# High temperature retardation mode in epoxy-aromatic amine networks

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Due to the specific nature of thermally stimulated creep (TSCr) experiments, complementary data on the high temperature retardation mode in epoxy-aromatic amine networks as observed in dynamic mechanical thermal analysis have been obtained. Two series of amine-cured diglycidyl ether of bisphenol A (DGEBA) networks were investigated by TSCr to characterize their anelastic properties. By systematically varying the amount of methylene dianiline (MDA) used as crosslinking agent, the effect of an excess of epoxy on the network structure was followed. The high temperature retardation mode associated with the glass transition was found to be shifted to higher temperatures with increasing hardener content. This reveals an important restriction of molecular mobility as the resin tends to full crosslinking. It is also important to note that the peak temperature of DGEBA–MDA depends on the crosslink density for aminohydrogen to epoxy ratio $r > 0.6$ and on number average molecular weight for $r < 0.6$.

**(Keywords: thermally stimulated creep; epoxy network; thermoset network; thermo-mechanical properties; retardation spectrum; glass transition)**

## INTRODUCTION

Thermosets based on crosslinked epoxies are known to have wide-ranging applications including adhesives and matrix materials for glass, aramide or carbon-fibre reinforced composites. The choice of particular prepolymers and crosslinking agents depends strongly on the mechanical properties and service requirements of the end product.

A better knowledge of the anelastic properties of epoxy resins is desirable if improved systems based on thermosets are to be developed. During the last two decades, the study of epoxy network structure has given rise to numerous investigations of their mechanical behaviour. Unfortunately, there is still no accurate and satisfactory method for defining such amorphous network structure.

In this work, thermally stimulated creep (TSCr) was applied to two series ($\bar{n}=0.03$ and $\bar{n}=0.15$) of aromatic epoxy resins of diglycidyl ether of bisphenol A (DGEBA) cured with methylene dianiline (MDA).

The aminohydrogen to epoxy ratio, $r$, was systematically varied below stoichiometric composition.

Complementary data have been obtained by differential scanning calorimetry (d.s.c.) and dynamic mechanical thermal analysis (d.m.t.a.). TSCr experiments[1] have already been carried out on a variety of systems such as amorphous[2] and semicrystalline homopolymers[3–5], copolymers[6] and blends[7]. After a brief description of the TSCr principle, the retardation spectra of crosslinked epoxies will be discussed.

## MATERIALS

The materials used, together with suppliers, molecular weight ($\bar{M}_n$) and epoxy equivalent weight (as determined by chemical titration), functionality and comments are listed in *Table 1*.

The structures of DGEBA epoxy resin and of MDA are shown in *Figure 1*. Two series of amine-cured epoxy resins were studied with number average degrees of condensation, $\bar{n}$, of the prepolymer of 0.03 and 0.15.

In the text, the formulations are identified by the aminohydrogen to epoxy ratio:

$$r=\frac{(4m_a/\bar{M}_{na})}{(2m_e/\bar{M}_{ne})} \tag{1}$$

where $m_a$ and $m_e$ are the initial weights of amine and epoxy prepolymer in the mixture, and $\bar{M}_{na}$ and $\bar{M}_{ne}$ are the number average molecular weights, respectively.

**Table 1** Details of materials used including molecular weight ($\bar{M}_n$), epoxy equivalent weight (EEW) and functionality ($\bar{F}_n$)

| Material | Supplier | $\bar{M}_n$ (g mol$^{-1}$) | EEW | $\bar{F}_n$ | Comments |
|---|---|---|---|---|---|
| DGEBA ($\bar{n}=0.03$) | Dow Chemical | 348 | 174 | 2 | DER 332 |
| DGEBA ($\bar{n}=0.15$) | Ciba-Geigy | 382 | 191 | 2 | BAK 164 |
| MDA | Fluka | – | – | 4 | Purity grade 98% |

