Polymer Vol. 37 No. 11, pp. 2195–2200, 1996

0032-3861/96/$15.00+0.00

Influence of cure schedule and stoichiometry on the dynamic mechanical behaviour of tetrafunctional epoxy resins cured with anhydrides

P. Guerrero, K. De la Caba, A. Valea, M. A. Corcuera and I. Mondragon*
Departamento Ingeniería Química y del Medio Ambiente, Escuela Universitaria Ingeniería Técnica Industrial, Universidad País Vasco/Euskal Herriko Unibertsitatea, Avda., Felipe IV, 1B, 20011 San Sebastián/Donostia, Spain
(Received 12 May 1995; revised 5 August 1995)

Epoxy networks based on N,N,N',N'-tetraglycidyl-4,4'-diamino diphenylmethane (TGDDM) prepolymer were prepared with *cis*-1,2,3,6-tetrahydrophthalic anhydride (THPA) curing agent at anhydride/epoxy group ratios varying from 0.3 to 1.0. For post-cured mixtures, dynamic mechanical tests show that the glass transition temperature reaches the maximum value at stoichiometric ratios between 0.8 and 0.9. This behaviour has been related to the crosslink density of the formed networks, and also to etherification reactions occurring during cure which lower the amount of anhydride needed in order to complete the curing process. The study of cure cycle variations on the viscoelastic properties showed that for epoxy/anhydride mixtures high post-cure temperatures could be needed to reduce the amount of unreacted epoxy groups after curing. Fourier transform infra-red spectroscopy has been used to analyse the residual epoxy groups and also to study the influence of the different cure reactions on the physical properties of these networks. Copyright © 1996 Elsevier Science Ltd.

(Keywords: epoxy; anhydride; dynamic mechanical behaviour)

INTRODUCTION

Although epoxy resins can be cured with different families of hardeners, most studies performed to date have been devoted to different aspects related to epoxy resins cured with aminic curing agents[1-8]. Nevertheless, despite the fact that anhydride-like hardeners become serious outsiders when choosing a curing agent, not so many papers have been devoted to epoxy/anhydride mixtures[9]. In fact, anhydride-like curing agents are preferred for electrical and electronic applications or when chemical safety has to be taken into account[9,10]. In cured epoxies, the three-dimensional molecular network structure formed—which is a function of the prepolymers and curing agents, and of the stoichiometric ratio used[1-3] and also of the advance of crosslinking[11,12]—determines the glass transition temperature and other physical properties of these materials[13-17]. Indeed, when highly heat-resistant materials are needed, tetrafunctional epoxides are preferred to bifunctional epoxide prepolymers[18].

On the other hand, although the main suppliers of anhydride hardeners suggest to use around 80–90 wt% of the anhydride/epoxy stoichiometric ratio in order to obtain better properties, there are few studies investigating the reasons for using this amount[9,10,19]. In addition, nowadays the influence of post-curing on the glass transition temperature and other physical properties of epoxy mixtures cured with aminic curing agents is well known[3,11,18,20,21].

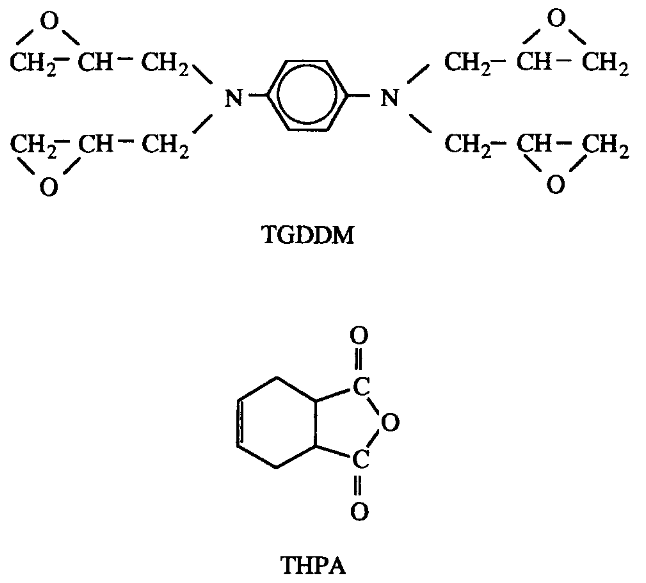
In the present study, the dynamic mechanical behaviour of a commercial epoxy system based on N,N,N',N'-tetraglycidyl-4,4'-diamino diphenylmethane (TGDDM) cured with tetrahydrophthalic anhydride (THPA) and containing different anhydride/epoxy stoichiometric ratios has been investigated. The variations obtained in the elastic modulus in the rubber region above the glass transition have been used to analyse the crosslink density of the networks. The influence of the cure schedule used on the dynamic mechanical behaviour has also been shown. The study of the variation of epoxy group conversion for mixtures cured with different cure schedules using Fourier transform infra-red spectroscopy (*FT*i.r.), along with analysis of the rubber modulus changes, allow us to correlate the reported physical behaviour to the internal structure of the crosslinked mixtures.

