Simultaneous differential scanning calorimetry and near-infra-red analysis of the curing of tetraglycidyldiaminodiphenylmethane with diaminodiphenylsulphone*

C. J. de Bakker, N. A. St John and G. A. George†
Department of Chemistry, The University of Queensland, Queensland 4072, Australia

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The crosslinking reaction of tetraglycidyl-4,4′-diaminodiphenylmethane with 27% 4,4′-diaminodiphenylsulphone at 150°C and 170°C was studied by near-i.r. spectroscopy while simultaneously recording the heat flow by isothermal differential scanning calorimetry (d.s.c.). From the absolute concentrations of primary, secondary and tertiary amine groups and the epoxy, hydroxyl and ether groups measured throughout the reaction, instantaneous rate curves were obtained and used along with reported reaction enthalpies to calculate heat flow curves for comparison with the d.s.c. data. It was found that previous assumptions of a constant reaction enthalpy were incorrect and values of -83 ± 2, -131 ± 9 and $-65\pm6\,\mathrm{kJ\,mol^{-1}}$ for epoxide reaction with primary amine, secondary amine and hydroxyl, respectively, gave the best fit between near-i.r. and d.s.c. data. Deviations between fitted and experimental data after gelation were attributed to heat capacity changes on vitrification and allowed a 'true' isothermal baseline to be constructed. From the corrected isothermal d.s.c. data and the absolute concentration of epoxide consumed, an average reaction enthalpy of $-92\pm1\,\mathrm{kJ\,mol^{-1}}$ was obtained. Reasons for discrepancies between these and scanning d.s.c. data are considered.

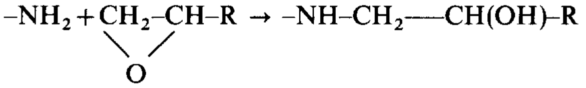
(Keywords: near-infra-red spectroscopy; differential scanning calorimetry; cure kinetics; epoxy resin)

INTRODUCTION

The epoxy resin system, tetraglycidyl-4,4′-diaminodiphenylmethane (TGDDM) crosslinked with 4,4′-diaminodiphenylsulphone (DDS) has been very closely studied because of the widespread use of the resin in advanced aerospace composite materials[1,2]. A detailed understanding of the rates of the many possible reactions over the duration of the cure cycle in which the liquid resin is transformed first to a rubber and then to a glass is essential in the development of optimum properties through a chosen temperature–time cycle[3]. Studies of the rheological changes have enabled time–temperature–transformation (TTT) diagrams to be constructed for similar systems for various ratios of resin to hardener (DDS)[4,5]. However, this cannot address the chemical reactions occurring as the network develops.

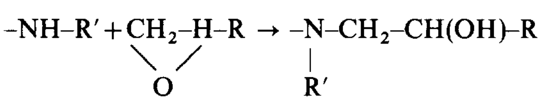
Differential scanning calorimetry (d.s.c.) has been the most common analytical technique employed in attempts to elucidate the cure kinetics[6]. While the method is experimentally very simple, it is only able to provide the overall extent of reaction, rather than the contributions of the individual chemical reactions to the instantaneous reaction rate at each point during cure[6,7]. It has recently been demonstrated[8,9] that, by making some assumptions about the individual reaction enthalpies and the relative reaction rates, it is possible to use d.s.c. data to calculate the concentration profiles of different groups formed over the whole range of cure and over the temperature range for network formation from 160–200°C. A similar attempt at modelling the reaction sequence[10] used existing functional group information from *FT*i.r. spectroscopy[11] together with other authors' d.s.c. data[2] to calculate rate constants for the three main reactions shown below:

Primary amine–epoxy addition



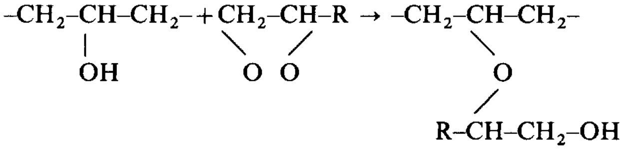
$$-NH_2+\underset{\diagdown\;O\;\diagup}{CH_2\text{–}CH}\text{–}R \rightarrow -NH\text{–}CH_2\text{—}CH(OH)\text{–}R \quad (1)$$