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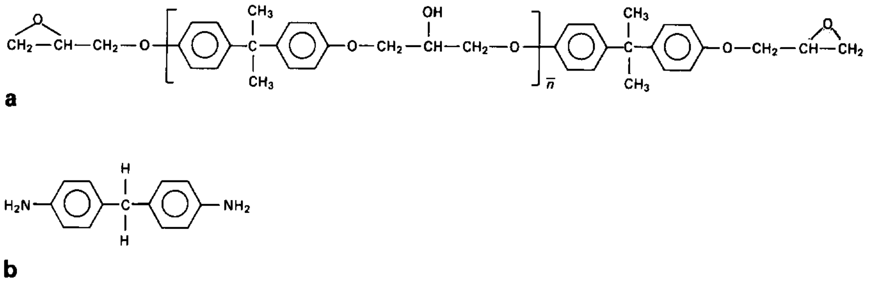

**Figure 1** Structures of (a) diglycidyl ether of bisphenol A (DGEBA) and (b) methylene dianiline (MDA)

*Sample preparation*

For each formulation, the indicated amount of hardener was ground prior to mixing with the resin at 70°C with mechanical stirring for 20 min. The mixture was then cast under vacuum in a $200 \times 200 \times 4\,\mathrm{mm}^3$ mould. The curing schedule was 110°C for 3 h and 190°C for 3 h, followed by slow cooling to room temperature.

D.s.c. scans of the cured resin revealed no exotherm and no increase in the glass transition temperature during a second scan. Therefore, we considered that the reaction between epoxy and amine groups was complete.

## METHODS

*Differential scanning calorimetry*

The Perkin-Elmer DSC-2 differential scanning calorimeter was used to determine the glass transition temperature ($T_g$) of each formulation. The d.s.c. analysis was performed in nitrogen at a heating rate of $20°\mathrm{C\,min}^{-1}$. The calorimeter was coupled to a scanning-auto-zero device which automatically optimized the baseline. Specimens weighing 8–12 mg were placed in aluminium pans and heated from room temperature to above $T_g$ and then quenched at $320°\mathrm{C\,min}^{-1}$. A second scan was then performed.

The first scan of the crosslinked epoxies clearly showed an enthalpy relaxation peak due to physical ageing of the material, resulting from storage at below $T_g$ (*Figure 2*).

In all cases, the values of $T_g$ were obtained from the midpoint temperature of the heat capacity deflection from the second d.s.c. scan.

*Dynamic mechanical thermal analysis*

Complementary data[8] were obtained using a dynamic mechanical thermal analyser (Polymer Laboratories) at 1 Hz. Samples were tested in double cantilever bending with a fixed displacement ($\pm 16\,\mu$m).

*Thermally stimulated creep*

The TSCr principle and the experimental apparatus used in this study have been described elsewhere[1,9,10].

*Principle*

A shear stress $\sigma$ is applied to the sample at a temperature $T_\sigma$ for a time $t_\sigma$ allowing polymer chains orientation. The viscoelastic strain is frozen in by a rapid quench to a temperature $T_0 \ll T_\sigma$. The release of the frozen-in strain is then monitored as the specimen is heated at a controlled rate: the most convenient rate was found to be $7°\mathrm{C\,min}^{-1}$.

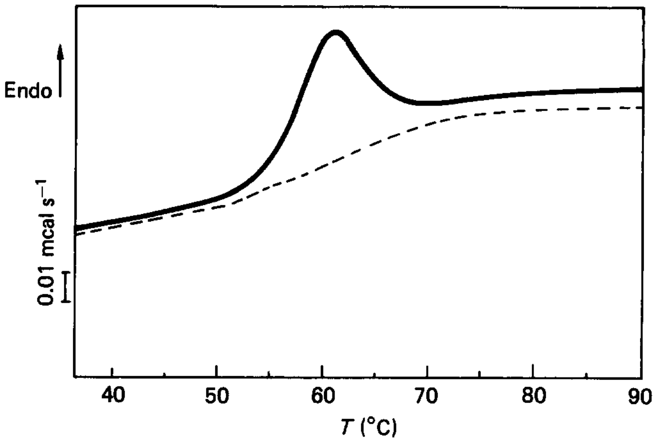

**Figure 2** D.s.c. thermograms of DGEBA ($\bar{n}=0.15$)–MDA, $r=0.5$. ——, First scan; ---, second scan

Thus, the frozen-in strain $\gamma(t)$, its derivative $\dot{\gamma}(t)$ and the temperature were simultaneously recorded as functions of time.

