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DYNAMIC AND MECHANICAL PROPERTIES OF DGEBA/POLY(PROPYLENE OXIDE) AMINE BASED EPOXY RESINS AS A FUNCTION OF STOICHIOMETRY

F. FERNANDEZ-NOGRARO, A VALEA, R. LLANO-PONTE and I. MONDRAGON*
Dpto. Ingeniería Química y M. Ambiente, Escuela Univ. Ingeniería Técnica Industrial, Universidad País Vasco/Euskal Herriko Unibertsitatea, Avda. Felipe IV, 1 B. 20011 San Sebastián, Spain

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Abstract—An investigation was carried out into the effect of stoichiometry on the dynamic and mechanical properties of epoxy resins cured with two different poly(propylene oxide) based amines. Glass transition temperatures as well as crosslink densities of the networks have been related to the stoichiometry of both mixtures as well as to the structure of the curing agent employed. Mechanical properties have been analyzed as a function of stoichiometry and chain structure of the components used. With the exception of mixtures with an amine/epoxy ratio of 0.6, the stiffness was a minimum around the stoichiometric composition for both systems. A good correlation between the toughness of these materials and their strength and ductility has been found. Toughness behaviour is explained as a function of the network homogeneity and the extensibility of the segments constituting the crosslinked structure.

INTRODUCTION

It is well known that thermosetting resins often show brittle behaviour which depends upon the structure of the components mixed, the stoichiometric ratio and also the cure schedule used, the latter two affecting the crosslink density of the network. In order to modify this behaviour, various basic solutions can be considered including the control of material structure or processing variables [1–7], the modification with other components [7–14], or the variation in stoichiometric ratio [15–18]. However, an alternative way can be employed by using curing agents with flexible chains which can lead to ductile networks [16, 19]. Epoxy resins cured with telechelic polymers can be included in this group. On the other hand, for a given matrix, the optimization of ultimate properties requires a better knowledge of the relationships between structure and properties.

This study considers the structure–property relationships of epoxy matrices prepared with low molecular weight telechelic polymers. The stoichiometric ratio, which is one important variable controlling the ultimate network structure, was changed systematically over a wide range to investigate its effect on the ultimate properties of the epoxy networks. Dynamic-mechanical studies at constant frequency have been performed to compare the structure of these mixtures, completing the characterization by infrared measurements. The influence of frequency and test rate on the dynamic-mechanical behaviour have also been analyzed. Flexural tests have been employed to determine the mechanical response as well as the fracture behaviour of the glassy crosslinked network.

The telechelic polymers used as curing agents were poly(propylene oxide) based polyamines of low molecular weight. The epoxy resin employed was diglycidyl ether of bisphenol A (DGEBA). In order to obtain different epoxy networks, the amine/epoxy stoichiometric ratio has been varied from 0.6 to 1.4. The stiffness, strength, ductility and toughness of these mixtures is correlated to the chemical structures of the crosslinked networks for all the stoichiometric range analyzed and compared to the small variations of chemical structure of the curing agents.

EXPERIMENTAL

Materials and mixing

Diglycidyl ether of bisphenol A (DGEBA), Rutapox VE/3966, epoxide monomer kindly provided by Bakelite, with an equivalent weight of epoxy groups equal to 184.5 g/equiv determined by chemical titration, was used in this study.

Two poly(propylene oxide) (PPO) based polyamines, Jeffamine D230 and T403, kindly supplied by Texaco, were used, The chemical structures of the amines and epoxide monomer are shown in Fig. 1. Mixtures with amine/epoxy ratios, *r*, ranging from 0.6 to 1.4 have been analyzed.

Before mixing, the DGEBA epoxy monomer was preheated at 60°C to melt any crystals present. Mixtures of the epoxy prepolymer and the curing agent were cast at room temperature, mechanically stirred for 5 min and subsequently degassed in a vacuum oven for 5 min.

These mixtures were cast into a mould with dimensions of 15 × 8 × 0.6 cm consisting of two glass plates and a steel frame, and cured at 60°C for 3 hr keeping them under vaccum for 60 min. Further curing at 180°C for 2 hr was conducted in an air circulating oven. The plates were then allowed to cool slowly in the oven to room temperature overnight.

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*To whom all correspondence should be addressed.

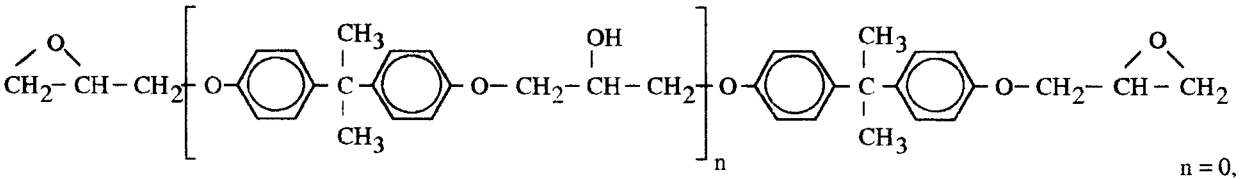
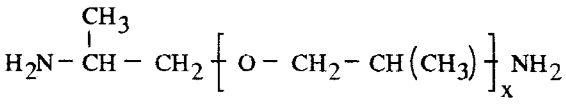
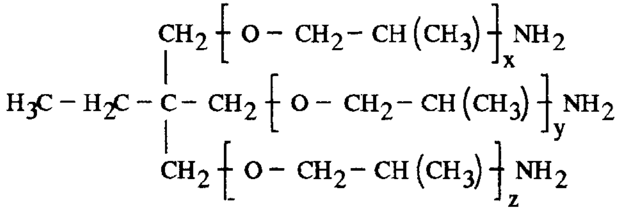
Product	Formula
Dyglicidyl ether of bisphenol A DGEBA Rutapox VE-3966 (Bakelite)	 n = 0,10
Poly(propylene oxide) diamine Jeffamine D230 (Texaco)	 $H_2N-\overset{\displaystyle CH_3}{\overset{\vert}{CH}}-CH_2\left[O-CH_2-CH(CH_3)\right]_x NH_2$ x ≅ 2,7
Poly(propylene oxide) triamine Jeffamine T403 (Texaco)	 $H_3C-H_2C-\overset{\displaystyle CH_2\left[O-CH_2-CH(CH_3)\right]_x NH_2}{\underset{\displaystyle CH_2\left[O-CH_2-CH(CH_3)\right]_z NH_2}{C}}-CH_2\left[O-CH_2-CH(CH_3)\right]_y NH_2$ x + y + z ≅ 5,3