EXPERIMENTAL

A commercial epoxy prepolymer, MY-9512 supplied by Ciba-Geigy, consisting largely of N,N,N',N'-tetraglycidyl-4,4'-diamino diphenylmethane (TGDDM), was cured with *cis*-1,2,3,6-tetrahydrophthalic anhydride (THPA), Fluka quality. They were used without further purification. The chemical structures are shown in *Scheme 1*.

---

* To whom correspondence should be addressed



Scheme 1 Chemical structures of the materials used

Samples were prepared by mixing both components at different stoichiometric ratios *r* ranging from 0.3 to 1.0, where *r* was defined as anhydride groups/epoxy groups. After degassing TGDDM at 50°C for 10 min, anhydride was added in small amounts by stirring in an oil bath at 100°C for 10 min. Plates of dimensions 150 × 50 × 10 mm were prepared using a steel mould coated with Frekote 44 releasing agent. Mixtures were subjected to the following cure schedules: 120°C for 2 h with degassing the earlier 15 min (schedule 1C); further curing at 170°C for 2 h after schedule 1C (schedule 2C); and post-curing at 200°C for 2 h after schedule 2C (standard cure schedule, 3C). Post-curing at 200°C led to a change in colour from straw yellow to deep orange, possibly because significant epoxide isomerization and/or oxidation occurred within the matrix at such a high cure temperature.

Specimens used for dynamic mechanical tests were machined to 60 × 12 × 10 mm from the above plates. Dynamic mechanical analysis was carried out in a Metravib viscoanalyser provided with a three-point bending device with a span length of 44 mm. Runs at 10 Hz were performed at a heating rate of 3°C min^{-1} over the temperature ranges described below. Elastic rubber modulus (E_r) values for all mixtures studied have been taken as those corresponding to a temperature around 40°C higher than that for the α relaxation peak.

Infra-red spectra of cured mixtures were obtained on a Perkin-Elmer FTIR spectrophotometer, model 16 PC, from 40 scans at a 4 cm^{-1} resolution in the range 400 to 4000 cm^{-1}. Samples were prepared from potassium bromide pellets mixed with a small amount of the epoxy mixture. The decrease in epoxy functionality was monitored by its characteristic 830 cm^{-1} absorption, taking as reference the band centred at 1612 cm^{-1} arising from phenyl ring stretching.

RESULTS AND DISCUSSION

Dynamic mechanical properties from −80 to 300°C for the stoichiometric TGDDM/THPA epoxy mixture cured with the standard cure schedule are shown in *Figure 1*.

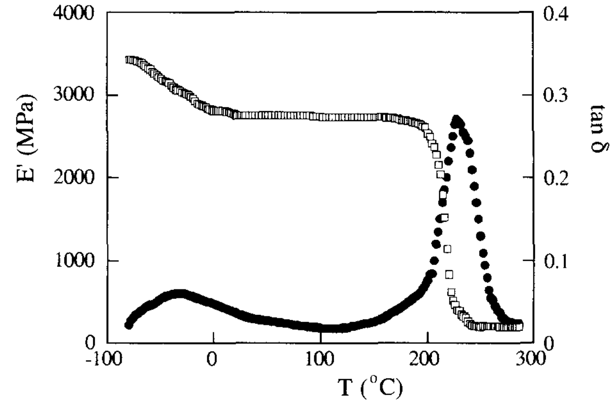


Figure 1 Dynamic mechanical spectra for the stoichiometric TGDDM/THPA mixture cured with the standard cure schedule: ●, loss factor; □, storage modulus

