Polymer Vol. 37 No. 9, pp. 1589–1600, 1996

0032-3861/96/$15.00+0.00

Dynamic and mechanical properties of epoxy networks obtained with PPO based amines/mPDA mixed curing agents

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(Received 9 March 1995; revised 25 July 1995)

Dynamic and mechanical studies of diglycidyl ether of bisphenol A (DGEBA) based epoxy resins cured with a mixture of two curing agents have been performed. One of the components of the mixed curing agent was an aromatic amine, *m*-phenylene diamine (mPDA), and the other was a poly(propylene oxide) based amine (Jeffamine D-230 or T-403). The mPDA content was changed in the 0–100 wt% range of the curing agent. Glass transition temperatures varied linearly as a function of the mPDA content in the curing agent and they increased with the crosslink density of the cured networks. Although a low amount of aliphatic amine lowered the rigidity of the mixture cured with mPDA, it resulted in an evident increase in resistance and toughness of the mixture, thus showing the potential interest of these systems for practical applications. Copyright © 1996 Elsevier Science Ltd.

(Keywords: epoxy networks; dynamic properties; mechanical properties)

INTRODUCTION

In many applications involving composites, the properties of the matrix can be of primary importance. In composites based on epoxy resins, the brittleness of the matrix, especially when it is cured with aromatic or cycloaliphatic curing agents, is an important aspect of the performance of the composite itself.

Enhancing the toughness of epoxy resins by the addition of a second component such as a rubber[1–3], or a thermoplastic modifier[4–6], or even a hard inorganic glass[7,8] has been widely documented in the last 20 years. The phase separation of this second component from the matrix triggers extrinsic toughening mechanisms that effectively shield the crack tip, thus improving the fracture toughness.

The mechanical properties corresponding to small deformations for highly crosslinked stoichiometric epoxy networks with aromatic amines can be lower than those for mixtures not reacted at all[9] or those for non-stoichiometric compositions[10]. This fact has been attributed to variations in the free volume of the networks at high conversion of epoxy groups. Fried and Hanna[11] reported for miscible rigid thermoplastic blends that a synergistic behaviour on elastic modulus can be obtained as a consequence of increasing the packing density due to specific interactions between the components of the mixture; this synergism involves a lowering on the ductility and impact strength of blends. These complementary observations seem to indicate that a modification of the segments involved in the interactions between elastic chains of crosslinked networks becomes the main key in order to improve the toughness of thermoset materials, simultaneously maintaining an acceptable level of other properties such as rigidity or thermal resistance.

Nowadays it is recognized that dynamic mechanical spectroscopy is a powerful tool to analyse the final properties of an ultimately cured epoxy mixture. Indeed, the influence of stoichiometry or extent of cure on the crosslink density and on the glass transition temperature has often been studied in the literature[12–17].

To further the understanding of the mechanical behaviour and fracture toughness of crosslinked epoxies, this paper reports structure–property studies of a stoichiometric epoxy–amine system in which the curing agent was mostly a mixture of an aromatic amine, *m*-phenylene diamine (mPDA), and an amine terminated poly(propylene oxide), either Jeffamine D230 or T403. Different epoxy networks were produced by varying the aromatic:aliphatic amine ratios. The physical properties, crosslink density, mechanical behaviour and fracture toughness of these epoxies crosslinked with mixed amines are reported and correlated with the chemical structure variations.

EXPERIMENTAL

Materials and mixing

Diglycidyl ether of bisphenol A (DGEBA), Rutapox VE-3966, epoxy monomer, kindly provided by Bakelite, with an equivalent weight of epoxy groups equal to

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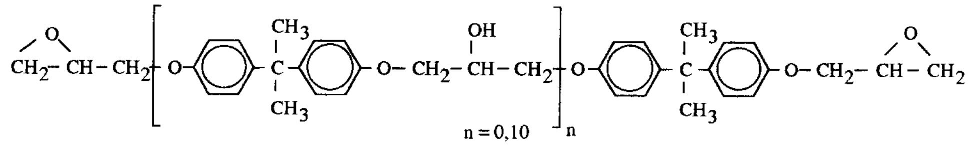
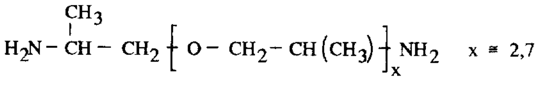
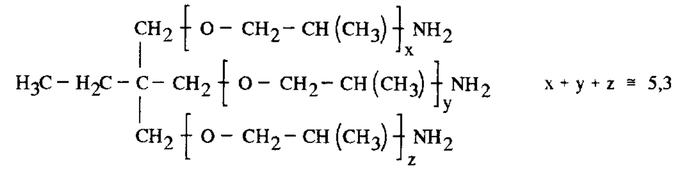
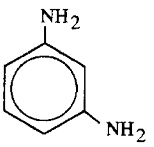
Table 1 Chemical structures of the epoxy prepolymer and amines used

Product	Formula
DGEBA (Rutapox VE-3966) Bakelite	
Jeffamine D-230 (Texaco)	 $H_2N-CH(CH_3)-CH_2[O-CH_2-CH(CH_3)]_xNH_2$ $x \cong 2,7$
Jeffamine T-403) Texaco)	 $H_3C-H_2C-C(CH_2[O-CH_2-CH(CH_3)]_xNH_2)(CH_2[O-CH_2-CH(CH_3)]_yNH_2)(CH_2[O-CH_2-CH(CH_3)]_zNH_2)$ $x+y+z \cong 5,3$
mPDA (Fluka)	

184.5 g/equiv. determined by chemical titration, was used in this study.

Two poly(propylene oxide) (PPO) polyamines, Jeffamine D230 and T430, kindly supplied by Texaco, were used. In addition, *m*-phenylene diamine (mPDA) Fluka quality, was used in various amounts. The chemical structures of the curing agent and epoxide monomer are shown in *Table 1*.

Before mixing, the DGEBA epoxy monomer was preheated at 60°C to melt any crystals present. Mixtures of the epoxy prepolymer and the corresponding amount of mPDA were cast at 75°C for 5 min, cooled to 60°C, and subsequently the PPO based polyamine was added and the mixture was mechanically stirred for 5 min. Stoichiometric mixtures were obtained for weight percentages of mPDA ranging from 0 to 100 in the curing agent. These mixtures were cast into a mould with dimensions 15 × 8 × 0.6 cm consisting of two glass plates and a steel frame, and cured at 70°C for 3 h, keeping them under vacuum for the first 60 min. Further cure at 180°C for 2 h was conducted in an air-circulating oven. The samples were then allowed to cool slowly in the oven to room temperature. This cure treatment allowed the maximum conversion for each mixture to be obtained as the glass transition temperatures remained constant after dynamical mechanical testing.

