Strain rate and temperature effects on the mechanical behaviour of epoxy mixtures with different crosslink densities

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The microstructure and the flexural behaviour of two highly crosslinked epoxy mixtures have been investigated. Besides the usual α and β relaxations appearing for any epoxy mixture, an additional ω relaxation, located slightly above room temperature, was evident for the mixture with higher crosslink density. This relaxation, which seems to be related to microstructural variations originating in a free volume increase, permits us to explain the lower mechanical properties of the larger higher crosslinked mixtures in the temperature range between the β and α relaxations. Whilst at room temperature the flexural modulus did not show any significant variation upon testing rate and the strength slightly increased for both epoxy mixtures. © 1997 Elsevier Science Ltd

INTRODUCTION

Epoxy resins are being used increasingly in structural applications such as matrices for composites or adhesives in the aircraft industry. The knowledge of the dependence of the mechanical behaviour upon chemical microstructure of these materials becomes of primary importance in order to attain the maximum performance for one chosen mixture. Nevertheless, despite using the best possible combination of constituents there are other factors such as crosslink density or free volume which can condition the ultimate properties of these materials[1-6]. These factors are dependent upon the cure schedule used[1,4,5]. Mechanical properties of polymers are strongly sensitive to temperature and strain rate[8-12], especially when the temperature approaches the glass transition temperature since in this region the viscoelastic nature of the material becomes highly strain-rate dependent.

The similar effects of testing rate and temperature on the fracture behaviour of epoxy resins have been described by several authors[8,9], whilst others have related the variation of fracture behaviour to the cure schedule used and/or to the crosslink density of the epoxy matrix[10,11]. Nevertheless, the importance of several relaxation processes which appear in epoxy resins through temperature as a consequence of chemical microstructural variations, has not been studied profoundly.

The aim of this study was, first, to evaluate the viscoelastic response through temperature for epoxy resins with different crosslink densities, and, secondly, to

investigate the mechanical behaviour of these resins as a function of testing rate and temperature as a function of the relaxation behaviour of these epoxy mixtures.

EXPERIMENTAL

Materials and mixing

The epoxy resins investigated were diglycidyl ether of bisphenol A (DGEBA) differing in their initial molecular chain length, DER 332 with an epoxide equivalent weight (EEW) of $174.3 \, \mathrm{g \, eq^{-1}}$ (determined by bromine titration), and Rutapox VE-3966 with an EW of $186 \, \mathrm{g \, eq^{-1}}$, both kindly supplied by Dow Chemical and Bakelite, respectively. Diaminodiphenylmethane (DDM), Ciba-Geigy quality, was used as an aminic curing agent in a stoichiometric ratio. Chemical structures of the amine and the resins are shown in *Figure 1*.

The amine was added to the heated liquid epoxy at 80°C, and mixing was done by mechanical stirring for 10 min. The resulting mixture was poured into a mould consisting of two glass plates and a steel frame, which had been sprayed with a mould release agent (Frekote 44) and preheated for 1 h at 80°C. Curing was made for 150 min at 80°C (under vacuum the first 90 min), 90 min at 140°C, and further post-curing at 200°C for 2 h.

Dynamic mechanical properties

Dynamic mechanical tests were carried out at 1 Hz and a heating rate of $3°\mathrm{C \, min^{-1}}$ in a dynamic mechanical thermal analysis unit (DMTA, Polymer Laboratories Ltd) and at 10 Hz and a heating rate of $3°\mathrm{C \, min^{-1}}$ using a Metravib viscoanalyser. Measurements were performed using the single cantilever or a three-point bending device

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Product	Structure
Diglycidil ether of bisphenol-A DGEBA	
Diaminodiphenyl methane DDM	

Figure 1 Chemical structures of the resins and the curing agent used

with a 14 mm or a 44 mm span, respectively. The specimen dimensions were $12 \times 12 \times 1$ mm or $60 \times 12 \times 6$ mm, respectively. The storage modulus, E', and the loss factor, tan δ, were measured from $-80°C$ up to a temperature beyond that for the rubbery state was attained. The glass transition temperature, T_g, was defined as the temperature corresponding to the maximum value of loss factor.

