Investigation of the Reaction Mechanism of Different Epoxy Resins Using a Phosphorus-Based Hardener

Russell J. Varley,[1] Weichang Liu,[2]* George P. Simon[2]

[1]CSIRO Molecular and Health Sciences, Clayton South, Victoria 3169, Australia
[2]Department of Materials Engineering, Monash University, Clayton, Victoria 3800, Australia

ABSTRACT: In this work, the fundamental kinetic and structure/property information for a novel phosphorus-based hardener, bis(4-aminophenoxy) phosphonate is cured with a range of common epoxy resins such as diglycidyl ether of bisphenol A, tri glycidyl p-amino phenol and tetra glycidyl diamino diphenyl methane (TGDDM) at various cure temperatures. The rate coefficients k_1 and k_2 for the primary and secondary amine epoxide addition reactions, respectively, were determined and were found to exhibit a positive substitution effect for the TGAP and TGDDM epoxy resins. Etherification or internal cyclization were shown to be important at higher levels of cure conversion, with these reactions being more significant for the TGAP/BAPP system. Some basic structure/property relationships were established between the glass transition temperature (T_g) and epoxide conversion. The master curve obtained for the superimposition of the various cure temperatures for each epoxy demonstrated the independence of the cure mechanism with temperature. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 99: 3288–3299, 2006

Key words: epoxy; phosphorous hardener; kinetics; NIR; cure mechanism

INTRODUCTION

The use of advanced composite materials has found widespread use in many industries because of their high strength to weight ratio, ease of processing, and corrosion resistance. However, for composite materials to find further applications, particularly in civil engineering and commercial aerospace industries, it is expected that they will be required to have a greater resistance to combustion and improved fire resistance. Because of increasingly stringent legislative requirements, commonly used halogenated fire retardants will no longer be used because of the safety and environmental concerns.[1] As a result, there is now a challenge to produce similar effective fire retardants that are more environmentally benign. This has led to considerable research in the area of phosphorus-based additives, which act through the promotion of a degradative process that produces a char layer because of the formation of polyphosphorous materials. This layer prevents the transfer of combustible products to the gaseous phase, therefore, reducing the fuel avail-able for combustion. The problem with the additive approach to reducing flammability is the necessity to add large amounts of fire retardant, sometimes up to 50% by weight. This level of addition can have deleterious effects upon the final mechanical properties and processability, and can greatly compromise their use in structural composite applications.

An alternative strategy has been the use of phosphorus-based species that are able to be incorporated into the polymer network through reactive terminal groups. In the case of epoxy amine thermosetting matrices, phosphorus-based compounds that contain reactive amine groups have been used as hardeners, thereby becoming inherently part of the network. In these instances, it has been shown that a much lower level of phosphorus content can be used to achieve similar levels of improvement in fire performance, compared to when it is a physically blended additive, thus, minimizing any deleterious effects upon the desirable mechanical and thermal properties.[2] A promising example of this type of fire retardant which is gaining considerable interest, is bis(4-aminophenoxy) phosphonate (BAPP), an aromatic diamine phosphine oxide-based compound, due to its ability to both improve fire performance considerably, while, at the same time, exhibit mechanical and thermal properties similar to other commercial, high performance epoxy resin systems.[3] This attribute, in particular, is expected to be a result of the rigid chain nature of the structure. The effectiveness of this hardener (or similar ana-
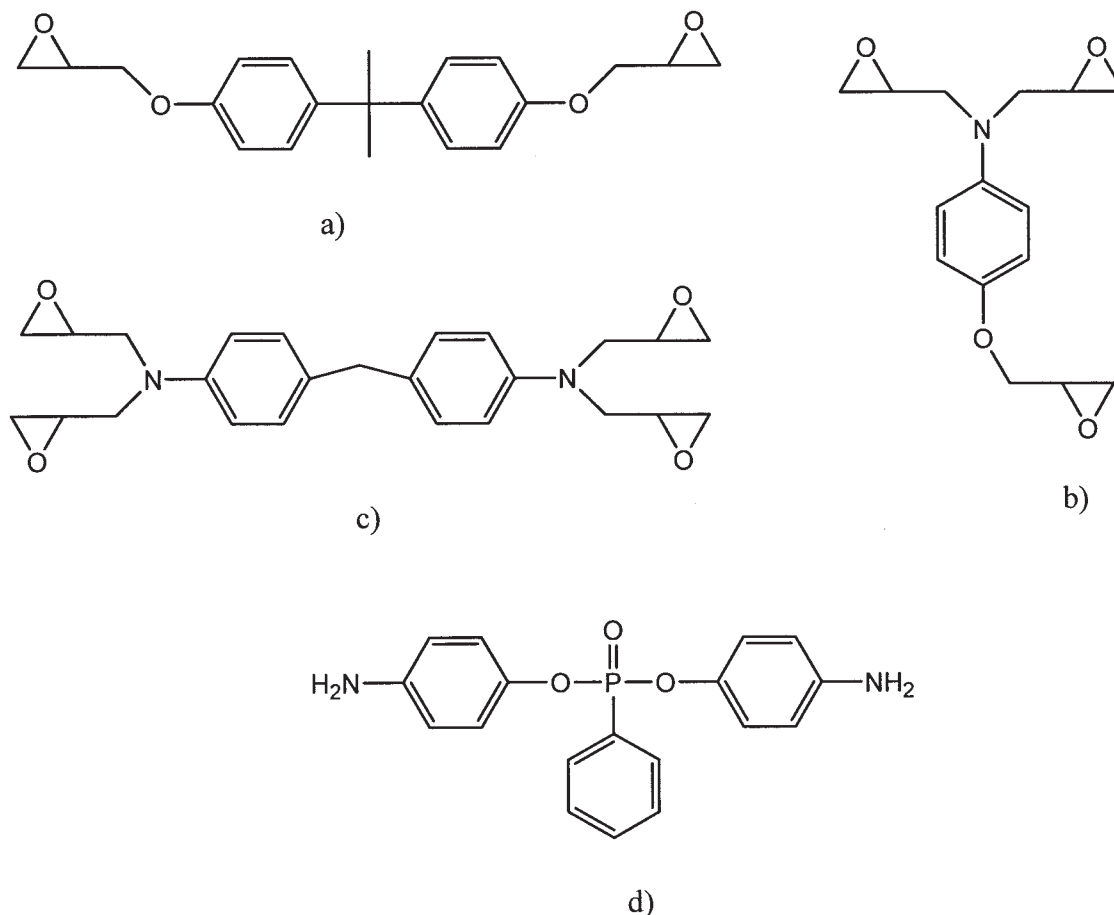
Figure 1 Chemical structures of materials used. (a) DGEBA, (b) TGAP, (c) TGDDM, and (d) BAPP.

logue) as a fire retardant to-date has been investigated by measuring the formation of the char layer using thermogravimetric analysis. Weichang et al.[4] compared the formation of the char layer in an air and nitrogen atmosphere for BAPP, with a range of commercially-available epoxy resins, using thermogravimetric analysis. It was found that the activation energy barrier to degradation increased with increasing levels of degradation, and were higher in an air atmosphere. This was attributed to the reducing nature of the phosphine oxide group and its reaction with oxygen, decreasing the oxidation of carbon to carbon monoxide and carbon dioxide and therefore promoting charring. An hydroxyl-terminated analogue of BAPP was used by Wang and Shieh[5] and the fire performance compared to a common tetra-brominated analogue. When both materials were prereacted with an epoxy resin, it was found that the phosphorus-based network displayed superior performance according to limiting oxygen index (LOI) and UL-94V measurements at lower levels of P content. In a study to build upon the fire retardance of BAPP alone, Wu et al.[6] showed that a synergistic improvement in fire performance, as measured using LOI, was obtained

when silicon and phosphorous species (in the form of BAPP) were incorporated into a diglycidyl ether of bisphenol A (DGEBA)/diphenyldiaminoemethane-based network. Hsiue et al.[7] reported a similar synergistic improvement using BAPP and silicone materials, and attributed the behavior to the low surface energy of the silicon (formed from degradation of a siloxane species), enabling it to migrate to the surface and further protect the phosphorus-rich char layer from oxidation.