Fourier transform infrared (*FT*i.r.) measurements were carried out on a Perkin Elmer model 16 PC infrared spectrophotometer. Samples were analysed in the form of KBr pellets.

Specimens for mechanical testing were machined to the required dimensions from cast plaques by cutting them with a circular saw, followed by milling.

Dynamic mechanical spectroscopy

Dynamic mechanical measurements were performed from 20 to 250°C at a frequency of 10 Hz and a heating rate of 3°C min^{-1} using a Metravib viscoanalyser equipped with a three-point bending device with a 44 mm span. The storage modulus E', and the loss factor, $\tan\delta$, were recorded. T_α was defined as the temperature corresponding to the maximum in the α relaxation. Despite the dependence of T_α upon test frequency, this temperature can be related to the glass transition temperature of the material. Elastic modulus in the rubber-like region was taken as the minimum value of storage modulus beyond the glass transition region.

Mechanical properties

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 text, 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.

Toughness studies

For fracture tests, single-edge notched specimens (SEN) with dimensions 60 × 12 × 6 mm were employed. A V-shaped notch was cut in the sample with a rotating cutter and a starter crack was initiated with a razor blade. The ASTM-E399 standard specification was 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 value is the average of at least five measurements. The critical stress intensity factor, K_{Ic}, was calculated

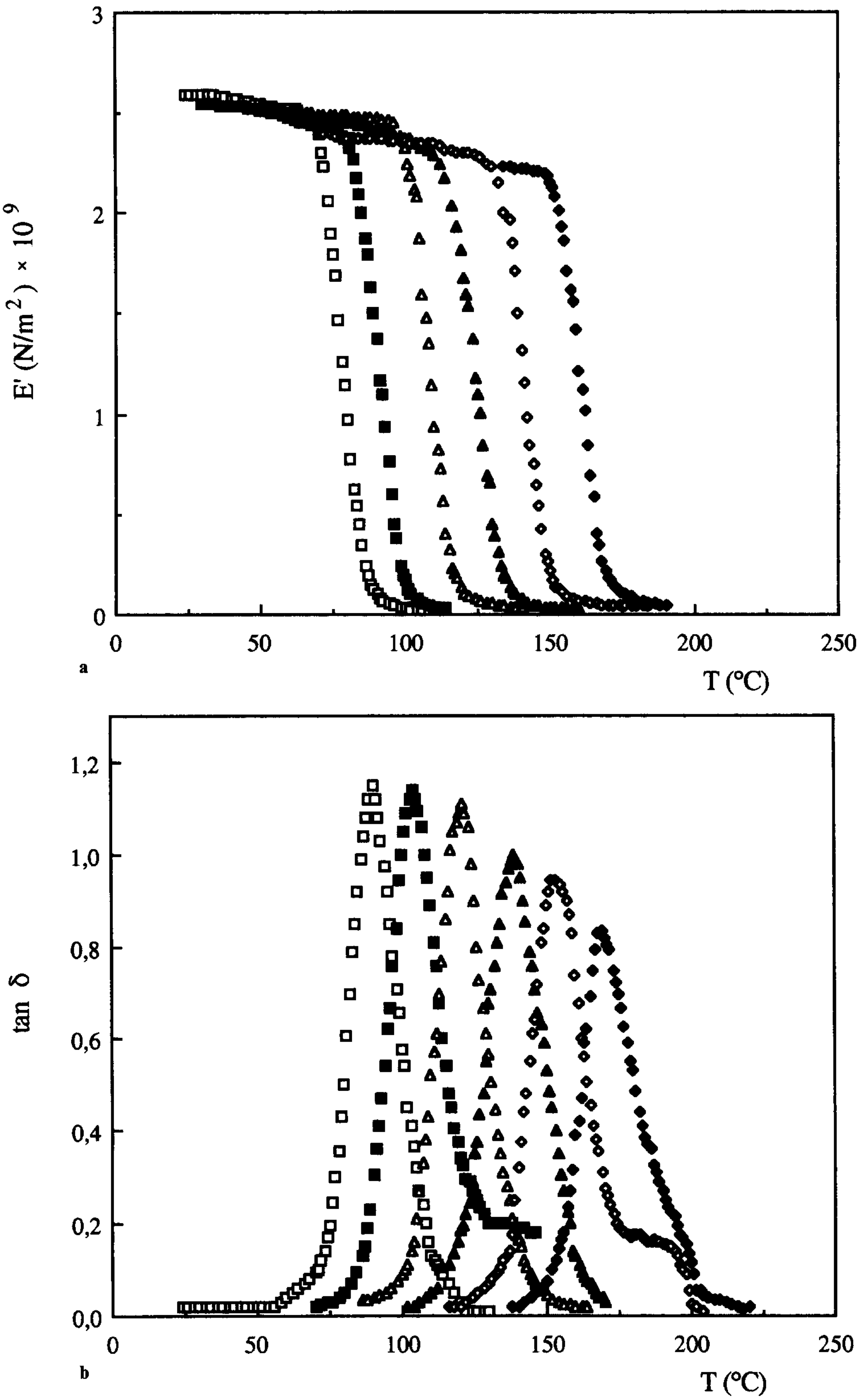


Figure 1 (a) Storage modulus evolution upon temperature for D230 containing mixtures with several mPDA percentages. □, 0% mPDA; ■, 20% mPDA; △, 40% mPDA; ▲, 60% mPDA; ◇, 80% mPDA; ◆, 100% mPDA. (b) Variation of the loss factor of D230 containing mixtures as a function of temperature with several mPDA percentages. Symbols as in (a)

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 the span length, f the shape factor, B the specimen thickness, and W the width of the specimen. The critical energy to fracture per unit area of crack, G_{Ic}, was calculated from the critical stress intensity factor as:

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

where v is Poisson's ratio taken as 0.35, and E the elastic modulus obtained from flexural testing.