Mechanical behaviour

Flexural properties were determined in a three-point bending device using an Instron universal testing machine, model 4206. Specimen dimensions were $80 \times 12 \times 6$ mm. Tests were carried out at $16 \times 10^{-4} \text{s}^{-1}$ over a temperature range between $-40°C$ and $180°C$, following the ASTM D790 standard specifications. In other series of tests carried out at room temperature, strain rates ranging from 10^{-4} to $5.12 \times 10^{-2} \text{s}^{-1}$ were used. Each test result reported here was an average of five test specimens.

RESULTS AND DISCUSSION

Viscoelastic properties of cured epoxy resins

The dynamic mechanical properties of both epoxy oligomers after curing with DDM determined at an excitation frequency of 10 Hz are shown in *Figures 2* and *3*. For both mixtures the typical viscoelastic behaviour usually shown by thermosetting resins was observed. The epoxy mixture formed by using the oligomer with a lower molecular weight, DER 332, showed a few less pronounced α relaxation peaks than that cured through the other epoxy oligomer, Rutapox VE-3966. The temperature corresponding to the α peak, T_α, was higher for the DER 332 containing mixture than that for the other resin. A broader and less pronounced β relaxation peak, similar in height for both mixtures, was also seen centred around $-50°C$ for both systems. This relaxation has been associated with the molecular motion of glycidylether groups though the motions of diphenylpropane groups can also have some contribution[13–17].

The loss factor variation, plotted in *Figure 2*, showed an intermediate ω relaxation which appeared at temperatures between 40°C and 100°C solely for the mixture cured from DER 332. Although this relaxation has been traditionally related to unreacted molecular segments and/or inhomogeneities in the sample arising from
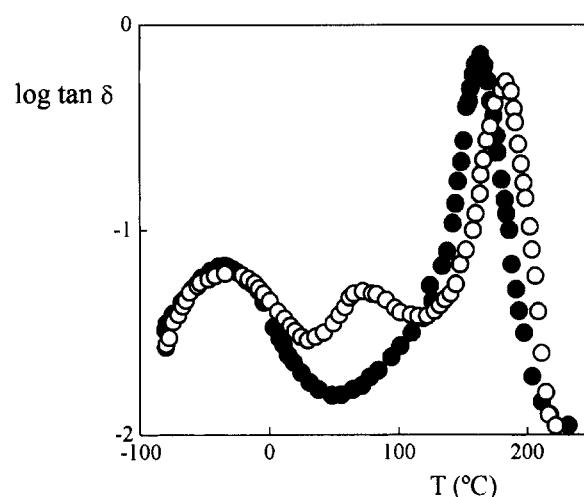
Figure 2 Loss factor variation upon temperature for both epoxy mixtures. O, DER 332/DDM; ●, Rutapox VE-3966/DDM
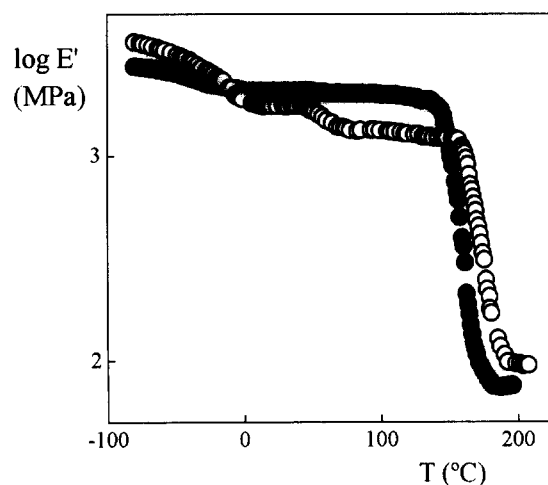
Figure 3 Storage modulus variation upon temperature for both epoxy mixtures. Symbols as in *Figure 2*

dissimilar crosslinking sites[14,16,18], recent work in our laboratories[6], along with the studies carried out by several techniques[3,7], including positron annihilation measurements[4,19] on variation of free volume at high crosslink density of these networks, seem to indicate that this relaxation can be related to local motions of chains in high crosslink density regions located inside the

