The effect of stoichiometry and thermal history during cure on structure and properties of epoxy networks

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An investigation was carried out into the effect of amine/epoxy stoichiometry and thermal history during cure on physical and mechanical properties of epoxy networks. The formulation studied consisted of a diglycidyl ether of bisphenol A epoxy resin and 4,4'-diaminodiphenyl sulfone curing agent. The experimental matrix was based upon three amine/epoxy ratios and seven different thermal histories during cure. Techniques used included dynamic mechanical and fracture analysis, and Fourier transform infra-red (FTi.r.) spectroscopy. The highest glass transition temperature (T_g) was observed in the stoichiometric formulation and the lowest in the epoxy-rich mixture. For a given stoichiometry, the value of $T_{g,infinity}$ was not a function of thermal history during cure except, interestingly, in the case when the initial temperature was 180 C. The highest rubbery state modulus and the lowest average molecular weight between crosslinks were also found in the stoichiometric formulation. Our findings were rationalized in terms of the varying degrees of crosslinking in different networks. The opposite trend was observed in the glassy state at 20 C, where the lowest flexular modulus belonged to the stoichiometric formulation. An explanation for those results was offered in terms of the free volume concept. FTi.r. analysis established clearly the existence of residual epoxy groups in all formulations, even after post-cure. Etherification reaction between epoxy and hydroxyl groups takes place during post-cure, but a complete conversion of epoxy groups cannot be attained owing to the topological constraints within the three-dimensional network in the later stages of cure. This finding is of particular significance in mechanistic kinetic models based upon the absolute value of epoxy concentration at all stages of cure.

(Keywords: epoxy resins; cure; networks)

INTRODUCTION

Since Castan's seminal work[1] over a half century ago, epoxy resins have graduated from a laboratory curiosity to a wide range of applications, becoming an integral component of the adhesive, electronics and aerospace industries. The most complete compilation of information on all aspects of chemistry, structure, properties and technology of epoxy resins can be found in the definitive reference book by May[2]. Among numerous epoxy formulations that are nowadays available, those composed of diglycidyl ether of bisphenol A (DGEBA) resin and 4,4'-diaminodiphenyl sulfone (DDS) curing agent (or hardener) are particularly interesting as they offer a highly desirable combination of high glass transition temperature and excellent mechanical properties. In the majority of reported studies with this and similar systems, however, the focus was either on chemorheology of cure or mechanical properties of cured networks. The effects

of thermal history during cure and amine/epoxy ratio, or stoichiometry, on physical/mechanical properties of these networks have not been studied systematically. We note at this point that the terms 'amine/epoxy ratio' and 'stoichiometry' are taken to have the same general meaning in this paper and will be used interchangeably, while 'the stoichiometric mixture' refers to the formulation with an equal initial concentration of epoxy groups and amine hydrogens.

An example of recent work on processing–structure–property correlations in epoxy networks is the study by Min et al.[3], who investigated the effect of cure temperature on fracture properties of the DGEBA/DDS system. But neither these authors nor others have addressed in a comprehensive manner the question of the effect that the variations in thermal history during cure and amine/epoxy ratio have on the properties of crosslinked networks. For instance, an interesting and equally important question is whether cure along different thermal paths (histories), but with common initial and final temperatures, can produce networks with different

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morphologies and hence physical/mechanical characteristics. A comprehensive investigation of this nature, that would account for the variations in network parameters such as the degree of cure, crosslink density and morphology, has not been reported.

The main objective of this study was to elucidate the effects of thermal history (the major processing parameter during cure) and amine/epoxy ratio on the physical/ mechanical properties of a series of DGEBA/DDS networks.

EXPERIMENTAL

Materials

A DGEBA epoxy resin (DER 332, $n = 0.03$; donated by Dow Chemical Company) and DDS (Fluka) curing agent were used in this study. Both materials were used without further purification.

Processing

Three different mixtures, with amine/epoxy ratios of 0.8, 1.0 and 1.2, were prepared at 130°C by dissolving DDS for 15 min in the previously heated epoxy resin. The mixture was poured into a mould preheated to the temperature of the first step in the cure schedule, and was kept there under vacuum for a desired period of time. Further cure was conducted in an air-circulating oven according to the conditions described in *Table 1*, where T_1, T_2 and T_3 are temperatures of the first, second and third stage, respectively, during cure, and t_1, t_2 and t_3, the corresponding times. In order to minimize the effect of thermal stresses, samples were allowed to cool slowly inside the oven. The mould consisted of two glass plates and a steel frame with a wall thickness of 5 mm. Glass plates were coated with Frekote 44.

As an extension of our experimental matrix we also prepared and investigated DGEBA/DDS formulations to which a thermoplastic polymer was added to increase toughness. Mixtures of the stoichiometric epoxy formulations and up to 15% by weight poly(methyl methacrylate) (PMMA), previously dried at 100°C for 24 h, were prepared by first dissolving the thermoplastic in methylene chloride and then adding the resin while stirring. Before the amine was added, the solvent was removed by gradual heating in an oil bath at 80°C for 10 h, followed by degassing under vacuum at the same temperature for 14 h. The amine hardener was then introduced into the DGEBA/PMMA homogeneous solution, stirred for 15 min and cured according to the following schedule: 140°C/2.5 h (of which 1.5 h in vacuum) + 180°C/4 h

+ 220°C/2 h. No other cure schedules were investigated for the PMMA-containing formulations.

