Quantitative analysis of the cure reaction of DGEBA/DDS epoxy resins without and with thermoplastic polysulfone modifier using near infra-red spectroscopy

B.-G. Min and Z. H. Stachurski
Department of Materials Engineering, Monash University, Clayton, Victoria 3168, Australia

and J. H. Hodgkin* and G. R. Heath
CSIRO, Division of Chemicals and Polymers, Clayton, Victoria 3168, Australia
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Near infra-red spectroscopy techniques were used to study the cure reactions of various epoxy resin formulations based on diglycidyl ether of bisphenol A (DGEBA) resins cured with 4,4′-diaminodiphenyl sulfone (DDS) hardener. Stoichiometric and non-stoichiometric DGEBA/DDS resin formulations, using neat as well as thermoplastic toughened systems containing two phenolic hydroxyl terminated polysulfones with different molecular weights were involved in this study. The infra-red absorption spectra of the prepared formulations were obtained on an *FT*i.r. spectrometer operating in the region of 11 000–4000 cm^{-1} and were analysed according to methods described in this paper. The chemical group peaks of interest in a DGEBA/DDS spectrum were identified by a comparative study with individual spectra of DGEBA and DDS monomers. Where necessary, special model compounds were used to identify unknown bands, such as the primary amine band at 4535 cm^{-1}. The absorption bands of interest were integrated to quantify the areas and then converted to molar concentrations. This series of quantitative analysis of the major chemical groups in several resin systems, led us to understand not only the reaction mechanism in each system but also the cure kinetics, which showed strong dependence on the formulation of the system. In this paper, the details of the quantitative analysis of the infra-red spectrum for various systems and the reaction mechanisms observed in stoichiometric DGEBA/DDS resin formulations are described.

(Keywords: near infra-red spectroscopy; epoxy resin; cure temperature; reaction mechanism; cure kinetics)

INTRODUCTION

Although epoxy resins have been used as matrix materials for many advanced composites, the intrinsic brittleness associated with their highly crosslinked structures still remains a major drawback. In the last few decades, extensive research work has contributed to methods of improving the relatively poor fracture properties of epoxy resins through (more or less successful) approaches based on reducing the crosslink density of the epoxy network or modifying commercially available epoxy resins with secondary components such as low molecular weight liquid rubbers[1–6], inorganic fillers[7], or ductile engineering thermoplastics[8–13].

The developing network structure of the epoxy resins, arrested at different times during the cure, will be influenced by various parameters according to the reaction mechanism, and the exact nature of this molecular network will determine the system properties. A clear understanding of this network structure, which would allow further improvements in fracture properties of epoxy resins, has not yet been achieved. This is due partly to the lack of visibility of the epoxy network to microscopic analysis methods. Various indirect approaches, such as the measurement of glass transition temperature[14,15], liquid absorption characteristics[16,17] or crosslinking density[18,19] of cured resins, have been followed as a means of characterizing network structure. These approaches have generally not been able to provide adequate information about the true network structure. Recently, the analysis of reaction mechanisms and cure kinetics, which determine the parameters of network formation during cure, have attracted much interest. A differential scanning calorimetry (d.s.c.) technique has been used frequently to investigate the cure kinetics of tetraglycidyl diaminodiphenylmethane (TGDDM) or diglycidyl ether of bisphenol A (DGEBA) epoxy resins cured with 4,4′-diaminodiphenyl sulfone (DDS)[15,20]. However, d.s.c. gives overall cure kinetics only. Solid state ^{13}C n.m.r.[17,21] and Fourier transform infra-red spectroscopy (*FT*i.r.)[22–25] have also been used within their applicable ranges for analysing cure reactions of epoxy resins. The epoxy group consumption has been used mainly as a parameter indicating the overall conversion of the curing system in these infra-red studies. Very recently, George and co-workers[26,27] have been successful in the quantitative analysis of the cure reaction of TGDDM epoxy resins

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* To whom correspondence should be addressed

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cured with 17–37 wt% DDS, using *FT*i.r. coupled with *in situ* fibre optics, and using simultaneous d.s.c. and near infra-red analysis methods. They analysed the reaction mechanisms and the cure kinetics involved in their resin system by monitoring the variations of functional group concentrations during the cure. Extensive side reactions, defined mainly as etherification, were also observed[27].

In this paper, the near infra-red technique is extended to stoichiometric and non-stoichiometric DGEBA/DDS epoxy resin formulations, and to polysulfone modified DGEBA/DDS epoxy resin systems. Detailed procedures used for the band assignments and for the quantitative analysis of the cure reaction (by measuring the variations of the interesting chemical groups in various systems) are described, together with the reaction mechanisms observed in the stoichiometric DGEBA/DDS system. Details of the results from non-stoichiometric systems, and from polysulfone-modified systems will be presented in subsequent papers.