Table 1 Height and peak temperatures of the main relaxations measured at 1 and 10 Hz

	ν (Hz)	h_β	T_β (°C)	h_ω	T_ω (°C)	h_α	T_α (°C)
RUTAPOX VE-3966	1	0.066	−52	—	—	0.70	162
	10	0.067	−34	—	—	0.71	165
DER 332	1	0.065	−50	0.043	71	0.51	175
	10	0.066	−32	0.051	74	0.52	189

overall matrix because in these regions the free volume would be higher than in the rest of the overall matrix. Therefore, it seems reasonable to suppose that the ω relaxation, appearing in highly crosslinked networks, arises from the motion of the same groups which are responsible for the β relaxation. As shown in a previous work[6], the temperature chosen for the early stage of a cure schedule has a clear influence on the shape of the ω relaxation of the corresponding post-cured stoichiometric mixture, possibly as a consequence of the existence of inhomogeneities in the cured epoxy mixture. Besides, the ω relaxation appears solely for the DER 332/DDM mixture once post-cured at high temperatures. All that may be related to the increasing free volume at the latter stages of curing[3,7]. Nevertheless, it is still not clear whether these variations are a consequence of microstructural differences produced at the early stage of curing or to chemical reactions occurring upon post-curing at high temperatures, though both factors together could explain the variations on the ω relaxation and could correspond to the increasing free volume around the inhomogeneities. These are obtained at the early stage of curing and only affect the dynamic behaviour at very high crosslink densities of the cured network.

As shown in *Figure 3*, for both mixtures the variation of storage modulus upon temperature showed similar shifts in the β and α relaxation regions with a slight decrement at the β relaxation and a sharp drop at the α relaxation then approaching a constant value in the rubbery region. The rubbery modulus was higher for the mixture cast from DER 332 than for that used from Rutapox VE-3966. Following the theory of rubber elasticity[20], the higher rigidity seen in the rubbery region for the mixture cast from the epoxy oligomer with a lower molecular weight indicated a higher crosslink density for the corresponding epoxy mixture after curing.

On the other hand, only the mixture cured from DER 332 showed a slight drop in the storage modulus at the ω relaxation region, which led to a clear lower rigidity for this mixture than that cured from Rutapox VE-3966 in the temperature range located between the ω and α relaxations. This behaviour once again indicates that, despite the higher crosslink density for the mixture cured from DER 332, slight microstructural variations, such as regions with higher crosslink density leading to higher free volume inside the network, on the cured network could lead to lower elastic modulus values for highly crosslinked epoxy networks in the temperature range corresponding to these microstructural relaxations. This interpretation could permit us to calculate the variations observed in the literature survey for small deformation mechanical properties shown for epoxy mixtures, lower for highly crosslinked stoichiometric mixtures, cured with different stoichiometric ratios or with various

Table 2 Flexural properties of both epoxy mixtures at room temperature

	E (MPa)	S (MPa)	r (mm mm^{-1})
RUTAPOX VE-3966	2870 ± 40	133 ± 11	0.077 ± 0.003
DER 332	2610 ± 45	126 ± 3	0.076 ± 0.005

crosslink densities[5,11,21–24]. This would also allow us to explain the higher value of storage modulus at low temperatures for the larger crosslinked network.

In the same way as shown in other studies[2,6], the glass transition temperature, defined as that corresponding to the peak of the α relaxation, decreased as crosslink density of the network decreased, see *Table 1*, and, conversely, the height of the relaxation increased.

As *Table 1* shows, despite the difference on specimen dimensions used in the DMTA and in the viscoanalyser, the relative dynamic mechanical behaviour shown above for both epoxy mixtures was not practically dependent on the frequency of the measurement, though all relaxations, and particularly the β one, appeared at lower temperatures as frequency decreased from 10 to 1 Hz.