Fig. 1. Chemical structures of the epoxy prepolymer and diamines used.

Dynamic-mechanical properties

Dynamic-mechanical tests were carried out at 10 Hz using a viscoanalyser Metravib, at a heating rate of 3°C $\min^{-1}$. Studies were performed using a three-point bending devide with a 44 mm span. The dimensions of specimens were 60 × 12 × 6 mm. The storage modulus, E', and the loss factor, $\tan \delta$, were measured from 20°C up to a temperature beyond that for which the rubbery state was attained. A transition temperature related to T_g was defined as the temperature corresponding to the maximum in the loss factor.

Mechanical behaviour

Flexural properties were determined in a three-point loading configuration using an Instron Universal Testing Machine, model 4206. Specimen dimensions were 80 × 12 × 6 mm. Tests were carried out at 20°C following the ASTM-D790 standard specifications. A support span length of 64 mm and a crosshead speed of 1.7 mm $\min^{-1}$ were employed. At least five specimens were tested for every datum point. In the following test, the subscripts m and b represent the yield point (or the point at which the sample broke when the yield point was not reached) and the breaking point, respectively.

Fracture toughness

For fracture tests, single-edge notched specimens, SEN, (60 × 12 × 6 mm) were employed. A "V" notch was cut in the sample with a rotating cutter, and a starter crack was initiated with a razor blade. The ASTM-E399 standard specifications were followed in three-point bending mode with a span of 48 mm. Tests were carried out at 20°C and a crosshead speed of 10 mm $\min^{-1}$ in the Instron machine. Each reported value is the average of at least five measurements. The critical stress intensity factor, K_{Ic}, was calculated according to the formula:

$$K_{Ic} = P_{\max} Lf / BW^{3/2} \qquad (1)$$

where $P_{\max}$ is the maximum load at crack initiation, L is the span length, f is the shape factor, B is the specimen thickness, and W is the width of the specimen in the crack direction. The critical energy to fracture per unit area of crack, G_{Ic}, was calculated from the critical stress intensity factor as:

$$G_{Ic} = (1 - \nu^2) K_{Ic}^2 / E \qquad (2)$$

where ν is Poisson's ratio, and E the elastic modulus obtained from flexural testing.

Infrared measurements

Infrared absorption spectra of the cured mixtures were recorded by a Fourier transform spectrophotometer (Perkin-Elmer, 16 PC model) in the range 4000–400 cm^{-1}. Samples were made and analyzed in the form of KBr pellets. The operating conditions for obtaining spectra involved 32 scans at a resolution of 4 cm^{-1}. The conversion of epoxy groups was obtained by normalizing the areas of the peak centered at 916 cm^{-1} to an internal reference band at 1610 cm^{-1} corresponding to the stretching of the aromatic ring.

RESULTS AND DISCUSSION

Physical properties

The dynamic-mechanical properties of DGEBA based epoxies were monitored in the 20–160°C range. Plots of the storage moduli of mixtures with various stoichiometries are shown in Figs 2a and 2b for DGEBA cured with D230 or T403 curing agents, respectively. The elastic moduli had an almost constant value up to the region of the glass transition at which they sharply decreased. It is worth noting that the stiffness remained unchanged to the highest temperatures for exact stoichiometry than for the other compositions in both polyamine containing mixtures. On the other hand, the drop on elastic modulus beyond to the glass transition occurred at lower temperatures as the stoichiometric ratio went far away from stoichiometry in both mixtures. Although the modulus variation was similar in both amine containing systems at compositions higher than the stoichiometric one, epoxy-rich systems showed a different behaviour as for each composition the elastic modulus of T403 based mixtures dropped at lower temperatures than for the D230 containing systems, thus showing that differences existed between both crosslinked networks. According to Morgan *et al.* [16], the flexibility of the segments of PPO based polyamines allows a wide variation in the ring structure of the epoxy networks formed. The earlier drop in elastic modulus for epoxy-rich compositions and especially for the $r = 0.8$ mixtures in T403 based mixtures should be a consequence of a loosening in their network structures compared to D230 containing mixtures.

The freedom of epoxy-rich mixtures based on T403 becomes more evident when the loss factor, $\tan \delta$, behaviour is analyzed, as shown in Figs 3a and 3b. Thus, for every epoxy-rich mixture the α relaxation appeared at lower temperatures in T403 based mixtures. A larger variation was observed for both mixtures the lower hardener content. Thus, it can be seen in Figs 3a and 3b that these systems showed two peaks. They originate in the inhomogeneity of these amine-poor compositions in which a low crosslinked network and a more or less branched backbone would coexist. Moreover, it becomes evident for epoxy-rich mixtures that the network loosening increased as the amine content went away from the stoichiometric ratio since the height of the $\tan \delta$ peak increased. The existence of two α relaxations for the $r = 0.8$ mixture containing T403 supports the higher inhomogeneity of these mixtures at epoxy-rich compositions.