THEORY

Beer's law[28], also referred to as the Beer–Lambert law or the Beer–Lambert–Bouquer law, which expresses the relationship governing the quantitative use of infra-red spectroscopy, is written in the form:

$$A = \log_{10} I_0/I = \varepsilon c l \tag{1}$$

where A is the absorbance, I_0 is the intensity of radiation entering the sample, and I is the intensity of radiation leaving the sample. For a given band, ε ($\mathrm{l\,mol^{-1}\,cm^{-1}}$) is the absorption coefficient or molar absorptivity of a component of the sample at the particular frequency, c ($\mathrm{mol\,l^{-1}}$) is the concentration of that component, and l (cm) is the path length of radiation within the sample. The absorption coefficient, ε, is a unique property of the component at the frequency and operating conditions for which it is determined. Therefore when it is used for the purpose of quantitative comparison it must be determined under those conditions.

The practical difficulty of preparing samples of uniform thickness can be overcome by deriving the effective thickness using an internal standard, which does not change during the cure.

The volume concentration, c, is difficult to measure in the DGEBA/DDS mixture, which consists initially of liquid and solid monomers. Therefore weight concentration of the component (expressed in $\mathrm{mol\,kg^{-1}}$), which can be calculated from the initial composition of the mixture, was used in this study. The use of weight concentration was based on the assumption that the densities of DGEBA and DDS monomer are quite close and therefore the errors associated with conversions between volume and mass are small. Meanwhile equation (1) can be expressed in a simplified form with standardized sample thickness:

$$A = ac \tag{2}$$

where $a = \varepsilon l$, and l is the standardized sample thickness. The parameter, a (expressed in $\mathrm{kg\,mol^{-1}}$) is referred to (in this paper) as the molar absorptivity of the component.

The absorbance of a combined band of more than two components is a sum of the individual absorbances of the components (if there is no interference). From equation (2), we write:

$$\Sigma A = A_1 + A_2 + A_3 + \cdots A_n = a_1c_1 + a_2c_2 + a_3c_3 + \cdots a_nc_n \tag{3}$$

where ΣA is the absorbance of the combined band, $A_1 \ldots A_n$ are the absorbances of the components, $a_1 \ldots a_n$ are the molar absorptivities of the components, and $c_1 \ldots c_n$ are the molar concentrations of the components.

EXPERIMENTAL

Materials and apparatus

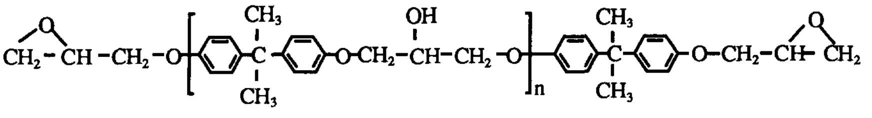
The epoxy resin used in this study was DGEBA (Epikote 8283, Shell Chemicals, $M_n = 380$, liquid) and the amine curing agent was DDS (Anchor Chemicals, $M_n = 248$, powder). Two phenolic hydroxyl-terminated polysulfones (PSF) of $\bar{M}_n = 6400$ and $\bar{M}_n = 10\,000$, used as modifiers, were synthesized from bisphenol A and dichlorodiphenylsulfone monomers by the conventional method described by Merriam and co-workers[29,30], and were incorporated into the DGEBA/DDS system. The chemical structures of the materials used are shown as *Structures 1–3*.

The infra-red apparatus employed in this study was an Alpha Centauri *FT*i.r. spectrophotometer (Mattson Instruments Inc., USA) for recording near infra-red absorption spectra in the region 11 000–4000 cm⁻¹. The operating conditions for obtaining the spectra involved 32 scans at a resolution of 8 cm⁻¹.

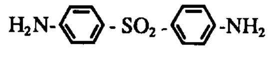
Sample preparation

The intimate mixtures of DGEBA and DDS in stoichiometric (1:1) and non-stoichiometric ratios (1:2 and 2:1), based on the functionality of the two monomers, were prepared in a rotary evaporator under vacuum starting from a temperature of 80°C and finishing at 120°C. In order to minimize chemical reactions between the monomers during the mixing process, the heating time was limited to less than 30 min. The flask was rotated at a constant speed during the process. When the temperature reached 120°C, the mixture became a clear, transparent solution. At that point, set volumes of the mixtures were cast into aluminium foil cups to form discs of about 15 mm diameter and 2 mm thickness. The samples were placed in an air oven at two different temperatures, 130°C and 205°C, for various intervals so that different degrees of cure were achieved. Samples prepared in this way were used for the near infra-red studies without further machining or preparation.

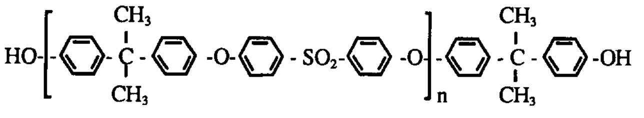
The polysulfone-modified mixtures, containing a stoichiometric amount of DGEBA to DDS and different levels of PSF, were prepared in a similar way. However, the DGEBA and PSF monomers were prereacted in the presence of a catalyst (tetramethylammonium hydroxide) prior to adding DDS. The mixtures were poured into a Teflon mould and cured, first at 140°C for 2 h, then at 180°C for 2 h, and finally post-cured at 205°C for 3 h. These fully cured epoxy bars (120 mm × 12 mm × 16 mm) containing 5–20 wt% PSF, were machined to 2.3 mm thickness and used for the near infra-red spectroscopy.