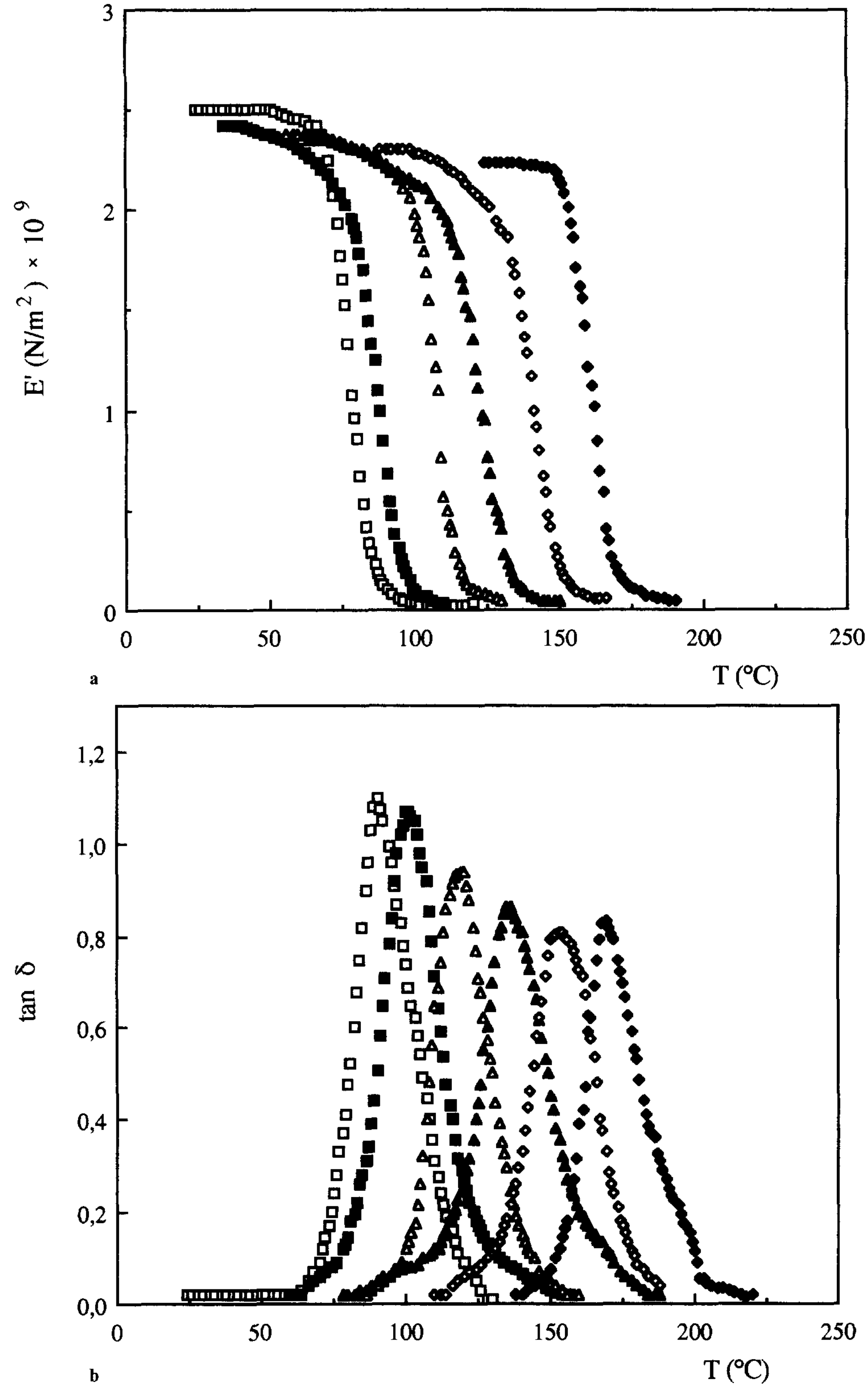


Figure 2 (a) Storage modulus evolution upon temperature for T403 containing mixtures with several mPDA percentages. Symbols as in *Figure 1a*. (b) Variation of the loss factor of T403 containing mixtures as a function of temperature with several mPDA percentages. Symbols as in *Figure 1a*

RESULTS AND DISCUSSION

Dynamic mechanical studies

Dynamic mechanical properties for stoichiometric formulations of epoxy mixtures cured upon PPO di- or triamine/mPDA mixed curing agents are shown in *Figures 1* and *2* as a function of the mPDA weight percentage in the curing agent. *Figures 1a* and *b* show the storage modulus, E', and damping, tan δ, as a function of temperature for various formulations of mixtures containing the PPO diamine, D230. The damping peak corresponding to the T_α of these mixtures was displaced to higher temperatures as mPDA content increased and a similar behaviour was observed in the sharp decrease of