Techniques

Specimens for mechanical testing were machined to the required dimensions from cast plates by cutting with a circular saw, followed by milling. Prior to testing, all samples were maintained in a controlled environment at 20°C for approximately the same time in order to minimize additional differences between samples which could result from various rates of structural relaxations in the glassy state. At 20°C, however, all samples are well below their glass transition temperatures (T_gs) and no appreciable difference in the rates of structural relaxation is expected.

A Metravib viscoanalyser, equipped with a three-point bending fixture with a 44 mm span, was used for dynamic mechanical testing. Measurements were carried out at a frequency of 10 Hz and a heating rate of 3°C min^{-1} over a temperature range from 20 to 300°C. Specimen dimensions were 60 mm × 10 mm × 5 mm. The T_g was taken as the temperature corresponding to the maximum in the loss factor.

Flexural properties were determined in a three-point loading configuration using an Instron Universal Testing Machine (model 4206). Specimen dimensions were 80 mm × 10 mm × 5 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.

For fracture tests, a V-shaped notch was cut in the sample with a rotating cutter, and a starter crack was introduced with a razor blade. The ASTM-E399 standard specification was followed. Tests were carried out at 20°C and a crosshead speed of 10 mm min^{-1}. The maximum load at crack initiation was used to calculate the critical stress intensity factor, K_{Ic}, and the critical energy per unit area of crack, G_{Ic}.

Fourier transform infra-red (*FT*i.r.) spectroscopy was carried out on a Perkin Elmer model 16 PC i.r. spectrophotometer. Samples were made and analysed in the form of KBr pellets. Twenty-five scans were collected at a 4 cm^{-1} resolution in the mid-i.r. range from 4000 to 400 cm^{-1}. The progress of reaction was monitored by the characteristic epoxide absorption peak at 916 cm^{-1}. *FT*i.r. studies of epoxy cure have been reported by several investigators[4-6]. The results obtained in this work were normalized to an internal reference band at 1507 cm^{-1}, corresponding to the stretching of the aromatic ring, in order to account for possible fluctuations in thickness and refractive index during cure[7]. The amount of hydroxyl groups after cure was approximated by calculating the area of the broad band between 3650 and 3150 cm^{-1}, using the same internal reference band at 1507 cm^{-1}.

Table 1 Summary of thermal histories during cure employed in this study. T_i and t_i are temperature and time of the *i*th step in the cure schedule

Cure schedule	T_1 (°C)	t_1 (h)	t_{vac} (min)	T_2 (°C)	t_2 (h)	T_3 (°C)	t_3 (h)
1	130	3	120	180	4	–	–
2	130	3	120	180	4	220	2
3	140	2.5	90	180	4	220	2
4	150	2	60	180	4	220	2
5	160	1.5	40	180	4	220	2
6	170	1.25	20	180	4	220	2
7	180	1	–	180	4	220	2

RESULTS AND DISCUSSION

α-Relaxation process

Attention is initially focused on the observed temperature dependence of dynamic mechanical loss in the temperature range of α-relaxation. The results for three different amine/epoxy ratios, each cured using three different cure schedules, are displayed in *Figures 1a–c*.

The breadth and magnitude of α-relaxation were slightly greater in the epoxy-rich formulations than in the stoichiometric and amine-rich mixtures, regardless of the cure schedule employed. This observation, together with the fact that the α-transition temperature was invariably lower in the epoxy-rich formulations, suggests the existence of a lower crosslink density network. Naturally, that is at least partly due to the below-stoichiometric amount of amino groups present in the mixture, which precludes completion of crosslinking reactions.

The effect of post-cure, on dynamic mechanical behaviour is shown in *Figures 2a* and *b* and is summarized in *Table 2*. Post-curing results in the completion of network formation in all formulations, as judged by an increase in the temperature of the α-relaxation peak; this is readily deduced by a direct comparison of *Figure 2a* with *2b*.

In *Figure 3*, the temperature of the α-relaxation peak is plotted as a function of amine/epoxy ratio, with cure schedule as a parameter. The small difference in T_g values of post-cured amine-rich and stoichiometric formulations suggests similar network morphologies in these systems. The lower T_g of epoxy-rich formulations is a direct consequence of the lower crosslink density in these systems, as pointed out above.

