

THERMALLY STIMULATED CREEP SPECTROSCOPY FOR THE STUDY OF DGEBA-DDM NETWORKS

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During the past two decades, Thermally Stimulated Creep Recovery (TSCR) has been used successfully to study molecular mobility in polymers. The main feature of this technique is its quite good sensitiveness: the sample undergoes a shear stress, so that the subsequent strain is linear in a range larger than in elongation or compression experiments. Furthermore, the low equivalent frequency of TSCR permits the resolution of normally overlapping peaks.

In this study, the TSCR technique has been used to investigate a series of DGEBA-DDM networks differing from the value of the amine- to-epoxy ratio which was systematically varied below stoichiometric composition. The magnitude of the β -mode (glassy region) is seen to decrease unexpectedly as the network gets looser, while its peak-temperature decreases. This result is interpreted in terms of 'internal antiplasticization'. Moreover, we show that the important shift of the α -peak associated with the glass transition has an essentially entropic origin.

Introduction

Thermosets based on epoxy resins are widely used as adhesives, coatings and matrices for reinforced composites. The choice of particular pre-polymers or crosslinking agents is dictated by end-use or service requirements.

Despite their good mechanical properties (e.g. high storage modulus), these materials 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 their molecular structure. It is therefore necessary to correlate the anelastic losses responsible for those mechanisms with the microstructure of the thermoset network. This is the purpose of the present study by carrying out TSCR experiments. The technique has already been utilized to study both amorphous and crystalline polymers [1-3], copolymers [4] and blends [5].

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In this work, the epoxy pre-polymer DGEBA (diglycidyl ether of bisphenol A)-average degree of polymerisation: 0.03- was crosslinked with the primary amine DDM (4,4' diamino diphenyl methane). The structural parameter is the amine-to-epoxy molar ratio r which varies between the values 0.5 and 1.

Thermally stimulated creep recovery (TSCR)

The TSCR principle and the torsion pendulum used for this work have been extensively described elsewhere [1, 6]. However, the general outlines are mentioned below.

Principle

The TSCR principle is shown in Fig. 1. A static shear stress σ is applied to the sample at a temperature T_σ for a time $t_\sigma = 2$ min to allow polymer chains orientation. The resulting viscoelastic strain is then frozen by quenching the sample to a temperature $T_0 \ll T_\sigma$. After 2 min at T_0 , a linear heating run is imposed to the sample:

$$T = T_0 + mt \quad (1)$$

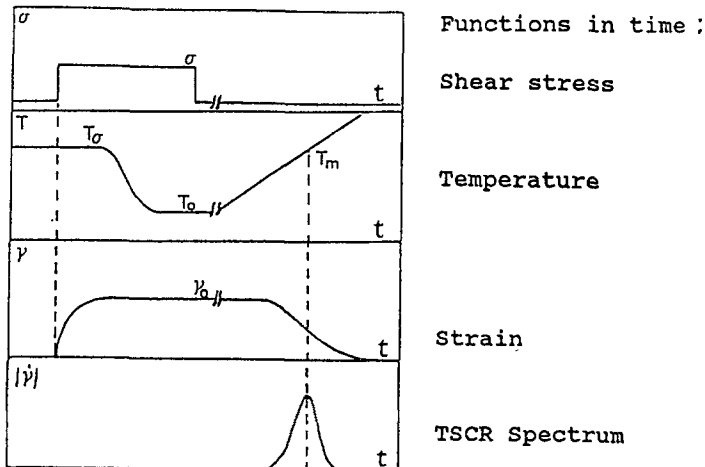


Fig. 1 Principle of thermally stimulated creep

During this scan the release of the frozen-in strain $\gamma(t)$ is observed. $\gamma(t)$, its time derivative $\dot{\gamma}(t)$, and temperature $T(t)$ are simultaneously recorded as functions of time. The plot of $\dot{\gamma}$ vs. T represents the TSCR complex spectrum.

Results on complex retardation modes

Low temperature retardation modes

Each sample was investigated in the glassy region with a stress $\sigma \approx 7$ MPa applied at $T_\sigma = -23, +27, +47,$ and -18° respectively in the order of increasing r values. T_σ was chosen in order that the peak temperature of each spectrum may be maximum, and to eliminate the overlapping of the β and ω peaks found for $r = 1$. Figure 2 shows the TSCR spectra thereby obtained. [For all spectra presented in this work, the heating rate was $m = 7$ deg/min.]