It thus appears that the use of BAPP as a hardener for epoxy resins has substantial potential in providing an alternative to traditional, high-performance epoxy resins. However, for new resin formulations to find acceptance in a commercial environment, it is important that the cure kinetics and structure–property relationships are well understood. This study, therefore, reports on a preliminary investigation using near infra-red (NIR) spectroscopy and differential scanning calorimetry (DSC) to determine some of these initial parameters. The cure kinetics and reaction mechanism of the BAPP/epoxy cure reaction has been investigated for three different epoxy resins, namely, DGEBA, tri glycidyl *p*-amino phenol (TGAP), and tet-
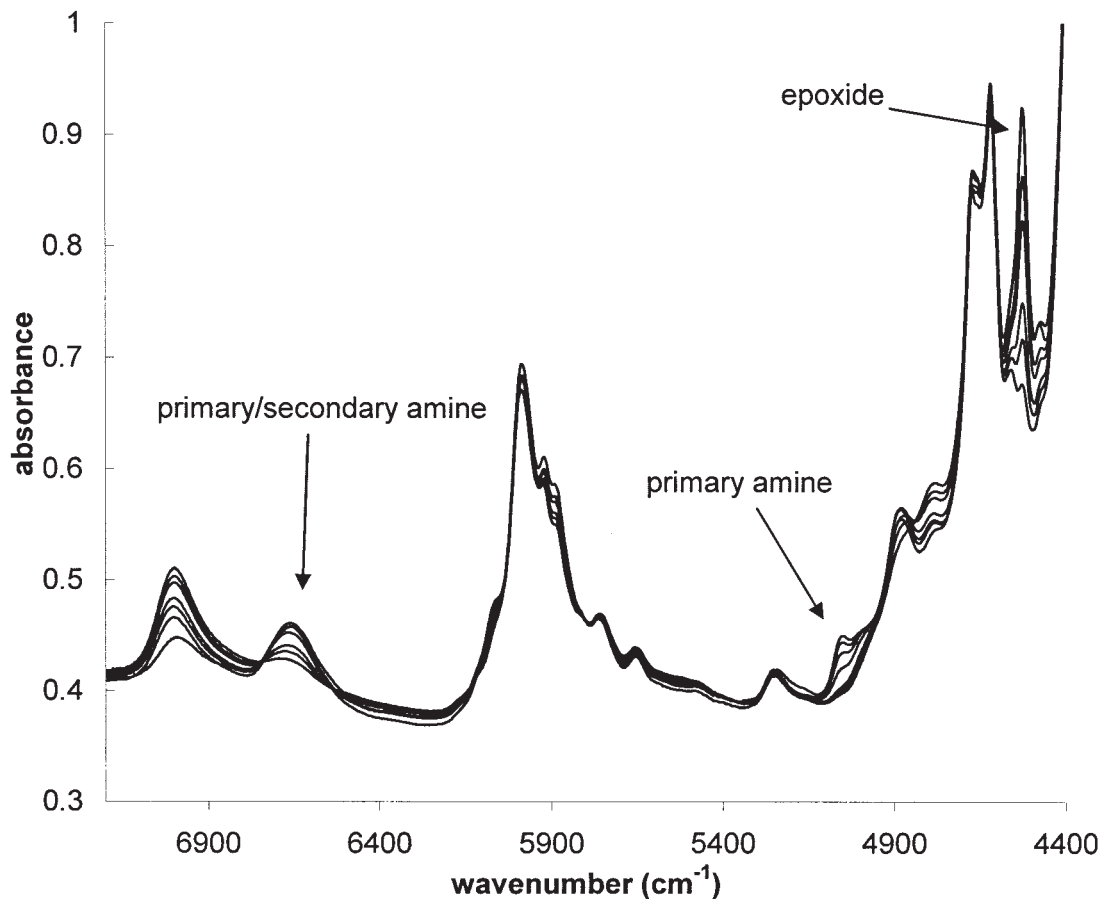
Figure 2 Examples of spectra measured during cure showing the decrease in the primary amine and epoxide peaks at 5052 and 4530 cm^{-1} and primary/secondary amine peak between 6500 and 6800 cm^{-1}.

raglycidyl methylene dianiline (TGDDM) at various cure temperatures. These latter, higher functionality resins (tri and tetra) are of particular importance because of their widespread use as components of aerospace resins in composite materials. Combining the NIR results with those obtained from DSC, some basic structure–property relationships (i.e., cure conversion *versus* glass transition temperature, T_g) can be determined and used as a means to further understand the robustness of the cure mechanism.

EXPERIMENTAL

Materials

BAPP was synthesized according to the procedure described by Weichang et al.[4] and used without further purification. The epoxy resins TGAP and TGDDM were obtained from Vantico (Australia) and are known under the trade names of MY0510 and MY720, respectively. The DGEBA (DER-331) was obtained from Dow Chemical (Australia). The chemical structures of the epoxy resins and BAPP are shown in Figure 1. All of the epoxy resins were used without further purification. Stoichio-metric ratios of the epoxy resins were blended with the BAPP on a rotary evaporator at 80°C, until the mixtures were homogenous and free of bubbles.

Techniques

A PerkinElmer 2000 spectrometer was used to record the NIR spectra from 8000 to 4000 cm^{-1} at a resolution of 4 cm^{-1} with 32 scans, with the indium detector cooled to 77 K. Isothermal NIR experiments were conducted using a hot stage Mettler FP90 central processor. The resins were placed between the microscope slides with a thickness of about 0.85 mm. The hot stage was placed into the NIR beam to allow the curing of the mixtures to be monitored *in situ* at various temperatures. The spectra were recorded at approximately every 2 min, at various cure temperatures ranging from 100 to 180°C. The differential scanning calorimeter used was Mettler 821e. Samples were cured isothermally for various lengths of time, then cooled and rescanned from 50 to 300°C, at 10°C/min, under a nitrogen blanket. The glass transition temperature (T_g) was taken from the midpoint of the step endotherm of the DSC thermogram.
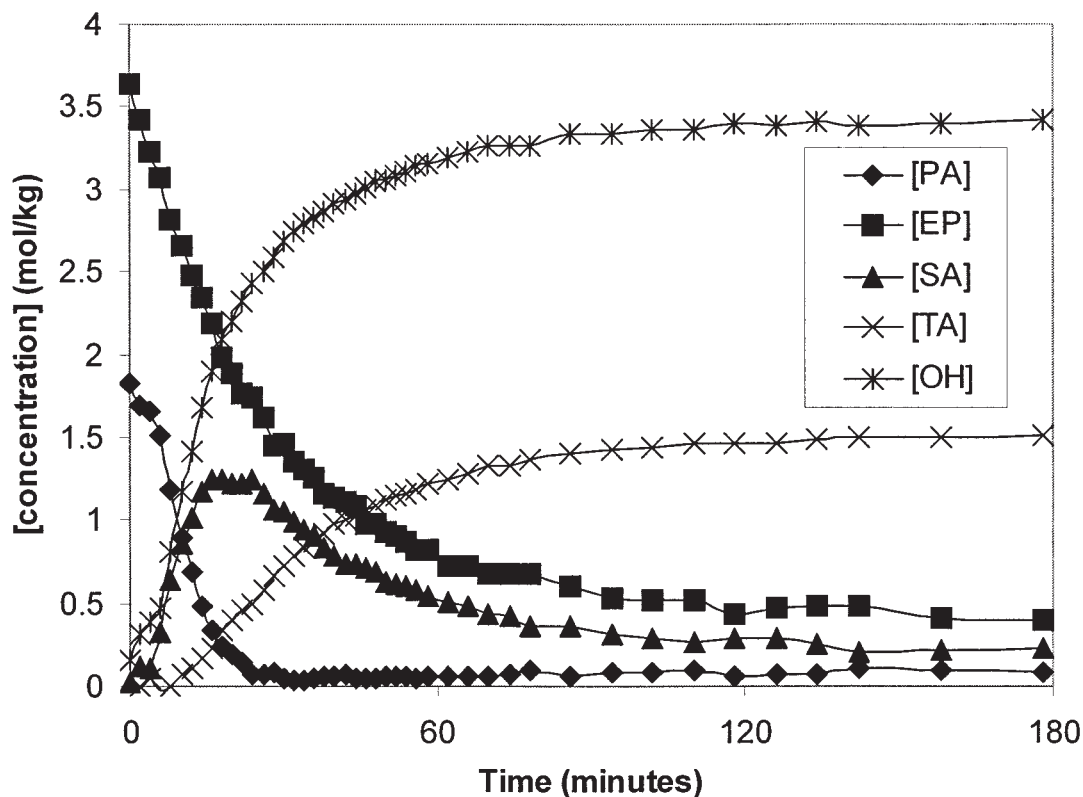
Figure 3 Typical changes in concentration changes of the functional groups with time during isothermal cure at 140°C for DGEBA/BAPP.

