

Molecular mobility associated with the T_g in DGEBA $_{\bar{n}}$ -DDM networks^a

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Abstract

Thermally stimulated creep (TSCr) spectroscopy has been used to investigate the molecular mobility associated with the glass transition in epoxy networks. A series of samples resulting from the crosslinking of DGEBA prepolymer (average degrees of condensation $\bar{n} = 0.03$ and 0.15) with the primary amine DDM was studied. The amino-hydrogen-to-epoxy ratio r was systematically varied below the stoichiometric composition. For all resins, a significant shift of the high temperature retardation mode is clearly observed as r is increased. The shift is about 100 °C between the formulations with $r = 0.5$ and $r = 1$. The complex TSCr spectra resolved into elementary peaks display a compensation law characteristic of the network structure and show that the shift of the peak temperature has an essentially entropic origin.

INTRODUCTION

Despite their good mechanical properties, thermosets based on epoxy resins display a disposition to cracking or fracture, which still remains a matter of concern for many researchers. The fracture mechanisms involved in the material are obviously related to the molecular structure. A better knowledge of the molecular mobility in epoxy networks is desirable if improved systems based on thermosets are to be developed.

In this work, thermally stimulated creep (TSCr) spectroscopy was applied to the two series ($\bar{n} = 0.03$ and $\bar{n} = 0.15$) of aromatic epoxy resins DGEBA $_{\bar{n}}$ -DDM. The amino-hydrogen-to-epoxy ratio r was systematically varied between 0.5 and 1.

After a brief recall of the TSCr principle, our results on the study of crosslinked epoxies will be presented.

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THERMALLY STIMULATED CREEP SPECTROSCOPY PRINCIPLE

During the past fourteen years, TSCr spectroscopy has been used successfully to study molecular mobility in polymers [1–4]. The main feature of this technique is its reasonably good sensitivity. The TSCr principle (Fig. 1) and the torsion pendulum used for this work have been extensively described elsewhere [1,2]; however, the general outlines are mentioned below.

The sample is subjected to a mechanical stress σ at T_g for 2 min, allowing complete orientation of the mobile units that one wishes to consider. The resulting viscoelastic strain ($\gamma \leq 10^{-3}$) is then frozen by quenching the sample to a temperature $T_0 \ll T_g$ and the stress is removed. The sample is subsequently warmed up at a controlled rate so that the mobile units can return to equilibrium at random. The strain $\gamma(t)$, its time derivative $\dot{\gamma}(t)$ and the temperature $T(t)$ are simultaneously recorded as functions of time. The plot of the normalized magnitude $|\dot{\gamma}/\sigma|$ versus T represents the complex TSCr spectrum.

RESULTS AND DISCUSSION

Complex retardation spectra

The TSCr spectra of DGEBA $_{\bar{n}}$ -DDM obtained by investigating the high temperature range between 40°C and 230°C are shown in Figs. 2 and 3. Each sample was submitted to a 0.1 MPa shear stress applied at $T_g + 40^\circ\text{C}$. The high temperature mode is labelled α . It is clear that the α -mode marks the glass to rubber transition and is associated with long range cooperative motions of the whole network; this was confirmed by T_g measurements performed on a DSC instrument.

As we can see in Figs. 2 and 3, for both the $\bar{n} = 0.03$ and the $\bar{n} = 0.15$ series, the magnitude of the peak decreases with increasing amino-hydrogen-

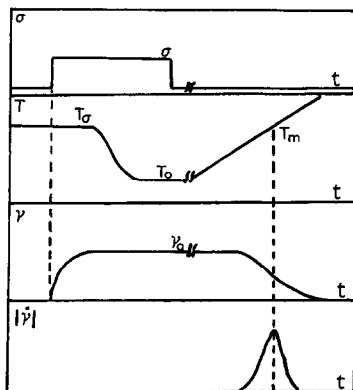


Fig. 1. Principle of thermally stimulated creep.