Secondary amine–epoxy addition



$$-NH\text{–}R'+\underset{\diagdown\;O\;\diagup}{CH_2\text{–}H}\text{–}R \rightarrow -\underset{R'}{\underset{|}{N}}\text{–}CH_2\text{–}CH(OH)\text{–}R \quad (2)$$

Hydroxyl–epoxy (etherification)



$$-CH_2\text{–}\underset{OH}{\underset{|}{CH}}\text{–}CH_2\text{–}+\underset{\diagdown\;O\;O\;\diagup}{CH_2\text{–}CH}\text{–}R \rightarrow -CH_2\text{–}\underset{\underset{\diagup}{\overset{\diagdown}{O}}}{CH}\text{–}CH_2\text{–} \atop \qquad\qquad R\text{–}CH\text{–}CH_2\text{–}OH \quad (3)$$

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[†] To whom correspondence should be addressed

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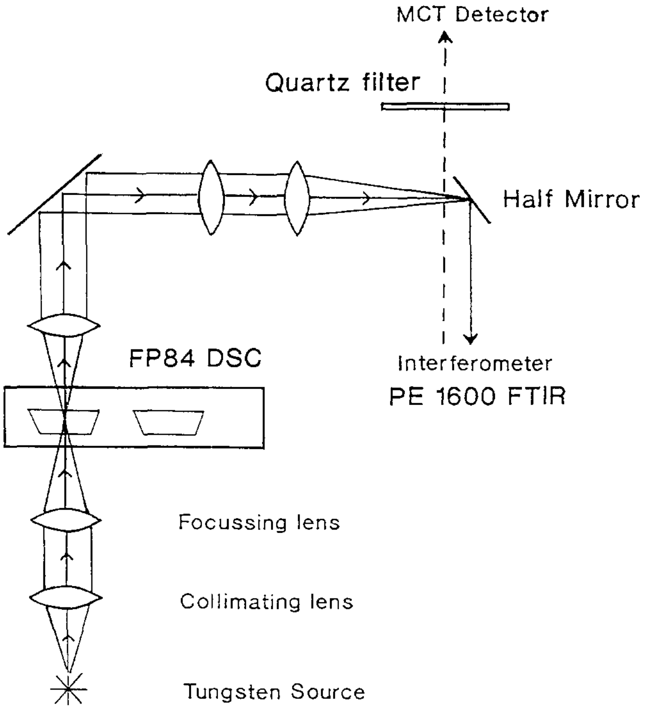

Figure 1 Schematic diagram of simultaneous d.s.c.–near-i.r.–*FT*i.r. experimental set-up

These reactions may be catalysed by impurities present in the resin or by hydroxyl and tertiary amine products formed as shown[9,12], resulting in autocatalysis. The insensitivity of the d.s.c. data to quite wide variations in the relative contributions of uncatalysed and catalysed reactions is the largest limitation of the technique in mechanistic studies, and has meant, for example, that the significance of reaction (3) has ranged from: dominant over reaction (2) at all temperatures[13]; important only at higher temperatures[10] and higher extent of cure[9]; to important under all conditions[6]. There does, however, appear to be general agreement that the fastest and dominant reaction is the chain extension reaction (1), and this is supported by spectroscopic[11,12] and model studies[14] using gel permeation chromatography. The latter technique may also be used on TGDDM/DDS to examine the sol fraction[15], but is restricted to the earlier stages of cure. Similarly, model studies cannot totally account for the interplay of steric, polarity and impurity effects in the crosslinking reactions of a complex system such as TGDDM/DDS, especially at higher extents of conversion.

Recently, we have described the use of near-i.r. spectroscopy to provide absolute concentration data for the reactants and products in reactions (1), (2) and (3) at 160°C and the resultant reaction rate data have shown that, while autocatalytic kinetics describe the reactions of primary and secondary amine, impurity reactions are significant early in the reaction and etherification is competitive with the secondary amine reaction[12]. The large amount of absolute rate data available in real time from such a technique suggests that it should provide an adjunct method to d.s.c. to enable the assumptions inherent in the derivation of reaction rate, and thus mechanistic data, to be tested. However, it has frequently been found that the small differences between experimental techniques in sample volume, thermal history and atmosphere make comparisons from separate experiments subject to uncertainty. It is therefore desirable that, in this case, the d.s.c. and near-i.r. experiments be performed on the same sample at the same time.