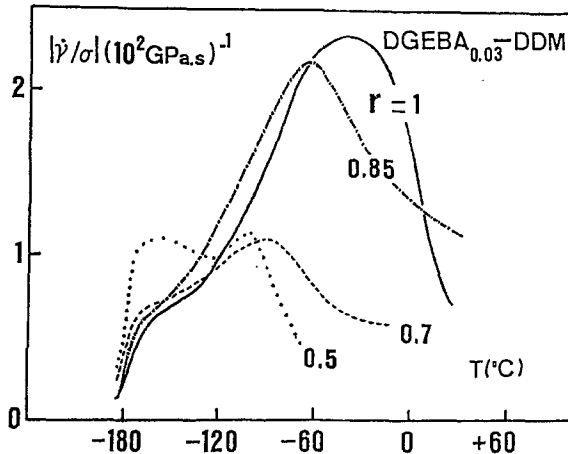


Fig. 2 Evolution of the β retardation mode with the amine/epoxy ratio r

The γ -mode found at about -160° regardless of the value of r , has been associated with the motion of the unreacted epoxy groups in the non-stoichiometric networks. Its magnitude increases as composition shifts from stoichiometry. It is interesting to note that the γ -mode appears as a shoulder for $r > 0.5$. Such a behaviour is typical for the most crosslinked resins.

The main retardation mode in the glassy region is the β -mode whose peak temperature is maximum at stoichiometry and shifts to lower tempera-

tures as the amine/epoxy ratio is decreased (Fig. 2). This result is in agreement with those reported in the literature [7, 8]. Here, a fault in stoichiometry corresponds to a depletion of the bulky, rigid phenyl segments of the DDM and consequently enhances local molecular mobility. It is generally accepted that the hydroxyether portions, produced during the curing of the network, do participate to a large extent in the localized motions [7-9].

The most striking result is the unexpected decline of the β -mode magnitude as r decreases (Fig. 2), while the evolution of its peak temperature seems to indicate greater mobility for the hydroxyether segments. This apparently paradoxical behaviour is similar to the so-called 'antiplasticizing effect' observed in the anomalous plasticization of some linear polymers, e. g. PVC, if low quantities of compounds with low molecular weight are added to the polymer [10, 11]. For the materials under study, the depression of the β -mode could be due to the unreacted epoxy groups, acting as anti-plasticizers, that would build up hydrogen bonds with the relaxing units and block the β -motions.

High temperature retardation mode

The TSCR spectra obtained by investigating the high temperature range are shown in Fig. 3. Each sample was submitted to a 0.1 MPa shear stress applied just above the peak-temperature of the relevant spectrum.

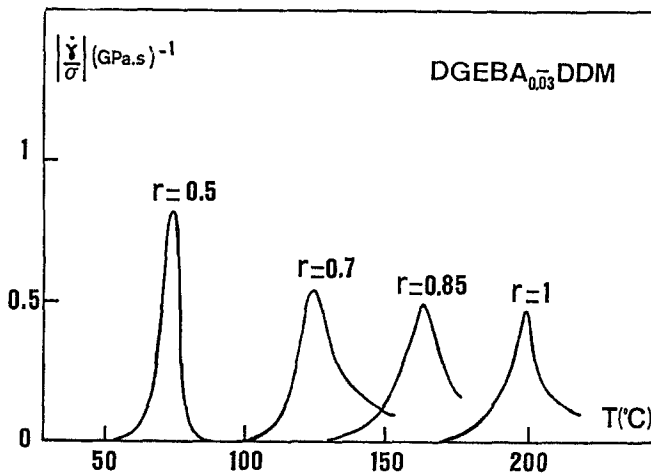


Fig. 3 Evolution of the α retardation mode with the amine/epoxy ratio r

The high temperature mode is labelled as 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 measurements of the glass transition performed with a DSC.

As r increases from 0.5 to 1, the α -mode is shifted from 72 to 198°. This may be attributed to an important restriction of molecular mobility as the network becomes more tightly crosslinked, the α -peak temperature reaching its maximum value at stoichiometry. This later result agrees quite well with those previously reported on epoxy-based networks [12, 13].

Fractional loading analysis

The complex TSCR spectrum is characterised by a distribution of mechanical retardation times. By applying fractional stresses to the sample, one can resolve the complex spectrum into elementary peaks.