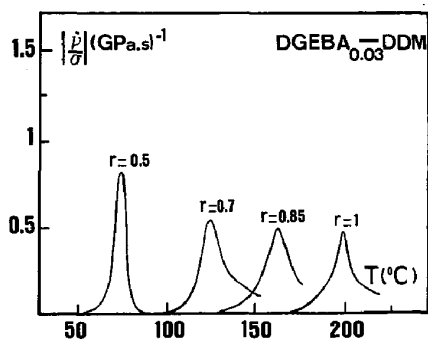


Fig. 2. TSCR complex spectra of DGEBA ($\bar{n} = 0.03$)-DDM for several stoichiometric ratios.

to-epoxy ratio (r). This effect may be assigned to a higher chain mobility for the least crosslinked networks. Furthermore, the magnitude of TSCR peaks is significantly increased for the higher value of \bar{n} (0.15), as might be expected because of the loosening of the network.

For both resins, a significant shift of the retardation mode to higher temperature is clearly observed as r is increased. The shift is about 100°C between the formulations with $r = 0.5$ and $r = 1$. This may be attributed to an important restriction of molecular mobility as the resin becomes more crosslinked.

Figure 4 shows on the same plot the T_α values for the two average degrees of condensation $\bar{n} = 0.03$ and $\bar{n} = 0.15$ as functions of r .

The plots of T_α vs. r exhibit a maximum for the peak temperature at $r = 1$. This result is in agreement with those obtained by several authors on crosslinked epoxy resins [5-7]. An excess of epoxy creates chain ends in the network which may markedly affect T_α . 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 $T_g + 40^\circ\text{C}$, which can be simply related to \bar{M}_c in rubber elasticity theory [8-10]. The

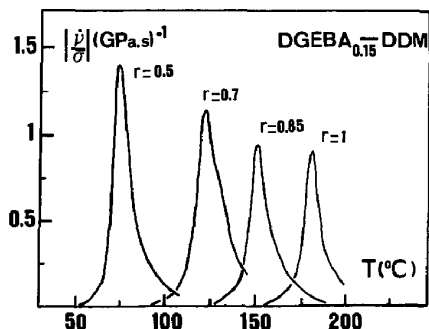


Fig. 3. TSCR complex spectra of DGEBA ($\bar{n} = 0.15$)-DDM for several stoichiometric ratios.

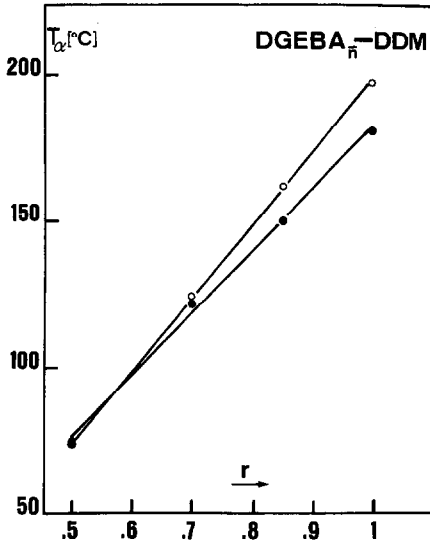


Fig. 4. Variation of T_α with the amino-hydrogen-to-epoxy ratio (r) for both DGEBA $_{\bar{n}}$ -DDM systems, $\bar{n} = 0.03$ (\circ) and $\bar{n} = 0.15$ (\bullet).

values of \bar{M}_c thereby obtained are 300 g mol^{-1} and 319 g mol^{-1} for the networks with $\bar{n} = 0.03$ 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 least crosslinked network should have the lowest T_α . It should be pointed out that, if r continues to decrease below a certain value (≈ 0.6 , the crossover composition), the trend is inverted: $T_\alpha(\bar{n} = 0.03)$ becomes lower than $T_\alpha(\bar{n} = 0.15)$; now the resins are lightly crosslinked, 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 $T_\alpha(\bar{n} = 0.15) > T_\alpha(\bar{n} = 0.03)$.