Structure 1 DGEBA, $n=0.14$



Structure 2 DDS



Structure 3 PSF, $n=13.96$ for $\bar{M}_n$ 6400 and $n=22.11$ for $\bar{M}_n$ 10000

RESULTS AND DISCUSSION

Identification of the chemical bands

The absorption spectra of DGEBA and DDS monomers are shown in *Figure 1*. The absorption bands of interest, including epoxy, primary amine, secondary amine, hydroxyl, methylene/methine and phenyl groups, were identified from the individual spectra, and are listed in *Table 1*. The bands used for quantitative analysis are underlined. The assignment of the bands generally agrees with those reported in published literature[26,31,32] except for an unknown band observed at 4535 cm^{-1} in the spectrum of DDS monomer in the solid state in *Figure 1*. This unknown band attracted our interest because it was observed at the same wavenumber as an epoxy group band in DGEBA which was considered as a suitable band for quantitative analysis because of its strong absorptivity. The absorption spectra of uncured and fully cured DGEBA/DDS mixtures are presented in *Figure 2*. The band at 4535 cm^{-1} was not observed in the spectrum of fully cured DGEBA/DDS, implying that the band at 4535 cm^{-1} observed in the spectrum of solid DDS monomer most likely corresponds to an amine group, which is the only group consumed during cure. At this stage, two questions were posed: (i) will the band be visible in DDS monomer in the liquid state? and (ii) does it correspond to either primary amine or secondary amine, or both? To answer the first question we obtained an infra-red spectrum of the DDS monomer in a solution of DDS in 1,2-dimethoxyethane solvent. The spectrum of the DDS monomer, obtained by subtracting the solvent spectrum, is presented in *Figure 3*. The second question was solved by obtaining spectra of two model compounds in the liquid state which have primary amine and secondary amine groups, respectively. The model compounds used were *p*-nitroaniline and *N*-methyl-*p*-nitroaniline. The band at 4535 cm^{-1} was observed only from *p*-nitroaniline having primary amine group in its structure. These two experimental results were enough to lead us to conclude that the band at 4535 cm^{-1} observed in the spectrum of DDS monomer is due to the primary amine group on the DDS and that it should also appear in the DGEBA/DDS spectrum combined with the epoxy group band.

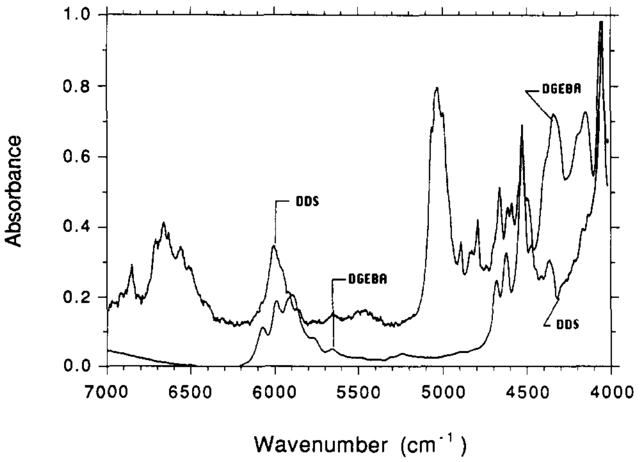
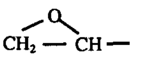
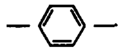


Figure 1 Near infra-red spectra of DGEBA and DDS monomers: the DGEBA monomer is in a liquid state, the DDS monomer is in a solid state

Table 1 Band assignments of the chemical groups from the infra-red absorption spectra of DGEBA and DDS monomers, and uncured DGEBA/DDS mixture

Chemical groups	Observed wavenumber (cm^{-1})
	<u>4535</u>[a], 6068
-NH$_2$	4535[a], <u>5012–5077</u>
-NH$_2$+-NH	<u>6577–6692</u>
-OH	4903, <u>6990</u>
	<u>4619–4682</u>
-CH$_2$+-CH	<u>5915–5990</u>

[a] Note that the absorption band at 4535 cm^{-1} (for epoxy group) occurs also for NH$_2$ group

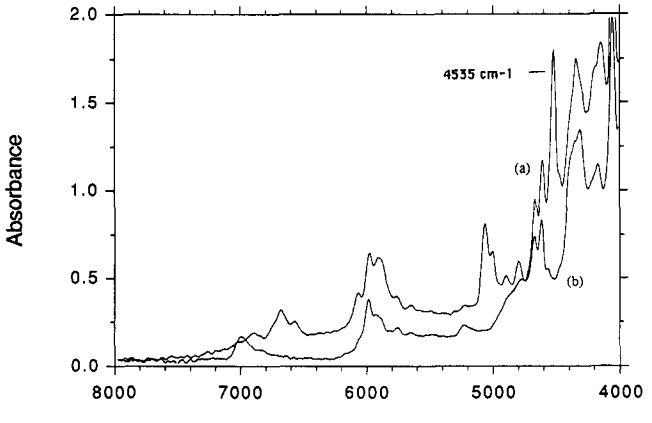


Figure 2 Near infra-red spectra of stoichiometric DGEBA/DDS formulations: (a) uncured and (b) fully cured at 205°C for 320 min. Note the disappearance of the band at 4535 cm^{-1} in spectrum (b)