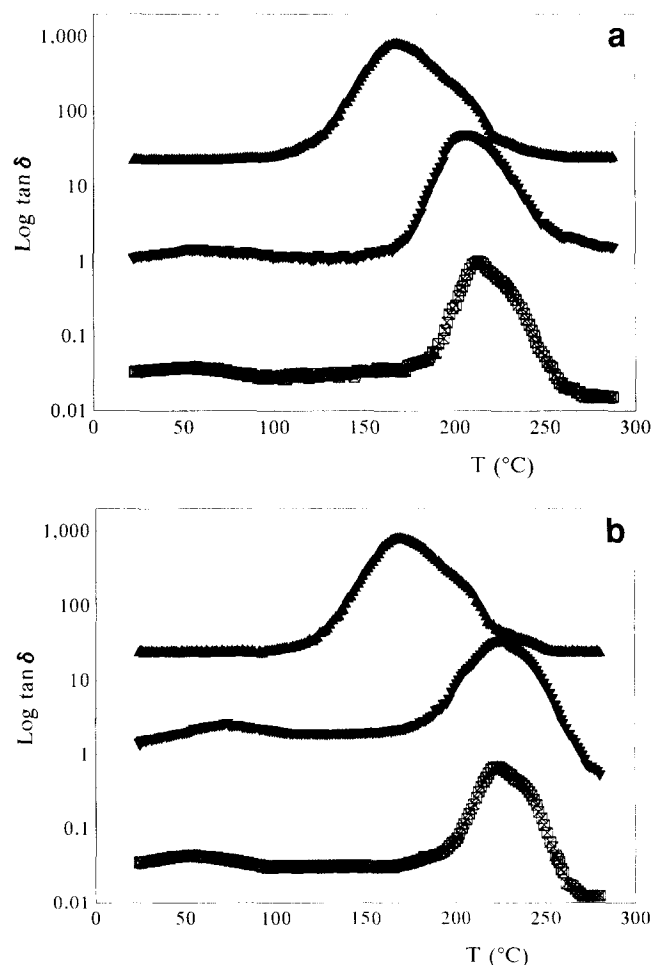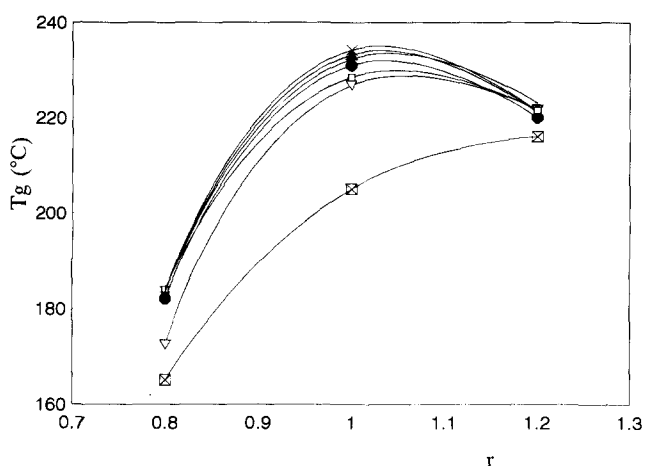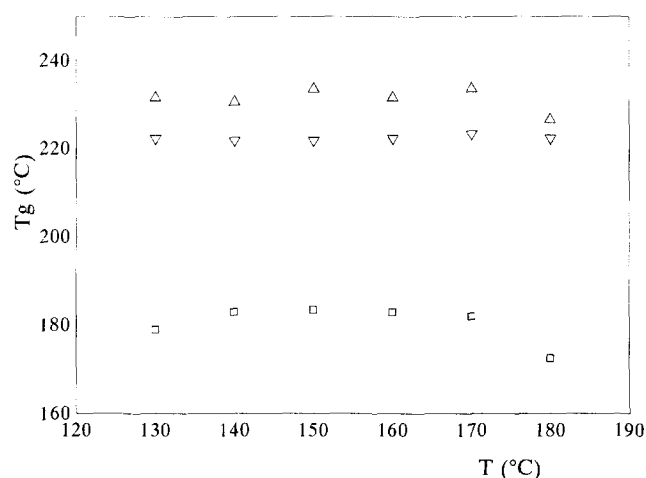An interesting observation was that the T_g of all post-cured epoxy-rich and stoichiometric mixtures was

Figure 1 Dynamic mechanical tan δ as a function of thermal history during cure with amine/epoxy ratio r as a parameter: ▲, 0.8; ▼, 1.0; ⊠, 1.2. Cure schedule temperature sequence: (a) 140/180/220°C; (b) 160/180/220°C; (c) 180/220°C

All systems show an α-relaxation, which is associated with the major relaxation process and which depends on both thermal history during cure and amine/epoxy stoichiometry. Another transition, termed ω-relaxation, was observed in the dynamic mechanical spectra above room temperature. The origin of ω-relaxation has been assigned to either the lower crosslink density sites in the epoxy network[7-9], or the β-relaxation overtones in the regions of higher crosslink density which are occluded in the lower crosslink density matrix[10-12]. This subject is discussed further in a forthcoming publication[13].

Figure 2 Dynamic mechanical tan δ as a function of thermal history during cure (130/180°C) with amine/epoxy ratio r as a parameter: ▲, 0.8; ▼, 1.0; □, 1.2. (a) Before post-cure; (b) after post-cure at 220°C

Table 2 Summary of measured (T_α and tan δ) and calculated (E_r and M_c) network parameters[a] as a function of amine/epoxy ratio (r) and thermal history during cure

Cure schedule	r = 0.8				r = 1.0				r = 1.2			
	T_α(°C)	tan δ	E_r	M_c	T_α(°C)	tan δ	E_r	M_c	T_α(°C)	tan δ	E_r	M_c
1	165	0.904	2.2	596	205.5	0.951	5.4	265	216	0.753	–	–
2	179	0.835	3.4	398	232	0.670	7.7	194	222	0.690	6.0	247
3	183	0.855	3.6	379	231	0.577	7.8	193	221.5	0.744	6.1	243
4	183.5	0.852	3.3	414	234	0.613	7.7	197	221.5	0.691	6.2	239
5	183	0.827	3.5	390	232	0.667	8.4	180	222	0.736	6.2	239
6	183	0.828	3.5	389	234	0.584	8.2	185	223	0.726	6.2	240
7	172.5	0.988	2.1	635	227	0.821	6.7	223	222	0.704	6.0	257