Mirabella[16,17] has demonstrated that the crystallization of polypropylene may be studied by simultaneous d.s.c. and mid-i.r. absorption spectroscopy by coupling a commercial d.s.c. microscopy stage to an *FT*i.r. spectrometer using a microsampling accessory and i.r. transparent KBr sample cups. In this paper we describe a similar approach which may be used in the near-i.r. region; however, the experimental arrangement is considerably simpler. In this way we have obtained absolute reaction rate data for TGDDM/DDS from near-i.r. at the same time as acquiring heat flow data using a d.s.c. microscopy unit. This has enabled an estimation to be made of the reaction enthalpies for each of the reactions (1) to (3). From these and the *FT*i.r. reaction rates, the heat flow during cure may be calculated and compared with isothermal d.s.c. data. It is then possible to discern changes in the d.s.c. baseline which are attributable to the decrease in heat capacity as the resin vitrifies.

Intrinsic to previous studies of this resin by d.s.c. have been assumptions both of relative reaction rates of primary and secondary amine[8,9] and the enthalpy and heat capacity changes described above[7,18,19]. It is the purpose of this paper to describe a technique by which these assumptions may be tested, and to indicate that by simultaneous d.s.c.–*FT*i.r., valuable new information on the cure kinetics may be obtained.

EXPERIMENTAL

Materials

Ciba Geigy epoxy resin MY721 which is approximately 92% epoxy group equivalence of TGDDM (of which 86% is pure monomer by h.p.l.c.) and Sigma Chemical Company laboratory reagent grade DDS were used. Resin samples were prepared by preheating the MY721 to 100°C and slowly adding a weighed portion of DDS, stirring until a clear mixture was obtained. The samples, 27% by weight DDS in MY721, were cooled then stored in a freezer until needed for d.s.c.–*FT*i.r. studies.

Near-i.r. spectroscopy using d.s.c. attachment

D.s.c.–*FT*i.r. studies in the near-i.r. region may be performed on extended-range *FT*i.r. instruments which may be configured for emission spectroscopy. We have used Perkin-Elmer model 1600 and Mattson Sirius instruments. A schematic of the apparatus used for simultaneous d.s.c.-*FT*i.r. is shown in *Figure 1*. Radiation from an external 11 W tungsten lamp was collimated and focused into a d.s.c. microscopy cell (Mettler FP84) which contained the sample of epoxy resin in a glass pan on a d.s.c. sensor. The filled pan contained 20 mg and produced an optical path length of 1 mm which resulted in an initial absorbance of 2.1 for the overlapped epoxy–primary amine bands at 4520 cm^{-1}. This provided optimum sensitivity for both calorimetry and spectroscopy of the curing resin. After the radiation passed through the sample it was captured and focused onto a half mirror situated in the sample position on the Perkin Elmer spectrometer. This mirror then launched the radiation into the interferometer in the reverse direction to that when using an internal source. (This is the same mode of operation employed for emission studies with this instrument.) The external source of the *FT*i.r. was switched off so the only source of radiation seen by the MCT detector on the external bench was the returning modulated beam from the interferometer which passed the half mirror. A quartz filter was placed before the MCT detector, which operates at 77 K, to remove background i.r. emission from the interferometer. Spectra from 4000 to 7800 cm^{-1} were obtained, co-adding 64 scans, at a resolution of 8 cm^{-1} every 2 min during cure of the epoxy resin.

For the Mattson Sirius instrument the experimental arrangement was simplified since access was achieved via an external port and the radiation after passing through the d.s.c. cell was focused on the Jacquinot stop. The instrument collected near-i.r. spectra from 11 000 to 4000 cm^{-1} using a quartz beamsplitter and an indium antimonide (InSb) photovoltaic detector cooled to 77 K.