Assignment of internal standard band

All samples used had slightly different thicknesses and so, for the purpose of quantitative analysis, internal

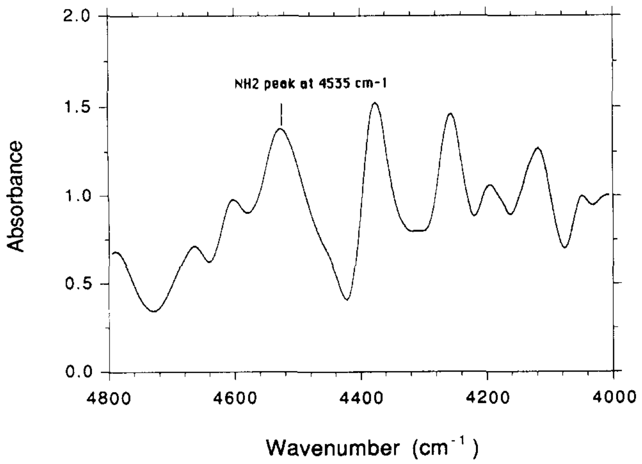


Figure 3 Near infra-red spectrum of DDS monomer from solution of DDS in solvent, obtained by subtracting the solvent spectrum

calibration of values based on the concentration of an internal standard was needed. The combined CH_2, CH band at 5915–5990 cm^{-1} and the phenyl group band at 4619–4682 cm^{-1}, which were believed not to be consumed or produced during the cure, were therefore examined and were chosen as suitable for internal standards. *Figures 4* and *5* show the plots of the band area and band intensity (height) of the nominated regions against the sample thickness in a stoichiometric DGEBA/DDS formulation. Both the band area and the band intensity appear to obey Beer's law in that they are proportional to sample thickness. Note that the lines of best fit extrapolate very close to zero for zero sample thickness. This observation allows us to use either of the two group bands as an internal standard. In resins modified by PSF the initial concentration of CH_2 and CH groups is more complicated to derive. Therefore, we used the phenyl group band as an internal standard for all systems.

The area of the band was used in preference to intensity, and converted to molar concentrations for each group. To obtain maximum accuracy, the band area was measured by integrating the band over a constant wavenumber range. It was also believed that this method can minimize the error occurring with irregular baseline.

Chemical group analysis

Initial molar concentrations of the chemical groups of interest were calculated from the formulations used and are listed in *Table 2*. Molar absorptivity of the phenyl group was obtained by dividing the band area by its initial molar concentration in the spectrum for 1.55 mm thick stoichiometric DGEBA/DDS sample. This value was found to be 4.61 kg mol^{-1}. This value was then used to calculate the standard band area of the phenyl group in other formulations by multiplying it by initially known phenyl group concentration. The molar absorptivities of the chemical groups of interest were calculated by the procedures described below, and are summarized in *Table 3*.

Epoxy and primary amine group analysis. From equation (3) we obtain the following relation in a specific form:

$$\Delta A_t = a_1[\mathrm{EP}]_t + a_2[\mathrm{PA}]_t \qquad (4)$$

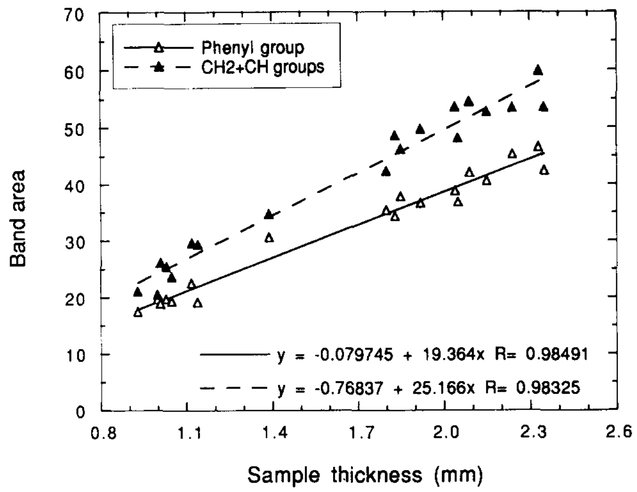


Figure 4 Band areas of the nominated internal standard groups *versus* sample thickness in the spectra of stoichiometric DGEBA/DDS formulations