On the other hand, as can be seen in Fig. 3b, stoichiometric, but above all amine-rich mixtures, showed a different behaviour since the glass transition temperatures were similar for both PPO polyamine based mixtures in spite of the height of the α relaxation for mixtures containing T403 being lower for those with D230, thus showing a higher packing density in the T403 based networks.

The glass transition temperatures of D230 and T403 based blends, taken as those corresponding to the peak of the α relaxation, are plotted in Fig. 4 as a function of stoichiometric ratio. As has also been reported for different epoxy mixtures [16, 20–23], both systems exhibited a maximum around the stoichiometric composition. The lower T_g values for epoxy-rich mixtures and slightly higher ones for amine-excess formulations in the case of networks cured with T403 agrees with the above considerations of network packing.

The dynamic-mechanical results were used to determine the crosslink density for these DGEBA based mixtures. By taking the values of log E' at $T = T_g + 30°\mathrm{C}$, the molecular weight between crosslinks can be calculated by means of the commonly used expression derived from rubberlike elasticity

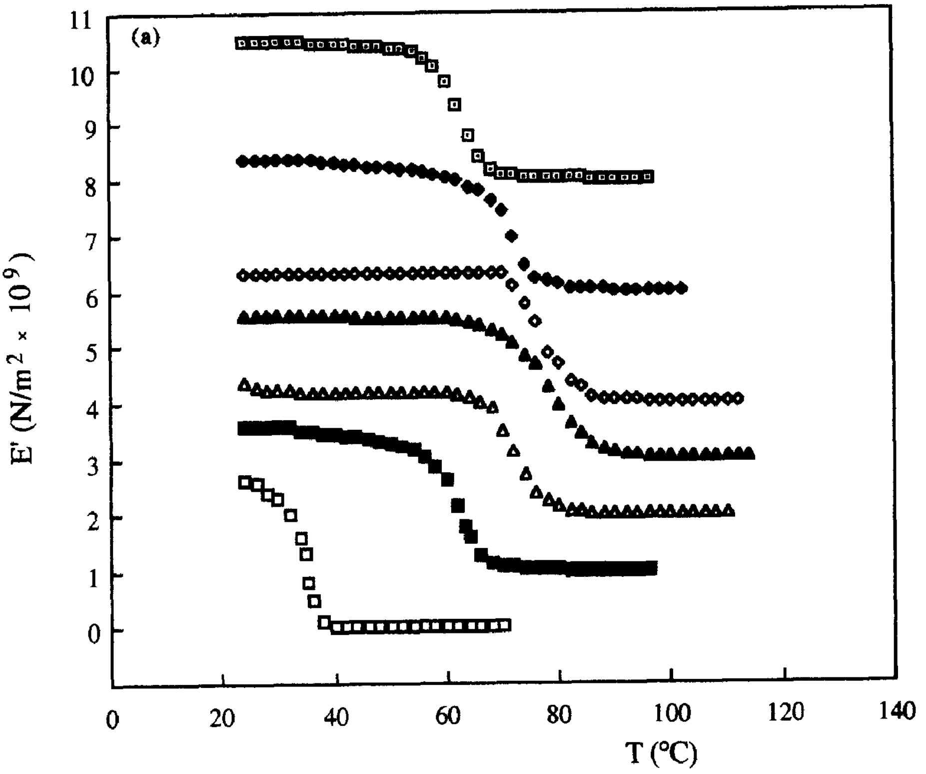


Fig. 2(a). Storage modulus evolution upon temperature for D230 containing mixtures for different epoxy/amine ratios. □, 0.6; ■, 0.8; △, 0.9; ▲, 1.0; ◇, 1.1; ◆, 1.2; ▣, 1.4. The E' scale is correct for $r = 0.6$. For other compositions, the scale is offset vertically from that of its immediate neighbours by 1.0 (for $r = 1.2$ and 1.4 the offset is +2.0).