The samples in glass d.s.c. pans were cured at 150 and 170°C with an empty glass pan as reference, and the heat flow was measured continuously by the FP84 d.s.c. and analysed by a PC, using modified Mettler software as the spectra were collected. The Mettler FP84 is a heat flux calorimeter of the Boersma type which is asymmetric with respect to sample and reference due to the arrangement for the passage of light through the sample pan. The calorimetric data are highly reproducible[20] though less easily understood in terms of mathematical analysis than those obtained from conventional heat flux and power compensation type d.s.c.s. The consequence of this is that the influence of sample heat capacity on measurements and thus the 'instrumental' baseline in an isothermal experiment is not well characterized for the FP84. Calibration for temperature and calorimetric measurement was done using indium as a standard. The data from the d.s.c. had a high uncertainty over the first 5 min when thermal equilibrium was re-established upon placing the d.s.c. pans in the preheated apparatus. After the isothermal runs a temperature scan to 300°C was used to determine a residual enthalpy value.

RESULTS AND DISCUSSION

Spectral analysis

The near-i.r. spectral region of an epoxy resin with amine curing agent is considerably simpler than that in the mid-i.r., the usual analytical region[21]. *Figure 2* shows the near-i.r. spectrum of the TGDDM/DDS resin contained in a glass pan held in the remote d.s.c. microscopy stage at 170°C as shown in *Figure 1*. The bands attributed to the functional groups shown in equations (1) to (3), which change on cure (epoxy, primary and secondary amine and hydroxyl), are marked. The bands appearing in the near-i.r. are overtones and combinations of the highly anharmonic C–H, N–H and O–H fundamentals which appear in the mid-i.r. spectrum. In the mid-i.r. these are overlapped with C–C, C–N, C–S and S=O vibrations so that quantitative analysis is difficult without Fourier self-deconvolution or curve-fitting procedures. These latter vibrations are of much lower intensity in the near-i.r. since they do not contain a light atom (which contributes to anharmonicity) and do not appear at the pathlength of 1 mm used in this study. The epoxy group appears at several positions in the near-i.r. spectrum, at 8627, 6060 and 4518 cm^{-1}; in previous studies we have found that the first two bands may be used to monitor the change in concentration during crosslinking[12,22]. However, the band at 8627 cm^{-1}, which is the first overtone of the CH combination band at 4518 cm^{-1}, is weak at the pathlength required for d.s.c. analysis and is also overlapped with an OH band which makes quantitation difficult. The overtone of the CH stretch in the epoxy group appears at 6060 cm^{-1} but requires Fourier self-deconvolution, and thus area measurements, for quantitative analysis. At narrow path lengths, the much more intense band observed at 4520 cm^{-1} may be used to determine the concentration of epoxy groups. However, this band is overlapped by a primary amine band of DDS at 4557 cm^{-1}; it is necessary to subtract the absorption due to this amine, whose intensity can be computed knowing the initial epoxy group concentration and the instantaneous amine concentrations during cure obtained as discussed below.

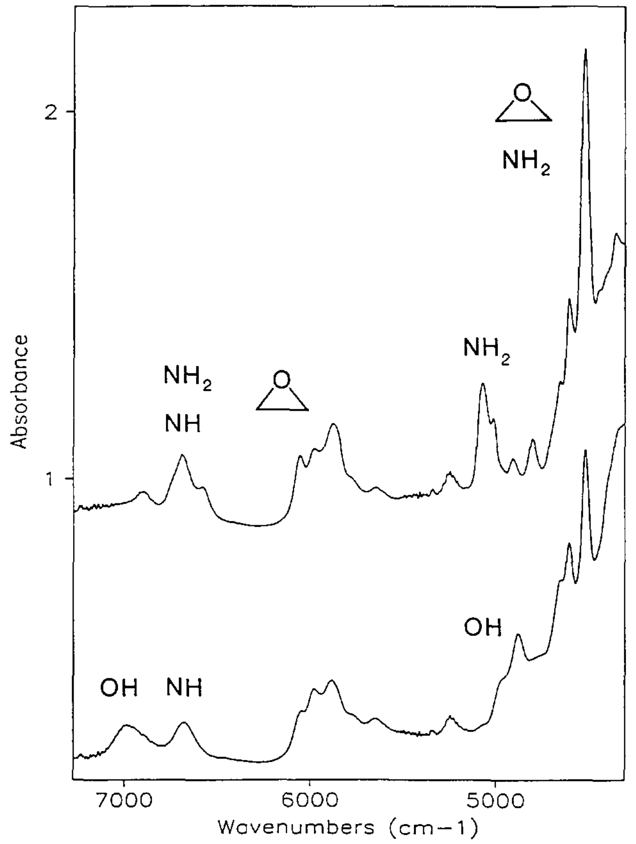

Figure 2 Near-i.r. spectra of MY721 + 27% DDS at 170°C in a glass pan recorded using simultaneous set-up after 2 min (top curve, offset) and 40 min (bottom curve)