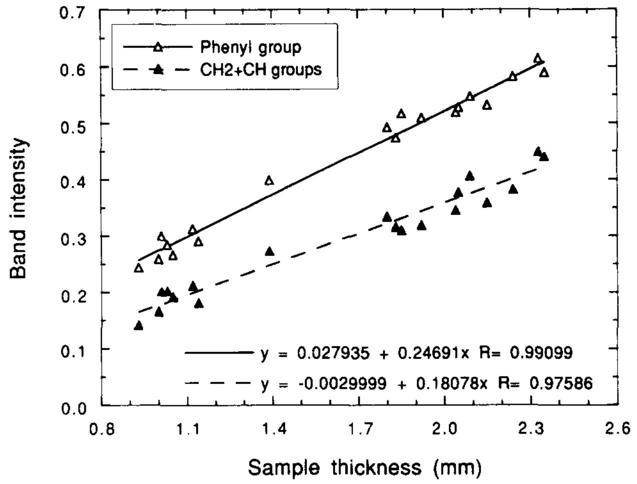


Figure 5 Band intensities of the nominated internal standard groups *versus* sample thickness in the spectra of stoichiometric DGEBA/DDS formulations

where ΔA_t is the combined band area of epoxy and primary amine groups at 4535 cm^{-1}, a_1 and a_2 are the molar absorptivities of epoxy and primary amine groups, respectively, at 4535 cm^{-1}, $[\mathrm{EP}]_t$ and $[\mathrm{PA}]_t$ are the molar concentrations of epoxy and primary amine groups, respectively, and the subscript, t, indicates the cure time.

The molar absorptivities of epoxy and primary amine groups at 4535 cm^{-1} were found to be 8.75 and 3.36 kg mol^{-1}, respectively, from spectra of DGEBA and DDS monomers. Additionally, the concentration of the primary amine group, at any time t, can be obtained from its separate band at 5012–5077 cm^{-1}. Finally, the epoxy group concentration, which is the only unknown in equation (4), can now be calculated. With the above data, the concentration of the epoxy group at 4535 cm^{-1} as a function of cure time was derived using equation (4).

The variation of the primary amine group concentration during the cure was monitored from its band at 5012–5077 cm^{-1}.

Secondary and tertiary amine group analysis. The secondary amine group appears at 6577–6692 cm^{-1} as a combined band with the primary amine group. It was

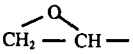
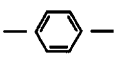
Table 2 Initial molar concentrations of monomers and chemical groups in various epoxy formulations (mol kg^{-1})

	Chemical group^a						
Formulation	$[B]_0$	$[EP]_0$	$[PA]_0$	$[OH]_0$	$[DGEBA]_0$	$[DDS]_0$	$[PSF]_0$
DGEBA	6.006	5.264	–	0.371	2.632	–	–
DDS	8.064	–	8.064	–	–	4.032	–
DGEBA/DDS(1:1)^b	6.511	3.968	1.984	0.280	1.984	0.992	–
DGEBA/DDS(1:2)	6.817	3.184	3.184	0.224	1.592	1.592	–
DGEBA/DDS(2:1)	6.294	4.524	1.132	0.319	2.262	0.566	–
DGEBA/DDS/PSFM_n 6400							
5 wt% PSF	6.642	3.772	1.886	0.282	1.886	0.943	0.0078
10 wt% PSF	6.766	3.572	1.786	0.283	1.786	0.893	0.0156
15 wt% PSF	6.896	3.376	1.688	0.285	1.688	0.844	0.0234
20 wt% PSF	7.020	3.175	1.588	0.286	1.588	0.794	0.0312
DGEBA/DDS/PSFM_n 10 000							
5 wt% PSF	6.642	3.772	1.886	0.276	1.886	0.943	0.0050
10 wt% PSF	6.766	3.572	1.786	0.272	1.786	0.893	0.0100
15 wt% PSF	6.896	3.376	1.688	0.268	1.688	0.844	0.0150
20 wt% PSF	7.020	3.176	1.588	0.264	1.588	0.794	0.0200

^{a}Initial molar concentrations of: $[B]_0$, phenyl group; $[EP]_0$, epoxy group; $[PA]_0$, primary amine group; $[OH]_0$, hydroxyl group; $[DGEBA]_0$, DGEBA monomer; $[DDS]_0$, DDS monomer; $[PSF]_0$, PSF

^{b}(1:1) etc. indicate stoichiometric ratios of DGEBA to DDS in the formulation, based on the functionality of the two monomers

Table 3 Molar absorptivity (a in equation (2)) of chemical groups, based on absorption band areas

Chemical group	Wavenumber of absorption band (cm^{-1})	Molar absorptivity, a (kg mol^{-1})
	4535	8.751
$-NH_2$	4535	3.364
	5012–5077	21.535
	6577–6692	17.011
-NH	6577–6692	9.223
	4619–4682	4.608

also analysed by subtracting the primary amine group concentration (which was obtained from its band at 5012–5077 cm^{-1}) from the combined area. Referring to equation (3) we write:

$$\Delta A_t = a_3[PA]_t + a_4[SA]_t \quad (5)$$

where ΔA_t is the combined band area of the primary and secondary amine groups, a_3 and a_4 are the molar absorptivities of the primary and secondary amine groups, respectively, $[PA]_t$ and $[SA]_t$ are the molar concentrations of the primary and secondary amine groups, respectively, and t has the same meaning as above. The value of a_3 is obtained when the secondary amine group concentration is zero at $t=0$, and a_4 is obtained on the assumption that the secondary amine is not involved in the reaction during the early stage of the cure due to its lower reactivity compared to that of the primary amine; the sum of the amine group concentrations is therefore conserved during the period. The calculated a_3 and a_4 values are presented in *Table 3*.