For this purpose, a 'temperature window' experiment has been carried out (Fig. 4): the sample undergoes a shear stress σ at the temperature T_{σ_1} for a time $\Delta t = 2$ min. The temperature is then lowered by ΔT to T_{σ_2} , ΔT , the 'temperature window', has been taken as 5° in this work. At T_{σ_2} the stress is removed and the specimen is allowed to recover partially for 2 minutes. The specimen is then quenched to $T_0 \ll T_{\sigma_2}$ where the viscoelastic strain is frozen. A linear heating run is then performed and the decay of the frozen-in strain $\gamma(t)$ is observed, together with its derivative $\dot{\gamma}(t)$.

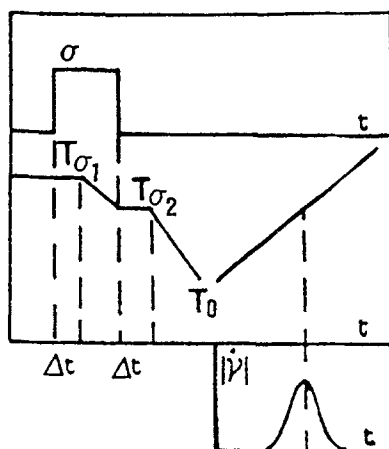


Fig. 4 Procedure of fractional loading in a TSCR experiment

The ratio $\gamma(t)/\dot{\gamma}(t)$ with the dimensions of time is typical of the relaxing system [14]. In other words, if one assumes a single retardation time for each recovery process, the i^{th} elementary peak obtained from the 'temperature window' experiment can be associated with a mechanical retardation time:

$$\tau_i = \left| \frac{\gamma_i(t)}{\dot{\gamma}_i(t)} \right| \quad (2)$$

It is clear from Eq. (2) that τ_i , commonly called the Bucci retardation time, is a function of time and therefore of temperature (see Eq. (1)). According to the theory of Thermally Activated States, $\tau_i(T)$ follows the Arrhenius equation:

$$\tau_i(T) = \tau_{oi} \exp(\Delta H_i/kT) \quad (3)$$

where τ_{oi} and ΔH_i are the pre-exponential factor and the activation enthalpy respectively for the i^{th} elementary processes, and k is Boltzmann's constant.

The pre-exponential factor can be related to ΔS_i , the corresponding activation entropy, by the Eyring equation (where h is Plack's constant):

$$\tau_{oi} = \frac{h}{kT} \exp\left(\frac{-\Delta S_i}{k}\right) \quad (4)$$

The values of τ_{oi} and ΔH_i attached to τ_i are deduced from a computer treatment of the experimental elementary peak, assuming a single retardation time. If the plot of $\log \tau_{oi}$ vs. ΔH_i yields a straightline, the material is said to display the kinetic 'compensation effect'.

Fine structure results

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.

β -mode

Figure 5 shows the plot of $\log \tau_o$ against ΔH for the DGEBA 0.03-DDM networks. For each sample, two compensation straight lines are clearly observed, revealing the existence of two different types of relaxing units. As discussed above, the β -mode in DGEBA-type networks is generally ascribed to the crankshaft motion of the hydroxyether segments. But some scientists [7, 8, 15] state that the diphenyl propane (DPP) groups are also involved in

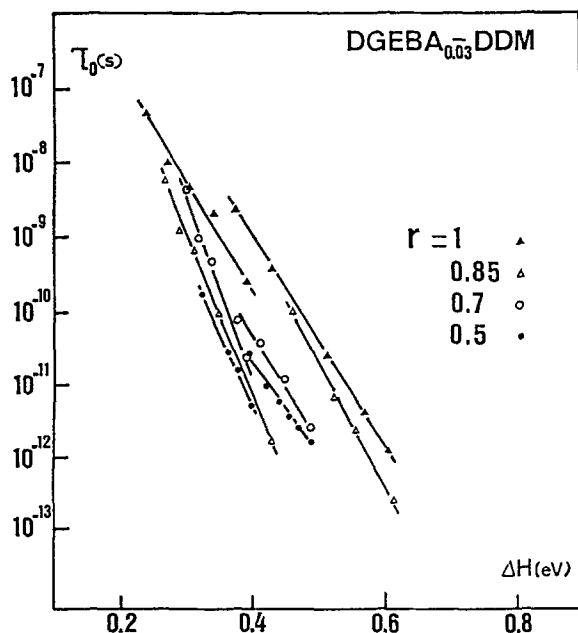


Fig. 5 Plots of the pre-exponential factor (τ_0) vs. activation enthalpy (ΔH) (β -mode) for different values of r

the β -mode motions. Our results support this contention. We suggest the β_1 sub-mode (at lower enthalpy or temperature) to be related to the motion of the DDP groups, while the β_2 sub-mode is attributed to the relaxation of the hydroxyether segments.