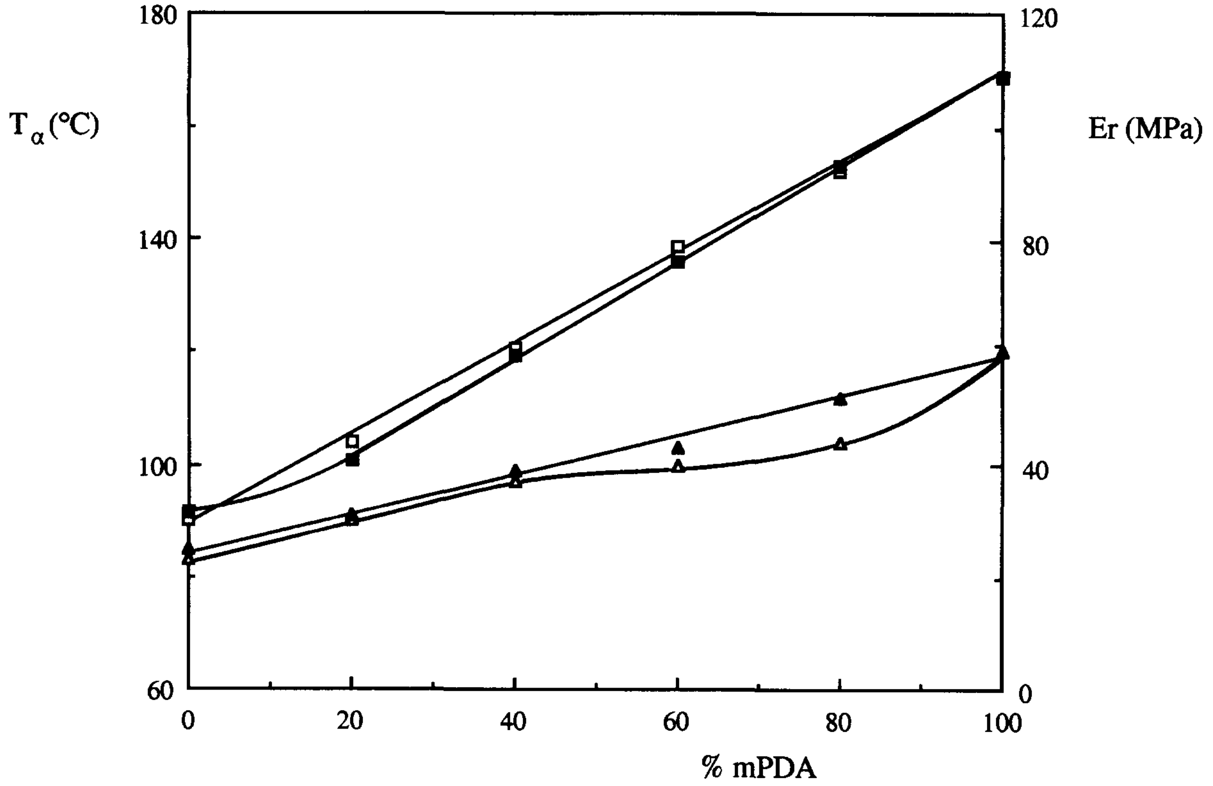


Figure 3 Variation of T_α and rubber modulus as a function of the mPDA percentage. □, T_α for D230 based mixtures; ■, T_α for T403 based mixtures; △, rubber modulus for D230 based mixtures; ▲, rubber modulus for T403 based mixtures

elastic modulus in the glass relaxation region. Beyond the glass transition, the elastic modulus of these epoxy mixtures steadied to a characteristic constant value which further increased for each composition. As can be seen in *Figures 2a–b*, similar shifts in the damping peak and elastic modulus were observed for crosslinked networks containing the PPO triamine, T403, as mPDA percentage increased.

The T_α of the cured networks containing D230 or T403 amines have been plotted as a function of the mPDA percentage in *Figure 3*. For both epoxy mixtures, T_α showed a linear dependence on the mPDA content, decreasing as the amount of the PPO based polyamine in the mixture was increased, therefore indicating that network structures corresponding to formulations with different aliphatic amine/mPDA ratios can be directly related to the amount of PPO in the curing agent.

On the other hand, the analysis of the shape of the α relaxation can provide additional information about the structure of the crosslinked networks[18,19]. Thus, the height of the α transition, h_α, for a thermoset mixture supplies information about the extent of cure, being lower as the distance between crosslinks becomes smaller (i.e. for DGEBA resins with equivalent weights of 177 and 184.5 cured with mPDA in a stoichiometric ratio under the same conditions that were used in this investigation, h_α values are 0.60 and 0.83 respectively). Besides, the width at the half-height decreasing on the α relaxation, σ_α, can be related to the network homogeneity as the α relaxation is broader as network loosening increases. As can be seen in *Table 2*, h_α increased in a similar way for both mixtures as the aliphatic amine content in the curing agent was higher, because chain length is higher for the aliphatic amines used than for mPDA. Moreover, the near-constant values on σ_α for both mixtures, independent of the composition of the curing agent, along with the σ_α results seem to indicate that the network compaction was similar for mixtures containing D230 and T403 amines, or in other words,the additional strand existing on T403 cured mixtures because of the chemical structure of the curing agent would compensate for the greater length of aliphatic chains between amine groups in T403 based systems with respect to that for D230 based mixtures.

Table 2 Variation of the height and the width at the half-height (in °C) of the α transition of the temperature (in °C) of the α relaxation, and of the rubber modulus (in MPa) with the mPDA percentage in the mixture for D230 and T403 containing mixtures

Curing agent		mPDA (wt%)					
		100	80	60	40	20	0
D230	h_α	0.83	0.94	1.02	1.11	1.16	1.17
	σ_α	23	22.5	24.5	21	22	20.5
	T_α	169	152.5	139	120.5	104	91
	E_r	60	44	40	37	30	23
T403	h_α	0.83	0.81	0.87	0.94	1.07	1.10
	σ_α	23	25.5	26	21.5	22.5	20.5
	T_α	169	152.2	136	119.5	100.5	90.5
	E_r	60	52	43	39	31	25

As is well known, the glass relaxation, linked to the sharp damping peak shown in *Figures 1* and *2*, can be attributed to the motion of chains between crosslinking points during the glass-to-rubber transition process. By assuming that the internal energy of the formed network is not affected above the T_α and by relating the changes

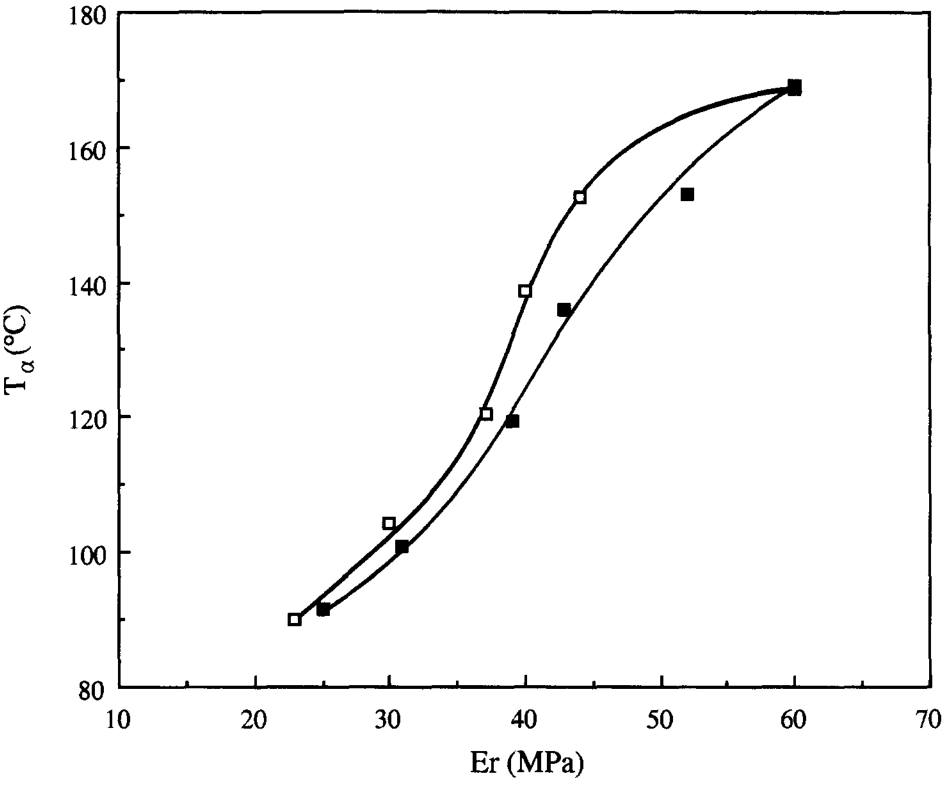


Figure 4 Rubber modulus *versus* T_α. □, DGEBA/D230/mPDA mixtures; ■, DGEBA/T403/mPDA mixtures