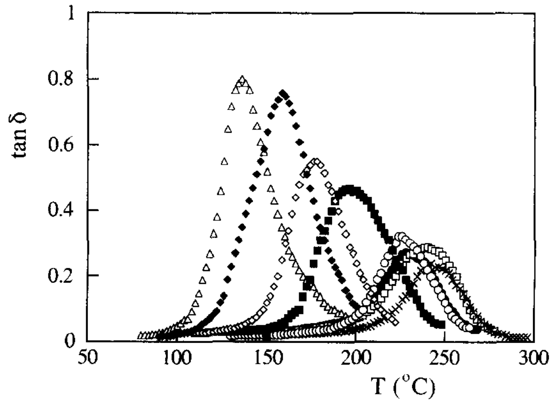


Figure 2 Dynamic mechanical loss tangent for epoxy mixtures cured with different amounts of anhydride: ●, *r* = 1.0; □, 0.9; ×, 0.8; ○, 0.7; ■, 0.6; ◇, 0.5; ◆, 0.4; △, 0.3

The mechanical loss factor (tan δ) showed two distinct peaks. The low temperature peak, usually noted as the secondary β relaxation, appeared centred at around −35°C. This relaxation has been related to the molecular motion of the anhydride portion incorporated into the network through diester linkages[22,23]. The elastic storage modulus (E') decreased slowly through the β relaxation. The maximum in the loss factor at high temperatures corresponding to the α relaxation is associated with the glass transition temperature (T_g) of the mixture. In this glass-to-rubber transition region, the elastic modulus showed a sharp drop of nearly two orders of magnitude before levelling out in the rubber region.

The relaxational behaviour in the range 20 to 300°C for mixtures with different stoichiometric ratios cured with the standard cure schedule is shown in *Figures 2* and *3* by means of the loss factor and the storage modulus, respectively. As shown in *Figure 2*, the peak temperature corresponding to the α relaxation of these mixtures increased as the stoichiometric ratio was raised up to $r \approx 0.8$–0.9 and decreased thereafter. Just the opposite trend was observed when the peak height of the α relaxation was analysed, since it decreased up to a stoichiometric ratio *r* of around 0.8 and then increased slightly. As shown below, this behaviour indicates that a more crosslinked network, and so a higher restriction on

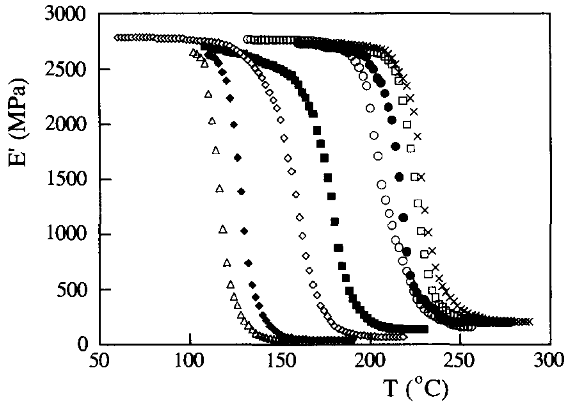


Figure 3 Storage modulus variation *versus* temperature for epoxy mixtures cured with different amounts of anhydride. Symbols as in *Figure 2*

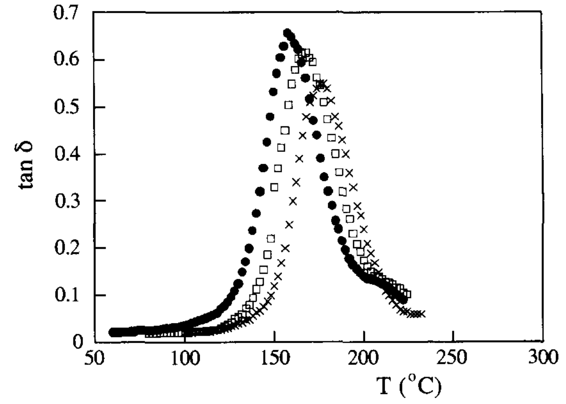


Figure 4 Dynamic mechanical loss tangent for epoxy mixtures with $r = 0.5$ cured with different cure schedules: ●, 1C; □, 2C; ×, 3C