[a] T_α, α-relaxation peak temperature; E_r, rubbery modulus; M_c, average molecular weight between crosslinks

Figure 3 Glass transition temperature (T_g) as a function of amine/epoxy ratio (r), with thermal history during cure as a parameter: ■, 130/180°C; +, 130/180/220°C; ⊠, 140/180/220°C; ×, 150/180/220°C; ▲, 160/180/220°C; ●, 170/180/220°C; ▼, 180/220°C

Figure 4 Glass transition temperature as a function of thermal history during cure with amine/epoxy ratio as a parameter: △, 0.8; ▽, 1.0; □, 1.2

independent of thermal history during cure, except in the case of the cure schedule that started at 180°C and resulted in a lower T_g. A probable cause for this effect lies in the faster reaction rate at that temperature, which results in the formation of a more inhomogeneous network. In an earlier study by Mijovic[14] on processing–property relationships in graphite/epoxy composites, it was found that different thermal histories prior to post-cure had an effect on the properties of composites. That effect, however, was 'erased' by the subsequent post-cure treatment.

Another informative way of evaluating the effect of thermal history during cure on network properties is by investigating how the T_g values of post-cured samples vary as a function of the initial temperature in each cure schedule. This is shown in *Figure 4*, where it is seen that a decrease in T_g occurred only in the non-stoichiometric formulations, and exclusively when the initial cure temperature was 180°C.

Rubbery region

A measure of the crosslink density of a polymer network is its rubbery state modulus, E_r, which is related to the average molecular weight between crosslinks, M_c, by the following equation from the theory of rubbery

elasticity:

$$E_r = 3dRT/M_c \qquad (1)$$

where d and T are network density and temperature, respectively. In his earlier work, Kaelble[15] used the theory of rubber elasticity to calculate the maximum network extensibility, which is proportional to the square root of the molecular weight between crosslinks. The use of either equation (1) or an empirical equation proposed by Nielson[16] to calculate the average molecular weight between crosslinks in highly crosslinked networks of the epoxy/amine type is approximate but useful in defining general trends, and has been successfully exploited by several authors in their studies of various epoxy systems. For instance, Fischer recently studied a series of epoxy formulations with different degrees of crosslinking and reported that rubbery moduli determined from dynamic tests were invariably higher than those obtained from static tests[17]. Similar trends were observed in our laboratory for DGEBA-type epoxies cured with various amines, including different amine-terminated poly(propylene oxide)s[18]. Therefore, the use of rubbery modulus as a measure of the average molecular weight between crosslinks, and hence the crosslink density, should be viewed as a valid tool only for comparative evaluations.

In this study, rubbery modulus was defined as the value of dynamic storage modulus at 30°C above its α-relaxation peak. The values of rubbery modulus (E_r), determined from dynamic mechanical scans, and the calculated values of the average molecular weight between crosslinks (M_c) for amine/epoxy ratios (r) of 0.8, 1.0 and 1.2, and seven different cure schedules, are summarized in *Table 2*. Even with an error of up to 10%, it is clear that E_r and T_g follow similar trends. This finding is expected on physical grounds, as both E_r and T_g should increase with an increase in crosslink density and a simultaneous decrease in M_c. In *Figure 5*, rubbery modulus is plotted as a function of amine/epoxy ratio, with cure schedule as a parameter. It is seen that, regardless of the cure schedule used, the highest modulus was observed in the stoichiometric mixtures, suggesting that the highest crosslink density is present in those systems. Thus the observed trends in α-relaxation, rubbery modulus and the average molecular weight between crosslinks are all in agreement.

Glassy state mechanical properties

Glassy state mechanical response of all formulations was studied next by performing stress–strain measurements in flexure. The stress–strain data, including flexural elastic modulus (E), flexural strength (σ), and ultimate

Table 3 Flexural modulus (E), strength (σ) and strain (ε) of epoxy networks at 20°C for various amine/epoxy stoichiometries (r) and thermal histories during cure

Cure schedule	$r = 0.8$			$r = 1.0$			$r = 1.2$		
	E	σ	ε	E	σ	ε	E	σ	ε
1	3313	148	6.38	2789	132	9.90	2801	140	9.77
2	3349	150	6.11	2573	132	9.42	2723	136	9.82
3	3173	146	6.40	2619	126	9.28	2750	134	9.34
4	2978	145	6.94	2547	129	9.08	2687	138	10.20
5	3170	151	7.31	2665	129	8.50	2727	138	9.99
6	3211	153	6.88	2879	126	8.01	2898	134	7.61
7	3352	159	6.90	2782	128	8.17	2847	134	8.98