The concentration of the tertiary amine group was estimated from the balance of produced and consumed secondary amine group concentrations:

$$[TA]_t = [PA]_0 - [PA]_t - [SA]_t \quad (6)$$

where $[TA]_t$ is the molar concentration of the tertiary amine group at time t, and $[PA]_0$ is the initial molar concentration of the primary amine group.

Hydroxyl group analysis. The molar absorptivity of hydroxyl groups was obtained from the spectra of the DGEBA monomer. The band intensity was used instead of the area, which is difficult to measure because it is combined with the dispersed band of hydrogen-bonded hydroxyl group at lower wavenumber. The hydroxyl group concentration obtained from the band intensity at 6990 cm^{-1} represents only the concentration of non-hydrogen-bonded hydroxyl group.

Reaction mechanisms in a stoichiometric DGEBA/DDS formulation

The epoxy group conversions monitored as a function of cure time during the cure at 130°C for 570 min and at 205°C for 320 min are shown in *Figure 6*. The epoxy group conversions increased almost linearly up to gelation (166 min at 130°C and 13 min at 205°C from dynamic mechanical thermal analysis (d.m.t.a.) measurements) and slowed down afterwards due to an increase of the system viscosity and depletion of reacting species. The maximum conversions, 89% at 130°C and 100% at 205°C, were achieved at and ahead of vitrification (325 min at 130°C and 141 min at 205°C from d.m.t.a. measurements), respectively. The consumption of the primary amine group, plotted against epoxy group conversion in *Figure 7*, shows that most of the primary amine groups were consumed by reaction with epoxy groups well before gelation (65% conversion of epoxy group from *Figure 6*). Note that the consumption of the primary amine during cure for two different temperatures,

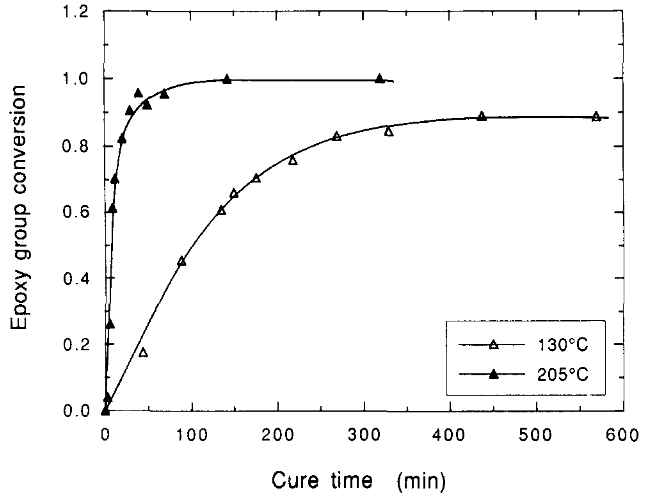


Figure 6 Plot of epoxy group conversion against cure time for stoichiometric DGEBA/DDS formulations

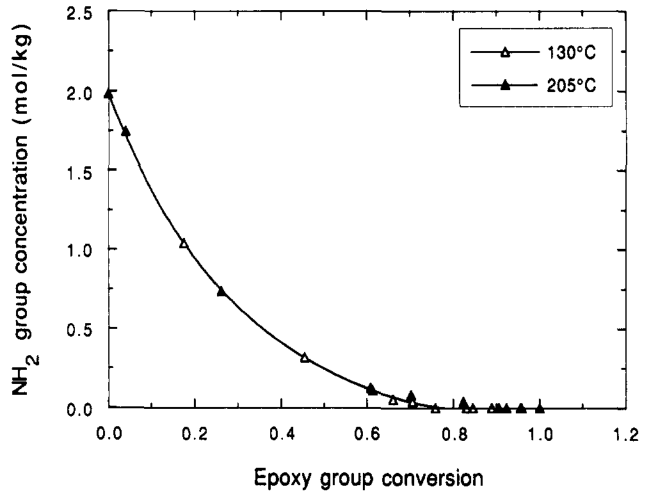


Figure 7 Plot of primary amine group concentration against epoxy group conversion for stoichiometric DGEBA/DDS formulations