*Experimental set-up*

The experimental set-up used for TSCr experiments was designed and carried out in our laboratory[1]. It consisted of a torsional pendulum placed in a cell which could be cooled by external nitrogen gas circulation and heated in a controlled helium atmosphere. The specimen was located in the lower part of the cryostat and maintained in a vertical position by two clamps, the upper one rigidly bound to the pendulum rod and the lower one fixed to the bottom of the cryostat. As the sample was heated, the release of the unrecovered frozen-in strain stimulated the rotation of the diaphragm above the photocell yielding $\gamma(t)$ and $\dot{\gamma}(t)$.

## RESULTS AND DISCUSSION

*Study of retardation spectra*

An example of a TSCr spectrum is shown in *Figure 3* for DGEBA ($\bar{n}=0.15$)–MDA with stoichiometric composition ($r=1$). A shear stress $\sigma = 0.1$ MPa was applied to the sample for 2 min at $T_\sigma = 187$°C. The temperature was then lowered to $T_0 = 77$°C and the stress was removed. The sample was subsequently heated at a rate of $7°\mathrm{C\,min}^{-1}$ (so that the mobile units could return at random). The strain $\gamma$ and its time derivative $\dot{\gamma}$ were recorded. *Figure 3* shows $\gamma$ and the normalized magnitude $|\dot{\gamma}/\sigma|$ *versus* temperature.

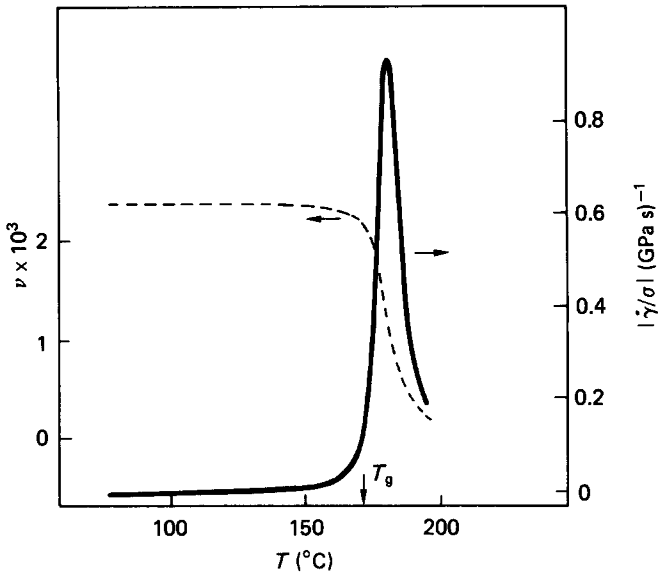

**Figure 3** TSCr spectrum of the stoichiometric ($r=1$) network DGEBA ($\bar{n}=0.15$)-MDA

**Table 2** Loading programme conditions and experimental results for two series of DGEMA-MDA

| | $r$ | Shear stress, $\sigma$(MPa) | Stress temp., $T_\sigma$(°C) | Peak temp., $T_\alpha$(°C) | Peak magnitude, $|\dot{\gamma}/\sigma|$(GPa s)$^{-1}$ |
|---|---|---|---|---|---|
| DGEBA ($\bar{n}=0.03$)-MDA | 0.5 | 0.20 | 87 | 75 | 0.82 |
| | 0.7 | 0.04 | 147 | 125 | 0.54 |
| | 0.85 | 0.08 | 197 | 163 | 0.52 |
| | 1 | 0.06 | 207 | 199 | 0.51 |
| DGEBA ($\bar{n}=0.15$)-MDA | 0.5 | 0.11 | 97 | 74 | 1.42 |
| | 0.7 | 0.26 | 127 | 122 | 1.14 |
| | 0.85 | 0.25 | 177 | 150 | 0.95 |
| | 1 | 0.16 | 187 | 181 | 0.93 |

Each spectrum was characterized by: its normalized magnitude $|\dot{\gamma}/\sigma|$ which depends on the number of relaxing species; the half-height width which accounts for the degree of homogeneity of the network; $T_\alpha$, the temperature at the maximum of the peak.