To determine the change in primary amine concentration, the combination band of the NH_2 bending fundamental (1625 cm^{-1}) and stretching fundamental (3450 cm^{-1}) which appears in the near-i.r. at 5067 cm^{-1} has been shown to be the most suitable for quantitative analysis[22] as it is well resolved and not overlapped. This band has been shown to obey Beer's law in the early stages of the cure of the TGDDM/DDS resin[22] and this forms the starting point for the quantitative analysis of the absolute concentration of the functional groups throughout the cure cycle, since a molar absorptivity for this band may be determined from the known molar mass and starting concentration of primary amine (DDS).

While the primary amine concentration may be determined directly, the secondary amine concentration requires the solution of a set of simultaneous equations, since the main absorption band at 6685 cm^{-1} is strongly

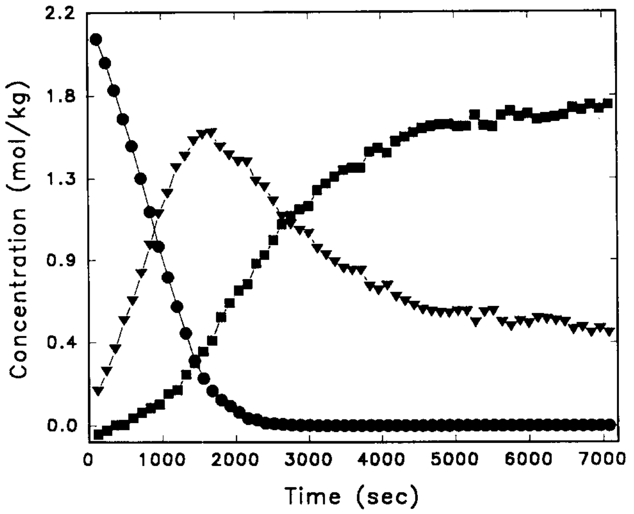

Figure 3 Plot of primary (●), secondary (▼) and tertiary (■) amine concentrations *versus* cure time at 170°C calculated using near-i.r. spectra

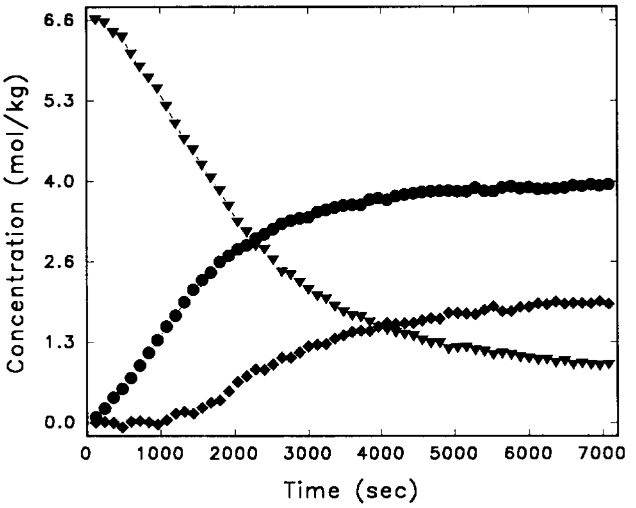

Figure 4 Plot of eopxy (▼), hydroxyl (●) and ether (◆) group concentrations *versus* cure time at 170°C calculated using near-i.r. spectra

overlapped by the overtones of the symmetric and assymetric stretching vibrations of the primary amine[21]. However, since the absolute concentration of primary amine at any time is known, the absolute secondary amine concentration may be determined with high precision. The only assumptions inherent in this analysis are: (1) that the secondary amine undergoes no reaction in the first 6 min of cure where the primary amine–epoxy reaction is dominant, which is supported by many independent studies[9,11]; and (2) that the secondary amine arises only from this primary amine–epoxy reaction.