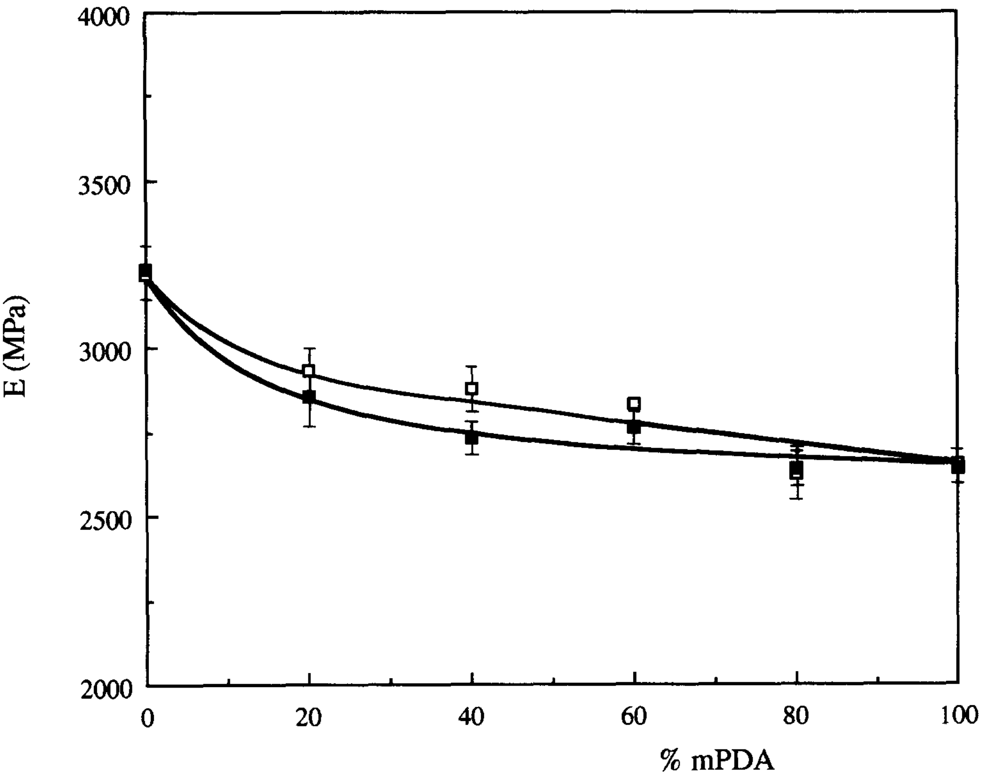


Figure 5 Flexural modulus *versus* mPDA percentage. □, D230 containing mixtures; ■, T403 containing mixtures

in entropy, due to the motion of segments amongst the network strands, to the average molecular weight between crosslinks, the rubber-like elasticity theory[20] relates in an approximate form the elastic modulus in the rubber-like region above the glass relaxation, E_r, to the average molecular weight between crosslinks, M_c, and density, ρ, by means of the commonly used expression:

$$E_r = 3\theta\rho RT/M_c \tag{3}$$

where R is the gas constant and T is the absolute

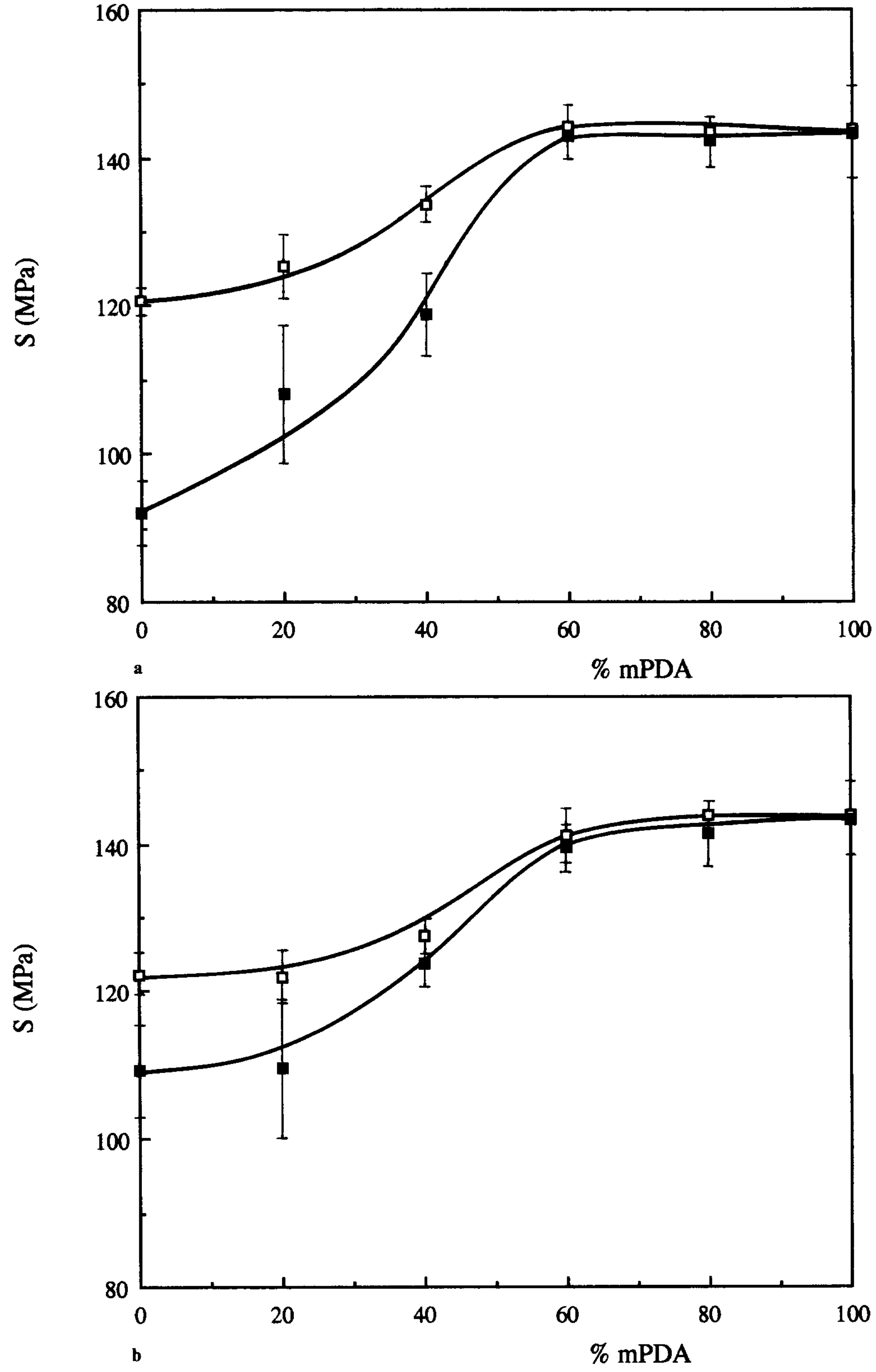


Figure 6 Flexural strength *versus* mPDA percentage for mixtures containing (a) D230 and (b) T403. □, Maximum strength; ■, strength to break

temperature. θ is the 'front factor', assumed to be equal to 1 (ref. 21).