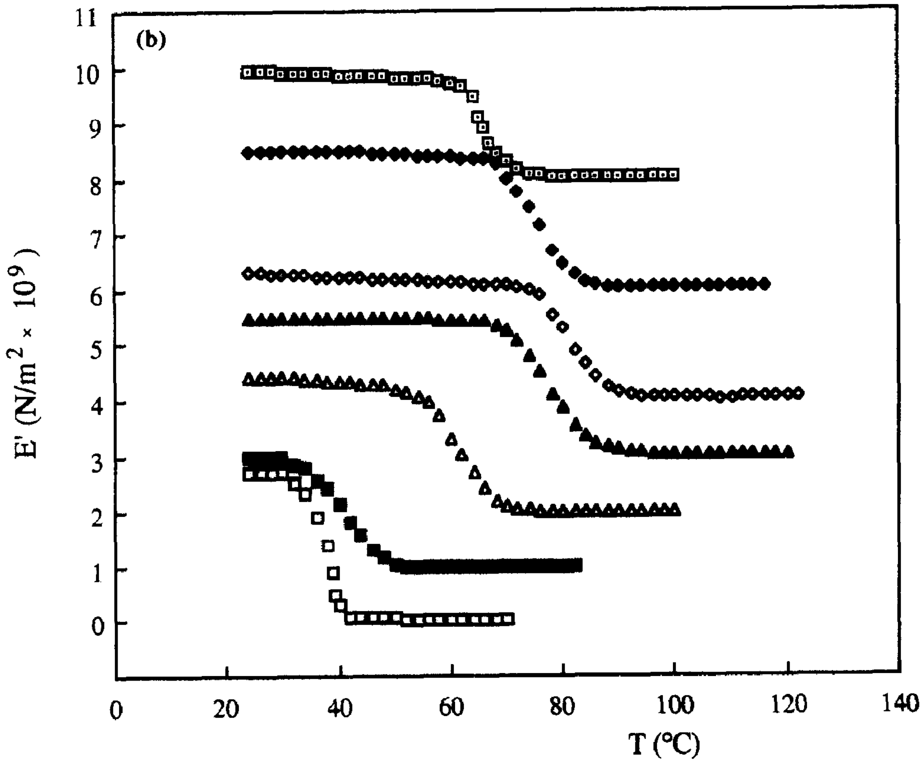


Fig. 2(b). Storage modulus evolution upon temperature for T403 containing mixtures for different epoxy/amine ratios. Symbols as in Fig. 2(a). The scale is correct for $r = 0.6$, and offset for other compositions as in Fig. 2(a).

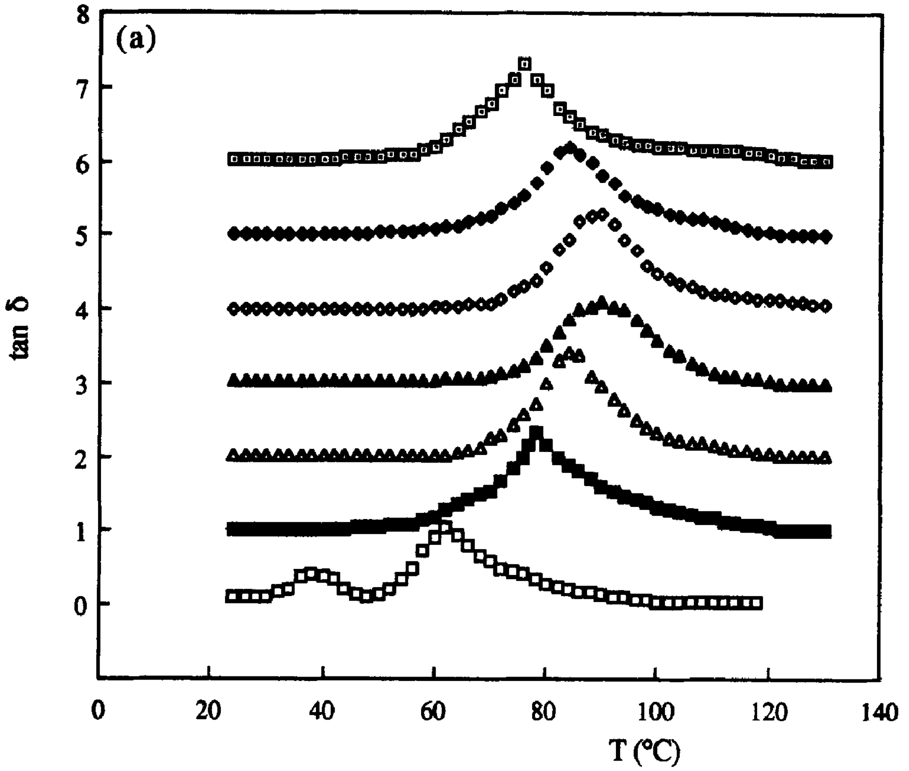


Fig. 3(a). Variation in loss factor of D230 containing mixtures as a function of temperature for several stoichiometries. Symbols as in Fig. 2(a). The scale is correct for $r = 0.6$. For other compositions, the scale is offset vertically from that of its immediate neighbours by 1.0.

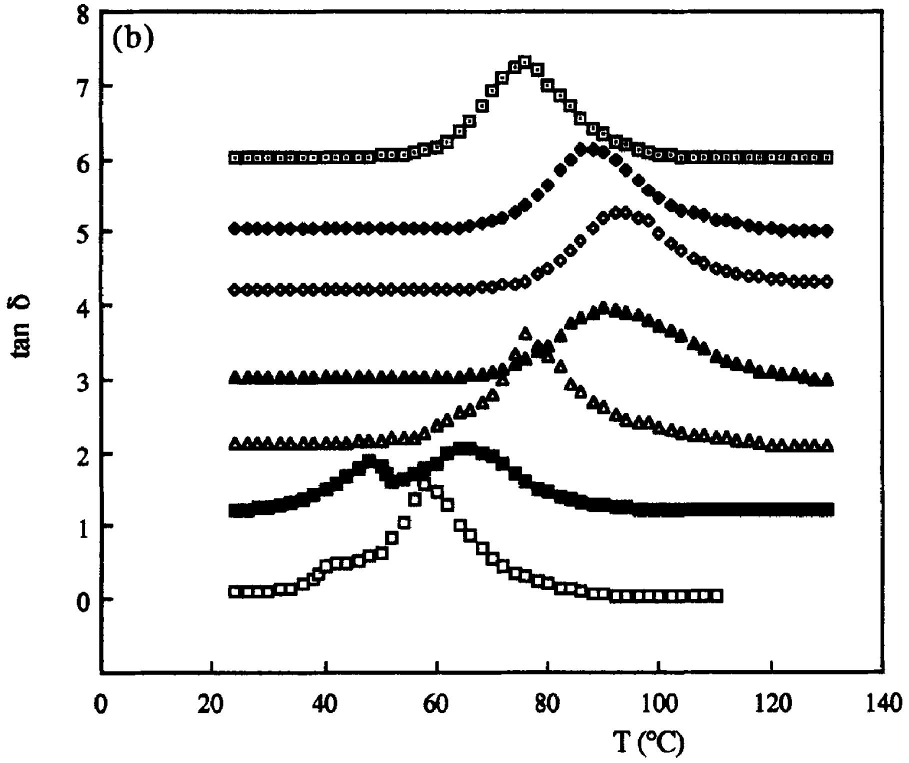


Fig. 3(b). Variation in loss factor of T403 containing mixtures as a function of temperature for several stoichiometries. Symbols as in Fig. 2(a). The scale is correct for $r = 0.6$, and offset for other compositions as in Fig. 3(a).