Fine structure analysis of the complex spectra

The complex TSCr spectra are characterized by a distribution of mechanical retardation times, and can be resolved by a fractional loading method [1,2]. For this purpose, a temperature window analysis was carried out: a static stress σ is applied at T_{σ_1} for a time $\Delta t = 2$ min. The temperature is then lowered by ΔT to T_{σ_2} (Fig. 5) where ΔT is the temperature window taken as 5°C in this work. At T_{σ_2} the stress is removed and the specimen is allowed to recover partially for $\Delta t = 2$ min. The specimen is then quenched to $T_0 \ll T_{\sigma_2}$ so that the viscoelastic strain ($\gamma \leq 10^{-3}$) is frozen-in at T_0 . A linear heating run is then performed and the decay of the frozen-in strain $\gamma(t)$ is observed together with its derivative $\dot{\gamma}(t)$.

In a creep experiment, if one assumes a single retardation time for each elementary recovery process obtained from the temperature window experi-

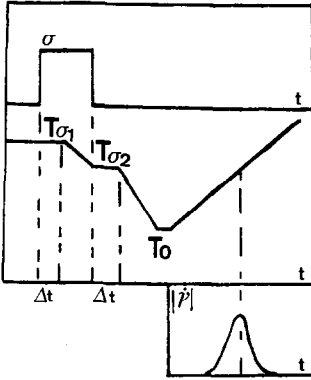


Fig. 5. Procedure of fractional loading in a TSCr experiment.

ment, this time τ_i can be associated with a mechanical retardation time

$$\tau_i(t) = \left| \frac{\gamma_i(t)}{\dot{\gamma}_i(t)} \right| \quad (1)$$

commonly called the Bucci relaxation time.

As temperature T is linear with time t , τ_i is also a function of T .

Thermally activated states theory predicts that $\tau_i(T)$ follows the Arrhenius equation

$$\tau_i(T) = \tau_{0i} \exp\left(\frac{\Delta H_i}{kT}\right) \quad (2)$$

where τ_{0i} is the pre-exponential factor, ΔH_i is the activation enthalpy and k is the Boltzmann constant. The activation entropy ΔS_i can be deduced from τ_{0i}

$$\tau_{0i} = \frac{h}{kT} \exp\left(-\frac{\Delta S_i}{kT}\right) \quad (3)$$

where h is the Planck constant.

Each elementary spectrum is characterized by an activation enthalpy (ΔH_i) and a retardation time τ_{0i} .

If a plot of $\ln \tau_{0i}$ versus ΔH_i yields a straight line, the material is said to display the 'kinetic compensation effect'.

In order to investigate the microstructure of the samples, each of them has been submitted to fractional stresses over the whole breadth of the corresponding complex spectrum.

Results of the investigation of the α -mode for the two resins ($\bar{n} = 0.03$ and $\bar{n} = 0.15$) are presented in Figs. 6 and 7. Each point corresponds to an elementary spectrum and each straight line corresponds to a complex spectrum.

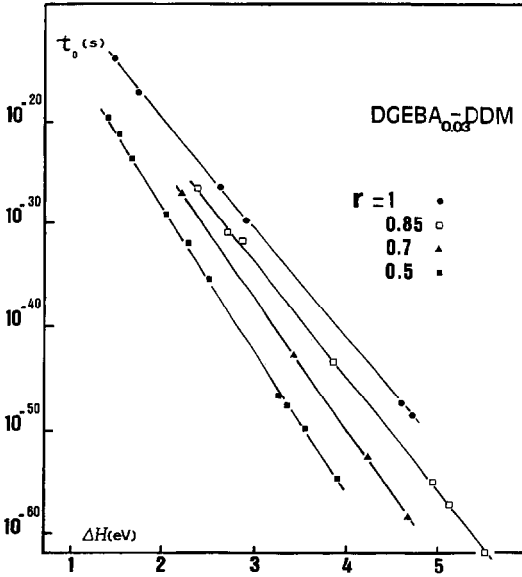


Fig. 6. Plots of the pre-exponential factor vs. activation enthalpy for different values of r .