Figure 7 Flexural strength at 20°C as a function of amine/epoxy ratio with thermal history during cure as a parameter. Symbols as in *Figure 3*
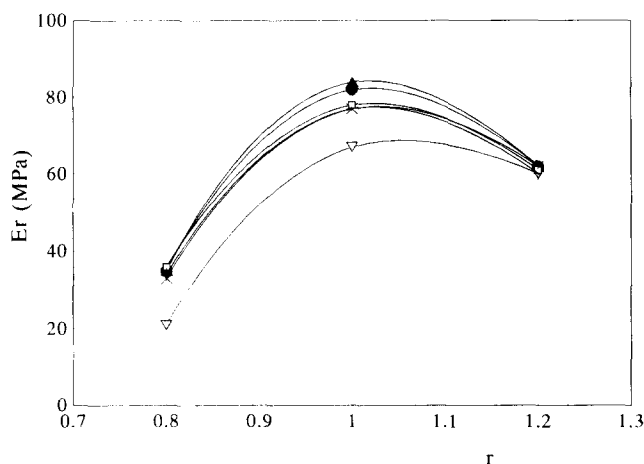

Figure 5 Elastic modulus in the rubbery state as a function of amine epoxy ratio with thermal history during cure as a parameter. Symbols as in *Figure 3*
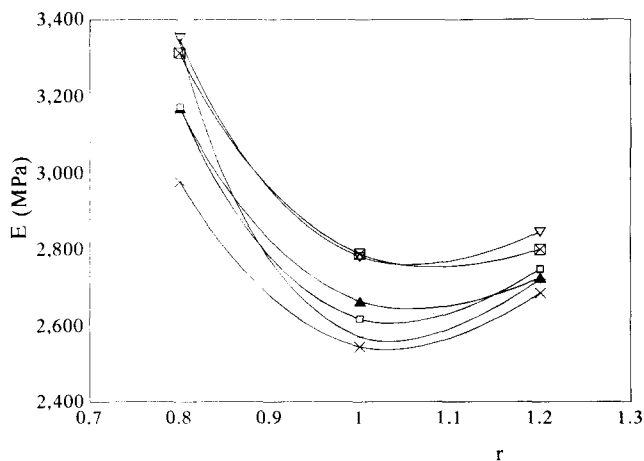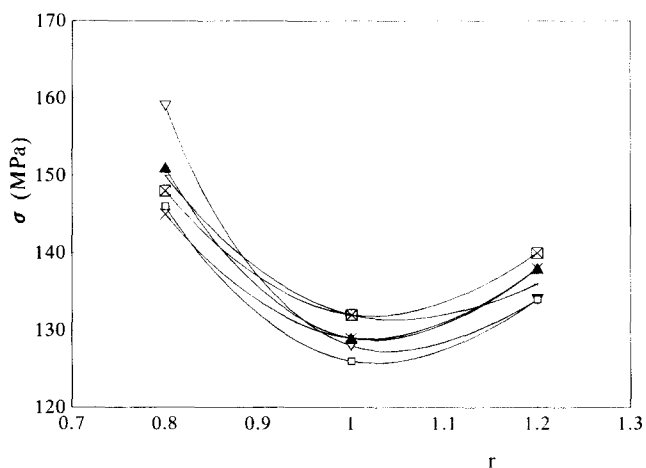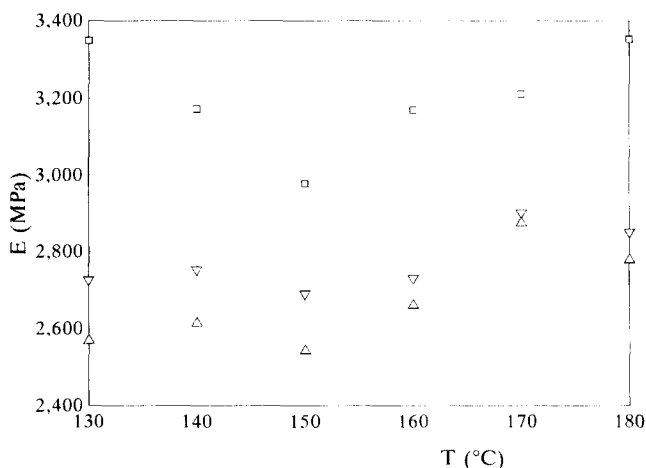

Figure 8 Flexural modulus at 20°C as a function of thermal history during cure with amine/epoxy ratio as a parameter. Symbols as in *Figure 4*

Figure 6 Flexural modulus at 20°C as a function of amine/epoxy ratio with thermal history during cure as a parameter. Symbols as in *Figure 3*

strain (ε), are summarized in *Table 3*, while in *Figures 6* and *7*, respectively, flexural elastic modulus and flexural strength are plotted as a function of amine/epoxy ratio, with cure schedule as a parameter. Flexural modulus and strength are replotted as a function of thermal history during cure in *Figures 8* and *9*, respectively. The obtained values of flexural modulus and strength are in excellent agreement with the literature[19].