The hydroxyl group appears as strong bands at 4897 cm^{-1} (the combination of stretching and bending vibrations) and at 6970 cm^{-1} (first overtone of the stretching fundamental) but these only represent the non-hydrogen-bonded species. While both bands increase throughout the cure cycle, the majority of hydroxyl groups are hydrogen bonded to amine and sulphone groups, which produces a broad underlying band unsuitable for quantitative analysis. However, it is possible to calculate the increase in hydroxyl groups since, as shown in equations (1) and (2), every molecule of amine reacting with epoxy produces a hydroxyl group, while the etherification reaction (3) produces no net increase in hydroxyl concentration.

Two key functional groups in equations (1) to (3) cannot be determined by spectral analysis in the near-i.r., since they have negligible intensity at the path length used in the d.s.c. cell. These are the tertiary amine (equation (2)) and the ether groups (equation (3)). The tertiary amine arises only from the reaction of secondary amines so it may be determined by the mass balance between the number of moles of secondary amine produced by equation (1) (i.e. the consumption of primary amine analysed at 5067 cm^{-1}) and the number determined by analysis at 6685 cm^{-1} to be present in the sample, i.e. at any time during cure the sum of primary, secondary and tertiary amine groups must be equal to the initial concentration of DDS.

The concentration of epoxy groups which are consumed by the etherification reaction (3) may be determined by comparing the number of moles of epoxide consumed in reactions (1) and (2) (by the change in amine group concentration described above) with the total number of moles analysed in the near-i.r. from the absorbance of the band at 4520 cm^{-1} after correction for the underlying primary amine band. Again, the concentration of ether linkages cannot be determined directly as this band carries no intensity in the near-i.r.

In the spectral analysis described above, the individual regions are expanded, corrected to a constant baseline and band areas used where possible for quantitation. By analysing spectra at 2 min intervals throughout the isothermal d.s.c. run it is possible to construct concentration–time plots of primary, secondary and tertiary amine, epoxide, hydroxyl and ether groups, as shown in *Figures 3* to *6*. The concentration–time data may then be differentiated to obtain instantaneous reaction rates for each group, which can be compared with the heat flow data generated at the same time.

Concentration profiles during cure

Figures 3 and *4* show absolute concentration changes in the functional groups of reactions (1) to (3) at 170°C while *Figures 5* and *6* show the data obtained at 150°C.

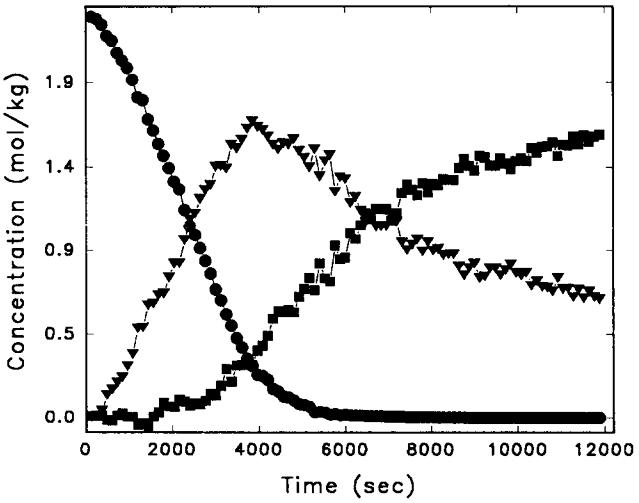

Figure 5 Plot of primary (●), secondary (▼) and tertiary (■) amine concentrations *versus* cure time at 150°C calculated using near-i.r. spectra