Spectral analysis

The analysis of the NIR spectral data has been treated in a manner previously reported in the literatures.[8,9] A range of spectra showing the changes taking place during cure are shown in Figure 2. For the purposes of this study, it is relevant to note that the spectral analysis is performed using three peaks in particular, namely, the epoxide peak at 4522 cm^{-1}, the amine peak at 5052 cm^{-1}, and the primary/secondary amine combination peak at 6674 cm^{-1}. The changes in the functional group concentrations (and subsequent cure conversions) for the epoxide and primary amine (PA) are determined using a knowledge of the initial starting PA and epoxide group concentrations (obtained from product suppliers), the effective extinction coefficients (as determined from initial spectra), and the changes in peak heights or areas during cure. The secondary amine (SA) concentration was determined by subtracting the known changes in PA concentration determined from the PA peak at 5052 cm^{-1} (assuming that there is no SA consumption occurring early in the cure). For more details, and a complete description on how the rate constants k_1 (PA reaction) and k_2 (SA reaction) were determined readers are referred to

TABLE I
Fractional Conversions at Gelation, and the Final Secondary Amine and Epoxide Conversions at Various Temperatures for the DGEBA, TGAP, and TGDDM Systems

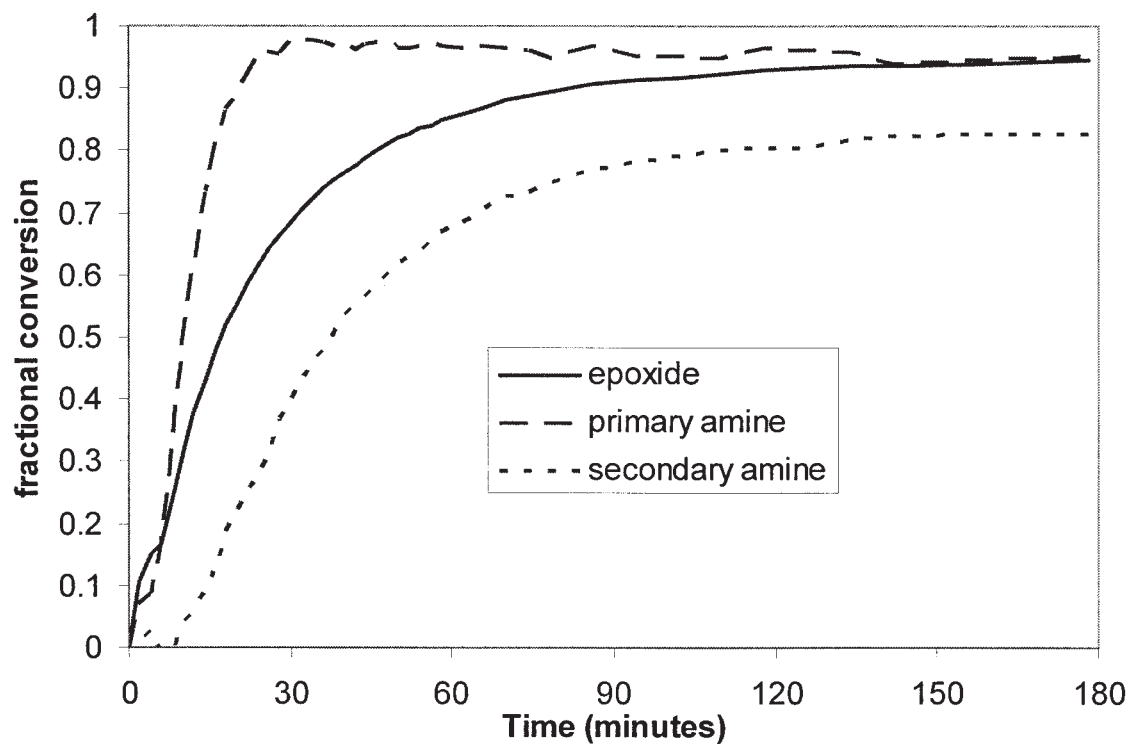| Temp. (°C)	DGEBA/BAPP			TGAP/BAPP			TGDDM/BAPP		
	$\alpha_{epoxide}$	α_{gel}	α_{SA}	$\alpha_{epoxide}$	α_{gel}	α_{SA}	$\alpha_{epoxide}$	α_{gel}	α_{SA}
100	0.58	0.69	0.71	0.41	0.33	0.51	0.52	0.25	0.54
110	0.59	0.67	0.77	*	*	*	*	*	*
120	0.55	0.72	0.86	0.50	0.59	0.65	0.59	0.42	0.69
130	0.55	0.78	0.89	*	*	*	0.64	0.63	0.75
140	0.59	0.83	0.95	0.52	0.74	0.72	0.64	0.52	0.76
160	0.66	0.86	0.94	0.49	0.79	0.80			0.86
180	0.69	0.89	1.00	0.52	0.82	0.91	*	*	0.92

*Not measured.