Values of E_r obtained from dynamical tests, which led to deviations from results from static tests for lack of relaxation due to dissimilar frequencies used[22], are represented against the mPDA content in *Figure 3* for D230 and T403 containing mixtures. For both epoxy systems the E_r variation followed the same trends as it was approximately inversely proportional to the mPDA percentage in the curing agent. The values of T_α, rubber elastic modulus, and average molecular weight between crosslinks of these epoxy mixtures are shown in *Table 2*.

Besides, the T_α values of both epoxy mixtures were inversely proportional to the average molecular weight

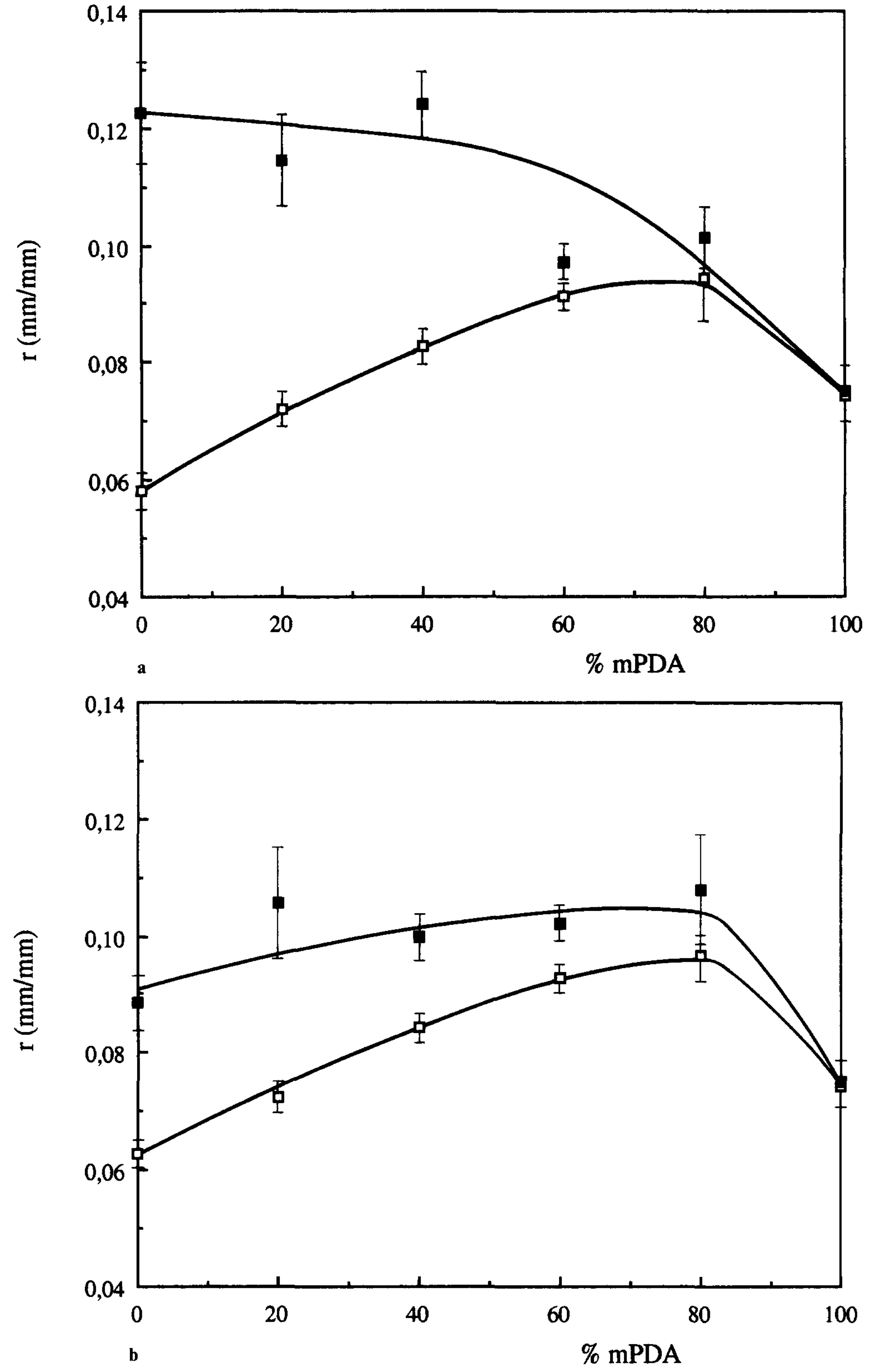


Figure 7 Strain behaviour as a function of the mPDA percentage for mixtures containing (a) D230 and (b) T403. □, Maximum strain; ■, strain to break

between crosslinks (the same behaviour as the storage modulus in the rubbery state), as can be seen in *Figure 4* for mixtures containing D230 and T403 curing agents, again showing clearly the high homogeneity of these networks independently of the PPO amine/mPDA ratio in the curing agent.

Influence of curing agent composition on static mechanical properties

The mechanical properties of the analysed epoxy mixtures such as flexural modulus, E, maximum stress, S_m, strength to break, S_b, strain to maximum strength, r_m, and strain to break, r_b, as well as the toughness