Changes in mechanical properties as a function of test temperature

Table 2 shows the flexural properties at room temperature for both epoxy mixtures measured at a strain rate of 2.07×10^{-4} s^{-1}. It becomes evident that small deformation properties such as flexural modulus, E, and strength, S, are slightly lower as crosslink density of the network was higher following the same trends as those shown by other authors[2,5,7]. Taking into account that the ω relaxation in the mixture prepared through DER 332, at the frequencies used in the dynamic mechanical tests, appeared in a temperature range slightly higher than the test temperature used, it is reasonable to consider that the lower values of these properties for the more crosslinked mixture are related to this relaxation since the frequency used in the static tests is clearly lower and so the relaxations have to occur at lower temperatures[8,25,26].

The temperature dependence of the flexural modulus, E, and strength, S, of DER 332 and Rutapox VE-3966 epoxy resins cured with DDM is shown in *Figures 4* and *5*, respectively. For both mixtures these mechanical properties decreased remarkably in the glass transition region. On the other hand, both epoxy mixtures showed a clear decrement in both properties at temperatures corresponding to their β relaxations, and decrease further in the temperature region located between their respective β and α relaxations. It is worth noting the similarity of the elastic modulus variation upon temperature with that shown by the storage modulus measured by dynamic mechanical testing (*Figure 3*).
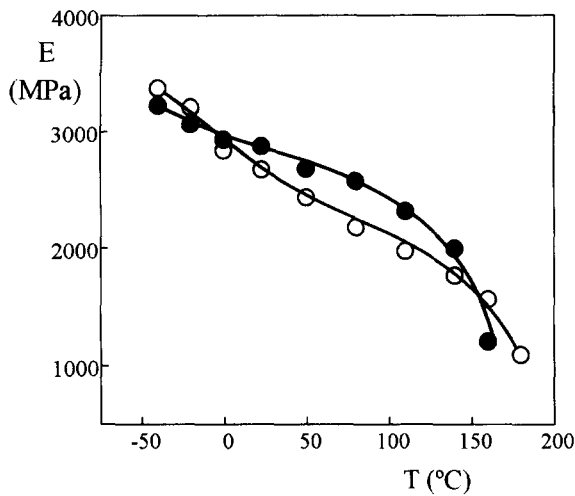
Figure 4 Flexural modulus as a function of testing temperature for both epoxy mixtures. Symbols as in *Figure 2*
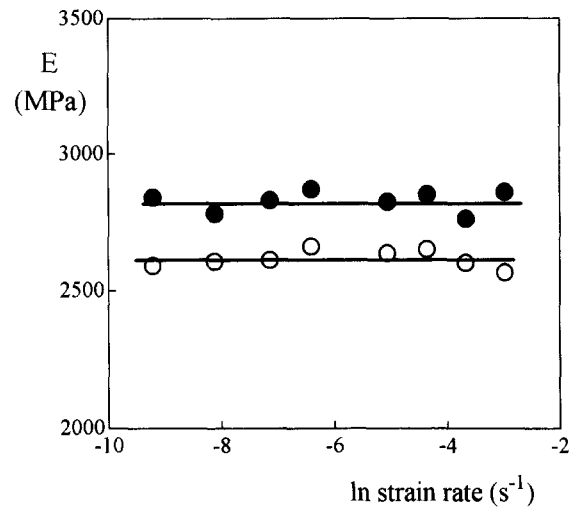

Figure 6 Plot of flexural modulus vs. strain rate at room temperature for both epoxy mixtures. Symbols as in *Figure 2*
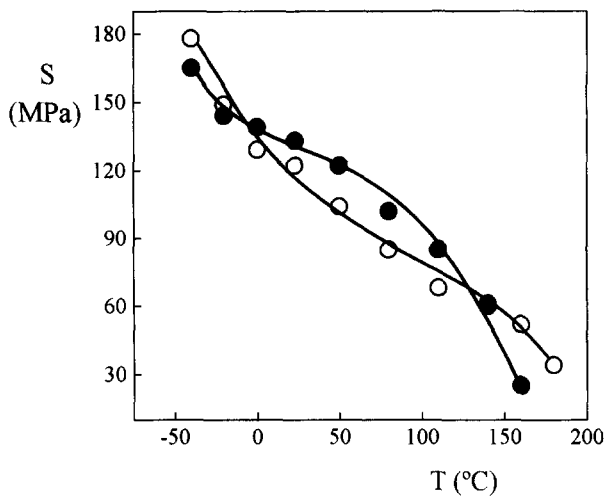