Figure 4 Plot of the fractional conversions for epoxide, primary, and secondary amine conversions for DGEBA/BAPP at 140°C.
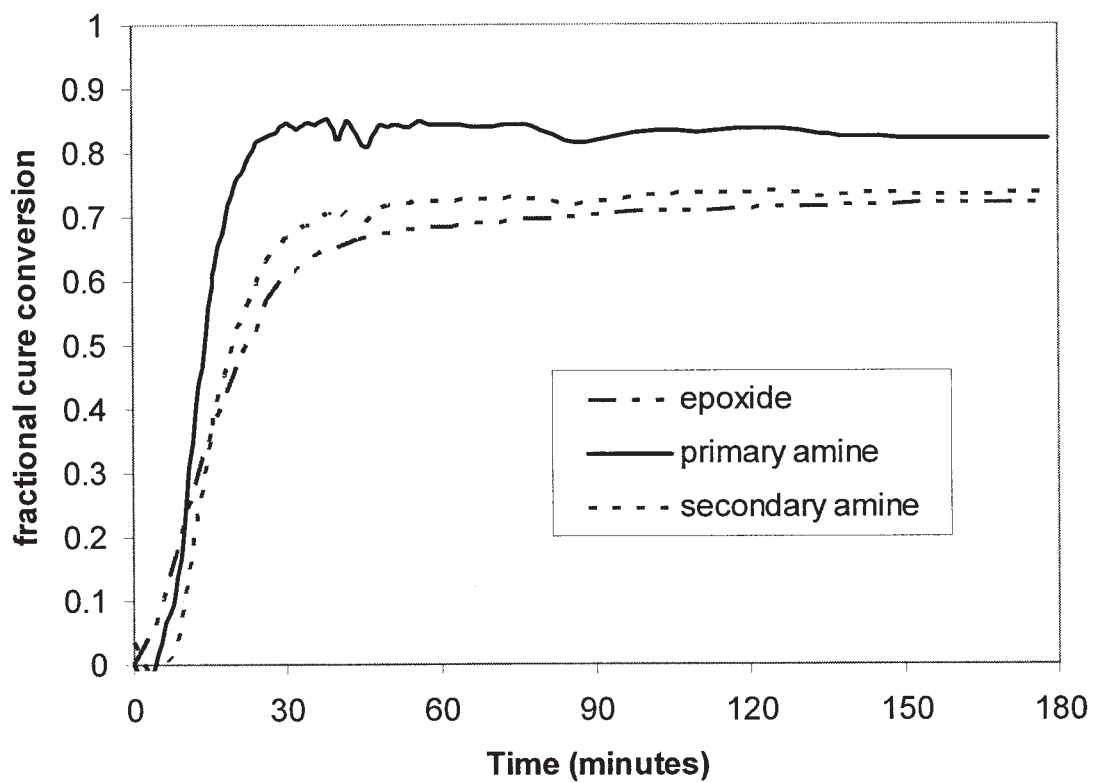

Figure 5 Plot of the fractional conversions for epoxide, primary, and secondary amine for TGAP/BAPP at 140°C.
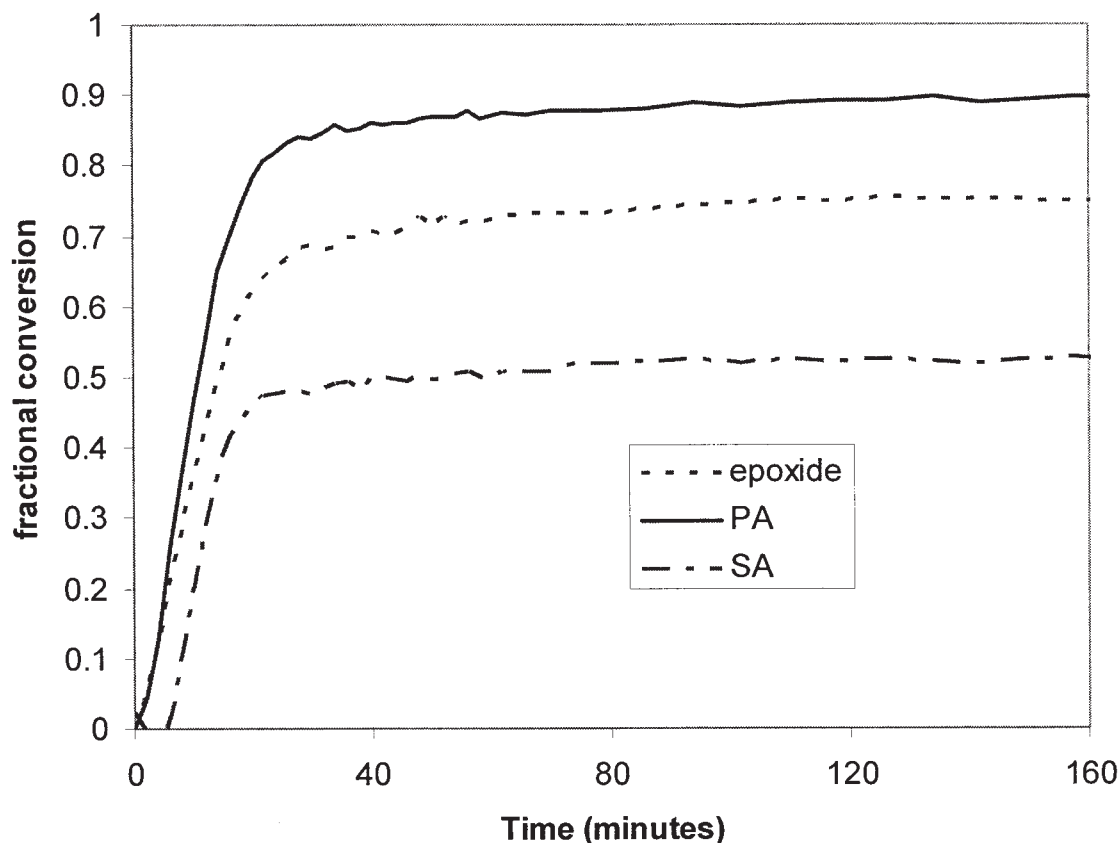
Figure 6 Plot of the fractional conversions for epoxide, primary, and secondary amine for TGDDM/BAPP at 140°C.

more comprehensive treatments available in the literatures.[8,9]

Particular attention should be drawn to the decrease in the epoxide and amine peaks at 4522 and 5052 cm^{-1}, respectively, demonstrating their clarity and, therefore, their usefulness in being used for quantifying changes in cure chemistry. It is also worth noting that the changes in the spectra region corresponding to the SA peak at 6674 cm^{-1} appear somewhat different to that typically found for epoxy amine spectra, being significantly broader and diffused, when compared to other NIR studies using more conventional amine hardeners.

RESULTS AND DISCUSSION

Reaction kinetics

The variation in concentration of the functional groups during cure at 140°C for the DGEBA/BAPP systems are shown in Figure 3. The behavior is typical of that found for the TGAP/BAPP, as well as for the

TABLE II
Rate Coefficients, k_1 and k_2, and Their Ratios as Determined for the DGEBA, TGAP, and TGDDM Systems