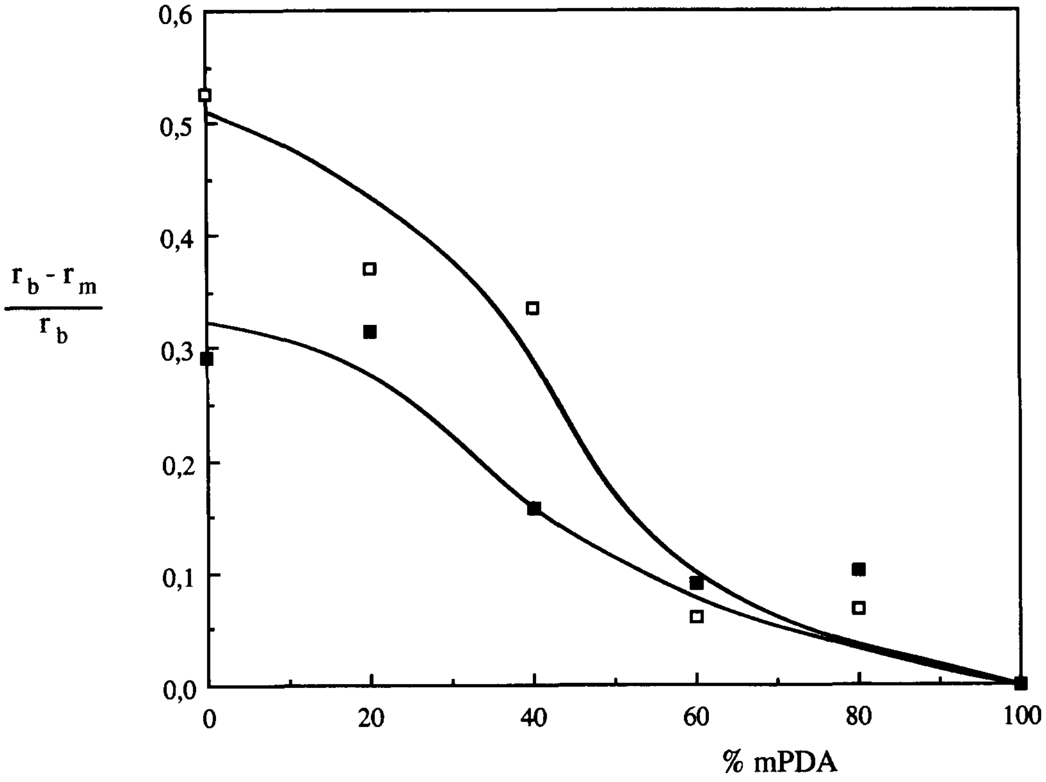


Figure 8 The ratio of non-linear elongation to breaking elongation *versus* mPDA percentage. □, D230 containing mixtures; ■, T403 containing mixtures

calculated as the critical stress intensity factor, K_{Ic}, or the critical strain energy release rate, G_{Ic}, have been studied.

Flexural moduli of both epoxy mixtures are shown in *Figure 5* as a function of mPDA percentage in the curing agent. The values are slightly lower than those corresponding to a linear rule of mixtures. Surprisingly, all mixtures including those containing solely the aliphatic amines, showed a higher stiffness than the mixtures cured solely with the aromatic amine, despite the chemical rigidity of networks built upon aromatic amines being higher for a similar extent of cure. Moreover, the higher crosslink density of mixtures cured with mPDA only with respect to that for those cured with each of the aliphatic amines should lead to a higher stiffness. In other words, the sole consideration of the network chemical rigidity would suppose that the mechanical stiffness of crosslinked networks built upon mPDA should be higher than that for those containing aliphatic amines. Therefore, in order to explain the elastic behaviour shown by these mixtures, effects other than the crosslink density have to be taken into account. As has been shown in the literature survey for stoichiometric epoxy mixtures[9,23], whilst at low and not too high extents of cure the crosslink density is the main factor controlling the elastic behaviour of crosslinked networks, when the crosslink density becomes very high, factors other than the network chemical rigidity should also be considered in order to analyse the elastic behaviour in the glassy state. Indeed, as has been stated[14,24], as a consequence of the lower molecular mobility of highly crosslinked networks, the segments of the network are less able to pack closely in the glassy state, thus supposing a higher free volume in the network and consequently a lower elastic modulus[24]. That is possibly the main factor that influences the stiffness behaviour of the epoxy mixtures studied since, as shown above, the networks were homogeneous. Nevertheless, the intensity of the β relaxation, not measured in this study, would also be one factor to take into account for mechanical values obtained at temperatures between that corresponding to this relaxation and T_α.

On the other hand, the higher chemical rigidity of chains between crosslinks on the mPDA cured mixtures in relation to that for the aliphatic amine cured systems influences the mechanical properties at larger deformations even more than the crosslink density of the cured networks. Indeed, as can be seen in *Figures 6a* and *b*, the maximum strength of the epoxy mixtures with high mPDA contents in the curing agent mixture was higher than that for formulations containing more aliphatic amine. (This variation was slightly more evident for systems containing the D230 curing agent (*Figure 6a*) than for those containing the T403 (*Figure 6b*), surely because of the longer chain flexibility in the T403 backbone due to a higher aliphatic segment/amine ratio in its chemical structure.)

Besides, the yield behaviour of these epoxy mixtures showed similar trends independently of whether the aliphatic amine used was D230 or T403, possibly as a consequence of the similar crosslink densities for both crosslinked networks at all mPDA contents in the curing agent. The higher chain flexibility of the aliphatic amines with respect to that for mPDA suggest a slight plasticization in high mPDA content mixtures as the strain to maximum strength, shown in *Figures 7a* and *b*, was higher for these mixtures that broke around the yield strength. Therefore, the maximum strength of mixtures

