEBA/D230 samples at $T_g - T \approx 10°C$. The vertical difference between two curves at the same ageing time is the shift factor a_x required to form the master curve for these two different crosslink density samples. Note that a_x is a function of ageing time until structural equilibrium is attained for both systems. Also note that at $t_e = 28$ min, $\log a_x = 0.004$ (see *Table 3*)

divinylbenzene crosslinked polystyrene[7], the ΔC_p for our networks changed by less than 10% over a range of molecular weights between crosslinks, M_c, from 2000 to 60 g mol^{-1}. Over the same range of M_c, T_g varied from -48 to 99°C. We are currently pursuing work using epoxies of higher functionality to investigate the reasons for this ΔC_p behaviour at T_g.

The ageing behaviour for different crosslink density epoxies did not differ greatly from that of the thermoplastic glasses described by Struik[6]. We observed that both the classical time–ageing time superposition and time–temperature superposition were valid for our networks. For the epoxy glasses studied here, the values of the double logarithmic shift rates, μ, were independent of temperature. At temperatures 10 and 5°C below T_g, we were able to age the materials into structural equilibrium. It was found that the time needed to reach structural equilibrium, t^*, increased as crosslink density increased

or M_c decreased. Furthermore, for different crosslink densities, time–crosslink density superposition was observed. However, since the values of t^* were different, at $t_e < t^*$, the crosslink density shift factor, a_x, is dependent on the ageing time; in the region of $t_e > t^*$, a_x was independent of ageing time. In conclusion, the results reported here are consistent with the principle of time–ageing time–temperature–crosslink density superposition for the thermosetting epoxy network glasses studied.

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