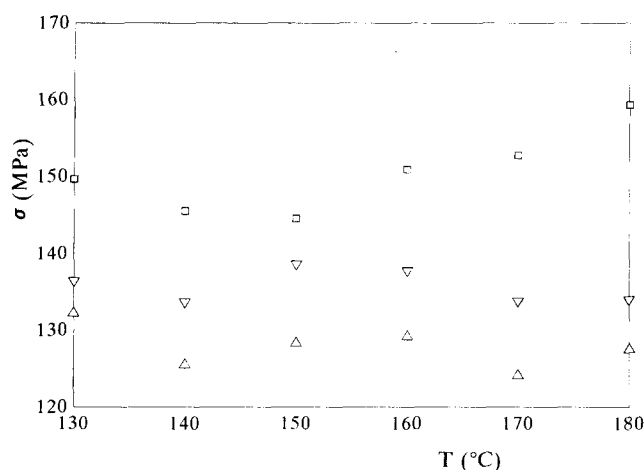Interestingly, the highest modulus and the highest strength were recorded in epoxy-rich mixtures. This

Figure 9 Flexural strength at 20°C as a function of thermal history during cure with amine/epoxy ratio as a parameter. Symbols as in *Figure 4*

finding, although in agreement with reported results for several epoxy systems[20,21], at first appears at odds with our findings regarding α-relaxation, rubbery modulus and the average molecular weight between crosslinks, all of which point to the presence of highest crosslink density in the stoichiometric mixture (*Table 2*). This apparent anomaly can be resolved by invoking the concept of free volume. The observed higher modulus and lower strength are a direct consequence of the lower specific volume, and hence higher density of these networks at 20 C. This phenomenon has been investigated and discussed in recent years by several investigators[22,23].

Fracture behaviour of neat and toughened formulations

Addition of linear thermoplastic polymers to toughen thermoset networks is nowadays generating considerable interest among polymer scientists and engineers[24-26]. PMMA is one such thermoplastic that has been the subject of recent investigations in our laboratory[27] and elsewhere[28]. In this study, we added up to 15% by weight PMMA to the stoichiometric DGEBA/DDS mixture, in order to increase the fracture toughness of the epoxy network. The observed change in elastic modulus as a function of PMMA content is shown in *Figure 10*. It is very interesting to note that the addition of only 2% PMMA causes a noticeable increase in modulus. Further addition of PMMA, however, has no effect on modulus. The possibility of chemical reactions occurring between epoxy formulation and the terminal groups on PMMA was not investigated in the course of this study, but will be looked at in the future.

The effect of PMMA on the fracture toughness of modified systems was expressed quantitatively in terms of the major fracture parameters, the critical stress intensity factor in mode I, K_{Ic}, and the critical strain energy release rate in mode I, G_{Ic}. These results are presented in plots of K_{Ic} and G_{Ic} as a function of PMMA content in *Figures 11* and *12*, respectively. Fracture toughness is observed to increase slowly, peak at about 5% PMMA, and then decrease at 15% PMMA to a value below that for the non-modified epoxy. Epoxy/ PMMA mixtures were clear (hence judged miscible

within the wavelength of light dimensions) before cure, but became opaque as the reactions progressed and the PMMA phase separated out. The observed behaviour indicates that, at the conditions of this study, PMMA was not an effective toughening agent, although we are continuing to look into this system. Our current studies are focusing on the chemical modification of PMMA and the influence of cure conditions on phase separation.
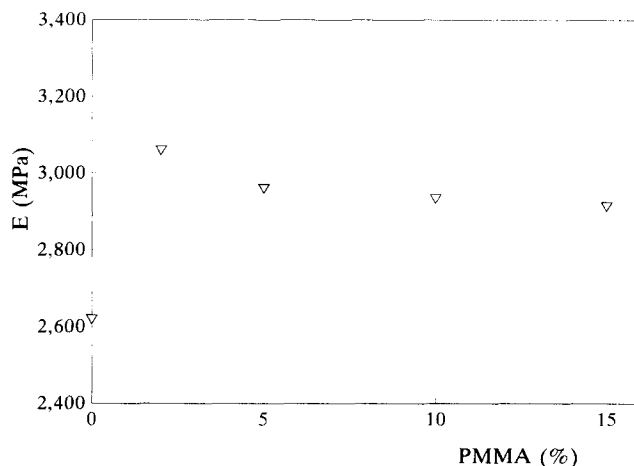

Figure 10 Elastic modulus as a function of weight percentage PMMA for the stoichiometric formulation
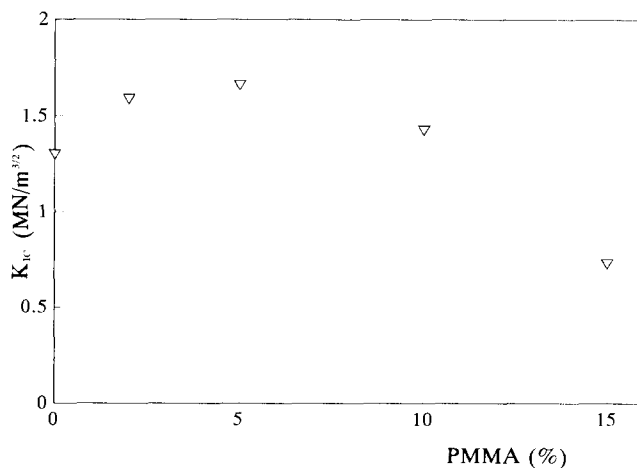