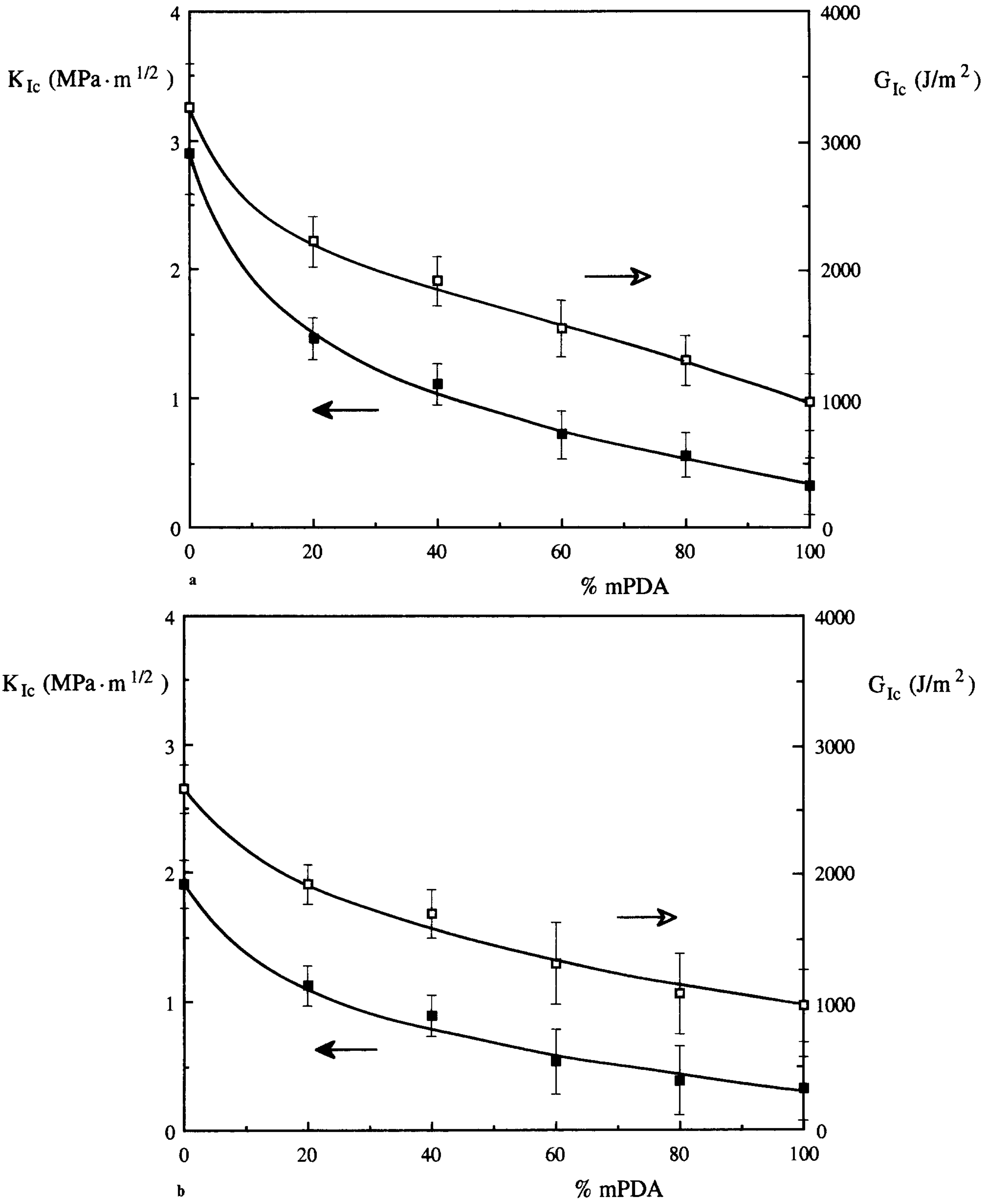


Figure 9 Fracture toughness *versus* mPDA percentage for mixtures containing (a) D230 and (b) T403. ■, Critical stress intensity factor K_{Ic}; □, critical strain energy release rate G_{Ic}

built upon a high mPDA content was similar to that for mixtures prepared with mPDA, thus showing the potential interest of this type of modification for high T_g epoxy resins.

As can be seen in *Figures 7a* and *b*, adding aliphatic amines to the mPDA curing agent clearly changed the mechanism of fracture of these mixtures (brittle for mPDA based mixture to ductile for systems containing PPO amines, since deformation to break became higher as aliphatic amine content increased). Nevertheless, despite the increased deformability for all amine compositions with respect to that for the mixture cured with mPDA, only mixtures with high contents of aliphatic amines yielded[25] because of the higher flexibility of the segments between crosslinks for these networks.

In addition, it is worth noting that the deformability of D230 containing mixtures was slightly higher than that for mixtures with T403 at high aliphatic amine contents in the curing agent. The lower values for mixtures with T403 are surely related to the relatively higher pendent methyl group/amine ratio with respect to that for the D230 backbone; besides, as shown in *Figures 6a* and *b*, there was a higher strength to break for mixtures built upon T403 than for those of D230 containing mixtures. This behaviour may be related to the small steric hindrance generated by the pendent methyl group which yields a lowering of chain mobility required for higher deformations.

As has been suggested recently[26], the ratio of the non-linear deformation to the breaking deformation $((r_b - r_m)/r_b)$ can be used to represent the ductility of these materials. This ratio has been plotted as a function of mPDA percentage in the curing agent in *Figure 8* for mixtures with different amounts of D230 and T403 amines. The slight plasticization shown above in mixtures with high mPDA contents may be clearly seen for mixtures containing 60 and 80% mPDA in the curing agent formulation. On the other hand, the higher ductility of mixtures with high aliphatic amine contents may be related to the higher flexibility of their chemical backbones with respect to that for mPDA, slightly higher in the D230 case as stated above.

On the other hand, the variation of the critical stress intensity factor, K_{Ic}, and the critical strain energy release G_{Ic}, with the mPDA content for both mixtures is shown in *Figures 9a* and *b*, respectively. K_{Ic} and G_{Ic} values decreased continuously as mPDA percentage increased in the mixtures. This variation of fracture toughness was similar to that shown above for the ductility. Indeed, the slightly higher toughness of mixtures containing D230 with respect to that for the T403 based systems seems to be a consequence of the higher deformability (the strength was similar, *Figure 7*) of the networks built up with D230 because of the higher mobility of their segments between crosslink points. As has been shown[27], K_{Ic} and G_{Ic} are strongly dependent upon the extent of reaction. In order to check whether the variation of mPDA percentage in the curing agent affected the extent of reaction in the different mixtures, Fourier transform infrared measurements have also been made. Results are shown in *Table 3*. In the same way as shown by other investigations[28], the conversion of the epoxy group did not reach 100% for all cured mixtures, but it was similar for all mixtures, thus indicating that the variations noticed for the mechanical properties were related to structural factors such as chemical structure.

CONCLUSIONS

In this study the dynamic and mechanical properties of epoxy resins cured with a curing agent formed by a mixture of mPDA and aliphatic amines have been analysed as a function of mPDA content. Results can be summarized as follows:

- the T_α of mixtures showed a linear dependence upon the mPDA content in the curing agent increasing with it;
- rubber modulus values increased as mPDA percentage in the curing agent was higher, indicating a good compaction in the mixtures;
- decrease in elastic modulus as mPDA content increased has been related to variations in the free volume of the mixtures as well as in their β relaxation;
- the evident increase in the strength of mixtures with high contents of mPDA with respect to that for the mixture cured solely with mPDA showed the potential interest for using a second aliphatic curing agent to cure epoxy resins crosslinked with aromatic amines;
- in the same way as for strength, the toughness of mixtures increased as aliphatic amine content was higher.

Table 3 Epoxy conversion (%) of the cured samples obtained by *FT*i.r. analysis

Curing agent	mPDA (wt%) 100	80	60	40	20	0
D230	94	94	94	96	96	94
T403	94	94	94	94	95	93

ACKNOWLEDGEMENT

The authors wish to thank Gobierno Vasco/Eusko Jaurlaritza for financial support (grant no. PI93/78).

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