The loading programme conditions and the experimental results are listed in *Table 2*.

### *Magnitude*

*Figure 4* shows the TSCr spectra of DGEBA ($\bar{n}=0.03$)-MDA and DGEBA ($\bar{n}=0.15$)-MDA for various stoichiometric ratios. It can be seen for both series that the magnitude of the peak decreases with increasing $r$. D.m.t.a. measurements[11] performed at 1 Hz give the same trend, i.e. a decrease of the peak magnitude when $r$ is increased (*Figure 5*). This effect may be assigned to a higher chain mobility for the least crosslinked networks.

Despite this interpretation, we also observe differences between the TSCr and d.m.t.a. data. Indeed, the magnitude of d.m.t.a peaks is only slightly affected by $\bar{n}$ (*Figure 5*) while the magnitude of TSCr peaks is significantly increased for the higher value of $\bar{n}$, as might be expected from the loosening of the network. The greater accuracy of TSCr experiments is probably due to the fact that spectra are recorded continuously at a low frequency.

### *Half-height width*

The dependence of half-height width $L$ on $r$ for TSCr and d.m.t.a spectra is shown in *Figure 6*. Each curve passes through a maximum. However, the maxima of the d.m.t.a. curves are only poorly defined. In contrast, significant variations can be observed in the TSCr results.

It is noteworthy that from the TSCr data, the $\bar{n}=0.03$ resins seem more homogeneous than the $\bar{n}=0.15$ resins, with $r<0.75$ (the cross-over composition). For $r>0.75$, the trend is reversed. The networks with $\bar{n}=0.03$ ($r=0.5$)