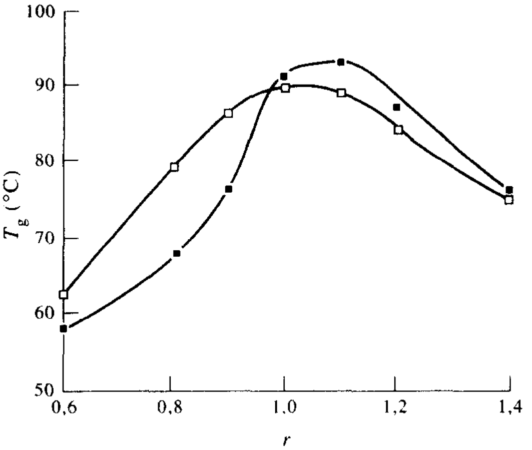


Fig. 4. Glass transition temperature as a function of stoichiometry for epoxy mixtures cured with: □, D230; ■, T403.

theory [24], which relates the elastic modulus of a rubber to the average molecular weight between crosslinks for small deformations:

$$E_r = 3\Phi\rho RT/M_c \qquad (3)$$

where Φ in the "front factor", assumed to be equal to 1 [5], E_r is the rubber modulus (MPa), ρ the density (kg/m^3), R the gas constant, T the absolute temperature (K), and M_c the average molecular weight between crosslinks (kg/mol).

The values of M_c determined as a function of hardener concentration are compared in Fig. 5, for D230 and T403 based systems. The variation of M_c values obtained for DGEBA/T403 mixtures was similar to that obtained by other workers [16–25] and for both systems were higher than those theoretically obtained by supposing homogeneous networks [25, 26]. The accuracy of the absolute values so obtained is discussed below. Nevertheless, the M_c values experimentally obtained may be used to make comparisons between the different mixtures in spite of the fact that, as shown by Fischer [27], equation (3) is solely an approximation to the real modulus of the network. The experimental data followed the same trends for both DGEBA/hardener epoxies. A more rapid increase in M_c with the stoichiometric ratio occurred in the epoxy-rich mixtures as the stoichiometric ratio decreased, than the relative low increase for amine-rich compositions. The differences in the crosslink densities between D230 and T403 based mixtures at both sides of the stoichiometric ratio correspond to the variations existing for the glass transition temperatures of these mixtures shown above, and they are possibly connected to the slight differences in the chain extension of the aliphatic segment.

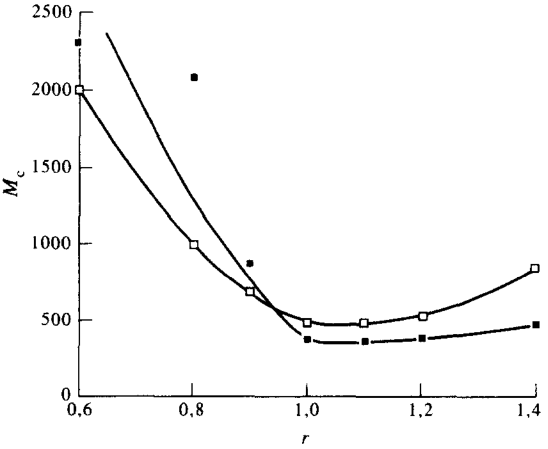


Fig. 5. Variation of the average molecular weight between crosslinks for epoxy networks with different stoichiometries cured with: □, D230; ■, T403.

Although some authors have noted a close correlation between the average molecular weight between crosslinks and the glass transition temperature [18], when Figs 3 and 4 are compared, it becomes evident that other factors than T_g of mixtures have to be taken into account since the differences existing in M_c variations for epoxy-rich or amine-excess containing mixtures do not correspond with the almost similar variations observed for the glass transition temperatures in this study and other investigations with T403 hardener [16]. On the other hand, the higher value of T_g in DGEBA/T403 mixture could arise from the value of the amine functionality used in this study, which could be different [25, 28–30].

In order to know if the elastic modulus data at temperatures above the T_g of these crosslinked mixtures may vary as a function of test conditions, various specimens of DGEBA/T403 stoichiometric mixtures have been analyzed by dynamic-mechanical measurements carried out at different heating rates (1–8°C/min at 10 Hz) and test frequencies (10–50 Hz at 3°C/min). As it has also been observed for other epoxy mixtures in our laboratories and by other investigators [27], neither the heating rate nor the exciting frequency employed modified significantly the rubber storage modulus of these mixtures, and therefore the study made on crosslink density seems to be correct. Nevertheless, in order to know the accuracy of the average molecular weight values so obtained, a static bending test was carried out according to the ASTM D-790 standard in an Instron mechanical testing machine, model 4206; in order to simulate the dynamic procedure, tests were carried out at 120°C, or $T = T_g + 30°C$, for the DGEBA/T403 stoichiometric composition. The elastic modulus value, averaged for five specimens, was 22.6 N/m^2. Indeed, the rubber modulus obtained by dynamic-mechanical testing was 1.21 times higher than the static one (it is worth noting that this ratio varies from one epoxy mixture to another), and thus the analysis of the molecular mass of the network strands, so often carried out by dynamical testing, has to be considered as approximative because of the lack of relaxation [27]. On the other hand, employing a higher frequency produced an increase of the peak temperature observed as has been shown in other works [3, 31]. On the contrary, the heating rate does not influence the value of T_g obtained, showing good temperature equilibration.