α -mode

The investigation of the α -mode by the fractional loading technique has revealed the results presented in Fig. 6. Each straightline corresponds to a complex spectrum.

The first observation that should be emphasized is that the width of the distribution of activation enthalpy is slightly affected by the variation of r between 0.5 and 1, in spite of the shift of the α -peak by about 126° (Fig. 3). In contrast, the pre-exponential factor τ_0 – for a specific ΔH value – increases considerably. By using Eq. (4), we have determined the values of the activation entropy ΔS at $\Delta H = 2.5$ eV for $r = 0.5$ and $r = 1$; we have found $\Delta S = 4.53 \times 10^{-3}$ eV/K and 2.48×10^{-3} eV/K, respectively.

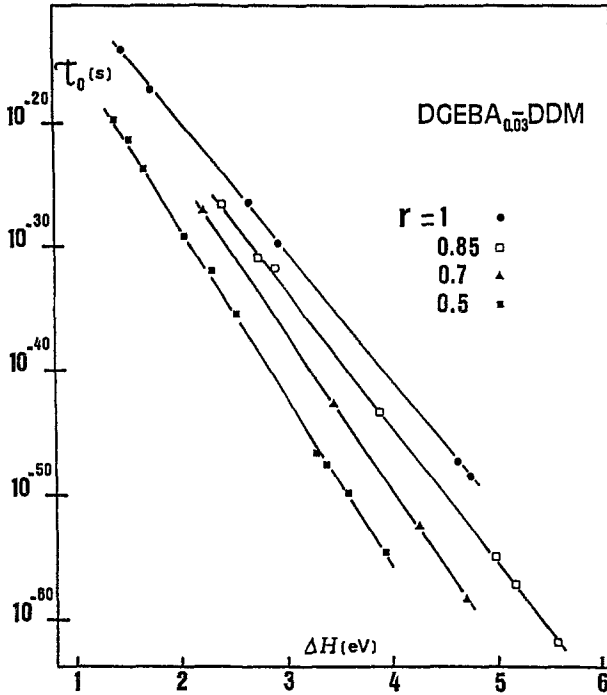


Fig. 6 Plots of the pre-exponential factor vs. activation enthalpy (α -mode) for different values of r

These results are of particular interest since peak shifts are commonly interpreted in terms of raise of activation enthalpy. Indeed, for our materials, the part played by the activation entropy must be taken into consideration.

Conclusion

The TSCR technique has been used to characterize a series of DGEBA_{0.03}-DDM networks. The β -mode observed in the glassy state is shifted towards lower temperatures by an excess of epoxy prepolymer, while its magnitude is lowered substantially. This behaviour, similar to the 'antiplasticizing effect', has been accounted for by the existence of intermolecular hydrogen bonds between the unreacted epoxy groups and the relaxing units. The study of its fine structure shows that the β -mode is the sum of two sub-modes, each of them corresponding to the motion of two different types of relaxing units.

The α -mode associated with the glass transition is found to shift to higher temperatures as the amine/epoxy ratio r increases. The resolution of the complex spectra into elementary peaks shows the important part played by the activation entropy in the shift of the α -peak of about 126° , as r increases from 0.5 to 1.

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Zusammenfassung – Thermisch stimulierte Kriecherholung (TSCR) ist eine Methode, die in den letzten 20 Jahren erfolgreich zur Untersuchung des mechanischen Fließverhaltens von Materialien eingesetzt wurde. Die Probe wird dabei einer konstanten mechanischen Belastung ausgesetzt, wobei nach einem gewissen Zeitintervall, der durch Viskoelastizität eingenommene Dehnungszustand durch rasches Abkühlen eingefroren wird. Durch eine anschließende Erwärmung mit einer linearen Aufheizrate ohne mechanische Belastung wird der Gleichgewichtszustand in einem materialabhängigen Temperaturintervall zurückgewonnen.

In der vorliegenden Arbeit wird das Verhalten von Proben eines vernetzten Epoxides eingehend beschrieben.