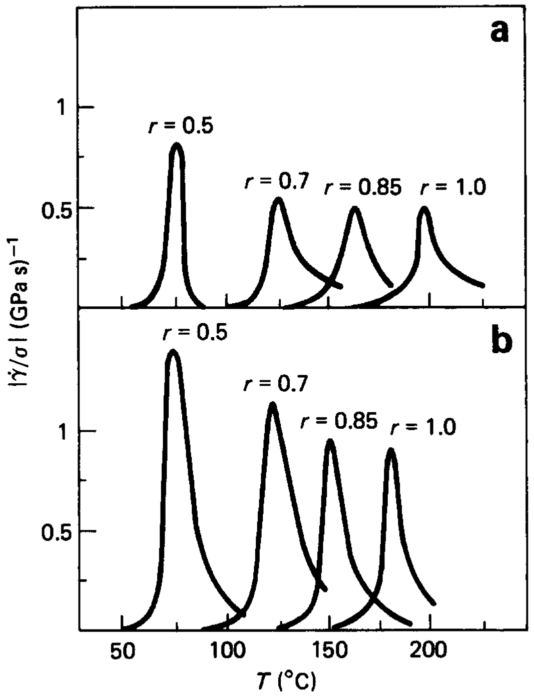

**Figure 4** TSCr spectra of (a) DGEBA ($\bar{n}=0.03$)-MDA and (b) DGEBA ($\bar{n}=0.15$)-MDA

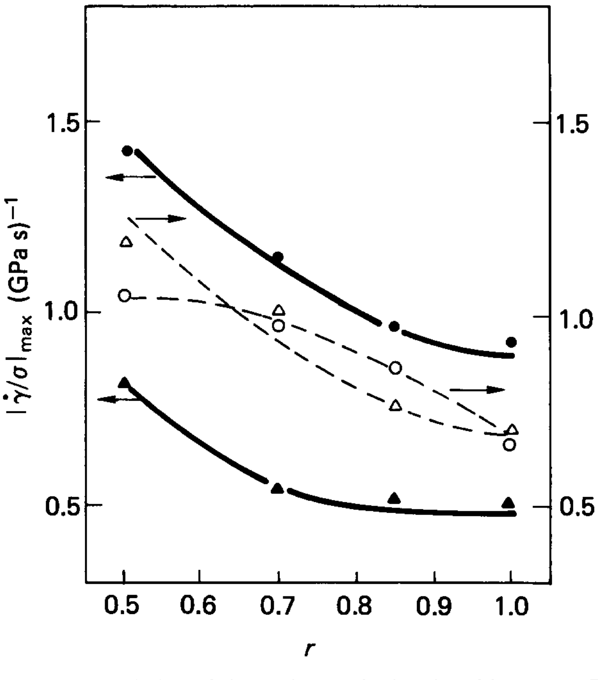

**Figure 5** Variation of the peak magnitude $|\dot{\gamma}/\sigma|$ with $r$. ——, TSCr spectra: ▲, $\bar{n}=0.03$; ●, $\bar{n}=0.15$. ---, D.m.t.a. spectra: △, $\bar{n}=0.03$; ○, $\bar{n}=0.15$

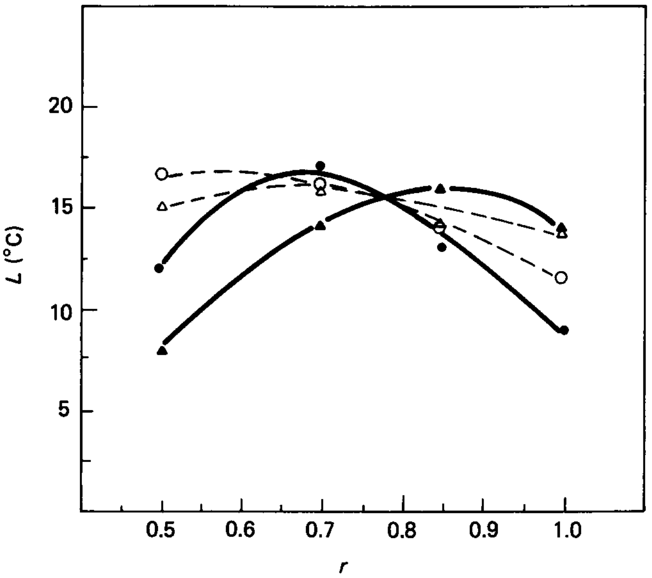

**Figure 6** Variation of the half-height width $L$ with $r$. ——, TSCr spectra: ▲, $\bar{n}=0.03$; ●, $\bar{n}=0.15$. - - -, D.m.t.a. spectra: △, $\bar{n}=0.03$; ○, $\bar{n}=0.15$

and $\bar{n}=0.15$ ($r=1$) show the greatest homogeneity (*Figure 6*). For both resins, as $r$ is varied between 0.5 and 1, regions of low crosslink density may occur in the material[12] and the resulting network becomes heterogeneous. However, the existence of such heterogeneities is still a matter of controversy.

### *Peak temperature*

For both resins, a significant shift of the TSCr retardation peak to higher temperatures is clearly observed as $r$ is increased (*Figure 4*). The shift is about 100°C between formulations $r=0.5$ and $r=1$. This may be attributed to an important restriction of molecular mobility as the resin becomes fully crosslinked.

For a thermoset network, the evolution of the retardation peak with $r$ is expected to be similar to that of the glass transition since both phenomena mark the glass-to-rubber transition which is associated with long range cooperative motion of the crosslinked network. This was confirmed by measurements of $T_g$ performed by d.s.c. (*Figure 7*).

Plots of $T_\alpha$ *versus* $r$ (*Figure 8*) exhibit a maximum at $r=1$. This is in agreement with results obtained by several authors[13–15] on crosslinked epoxy resins. An excess of epoxy creates chain ends in the network[16] which markedly affect $T_\alpha$.