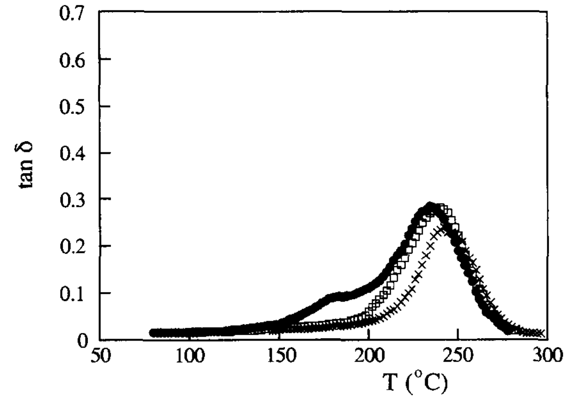


Figure 5 Dynamic mechanical loss tangent for epoxy mixtures with $r = 0.8$ cured with different cure schedules. Symbols as in *Figure 4*

molecular mobility, was obtained for compositions containing a low epoxy excess, $r = 0.8$–0.9, so agreeing with the advice given by resin suppliers and with findings in the literature[9,10,19].

A similar behaviour was obtained for the storage modulus, *Figure 3* showing that it decreased in the glass transition region. Moreover, for epoxy-rich mixtures cured with the standard cure schedule, the elastic modulus corresponding to the rubber region increased with the stoichiometric ratio to $r = 0.8$ and then decreased. This behaviour is in accordance with that shown by the loss factor in the glass transition region with respect to the stoichiometric ratio of these mixtures. Applying an approximation of the kinetic theory of rubber elasticity used by other authors[24–28] (in which the rubber modulus is given by $E_r \approx 3\rho RT/M_c$, where ρ, the density of the network, was almost invariant for all mixtures [1.22–1.23 g cm^{-3}], T is the temperature in K and M_c is the molecular weight between crosslinks), it can be seen that the crosslink density was higher since E_r increased with r up to $r \approx 0.8$, and then steadied to a nearly constant value.

As has been shown[10,29], in the absence of catalysts, epoxy/anhydride polymerization reactions mainly occur through consecutive addition–esterification steps involving carboxylic acid group intermediates and simultaneous addition–etherification. According to investigations carried out by Steinmann[30,31], polymerization of an epoxy resin with an anhydride similar to that used in this study may be complicated by some chain anhydride formation and an isomerization reaction of the anhydride; this would lead to some consumption of reactive anhydride groups and thus the supposition that an excess of anhydride should be used to complete the polymerization reactions. However, the fact that the more crosslinked networks were obtained for mixtures with a slight epoxy excess can be attributed to the competing addition–etherification reactions between epoxide groups and initial or reaction-formed hydroxyl groups in the presence of anhydrides or carboxylic acids.

In order to study the dependence of the dynamic mechanical properties on the cure schedule used, all mixtures were cured with the three different cure conditions described in the Experimental section. *Figures 4* and *5* show the changes of the loss factor as a function of the cure schedule for stoichiometric ratios of 0.5 and 0.8. It is note worthy that the first cure step at 120°C for 2 h was sufficient to obtain a high T_g for both mixtures (indicating a high cure conversion), in contrast to the behaviour observed for the non-catalysed polymerization of bifunctional epoxy resins cured with similar curing agents[11,12,19], possibly as a consequence of a higher amount of hydroxyl groups in the starting TGDDM epoxy resin. For both mixtures, but especially for that with $r = 0.5$, the subsequent cure steps increase (though not by much) the T_g of that mixture, so indicating the completion of cure reactions. Surprisingly, for both mixtures (although to a higher extent for the $r = 0.8$ formulation), the T_g reached after the 120°C cure step was higher than the cure temperature used. This behaviour is similar to that shown for other epoxy/anhydride mixtures[12] and could be related to etherification and/or more esterification reactions occurring amongst the unreacted epoxide and formed hydroxyl groups and the unreacted acid esters: the exothermy of the cure reactions in the mixtures could increase the temperature of the bulk mixtures inside the mould, so promoting other reactions because of the proximity of these reacting groups in the forming network. The subsequent cure steps did not clearly increase the T_g, possibly because most epoxide groups were already reacted and the steric hindrance in the tight network thus formed prevented further reaction.