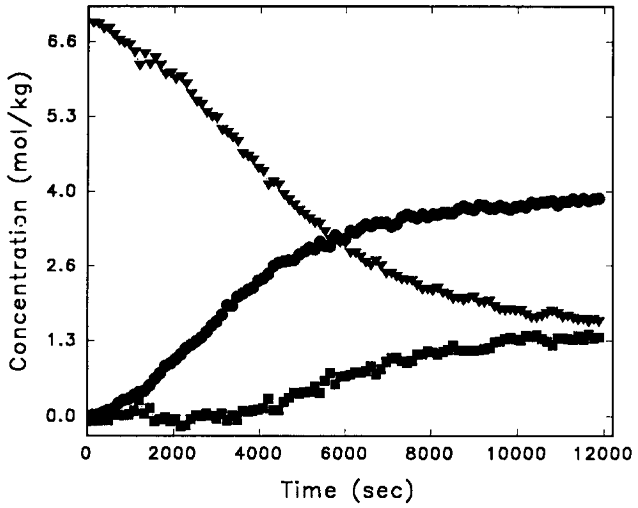

Figure 6 Plot of eopxy (▼), hydroxyl (●) and ether (■) group concentrations *versus* cure time at 150°C calculated using near-i.r. spectra

In both cases the data are collected to the point where negligible further heat flow in the d.s.c. has occurred. It may be seen that this corresponds to an extent of reaction of epoxide of 0.87 and 0.76, respectively. The curve profile for epoxide consumption is consistent with an autocatalytic reaction mechanism involving the hydroxyl group[23].

It is of particular interest to compare the profile for etherification with that for tertiary amine production, since this compares the competition between reactions (2) and (3). This comparison must be made after the first 6 min of reaction since the determination of the concentration profile of the secondary amine is made by deconvolution of the i.r. spectra, assuming that primary amine groups are the only reactive centres in the very early stages of cure at all temperatures. It is seen that at 170°C the concentration of tertiary amine groups is comparable to that of ether groups calculated from the excess epoxy reaction. At 150°C the etherification is less significant, which reflects the higher activation energy for reaction (3) compared to reaction (2). The etherification reaction was totally ignored in many early d.s.c. studies of cure kinetics[6] and later studies showed it to be favoured at higher temperatures[11]. Most recent modelling studies have shown that it is necessary to include reaction (3) in order to obtain curve fits to d.s.c. data, but these have been limited by assumptions of equal reactivity of primary and secondary amine[8,9]. Gupta *et al.*[13] in a comparative study of the cure of N,N'-dimethyldiphenylsulphone mixed with DDS concluded that secondary amine–epoxy reactions were negligible and that etherification must therefore be the dominant reaction at their cure temperature of 177°C. This single observation appeared to conflict with the results from d.s.c. of a constant reaction enthalpy which had been interpreted by assuming complete reaction of the secondary amine and equal reaction enthalpies[7,19]. The concentration profiles of *Figures 3* to *6* clearly show that the consumption of secondary amine is not complete at the stoichiometry used here, and the competition of etherification with secondary amine reaction produces a network with a completely different structure than had previously been supposed. For example, the etherification reaction results in a lower ratio of hydroxyl groups per mole of epoxide consumed, since there is no net increase in hydroxyl concentration in reaction (3) while there is if reaction (2) is occurring. It has also been suggested, based on n.m.r. data on model compounds[23], that much of the etherification reaction is intramolecular, leading to cyclization and no increase in crosslink density. This is less likely to be occurring at the early stages of cure where the mobility is high and a significant fraction of the linkages should be intermolecular. Cyclization due to intramolecular reaction of the secondary amine is more likely in the glassy state, where the lack of mobility prevents increased crosslinking and there is evidence from n.m.r. that such structures are formed[24].

From the concentration profiles in *Figures 3* to *6* the instantaneous reaction rates for the reactions (1) to (3) may be determined throughout cure. These may then be compared to the heat flow over the same time period from the calibrated isothermal d.s.c. trace.