The first observation that should be emphasized is that, for a given r value (except for $r = 0.5$), an increase of the average degree of condensation (\bar{n}) results in a diminution of the width of the distribution of activation enthalpy (ΔH).

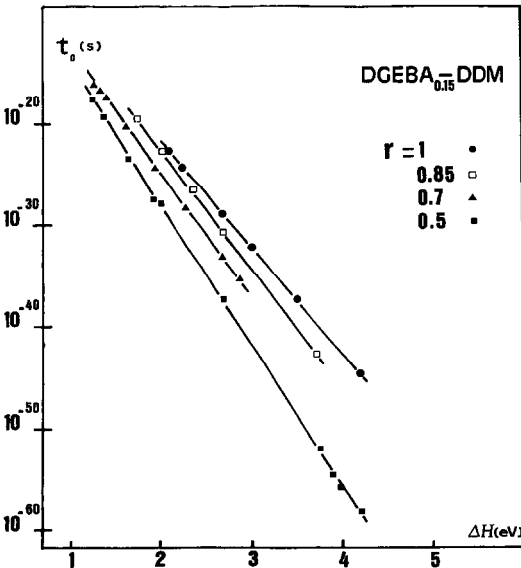


Fig. 7. Plots of the pre-exponential factor vs. activation enthalpy for different values of r .

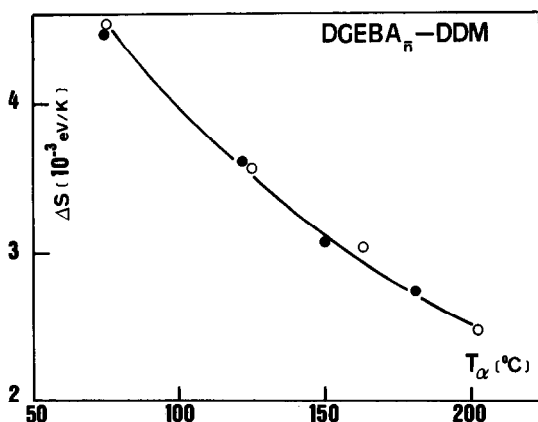


Fig. 8. Variation of the activation entropy vs. T_α for $\Delta H = 2.5$ eV, $\bar{n} = 0.03$ (○) and $\bar{n} = 0.15$ (●).

For both resins, if we consider a particular value of ΔH , an increase of r appears as a diminution of the activation entropy (ΔS). The influence of the entropic factor diminishes for the lowest values of ΔH .

The activation entropy associated with each complex spectrum has been calculated by using eqn. (3). In this equation the temperature has been taken as the harmonic average value (T_H) of the temperature of the N elementary peaks which obey a compensation law

$$T_H = \frac{N}{\sum_i \frac{1}{T_{m_i}}} \quad (4)$$

where T_{m_i} is the peak temperature of the i th elementary peak.

Figure 8 shows the variation of ΔS vs. T_α for the two resins. ΔS diminishes monotonically as T_α increases. Note that this curve is the same for the two values of \bar{n} .

The relatively large variation of ΔS as r varies between 0.5 and 1, compared with the slight variation of ΔH , shows that the 100°C shift of T_α has essentially an entropic origin.

CONCLUSION

For both resins, the α -mode associated with the glass transition is found to shift to higher temperatures as the amino-hydrogen-to-epoxy ratio r increases. The shift is about 100°C between formulations with $r = 0.5$ and $r = 1$. A quantitative analysis of TSCr spectra shows that T_α is mainly governed by the crosslink density for $r > 0.6$ and by \bar{M}_n for $r < 0.6$.

The resolution of the complex spectra into elementary peaks by the fractional stresses method shows the important part played by the activation entropy in the 100°C shift of the α -peak as r increases from 0.5 to 1.

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