130°C and 205°C, follows in exactly the same path (against epoxy group conversion). This observation indicates that at least the reaction between epoxy and primary amine groups is not affected by cure temperature. We believe that this is due to the fact that the system viscosity, determining the mobility of the reactant species in the curing system, is low enough even at low temperature for autocatalytic reaction up to the gel point, at which point the epoxy–primary amine reactions are already exhausted. Meanwhile the secondary amine group is produced by the reaction between epoxy and the primary amine groups, and consumed by the reaction with another epoxy group to produce tertiary amine group. Therefore the concentration of the secondary amine group at time t is governed by a relationship already introduced in equation (6). The concentration of the secondary and tertiary amine groups is presented in *Figures 8* and *9*, respectively. The concentration of the secondary amine group in the system increases to reach its maximum value at about 50% conversion due to the high reaction rate of the primary amine group compared to that of the secondary amine group in the early stage of the cure. At the transition point (at 50% conversion) the rates of production and consumption of the secondary amine groups are equivalent, or in other words the rates of reaction of the primary and the secondary amine groups are similar. This relationship can be seen more clearly in the plot shown in *Figure 10*. Above the transition point the rate of reaction of the secondary amine becomes higher than that of the primary amine. Note that the transition point is close to the onset of gelation. Theoretical calculation $[(P_{gel})^2 = 1/(f-1)(g-1)]$ gives $P_{gel} = 58\%$, whereas experimental results from d.s.c. and d.m.t.a. measurements give a figure of about 65%.

The conversion of the secondary amine group was calculated from the production of the tertiary amine group. It is noteworthy that 88% of the primary amine groups are converted to the secondary amine groups at the 50% transition point, whereas only 13% of the secondary amine groups have reacted with epoxy groups and converted to tertiary amine groups, showing that the reaction between epoxy and secondary amine starts only when most of the primary amine groups are consumed. The reaction is considered to be diffusion controlled due to the rapid increase of the system viscosity after gelation. The plots of the secondary amine conversion at cure temperatures of 130°C and 205°C in *Figure 10* are not

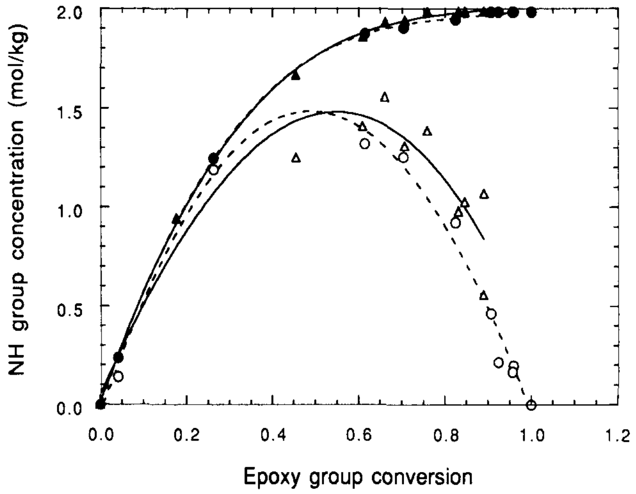


Figure 8 Plot of secondary amine group concentration against epoxy group conversion for stoichiometric DGEBA/DDS formulations: —△—, 130°C, remaining NH; --○--, 205°C, remaining NH; —▲—, 130°C, produced NH; --●--, 205°C, produced NH

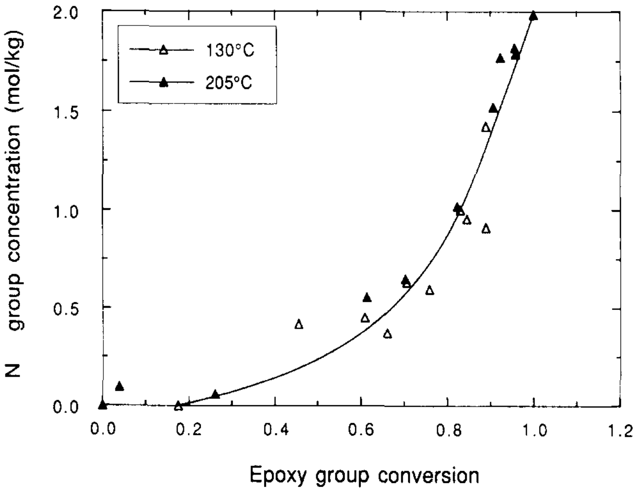


Figure 9 Plot of tertiary amine group concentration against epoxy group conversion for stoichiometric DGEBA/DDS formulations

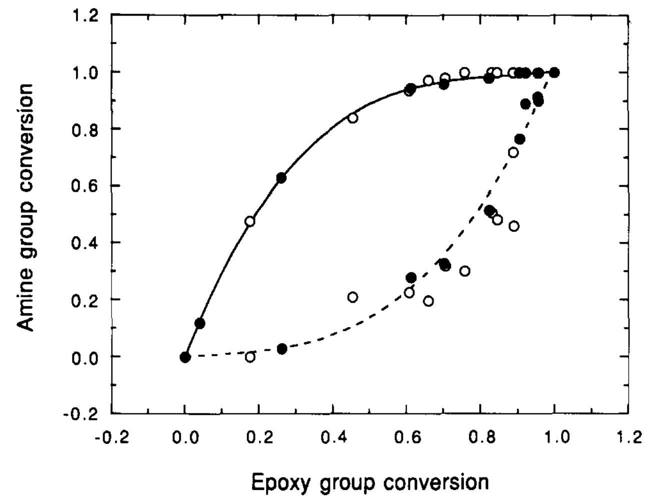


Figure 10 Plot of primary (——) and secondary (- - -) amine group conversions against epoxy group conversion for stoichiometric DGEBA/DDS formulation, during the cure at 130°C (○) and 205°C (●)