In order to establish whether the crosslink density of the networks prepared with D230 or T403 had any structural difference to each other, infrared measurements of all cured mixtures have also been performed.

Table 1. Epoxy conversion (%) in the cured mixtures as a function of the amine/epoxy ratio, r

	r						
Curing agent	0.6	0.8	0.9	1.0	1.1	1.2	1.4
D230	54	80	84	89	93	95	96
T403	50	75	80	87	92	94	95

As can be seen from Table 1 for epoxy-rich mixtures, the conversion of the epoxy group was higher for D230 containing formulations possibly as a consequence of the steric hindrance produced by the pendant methyl groups, in a higher proportion in T403, which constrains the flexibility of the overall structure of the hardener so obstructing the accessibility to the amine groups. Therefore, the higher packing density and glass transition temperatures for D230 containing mixtures at epoxy-rich compositions can be explained as a function of the lower loosening of the corresponding networks. Instead, the lower aliphatic chain amine group ratio of each network segment corresponding to the T403 hardener explains the slightly higher values of molecular weight between crosslinks, and also of T_g for T403 mixtures at amine-rich formulations because the epoxide conversion was similar for both kind of mixtures. Moreover, it becomes clear that an amine-excess was necessary to obtain the maximum conversion of epoxy groups.

Mechanical properties

The elastic modulus, determined from static tests, for both poly(propylene oxide) polyamine based epoxy mixtures was measured in flexure at room temperature. Figure 6 shows the flexural moduli of DGEBA/D230 mixtures as a function of the amine/epoxy ratio and Fig. 7 those corresponding to the T403 based mixtures. For both systems a maximum appeared at epoxy-rich compositions around a stoichiometric ratio of 0.8–0.9, and at lower epoxy contents the modulus dropped sharply to significantly lower values due to the increasing proximity of the testing temperature to the glass transition region, as can be seen in Figs 3a and 3b. A similar behaviour has been reported for DGEBA/T403 mixtures [16] and other epoxy mixtures [18]. On the contrary, at high amine/epoxy ratios, elastic moduli remained nearly constant.

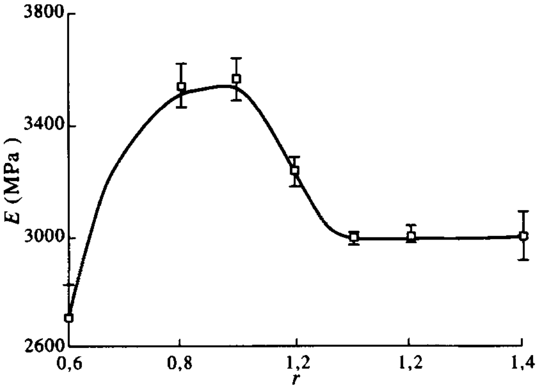


Fig. 7. Flexural modulus versus stoichiometric ratio for DGEBA/T403 mixtures.

The similar trends observed for different stoichiometric ratios between the behaviour of the flexural modulus for glassy mixtures and the values of average molecular weight between crosslinks obtained in the rubber state, could indicate that a close relationship exists, but as has been shown for many cured epoxy systems [16–18, 23], that is not so since above the glass transition temperature entropic contributions are the key to determine the elastic behaviour of these materials, whilst at temperatures lower than T_g, the variations in the internal energy of the systems become considerable. Instead, factors such as free volume [16, 32, 33] which may vary on aging [34], or β relaxation [35–37] or, in other words, besides the glassy-state packing, other factors depending on the chemical structure and composition of the network built up have to be considered to explain the modulus variations in the glassy state of crosslinked networks.

The yield, σ_m, and break, σ_b, stresses for both DGEBA based mixtures are plotted in Figs 8 and 9, respectively, as a function of the stoichiometric ratio. In the case of D230 based blends, with the exception of the lower stoichiometric ratio employed, all mixtures yielded, so showing a significant ductility. Mixtures prepared with T403 showed the same

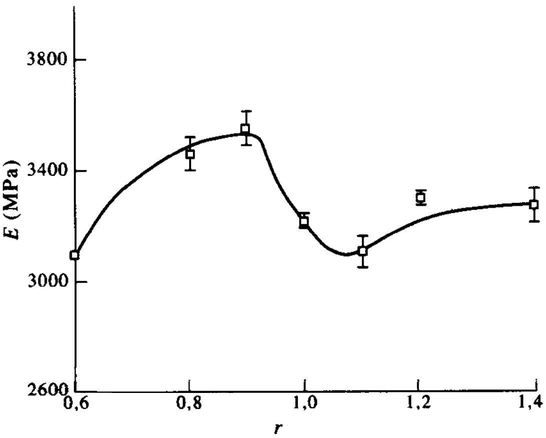


Fig. 6. Flexural modulus versus stoichiometric ratio for DGEBA/D230 mixtures.