Figure 11 Stress intensity factor in mode I as a function of weight percentage PMMA for the stoichiometric mixture
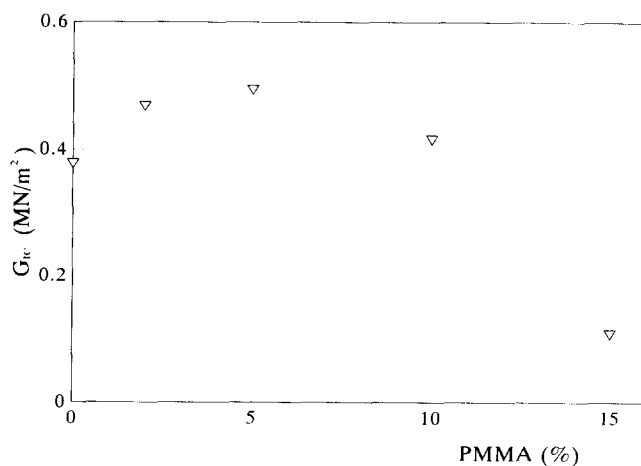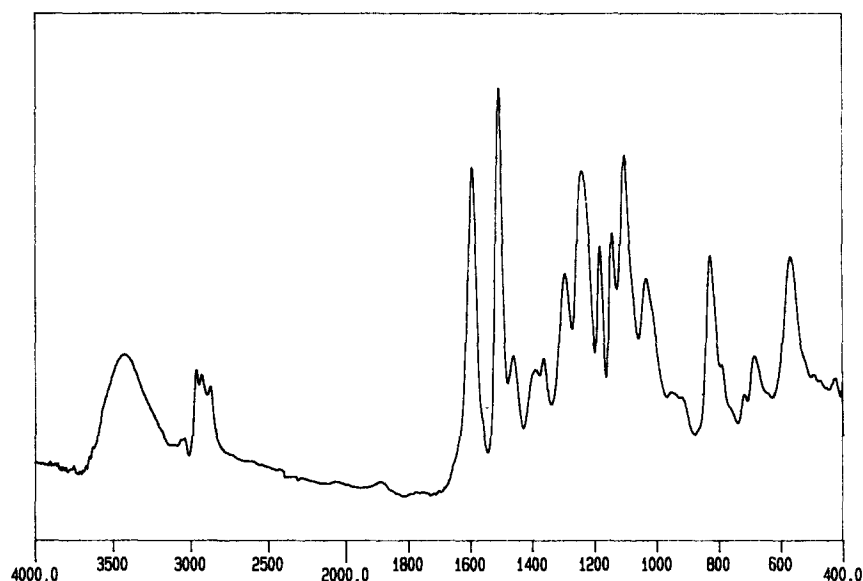

Figure 12 Strain energy release rate in mode I as a function of weight percentage PMMA for the stoichiometric mixture

Table 4 Percentage of residual epoxy groups in networks with different amine/epoxy stoichiometries (r) and thermal histories during cure

Cure schedule	$r = 0.8$		$r = 1.0$		$r = 1.2$	
	Epoxy (%)	A_{3400}/A_{1507}	Epoxy (%)	A_{3400}/A_{1507}	Epoxy (%)	A_{3400}/A_{1507}
1	18.1	5.90	11.8	6.24	7.6	7.16
2	15.4	5.01	9.9	5.69	6.8	6.66
3	15.0	4.79	10.2	5.63	7.5	6.74
4	14.6	5.17	9.9	5.88	7.7	6.67
5	15.5	4.89	10.3	5.89	6.9	6.12
6	15.3	5.11	9.2	5.36	7.5	6.81
7	16.1	4.39	8.9	5.33	7.8	6.81

Figure 13 Fourier transform infra-red spectrum of a sample of the stoichiometric mixture following cure schedule no. 4 (*Table 2*)

Fourier transform infra-red spectroscopy

FTi.r. spectroscopy was utilized to investigate the chemical state of different crosslinked networks. An FTi.r. spectrum of the stoichiometric formulation cured in a 150/180/220°C sequence (cure schedule 4, *Table 2*) is shown in *Figure 13*. The relative extent of reaction of epoxy groups was calculated from the area of the epoxy band at 916 cm^{-1}. Formation of hydroxyl groups, which are produced every time an epoxy group reacts, was monitored using the broad band between 3650 and 3150 cm^{-1}. The aromatic ring band at 1507 cm^{-1} was used as the internal standard. Percentages of residual epoxy and hydroxyl groups, calculated from the transmittance spectra, are summarized in *Table 4*. It is evident that the conversion of epoxy groups increases with amine content for all cure schedules, which is in agreement with an earlier study of a DGEBA/DDM system[29]. Another interesting observation is that in the systems judged fully cured by various mechanical measurements, there remains, in fact, a measurable portion of unreacted epoxy groups. This phenomenon, we believe, has its origin in the topological constraints in highly crosslinked networks that render inaccessible a fraction of epoxy groups during the final stages of cure. The post-cure step in the

stoichiometric and epoxy-rich formulations causes an additional reduction in the concentration of unreacted epoxy groups of about 20% and 15%, respectively, as deduced from *Table 4* by a comparison of cure schedule 1 (not post-cured) with cure schedules 2–7 (post-cured). This relatively small additional decrease in residual epoxy groups is particularly important, since it simultaneously leads to a considerable increase in the glass transition temperature, as seen in *Table 2*. On the molecular level, epoxy groups are consumed during post-cure by etherification, which is known to occur in epoxy-rich systems, at higher temperature and in the later stages of cure[30-34].

A somewhat different behaviour is observed in the amine-rich systems, where the excess of amino groups contributes to additional consumption of epoxy groups before post-cure, resulting in a lower percentage of the residual epoxy groups. But the topological constraints imposed in the network at that stage appear insurmountable and further post-cure has no appreciable effect on either the glass transition temperature or the percentage of the residual epoxy. The fact that a complete conversion of epoxy groups is not achieved in any system is particularly important in kinetic models built upon the knowledge of absolute epoxy conversion.