The $r = 0.8$ mixture cured at 120°C only showed a shoulder around 180°C in the α relaxation (this shoulder also appeared for all mixtures with $r > 0.6$ cured solely at

Table 1 Rubber modulus, glass transition temperature and height of the α relaxation peak, for mixtures with different stoichiometrics cured with several cure schedules

	Cure schedule	r 0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
E_r (MPa)	1C	12.8	31.5	53.5	87.8	147	171	210	202
	2C	14.5	35.0	59.6	101	156	221	215	213
	3C	22.5	34.3	70.5	140	168	210	210	205
T_g (°C)	1C	87 (105)	131.5	158.5	189.9	(172) 223	(180) 235	(182) 235	(174) 226
	2C	110.5	145.0	167.0	192.6	220.4	239.5	237.0	224.5
	3C	135.8	157.6	176.5	196.5	225.0	242.5	241.0	228.0
h_α	1C	(0.58) 0.60	0.639	0.656	0.592	0.348	0.287	0.282	0.296
	2C	0.902	0.731	0.618	0.537	0.354	0.285	0.286	0.303
	3C	0.803	0.758	0.550	0.473	0.320	0.236	0.291	0.271

120°C, see *Table 1*), indicating that further cure steps were needed to complete the cure reactions between the constituents of the mixture. On the other hand, although not shown, the mixture with a very low amount of anhydride ($r = 0.3$) showed two loss peaks at low temperatures, 87 and 105°C, possibly because of the highly loose nature of the network so obtained. These peaks transformed to only peak at higher temperatures as subsequent cure steps were carried out, possibly as a consequence of the initial low amount of anhydride that allowed addition–etherification to occur at higher cure temperatures because of the high amount of unreacted epoxy groups in these epoxy-rich mixtures.

The variations of the most significant characteristics of the α relaxation (T_g and peak height, h_α), as well as the corresponding rubber modulus, are plotted against the stoichiometric ratio in *Figures 6–8* for the three cure schedules used. Values are also shown in *Table 1*. Independently of the cure schedule used, both the T_g and the rubber modulus clearly increased, and the height of the α relaxation decreased, up to a $r = 0.8$ (up to $r = 0.9$ when curing was carried out at 120°C only), so showing the importance of the subsequent mono- and diester formation in the development of the network structure. With the exception of the mixtures with a very low anhydride content, the values of these properties remained almost constant after the second cure step at 170°C was performed, possibly because the network structure obtained after curing at 170°C was practically the best that could be obtained for each composition. The changes evident obtained in these properties for the $r = 0.3$ mixture cured with the 2C and 3C cure schedules correspond mainly to additional etherification reactions as a consequence of the excess of epoxy groups. On the other hand, for mixtures cured solely at 120°C, the variation of these properties with the stoichiometric ratio was slightly different since the maximum of T_g was not obtained until $r = 0.9$, possibly because some curing reactions could not be completed at this temperature due to steric hindrance in the forming network. Moreover, the rubber modulus values for mixtures with high epoxy contents were lower than those obtained after the other cure steps were performed; this fact was due to the greater broadness (two peaks for $r = 0.3$) of the α relaxation at this cure condition that indicated a looser nature in the formed network. As shown in *Table 1*, increase of T_g upon further cure steps for all compositions indicated that some etherification reactions may have occurred at those cure conditions for all formulations, but especially for those with high epoxy contents since the T_g increases were higher.

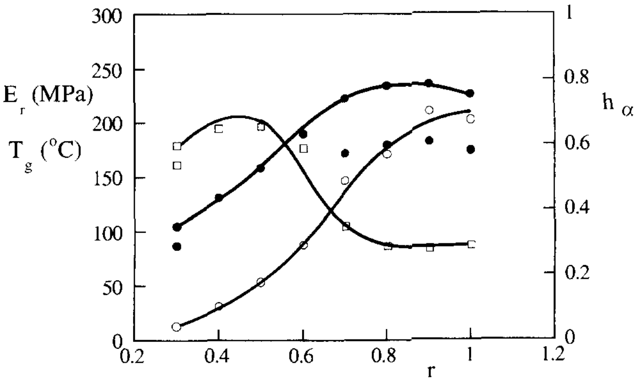


Figure 6 Effect of stoichiometric ratio on the magnitude of several dynamic mechanical properties for mixtures cured at 120°C: ●, glass transition temperature; ○, rubber modulus; □, height of the α relaxation peak