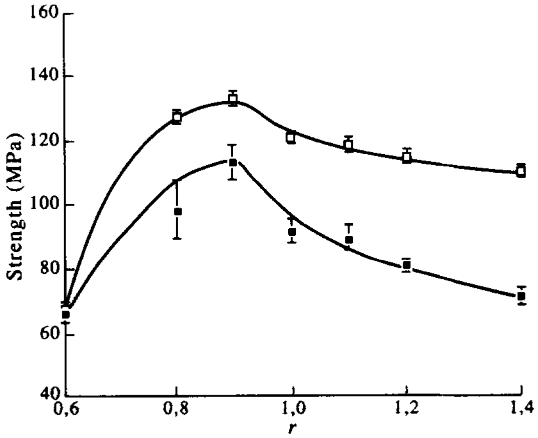


Fig. 8. Flexural strength versus stoichiometric ratio for DGEBA/D230 mixtures: □, flexural strength; ■, strength to break.

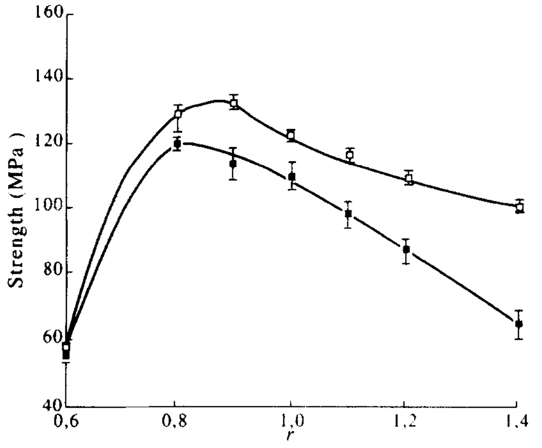


Fig. 9. Flexural strength versus stoichiometric ratio for DGEBA/T403 mixtures: □, flexural strength; ■, strength to break.

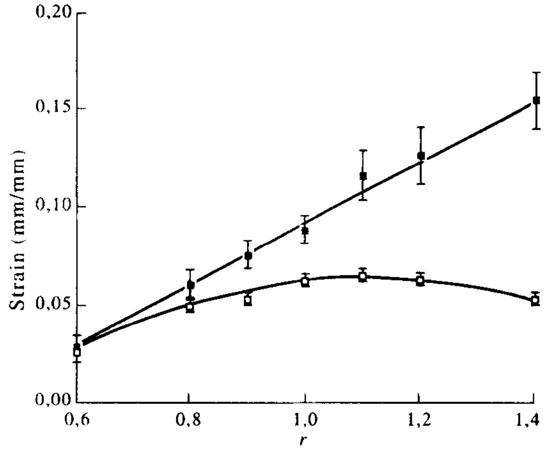


Fig. 11. Strain behaviour as a function of stoichiometric ratio for DGEBA/T403 mixtures: □, yield strain; ■, strain to break.

behaviour but only yielding beyond the 0.8 stoichiometric ratio, so apparently showing a little lower ductility at epoxy-rich compositions than those containing D230. The lower strength presented by the mixtures richer in epoxy was undoubtedly due to network imperfections like holes, chain-ends uncrosslinks, or others, to be a result of the increasing proximity of the T_g to the test temperature. On the other hand, at stoichiometric and amine-rich compositions the yield stress and the strength at break slow down as amine content increased but no minimum was apparent in a different way to that shown by elastic modulus. In order to understand this behaviour, it has to be borne in mind that, despite the fact that strength and elastic modulus are determined by the glassy-state packing and free volume [16], the deformation at which elastic modulus and strength are measured is different and so results do not have to show the same behaviour since at larger deformations, as those implied in yielding, viscous contributions have to be considered in the deformation mechanisms of these relatively ductile epoxies.

As it can be seen from Figs 10 and 11, in which yield and break strain are plotted against composition, all mixtures with $r > 0.8$, and also for $r = 0.8$ for blends containing D230, were ductile. These results are similar to those reported in tensile tests by Morgan *et al.* [16] for DGEBA/T403 mixtures in the 0.6–1.2 stoichiometric range, but they differ at high amine contents possibly because of the different kind of tests employed.

In order to compare the ductility of these mixtures, and following the method recently applied by Min *et al.* [7], in which the ratio of the non-linear strain to the breaking strain, $(\epsilon_b - \epsilon_m)/\epsilon_b$, is expected to represent the ductility of the materials [38], the values of this ratio calculated from the flexural measurements have been analyzed. Results so obtained are shown in Fig. 12 for DGEBA/D230 and DGEBA/ T403 mixtures. For both mixtures ductility increased as amine content was higher. However, values for stoichiometric and amine-rich mixtures based on D230 were almost constant, whereas ductility increased continuously in T403 containing mixtures at these formulations, so again showing the differences existing in the crosslinked networks of these systems.

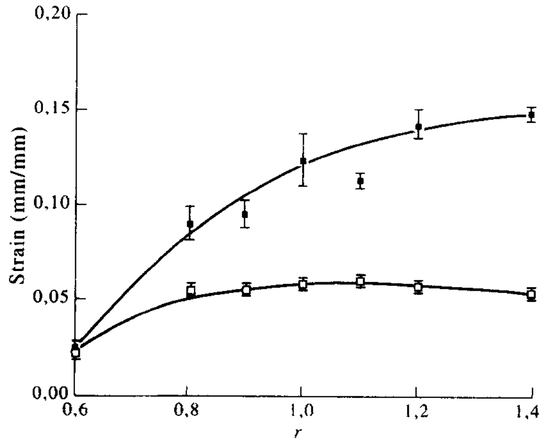


Fig. 10. Strain behaviour as a function of stoichiometric ratio for DGEBA/D230 mixtures: □, yield strain; ■, strain to break.