CONCLUSIONS

We have completed an investigation of the effects of stoichiometry and thermal history during cure on physical and mechanical properties of DGEBA/DDS epoxy networks. It was found that the stoichiometric formulation had the highest glass transition following post-cure, the highest rubbery state modulus and the lowest molecular weight between crosslinks, all as a direct consequence of the highest crosslink density in that formulation. For all amine/epoxy ratios studied, however, differences in network properties imparted by the variations in thermal history during cure were 'erased' during the common post-cure step. An exception was observed in the case when the initial temperature was 180°C.

The lowest modulus at 20°C was observed in the stoichiometric formulation, and an explanation was offered in terms of the free volume concept.

Residual epoxy groups were detected in all post-cured systems, as a consequence of topological constraints in the epoxy network at later stages of cure.

ACKNOWLEDGEMENT

REFERENCES

1   Castan, P. Swiss Patent No. 211116, 1940
2   May, C. A. (Ed.) 'Epoxy Resins Chemistry and Technology', Marcel Dekker, New York, 1988
3   Min, B. G., Hodgkin, J. H. and Stachurski, Z. H. *J. Appl. Polym. Sci.* 1993, **48**, 1303
4   Morgan, R. J. *Adv. Polym. Sci.* 1985, **72**, 1
5   Golub, M. A., Lerner, N. R. and Hsu, M. S. *J. Appl. Polym. Sci.* 1986, **32**, 5215
6   Mijovic, J., Fishbain, A. and Wijaya, J. *Macromolecules* 1992, **25**(2), 986
7   Keenan, J. D., Seferis, J. C. and Quinlivan, J. T. *J. Appl. Polym. Sci.* 1979, **24**, 2375
8   Ochi, M., Iesako, H. and Shimbo, M. *J. Polym. Sci., Polym. Phys. Edn* 1986, **24**, 1271
9   Mikolajczak, G., Cavaille, J. Y. and Johari, J. P. *Polymer* 1987, **28**, 2023
10   Mijovic, J. and Tsay, L. *Polymer* 1981, **22**, 902
11   Hofer, K. and Johari, J. P. *Macromolecules* 1991, **24**, 4978
12   Sasuga, T. and Udagawa, A. *Polymer* 1991, **32**, 402
13   Sanz, G., Garmendia, J., Andres, M. A. and Mondragon, I. *J. Appl. Polym. Sci.* in press
14   Mijovic, J. *Polym. Commun.* 1984, **25**, 271
15   Kaelble, D. H. in 'Epoxy Resins Chemistry and Technology' (Eds C. A. May and Y. Tanaka), Marcel Dekker, New York, 1967, Ch. 5
16   Nielsen, L. E. *J. Macromol. Sci.* 1969, **C3**, 69
17   Fischer, M. *Adv. Polym. Sci.* 1992, **100**, 313
18   Fernandez, F., Valea, A., Llano-Ponte, R. and Mondragon, I. *Eur. Polym. J.* in press
19   Mika, T. F. and Bauer, R. S. in 'Epoxy Resins Chemistry and Technology' (Ed. C. A. May), Marcel Dekker, New York, 1988, Ch. 4, pp. 465–550
20   Gupta, V. B., DrZal, L. T. and Rich, M. J. *Polym. Eng. Sci.* 1985, **25**, 812
21   Palmese, G. R. and McCullough, R. L. *J. Appl. Polym. Sci.* 1992, **46**, 1863
22   Cizmecioglu, M., Gupta, A. and Fedors, R. F. *J. Appl. Polym. Sci.* 1986, **32**, 6177
23   Pang, P. and Gillham, J. K. *J. Appl. Polym. Sci.* 1989, **37**, 1969
24   Bucknall, C. B. and Partridge, I. K. *Polymer* 1983, **24**, 639
25   Yamanaka, K. and Inoue, T. *Polymer* 1989, **30**, 622
26   Hedrick, J. L., Yilgor, I., Jurek, M., Hedrick, J. C., Wilkes, G. L. and McGrath, J. E. *Polymer* 1991, **32**, 2020
27   Franco, M. and Mondragon, I. unpublished results, 1994
28   Gomez, C. M. and Bucknall, C. B. *Polymer* 1993, **34**, 2111
29   Mondragon, I. and Bucknall, C. B. *Plast. Rubber Comp. Proc. Applic.* in press
30   Dusek, K., Bleha, M. and Lunak, S. *J. Polym. Sci., Polym. Chem. Edn* 1977, **15**, 2393
31   Bokare, U. M. and Gandhi, K. S. *J. Polym. Sci., Polym. Chem. Edn* 1980, **18**, 857
32   Gupta, A., Cizmecioglu, M., Coulter, D., Liang, R. H., Yavrouian, Y., Tsay, F. D. and Moacanin, J. *J. Appl. Polym. Sci.* 1983, **28**, 1011
33   Riccardi, C. C. and Williams, R. J. J. *J. Appl. Polym. Sci.* 1986, **32**, 3445
34   Morgan, R. J. and Mones, E. T. *J. Appl. Polym. Sci.* 1987, **33**, 999