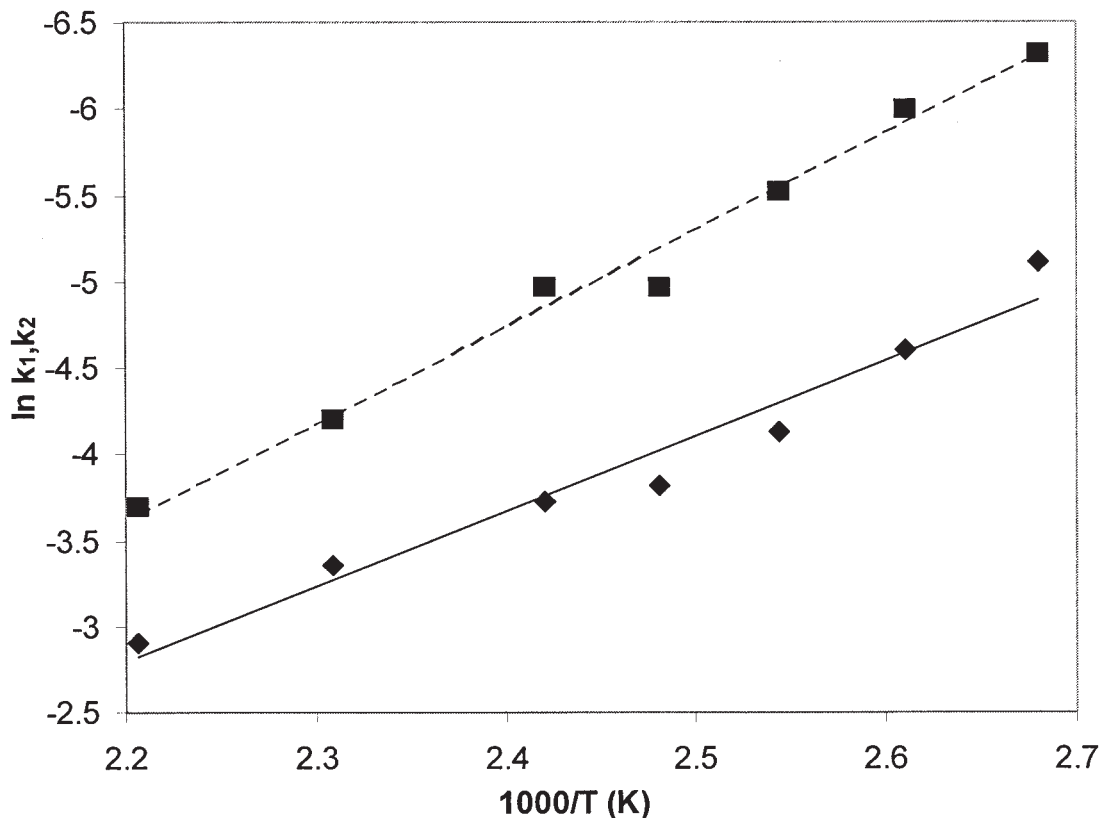| Temperature (°C)	DGEBA/BAPP rate coefficients (kg^{-3} mol^{-2} min^{-1})			TGAP/BAPP rate coefficients (kg^{-3} mol^{-2} min^{-1})			TGDDM/BAPP rate coefficients (kg^{-3} mol^{-2} min^{-1})		
	k_1	k_2	k_2/k_1	k_1	k_2	k_2/k_1	k_1	k_2	k_2/k_1
100	6	1.8	0.30	2	0.15	0.075	1.8	0.3	0.17
110	10	2.5	0.25	*	*	*	*	*	*
120	16	4.0	0.25	4	1.10	0.28	3.0	2.5	0.83
130	22	7.0	0.32	*	*	*	5.0	4.0	0.80
140	24	7.0	0.30	6	3.50	0.58	8.0	7.5	0.94
160	35	15.0	0.43	12	7.50	0.63	10.0	10.0	1.00
180	*	*	*	14	10.0	0.71	14.0	*	*

*Not measured.

Figure 7 Arrhenius plot of the rate coefficients for the DGEBA/BAPP cure.

TGDDM/BAPP systems and complements other reports in the literatures using more widely reported epoxy amine systems.[10,11]

The changes show that during the cure, where the reaction remains kinetically-controlled, the mechanism is dominated by the PA epoxy addition reaction. This is seen by an exponential decrease in both the PA and epoxide groups. As the PA is being consumed, SA and hydroxyl functional groups are produced. As the PA groups reach complete consumption, the SA concentration reaches a maximum, and begins to decrease as chemical reaction with other epoxide functional groups begins. This point has sometimes been identified with the onset of gelation[9] and the initial formation of a three dimensional network, where the material transforms from a sol to an intractable material. At this point, the chemical reaction changes from being dominated by a chain branching/extension process to a crosslinking mechanism which provides the significant increase in mechanical and thermal properties. Table I shows the epoxide conversions at gelation for the different epoxy amine systems at the various cure temperatures. The conversion at gelation is expected to remain relatively constant regardless of cure temperature due to the fact that it is a chemical process that is largely determined by the chemical stoichiometry of the resin blend, as proposed by Flory's model.[12] The epoxide conversions at gelation for the DGEBA/BAPP system were found be very consistent, particularly at lower cure temperatures, varying between 55 and 59% cure conversion between the cure temperatures of 100 and 140°C and correlates very well with the predicted value of 58% conversion, using Flory's theory. At the higher cure temperatures of 160 and 180°C, the epoxide conversion at gelation, however, was measured to be 66 and 69%, suggesting increasing levels of etherification at higher cure temperatures. The conversion at gelation as predicted by Flory's theory for the TGAP/BAPP and TGDDM/BAPP systems are calculated to be 41 and 33% respectively. The values determined experimentally for both systems, while fairly consistent across the temperature range, were both found to be significantly higher than

TABLE III
Acchenius Parameters for k_1 and k_2 as Determined Using NIR Spectroscopy for the DGEBA, TGAP, and TGDDM Systems

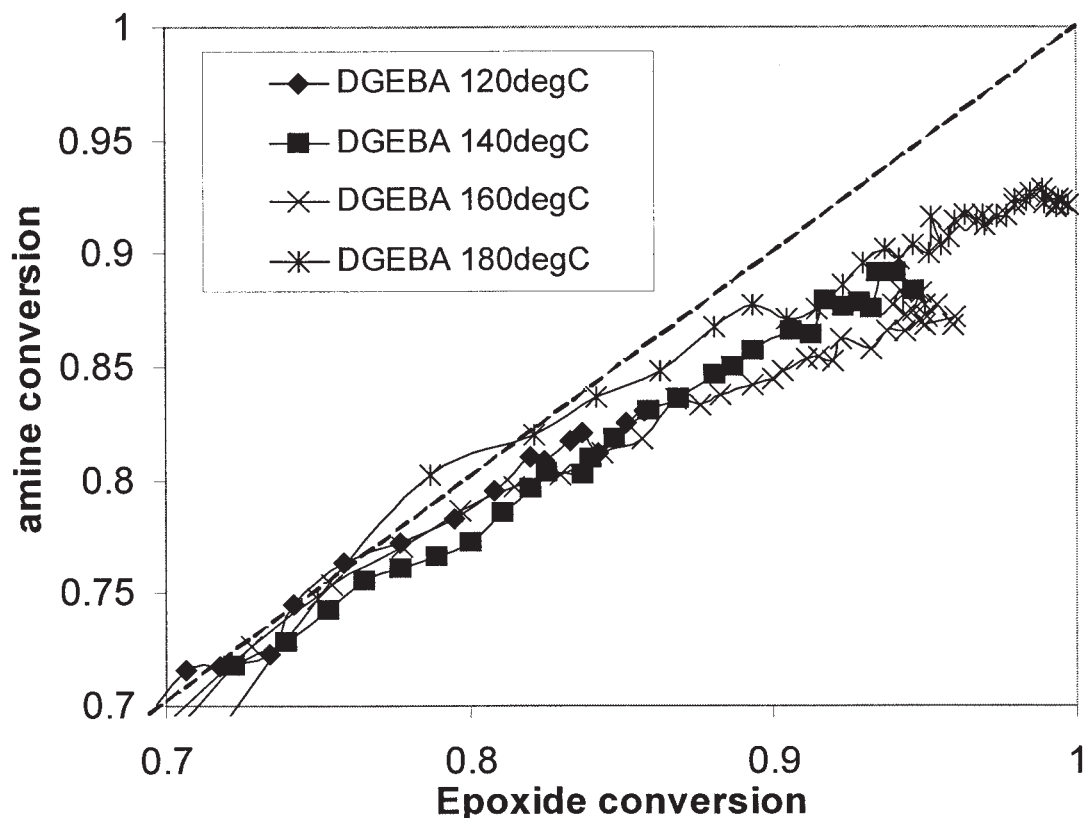| System	Ea_1 (kJ/mol)	$\ln A_1$	Ea_2 (kJ/mol)	$\ln A_2$
DGEBA/BAPP	36.5	6.87	46.6	8.71
TGAP/BAPP	34.9	5.07	69.1	13.96
TGDDM/BAPP	37.3	5.78	79.4	17.91

Figure 8 Total amine conversion plotted *versus* epoxide conversion. Deviation from linearity indicative of presence of homopolymerisation.

the experimental value. The TGAP/BAPP values were found to vary between 41 and 52% conversion, while the TGDDM/BAPP values varied between 52 and 64%. The large differences in these values as those predicted from the theory, in particular the TGDDM/BAPP system, may be attributed to higher levels of etherification occurring for these highly crosslinked systems occurring via internal cyclization as well as crosslinking. It is also anticipated that the level of sensitivity of the spectral technique can also impact the accuracy of the values determined. The conversion at gelation was determined in this work from the point where the PA was initially consumed. Although used elsewhere as a measure of gelation, it is also an arbitrary designation, which for the purposes of this work has demonstrated the expected changes in conversion as a function of temperature and has also more than likely overestimated the values for the TGDDM/BAPP system in this case.