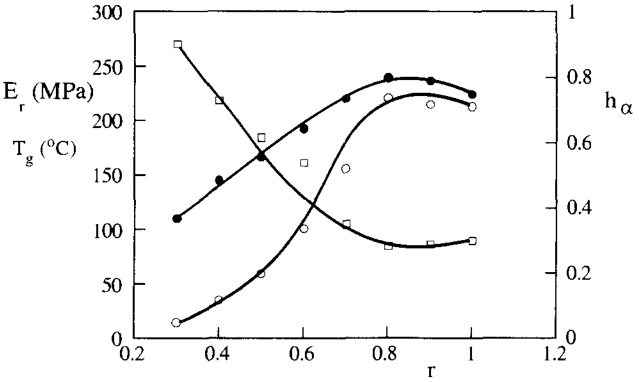


Figure 7 Effect of stoichiometric ratio on the magnitude of several dynamic mechanical properties for mixtures cured at 120–170°C. Symbols as in *Figure 6*

On the other hand, the variation of T_g with the stoichiometric ratio, shown in *Figures 6–8*, was quite

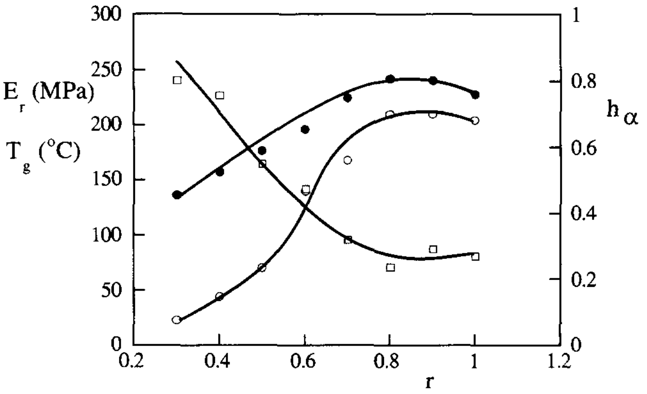


Figure 8 Effect of stoichiometric ratio on the magnitude of several dynamic mechanical properties for mixtures cured with the standard cure schedule. Symbols as in *Figure 6*

Table 2 Epoxy conversion, X, obtained by *FT*i.r. for mixtures with different stoichiometries cured with several cure schedules

Cure schedule	r							
	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
1C	0.30	0.26	0.23	0.21	0.18	0.17	0.15	0.14
2C	0.28	0.24	0.22	0.19	0.17	0.16	0.14	0.14
3C	0.21	0.20	0.19	0.18	0.16	0.15	0.14	0.13

similar for all mixtures to that shown for the rubber modulus, thus revealing the strong dependence of that property upon the crosslink density of the network which, as shown in *Figure 2*, also led to an evident variation of the height corresponding to the α relaxation. As stated by Noordam *et al.*[32], for both completion of the cure schedule and increase of stoichiometric ratio up to 0.8–0.9, a higher degree of cure (see below) results in a higher crosslink density (i.e. higher E_r) and hence in matrices with a higher T_g.

The above variations in the dynamic mechanical properties can be related to the epoxy group conversion, X, obtained after each cure step was carried out. Indeed, as inferred from infra-red analysis (the results of which are shown in *Table 2*), the higher differences between these properties observed at epoxy-rich compositions after the different cure steps were a consequence of the higher differences existing in the conversion of epoxy groups, especially after the ultimate cure step was performed. On the contrary, at stoichiometric ratios higher than 0.7, the last cure steps practically did not produce more reactions as differences between the conversions for the different cure schedules were $< 2\%$, and so the networks formed corresponding to these compositions did not show an evident variation upon cure schedule changes. On the other hand, the epoxy conversion was higher for mixtures with high stoichiometric ratios independently of the cure schedule used, indicating greater completion of the cure reactions for these compositions. The significant decrease in the T_g of epoxy-rich mixtures with $r < 0.7$, compared with mixtures having a composition near to stoichiometry could be attributed to the fact that unreacted epoxy groups can have some plasticization effect on the crosslinked networks.