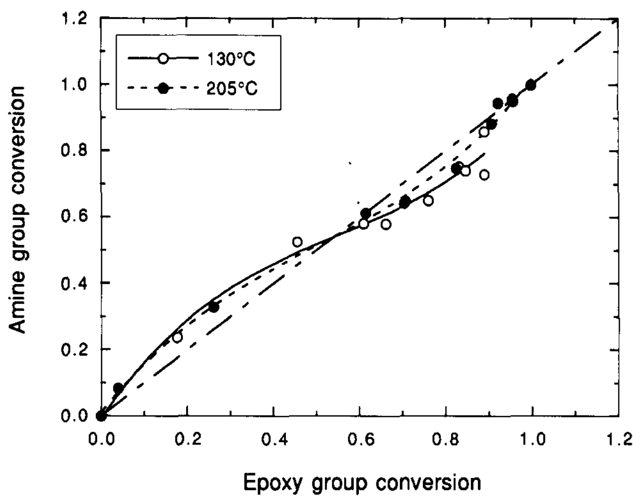


Figure 11 Plot of amine group conversion against epoxy group conversion for stoichiometric DGEBA/DDS formulation: ———, ideal reaction line

noticeably different from each other; a similar match of the conversion curves is seen in the primary amine group conversion. But with the 130°C cure, a considerable amount of the secondary amine species remained unreacted, as was observed in the epoxy group conversion in *Figure 6*.

In the study of reaction mechanisms, the occurrence of the side reactions has been an interesting subject in that these affect the formation of the network structure and final properties of the network. In recent publications it was reported that side reactions occur only in the presence of the catalyst in the DGEBA/DDS resin system[17] while it was observed even in a non-catalytic environment in the TGDDM/DDS resin system[26,27]. The reasons for the occurrence of side reactions are not clearly understood. In our stoichiometric DGEBA/DDS system, the side reactions, which we expect to be mainly the etherification reaction and the epoxy group homopolymerization, could be detected by monitoring the relationship between the conversions of epoxy and amine groups during cure. Based on the assumption that the amine group is consumed only by the reaction with an epoxy group, the following relationship can be established when only the ideal reactions occur:

$$\alpha_{\mathrm{EP}t}=\alpha_{\mathrm{A}t}=\frac{\alpha_{\mathrm{PA}t}+\alpha_{\mathrm{SA}t}}{2} \qquad (7)$$

where $\alpha_{\mathrm{EP}t}$ is the conversion of epoxy group at time t, $\alpha_{\mathrm{A}t}$ is the conversion of the amine group at time t, $\alpha_{\mathrm{PA}t}$ is the conversion of the primary amine group at time t and $\alpha_{\mathrm{SA}t}$ is the conversion of the secondary amine group at time t. Any deviation from this relationship would suggest the occurrence of side reactions in the system. *Figure 11* shows a plot according to equation (7) obtained for our stoichiometric DGEBA/DDS formulation. Up to the transition point (the onset of gelation) we see a greater conversion of amine groups than is dictated by the ideal reactions defined by equation (7). This trend is reversed for conversions above the transition point. Meanwhile for the 130°C cure, 89% of epoxy group and 80% of amine group were consumed, whereas 100% of epoxy and amine groups were consumed at the 205°C cure. The excess 9% conversion of epoxy group at 130°C can be treated as the amount converted by the side reaction. The side reaction observed at low temperature cure may be attributed to the higher system viscosity; this is especially true after gelation, which reduces the mobility of reactant chains and finally allows the slight possibility of side reactions to occur between nearby unreacted species. It was not possible to distinguish between the two likely side reactions in this study due to insufficient information about the hydroxyl group concentrations. The appearance of a broad hydrogen-bonded hydroxyl group band in the infra-red spectrum prevents accurate hydroxyl measurement.

CONCLUSIONS

Near infra-red spectroscopy was used for quantitative analysis of cure reactions in DGEBA/DDS and DGEBA/DDS/PSF systems. Quantitative analysis methods for epoxy, primary amine, secondary amine, tertiary amine and free hydroxyl groups are described. The combined band of epoxy and primary amine groups at 4535 cm^{-1} was identified from the spectra of model compounds and DDS monomers in the solid and liquid state. The work has shown that the quantitative analysis of chemical groups during the cure, using near infra-red spectroscopy, provides an understanding of the reaction mechanisms in various resin systems and an estimate of the network structure of each system. The experimental data for the stoichiometric DGEBA/DDS formulation have confirmed a straightforward reaction mechanism in the formulation. Side reactions were not observed at high temperature cure while at low temperature cure 9% of epoxy groups were consumed by the side reactions. The high system viscosity found in such a low temperature cure, especially after gelation, was considered a major factor contributing to the occurrence of side reactions. As we consider that 130°C is a rather low temperature to be employed in practical (uncatalysed) cures of DGEBA/DDS, we can conclude that this side reaction is not significant in a stoichiometric DGEBA/DDS system.

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