Figure 5 Flexural strength vs. testing temperature. Symbols as in *Figure 2*
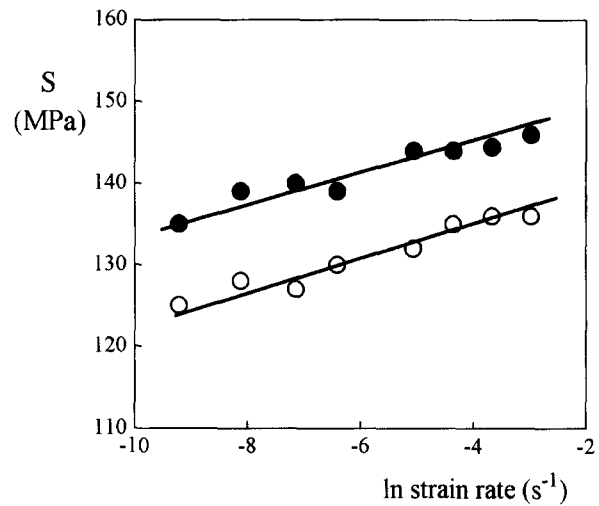

Figure 7 Flexural strength vs. strain rate at room temperature for both epoxy mixtures. Symbols as in *Figure 2*

Thus, at low temperatures, i.e. for the unrelaxed networks, the elastic modulus, and also the flexural strength, was higher for the more crosslinked mixture, but once the β relaxation was overcome the behaviour was the opposite. Moreover, at temperatures higher than the ω relaxation the differences in these properties became more important, and the network with higher crosslink density had lower values upon temperature. As described in the previous section, this behaviour seems to be related to the higher free volume existing in the mixture with higher crosslink density. On the other hand, the stiffness and the strength of both epoxy mixtures decreased significantly at temperatures close to those for their respective α relaxations.

Influence of strain rate on the mechanical properties

Both flexural modulus and strength, which were gathered at various strain rates at room temperature, are shown in *Figures 6* and *7*, respectively. As it can be seen in *Figure 6*, the flexural modulus did not show any significant variation in the range of strain rate used, and it was higher for the less crosslinked mixture. On the other hand, both mixtures had a relatively constant strength to fracture, though slightly increased, over the range of testing rate investigated.

In the same way as for the modulus, flexural strength was higher for the mixture with a lower crosslink density at all loading rates used in this study. This behaviour has to be related to the ω relaxation, and its connection to the free volume of the network, appearing only for the more highly crosslinked network. Alternatively, as shown in *Figure 7*, in the same way as that reported for several glassy polymers tested in tension or compression[12,27-29], for both mixtures the fracture strength increased linearly upon the testing rate, surely because final fracture occurred with the same mechanism in the brittle materials studied.

CONCLUSIONS

In this study, the flexural behaviour of two epoxy mixtures differing in their crosslink densities has been investigated in a wide range of temperatures and testing rates. The changes observed in elastic modulus and flexural strength have been related to the relaxational variations existing from one system to the other as a consequence of microstructural differences in the mixtures originated as a consequence of the distinct molecular weight of the respective initial oligomers.

Despite the higher crosslink density of the epoxy

mixture prepared from the epoxy oligomer with lower molecular weight, which consequently had a higher glass transition temperature, its mechanical properties at room temperature were lower at all testing rates used than for the other epoxy mixture. This behaviour has been related to the existence of the ω relaxation appearing only for the more crosslinked mixture.

The variation of both flexural modulus and strength upon temperature for both epoxy mixtures was similar to that shown by the dynamic storage modulus, and it was a consequence of the relaxational changes occurring in these mixtures. Thus, the more crosslinked network showed higher mechanical properties at temperatures below the β relaxation but lower ones once test temperature was in the range or higher than the ω relaxation, which has been related to the higher free volume existing in the networks with higher crosslink density.

ACKNOWLEDGEMENT

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