Moreover, despite the fact that some epoxide isomerization and oxidation reactions could occur at high temperatures for the epoxy resin used[33], the higher increase of epoxy conversion for anhydride-poor mixtures, especially when the 200°C cure step was carried out, corresponds to some etherification reactions occurring for these compositions between the unreacted epoxy groups as a consequence of an important amount of epoxy groups not having reacted after the first cure step at 120°C. As can be seen in *Figure 9* for the $r = 0.3$ formulation, besides the bands corresponding[10,19] to the branched ether groups obtained at 120°C appearing in the 1100–1200 cm^{-1} region, two small peaks appeared at 1070 and 1350 cm^{-1} which correspond to new ether

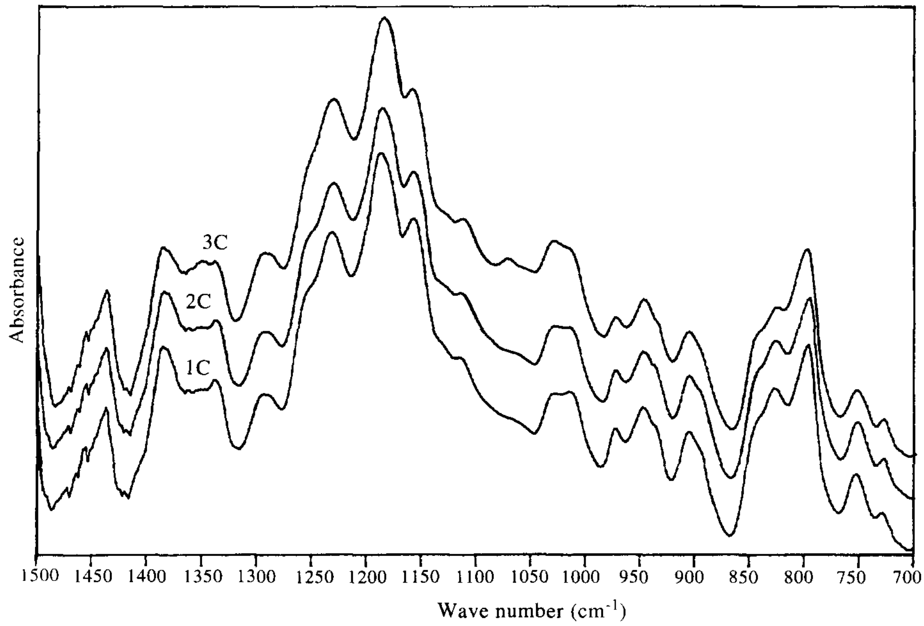


Figure 9 *FT*i.r. absorption spectra in the range 1500–700 cm^{-1} for the $r = 0.3$ mixture cured with different cure schedules

linkages[10,19] formed through reactions of the epoxy groups, since the band centred at 830 cm^{-1} clearly decreased after the 200°C cure step was performed. Although the 1070 and 1350 cm^{-1} peaks were lower, a similar behaviour was obtained for all mixtures after curing at 200°C, indicating that etherification reactions at high temperatures contributed to the network structures formed in these epoxy/anhydride mixtures. These reactions could be responsible for the higher T_g obtained for mixtures with a slight excess of epoxy groups.

CONCLUSIONS

The dependence of the dynamic mechanical behaviour of TGDDM/THPA mixtures upon cure schedule and stoichiometric ratio has been discussed, based on changes of the crosslink density and epoxy conversion of the networks.

In common with other epoxy mixtures, T_g was found to increase as the anhydride/epoxy ratio increased. Nevertheless, the higher T_g did not appear for the epoxy mixture cured with the stoichiometric ratio of THPA, but for mixtures with stoichiometric amounts in the range 0.8–0.9. This behaviour has been related to competitive etherification and esterification reactions occurring during cure of these mixtures.

Post-curing at high temperatures increases the conversion of epoxy groups and modifies the crosslink density of these epoxy/anhydride networks. The effects of post-curing on the viscoelastic properties become more significant for epoxy-rich mixtures mainly owing to, as shown by *FT* i.r. analysis, additional etherification reactions between the unreacted epoxy groups.

The T_gs of the mixtures have been related to the crosslink density and also to the height of the α relaxation. The T_gs actually showed a direct dependence on the rubber modulus for all stoichiometries and cure schedules studied. Conversely, the height of the α relaxation decreased when T_g increased, as the stoichiometry of the mixtures increased and/or when the cure schedule was more complete. This behaviour is a consequence of the higher homogeneity of the crosslinked networks with higher epoxy conversion obtained in these conditions.