Irrespective of the epoxy compound considered $T_\alpha$ depends linearly on $r$. As expected, at stoichiometry ($r=1$) $T_\alpha(\bar{n}=0.03)$ is greater than $T_\alpha(\bar{n}=0.15)$. For the two stoichiometric networks, the average molecular weight between crosslinks, $\bar{M}_c$, was calculated from the measurement of the shear storage modulus at $T_g+40$°C, which can be simply related to $\bar{M}_c$ in rubber elasticity theory[16–18]. The values of $\bar{M}_c$ thereby obtained are 300 g mol$^{-1}$ and 319 g mol$^{-1}$ for the networks $\bar{n}=0.03$ and $\bar{n}=0.15$ respectively. Since $\bar{M}_c(\bar{n}=0.15)$ is greater than $\bar{M}_c(\bar{n}=0.03)$, it is natural that the most loosely crosslinked networks have the lowest $T_\alpha$. It should be pointed out that if $r$ continues to decrease below a certain value (the crossover composition, $r \simeq 0.6$) the trend is reversed: $T_\alpha(\bar{n}=0.03)$ becomes lower than $T_\alpha(\bar{n}=0.15)$. In this situation the resins are lightly crosslinked and the peak temperature is mainly governed by the molecular weight $\bar{M}_n$, and $\bar{M}_n(\bar{n}=0.15) > \bar{M}_n(\bar{n}=0.03)$ implies $T_\alpha(\bar{n}=0.15) > T_\alpha(\bar{n}=0.03)$.

## CONCLUSION

Due to the specific characteristics of TSCr experiments, complementary data on the high temperature retardation mode ($\alpha$) in epoxy-aromatic amine networks as observed in d.m.t.a., have been obtained.

The analysis of TSCr spectra gives first indications about molecular mobility: $|\dot{\gamma}/\sigma|$ decreases and $T_\alpha$ increases as $r$ increases. The variation of the half-height width of the TSCr spectra accounts for the variation of homogeneity with the crosslink density.

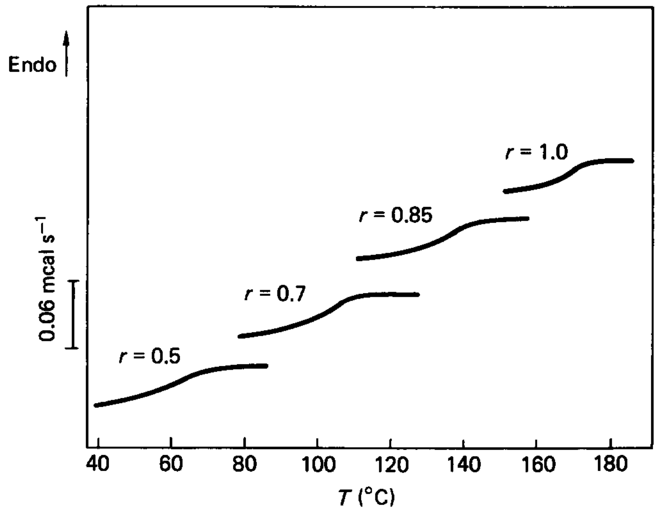

**Figure 7** D.s.c. traces of DGEBA ($\bar{n}=0.15$)–MDA specimens

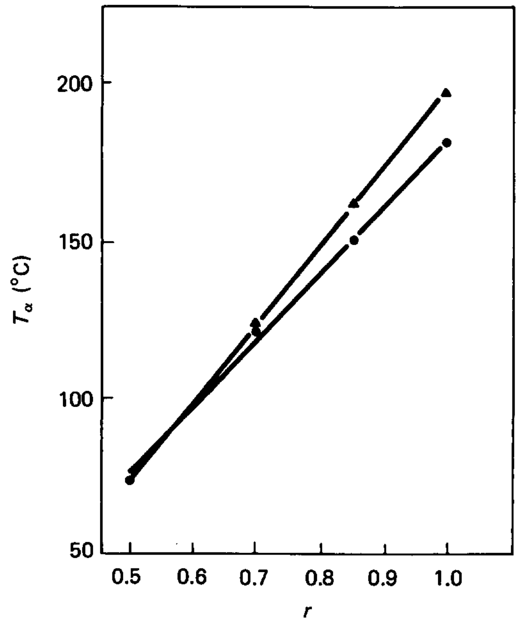

**Figure 8** Variation of $T_\alpha$ with $r$ for ▲, DGEBA ($\bar{n}=0.03$)–MDA; ●, DGEBA ($\bar{n}=0.15$)–MDA

A quantitative analysis of TSCr spectra shows that $T_\alpha$ is mainly governed by the crosslink density for $r>0.6$ and by $\bar{M}_n$ for $r<0.6$. It is important to note here that by using the fractional stresses procedure, the fine structure of TSCr spectra can be explored and related to the network structure. These data will be presented in a future publication.

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