Figures 4–6 show the plots of the fractional conversion of epoxide (EP), PA, and SA groups with time at 140°C for the DGEBA, TGAP, and TGDDM systems, respectively. These results are presented graphically to highlight the effect that the epoxy resin has upon the relative reaction rates of the PA and SA reactions. Figure 4 reflects the changes in the DGEBA/BAPP

reaction, which exhibits a rapid increase in PA conversion until near completion, while the SA groups that are consumed somewhat more slowly and at longer times go only to around 85% completion. The same plots for the TGAP and TGDDM systems are shown in Figures 5 and 6, where the differences in the cure mechanism with the DGEBA-based system are evident. The rates of the SA cure conversion appear significantly faster than that for the DGEBA system. In fact, the SA reaction rates appear to be quite comparable to that of the PA cure conversion for the TGAP and TGDDM systems. The differences are possibly a result of the fact that the PA addition to the DGEBA system occurs through a chain extension process and results in a fairly high degree of spatial separation of the functional groups prior to gelation and the onset of SA addition, consequently making SA addition more difficult. In contrast, the initial PA epoxide addition to the TGAP and TGDDM species, being tri and tetra functional epoxy resins, produce a highly branched polymer prior to crosslinking, and the reactive species may be closer in spatial proximity to each other and facilitate the SA reaction.

The rate coefficients, k_1 (PA addition to epoxide group) and k_2 (SA addition to epoxide group), determined over a range of cure temperatures as shown in
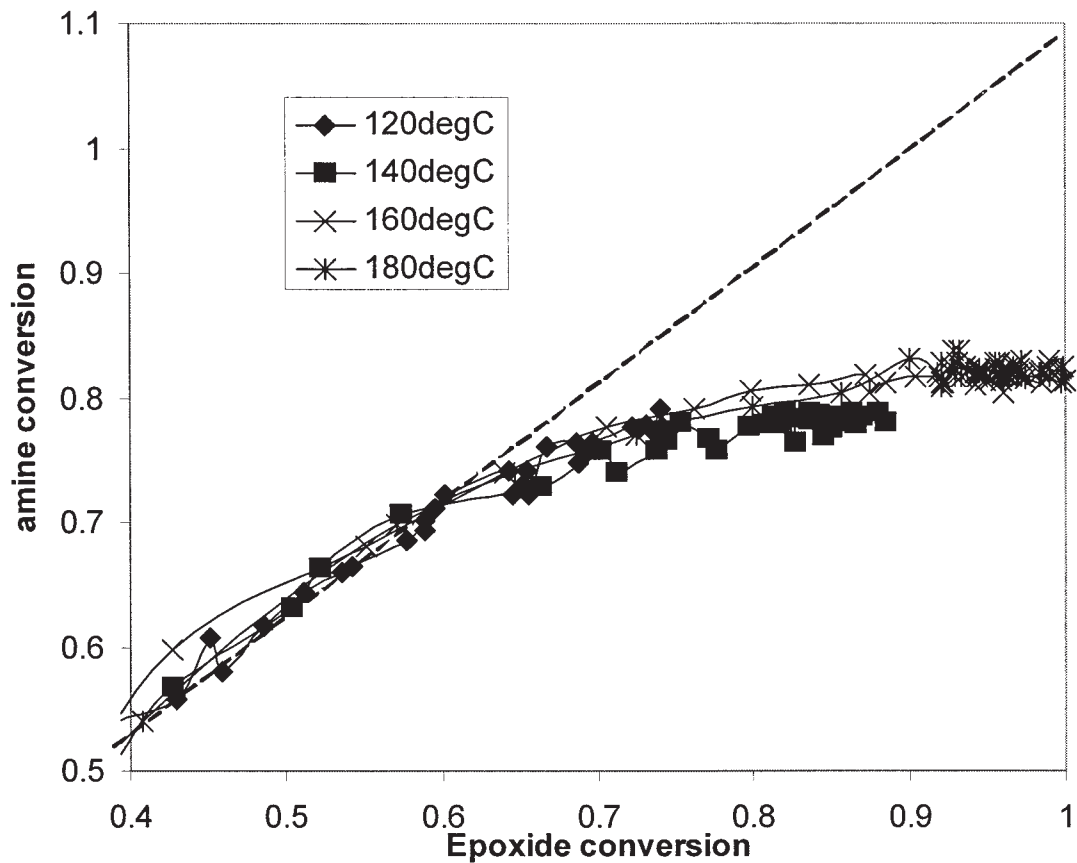
Figure 9 Total amine conversion plotted *versus* epoxide conversion for the TGAP/BAPP cure.
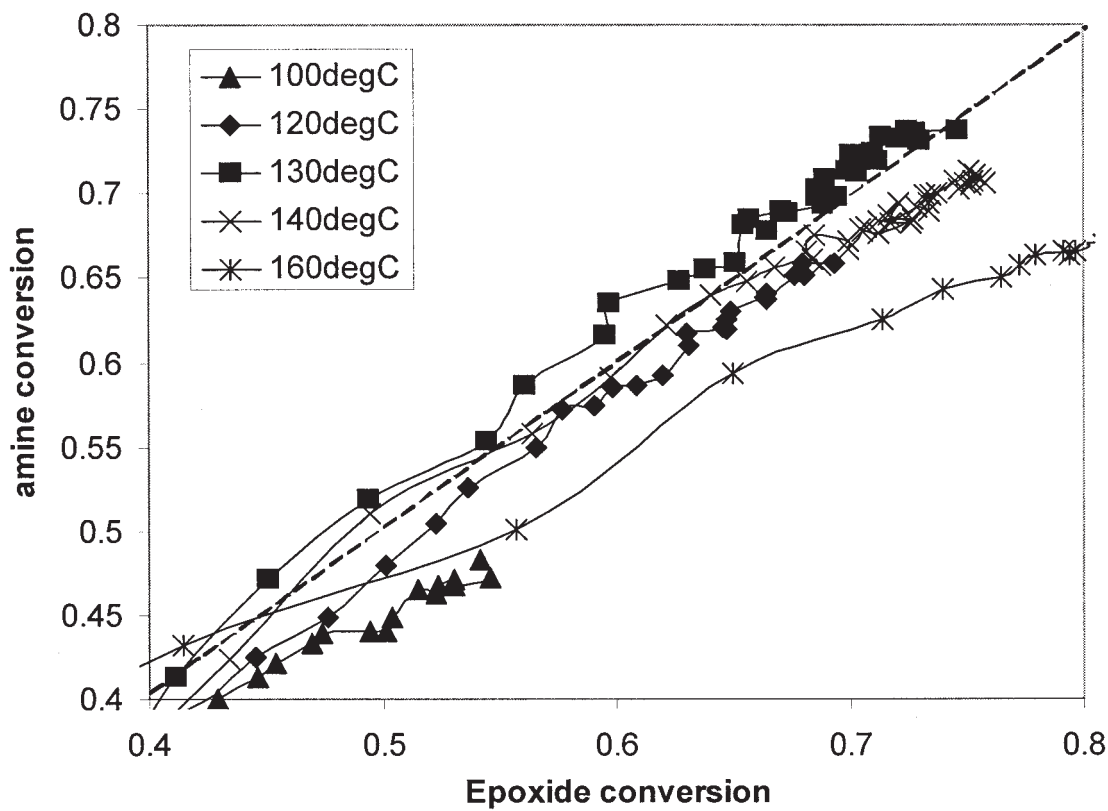