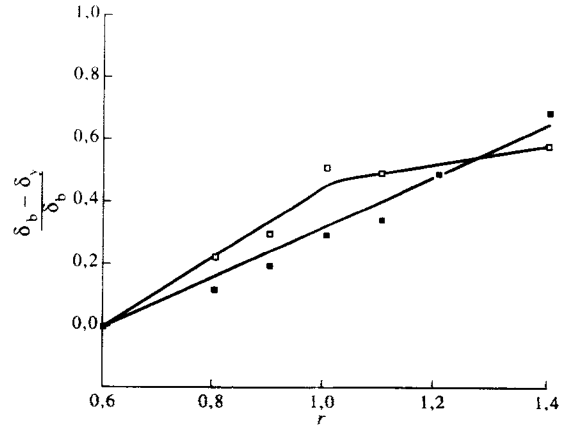


Fig. 12. The ratio of non-linear deformation to breaking deformation versus stoichiometric ratio for epoxy mixtures cured with: □, D230; ■, T403.

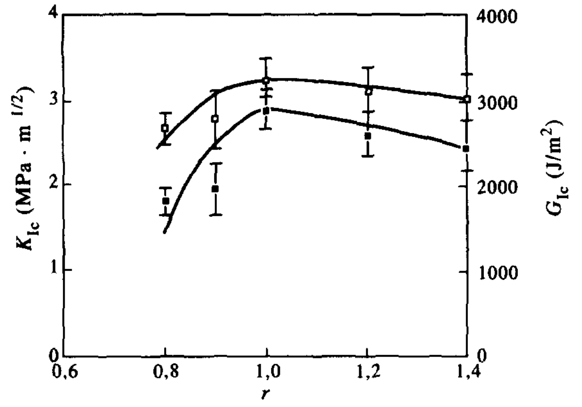


Fig. 13. Fracture toughness versus stoichiometric ratio for DGEBA/D230 mixtures: □, critical stress intensity factor, K_{Ic}; ■, critical strain energy release rate, G_{Ic}.

Fracture toughness

Results for the critical stress intensity factor, K_{Ic}, and the critical energy release rate, G_{Ic}, are shown in Fig. 13 for DGEBA/D230 epoxy mixtures at different stoichiometric ratios. Each data represents at least five measurements. Results for mixtures with $r = 0.6$ are not shown because the high brittleness of these samples did not permit notching and precracking. Both properties, K_{Ic} and G_{Ic}, presented a maximum value at the stoichiometric composition reducing at both sides of this composition. Toughness may be taken as a property related to the strength and ductility of the material, and thus it depends on factors such as crosslink density, chemical structure, intermolecular packing and molecular building of the network. Indeed, it seems that the decrease of toughness at compositions higher than the stoichiometric may be a direct consequence of the strength decreasing for the amine-rich mixtures with respect to that for the stoichiometric system, whilst the higher brittleness of the materials at low amine contents seems to be responsible for the lower toughness observed.

Figure 14 illustrates the K_{Ic} and G_{Ic} variations for DGEBA/T403 mixtures as a function of stoichiometric ratio. A similar behaviour to that presented by D230 based blends was observed but the maximum in both properties appeared at higher amine contents. The sharp decrease in toughness for the $r = 1.4$ mixture should be connected with the lower strength of the DGEBA/T403 mixture at this composition.

The higher toughness values for both mixtures around the stoichiometric composition must be related to the higher homogeneity of these crosslinked networks [16, 36] and also to the higher flexibility of the network segments because of the higher flexibility of the chains of the curing agent with respect to that corresponding to the resin.

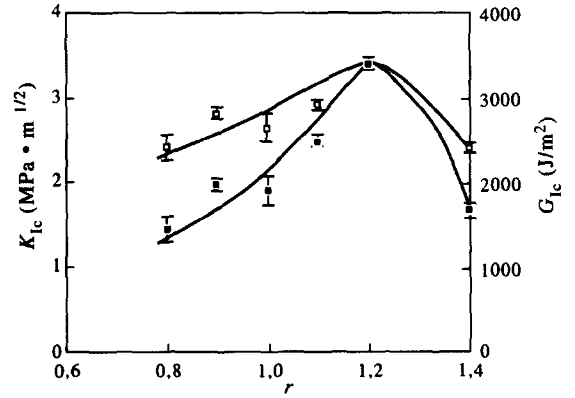


Fig. 14. Fracture toughness versus stoichiometric ratio for DGEBA/T403 mixtures: □, critical stress intensity factor, K_{Ic}; ■, critical strain energy release rate, G_{Ic}.

CONCLUSIONS

The main objective of this study was to relate the dynamical and mechanical behaviour with the structure of epoxy resins cured with flexible curing agents like poly(propylene oxide) based amines. The work has been made for a wide range of stoichiometries. Two curing agents have been used in order to compare the influence of their chain length and other factors like steric hindrance in the final properties of these epoxy mixtures. Results can be summarized as follows.

—Stoichiometric mixtures showed the higher glass transition temperatures for the corresponding epoxy/amine series. Differences in homogeneity were especially remarkable in epoxy-rich mixtures.

—Variations in crosslink density of these mixtures have been related to the chain extension and steric hindrance of methyl groups contained in the curing agent.

—The loss peak temperature has been shown to be a function of the test frequency but not of the heating rate of tests in the interval studied.

—The lower elastic modulus appeared around the stoichiometric composition in both mixtures. The strength of these flexible mixtures which yielded showed a slightly different behaviour at amine-rich contents. The variations existing between both types of mixtures have been correlated to the steric hindrance of methyl groups contained in the curing agent.

—For both mixtures the toughness attained the maximum value at a composition greater than the stoichiometric one. These values have been explained as a function of strength and ductility of the mixtures and they are connected with the homogeneity of the network and the extensibility of the basic chains.

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