ACKNOWLEDGMENT

The authors wish to thank the Universidad Pais Vasco/Euskal Herriko Unibertsitatea (PI-112.263-E093/91) for the fininacial support of this work.

REFERENCES

1 Murayama, T. and Bell, J. P. *J. Polym. Sci., Part A* 1970, **2**, 437

2 Arridge, R.G. C. and Speake, J. H. *Polymer* 1972, **13**, 443

3 Keenan, J. D., Seferis, J. C. and Quinlivan, J. T. *J. Appl. Polym. Sci.* 1979, **24**, 2375

4 Mijovic, J., Williams, J. G. and Donnellan, T. *J. Appl. Polym. Sci.*, 1985, **30**, 2351

5 Charlesworth, J. M. *Polym. Eng. Sci.* 1988, **28**, 221

6 Grillet, A. C., Galy, J., Gérard, J.-F. and Pascault, J.-P. *Polymer* 1991, **32**, 1885

7 Stutz, H. and Mertes, J. *J Polym. Sci. Part A: Polym. Chem. Edn* 1993; **31**, 2031

8 de Nograro, F., Guerrero, P., Corcuera, M. A. and Mondragon, I. *J. Appl. Polym. Sci.* 1995, **56**, 177

9 Ellis, B. 'Chemistry and Technology of Epoxy Resins', Blackie Academic & Professional, Chapman & Hall, London 1993

10 Stevens, G. C. *J. Appl. Polym. Sci.* 1981, **26**, 4259

11 Stevens, G. C. and Richardson, M. J. *Polymer* 1983, **24**, 851

12 Fisch, W., Hofmann, W. and Schmid, R. *J. Appl. Polym. Sci.* 1969, **13**, 295

13 Sanz, G., Garmendia, J., Andrés, M. A. and Mondragon, I. *J. Appl. Polym. Sci.* 1995, **55**, 75

14 Gérard, J.-F., Galy, J., Pascault, J.-P., Cukierman, S. and Halary, J. L. *Polym. Eng. Sci.* 1991, **31**, 615

15 Mikolajczak, G., Cavaille, J.Y. and Johari, G. P. *Polymer* 1987, **28**, 2023

16 Hofer, K. and Johari, G. P. *Macromolecules* 1991, **24**, 4978

17 Mondragon, I. and Bucknall, C. B. *Plast. Rubber Compos. Proc. Applic.* 1994, **21**, 275

18 Chu, H. S. and Seferis, J. C. *Polym. Compos.* 1984, **5**, 124

19 Stevens, G. C. *J. Appl. Polym. Sci.* 1981, **26**, 4279

20 Pangrle, S., Wu, C. S. and Geil, P. H. *Polym. Compos.* 1989, **10**, 173

21 Wisanrakkit, G. and Gillham, J. K. *J. Appl. Polym. Sci.* 1991, **42**, 2465

22 Shimbo, M., Ochi, M. and Iesako, H. *J. Polym. Sci.: Polym. Phys. Edn.* 1984, **22**, 1461

23 Ochi, M., Iesako, H., Nakajima, S. and Shimbo, M. *J. Polym. Sci.: Polym. Phys. Edn.* 1984, **24**, 251

24 Tobolsky, A. V., Carlson, D. W. and Indicator, N. J. *J. Polym. Sci.* 1961, **54**, 175

25 Charlesworth, J. M. *Polym. Eng. Sci.* 1988, **28**, 230

26 Vratsanos, M. S. and Farris, R. J. *Polym. Eng. Sci.* 1989, **29**, 806

27 Wingard, C. D. and Beatty, C. L. *J. Appl. Polym. Sci.* 1990, **41**, 2539

28 Sasuga, T. and Udagama, A. *Polymer* 1991, **32**, 402

29 Fisch, W. and Hofmann, W. *J. Polym. Sci.* 1954, **XII**, 497

30 Steinmann, B. *J. Appl. Polym. Sci.* 1989, **37**, 1753

31 Steinmann, B. *J. Appl. Polym. Sci.* 1990, **39**, 2005

32 Nooram, A., Wintraecken, J. J. M. H. and Walton, G. in 'Crosslinked Epoxies', Walter de Gruyter & Co., Berlin, 1987, p. 373

33 Morgan, R. J. *Adv. Polym. Sci.* 1985, **72**, 1