Figure 10 Total amine conversion plotted *versus* epoxide conversion for the TGDDM/BAPP cure.
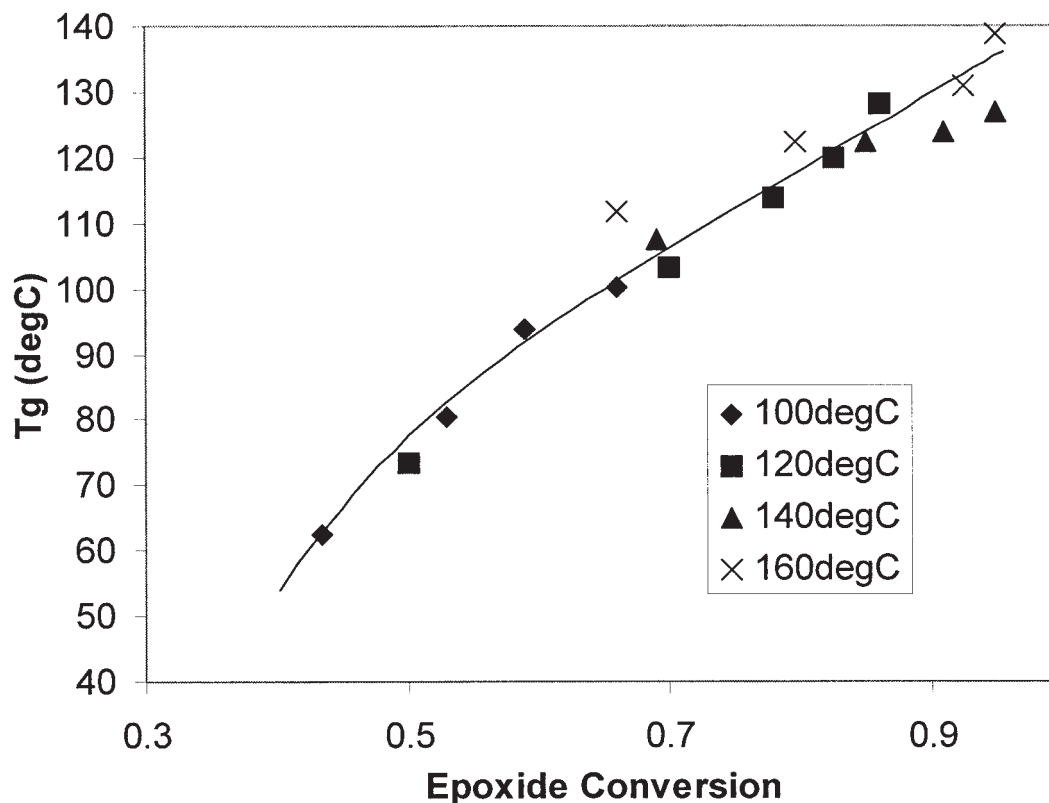
Figure 11 T_g *versus* epoxide conversion for the DGEBA/BAPP cure at varying cure temperature, displaying the independence of the cure mechanism to cure temperature.

Table II, highlight that the abovementioned considerations are independent of cure temperature. While there is some scatter in the results, the k_2/k_1 ratio as also shown in Table II, further illustrates this point. The values of 0.25–0.4 for the DGEBA/BAPP system are similar to that found by Liu et al.,[8] and reflect linear chain branching/extension, followed by the crosslinking mechanism discussed above. Liu et al.[8] also found that for other hardeners, such as diethyltoluenediamine and dimethyldithiotoluenediamine, the k_2/k_1 ratio was higher for TGAP and TGDDM, compared to that found for DGEBA. These results were attributed to the increasing deconjugation of the aromatic pi electrons of the amine with the lone pair of electrons on the N atom with increasingly bulky substituents. This in turn increases the basicity of the SA (due to it becoming more aliphatic in nature) and the rate of SA addition to another epoxide species, and explains the order of k_2 as being TGDDM > TGAP > DGEBA.

In comparing the values of k_1 and k_2 for the BAPP system to those of Liu et al.,[8] it can be seen that the BAPP hardener generally results in a cure process, which reacts significantly faster than both the diaminodiphenylsulphone and the dimethyldithiotoluenediamine system and modestly faster than diethyltoluenediamine. Figure 7 shows an example of the

Arrhenius plot of the rate coefficients k_1, k_2 for the DGEBA/BAPP system, and the resultant activation energies of the reaction are shown in Table III. The values reported here are somewhat lower than the other values reported in the literatures[8,13,14] and reflect the higher rate of reaction of the BAPP hardener. This may be attributed to the above-mentioned deconjugation affecting, k_2 and the flexible P-O-C linkage, as reported by Weichang et al.[4]

Network structure

An important aspect of the investigation of the structure–property relationships for epoxy amine networks is the behavior of the cure process when the reaction becomes more diffusion-controlled at higher cure conversions, compared to the initial kinetically-controlled process. When the material approaches vitrification, increasing levels of etherification or internal cyclization are able to take place.[15] The level of etherification occurring can be investigated by plotting the total amine conversion *versus* epoxide conversion.[11] If all reaction occurs via epoxy amine addition, then this relationship is linear and any deviation indicates the presence of side reactions. Figures 8–10 shows these plots for the range of temperatures used for the DGEBA,
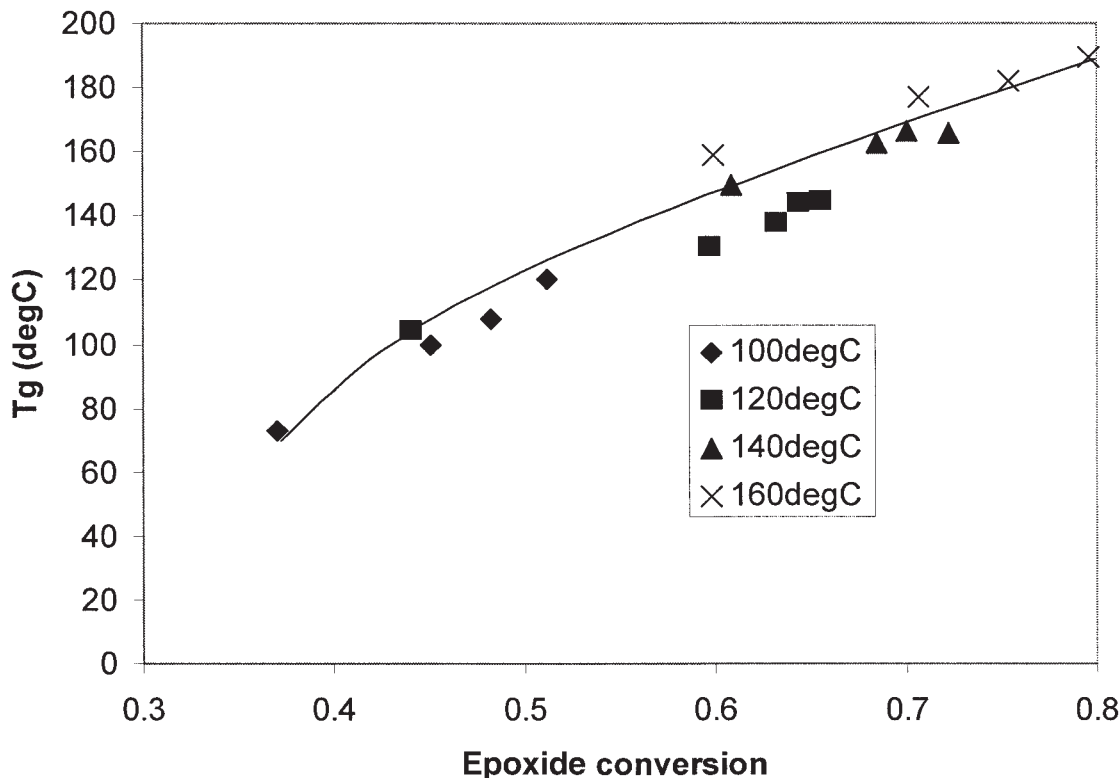
Figure 12 T_g *versus* epoxide conversion for the TGAP/BAPP cure at varying cure temperature, displaying the independence of the cure mechanism to cure temperature.

TGAP, and TGDDM systems, respectively. The DGEBA and TGDDM plots indicate that very little etherification occurs until late in the cure process, in contrast to the TGAP plot that shows significantly higher levels of etherification occurring.

Table I also shows the final level of cure conversion (epoxide and SA) achieved for each of the systems. As can be seen, the DGEBA/BAPP final conversions tend to be higher than that of the TGAP and TGDDM systems, which can be attributed to an increased level of steric hindrance in the glassy state due to the highly branched and bulky nature of the epoxy species.

Initial structure–property relationships for the epoxy/BAPP blends have been established and are shown in Figures 11–13. The glass transition temperatures, determined independently from DSC measurements, are plotted against the epoxide cure conversion. As can be seen, there is an excellent correlation over a range of cure temperatures for each system as demonstrated by the formation of a master curve from the superposition of the results obtained from the different cure temperatures. These plots have been reported widely[16,17] and are used to show that the reaction mechanism operating during cure is independent of temperature, regardless of other side reactions that may be occurring.

CONCLUSIONS

In conclusion, this work has sought to report and establish some of the basic kinetic and structure/property information for a novel phosphorus-based hardener cured with a range of common epoxy resins such as DGEBA, TGAP, and TGDDM. It is important to characterize the behavior of new hardeners in terms of their processability and performance for new hardeners to be accepted and used commercially. Phosphorus-based hardeners are particularly important, given the commercial imperative to develop composite materials with improved fire and environmental performance. The rate coefficients k_1 and k_2 have been determined and appear to be modestly faster than the commercially-available DETDA, and significantly faster than the other commercially important hardener diamino biphenyl sulfone. The relative ratio of the rate coefficients k_2/k_1 was shown to exhibit a positive substitution effect for the TGAP and TGDDM systems. Side reactions such as etherification or internal cyclization were shown to be important only at higher levels of cure conversion for the TGDDM and DGEBA systems, while significantly more etherification was determined to occur for the TGAP/BAPP system. Plots of the glass transition temperature *versus* epoxide con-
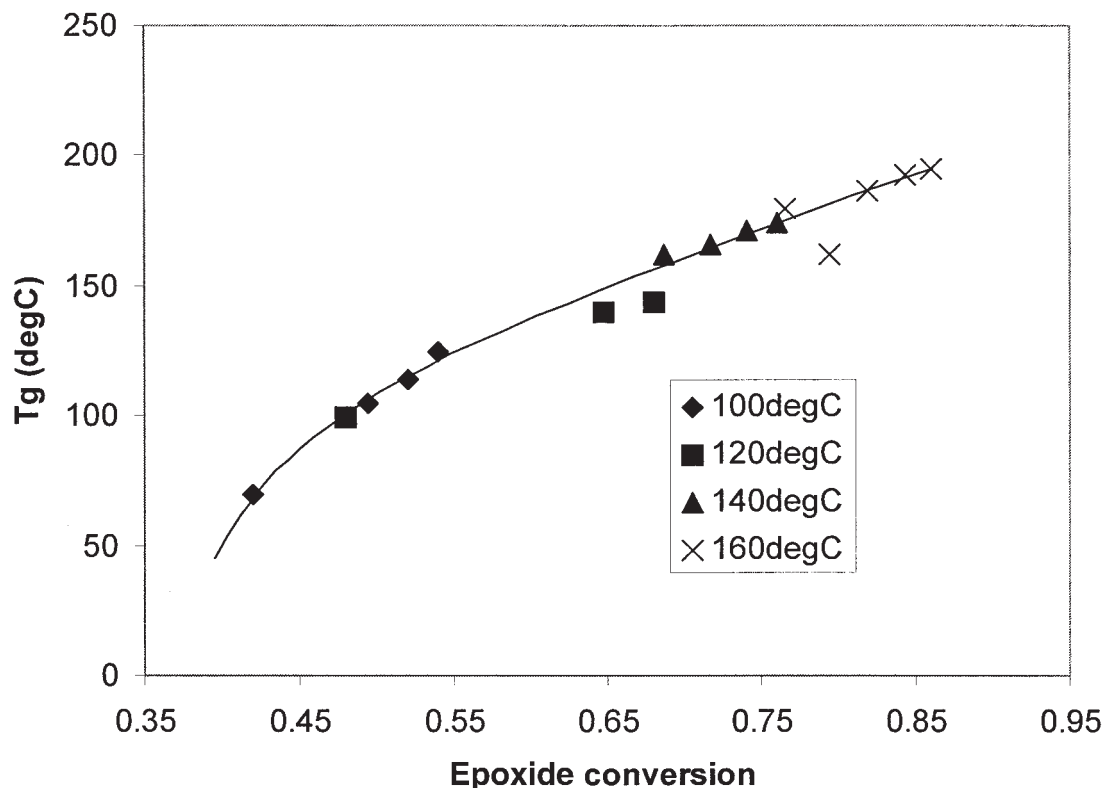
Figure 13 T_g *versus* epoxide conversion for the TGDDM/BAPP cure at varying cure temperature, displaying the independence of the cure mechanism to cure temperature.

version indicated that the cure mechanism was independent of temperature.

References

1. Murphy, J. Reinforc Plast 2001, Oct., 42.
2. Sprenger, S.; Utz, R. J Adv Mater 2001, 33, 24.
3. Weichang, L.; Varley, R. J.; Simon, G. P. Polym, in press.
4. Weichang, L.; Varley, R. J.; Simon, G. P. J Appl Polym Sci 2004, 92, 2093.
5. Wang, C.-S.; Shieh, J. Y. Eur Polym J 2000, 36, 443.
6. Wu, C. S.; Liu, Y. L.; Chiu, Y. S. Polymer 2002, 43, 4277.
7. Hsiue, G. H.; Ying, L. L.; Tsiao, J. J Appl Polym Sci 2000, 78, 1.
8. Liu, H.; Uhlherr, A.; Bannister, M. K.; Varley, R. J J Polym Sci Part A: Polym Chem 2004, 42, 3143.
9. St. John, N. A.; George, G. A. Prog Polym Sci 1994, 19, 755.
10. Musto, P.; Martuscelli, E.; Ragosta, G.; Russo, P. High Perform Polym 2000, 12, 155.
11. Min, B.-G.; Stachurski, Z. H.; Hodgkin, J. H. Polymer 1993, 34, 4908.
12. Flory, P. J. J Am Chem Soc 1941, 63, 3083.
13. Barton, J. M. Br Polym J 1986, 18, 37.
14. Opalicki, M.; Kenny, J. M.; Nicolais, L. J Appl Polym Sci 1996, 61, 1025.
15. DeBakker, C. J.; George, G. A.; St John, N. A. Polymer 1993, 34, 716.
16. Varley, R. J.; Heath, G. R.; Hawthorne, D. G.; Hodgkin, J. H.; Simon, G. P. Polymer 1995, 36, 1347.
17. Simon, S. L.; Gilham, J. K. J Appl Polym Sci 1994, 53, 709.