Comparison of absolute reaction rates with heat flow data at 170°C

The fundamental assumption in d.s.c. analyses of the cure of epoxy resins[6] including the TGDDM/DDS system[7] has been that reactions (1) to (3) have equal reaction enthalpies so the d.s.c. heat flow curve under isothermal conditions represents the instantaneous rate of reaction of the epoxide. Evidence to support this simplifying assumption has been the observation[19] that the total heat of reaction of TGDDM/DDS is insensitive to variations in the amine to epoxide mole ratio from 0.61 to 1.14, and the heat released in the reaction model systems (phenylglycidyl ether-aniline) increased linearly with conversion[23]. Consequently, it would be expected that the epoxy consumption rate obtained by differentiating the concentration–time curve in *Figure 4*, when multiplied by the average reaction enthalpy, would be identical to the isothermal d.s.c. curve obtained on the same sample at the same time. There is agreement from several authors[7,9] that if the assumption of equal reaction enthalpy is made, then the reaction enthalpy for epoxy–amine and epoxy–hydroxyl reactions is around $-105\,\mathrm{kJ\,mol^{-1}}$ epoxide. *Figure 7* shows the experimental heat flow data at 170°C together with the calculated heat flow curve using the epoxy consumption rate and scaling

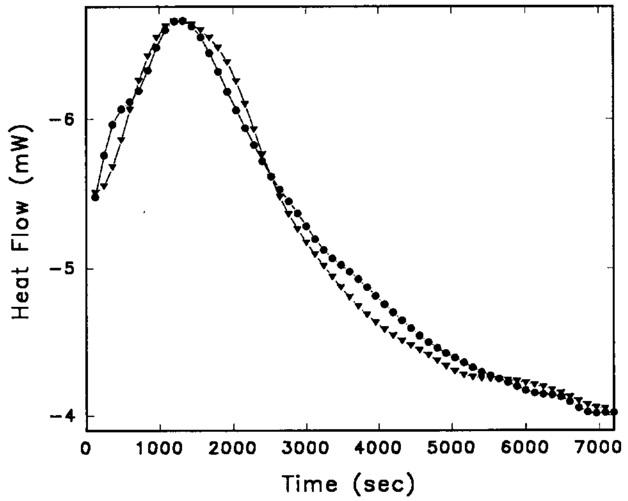

Figure 7 Plot of heat flow *versus* cure time at 170°C from isothermal d.s.c. (●) and calculated using epoxy data from near-i.r. assuming constant enthalpy for epoxide reactions (▼)

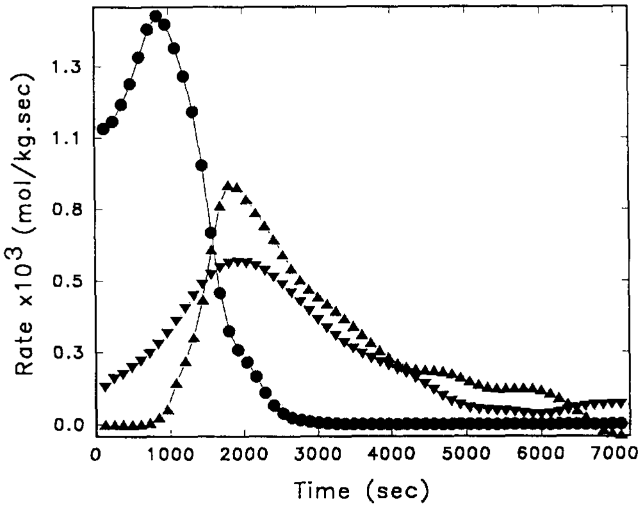

Figure 8 Plot of instantaneous reaction rates, d[PA]/d*t* (●), d[TA]/d*t* (▼) and d[ET]/d*t* (▼) *versus* cure time at 170°C calculated from near-i.r.

to a common maximum and end point, assuming a constant reaction enthalpy which in this case was found to be $-60\,\mathrm{kJ\,mol^{-1}}$. It is seen that there is a qualitative similarity between the two curves which could be within reproducibility if the experiments were performed separately. However, there are sufficient differences between the curves in this simultaneous method to warrant closer investigation. Also notable is the very low average enthalpy value of $-60\,\mathrm{kJ\,mol^{-1}}$ compared to the literature value of $-105\,\mathrm{kJ\,mol^{-1}}$.

Reaction enthalpies

In order to obtain a closer fit between the calculated and observed heat flow curves in the early stages of cure it is necessary to remove the constraint of equal reaction enthalpies for reactions (1) to (3). This involves using the instantaneous reaction rates from primary amine, secondary amine and etherification reactions at 170°C obtained by differentiating the curves shown in *Figure 4*. The resulting rate curves are shown in *Figure 8* and these data were fitted to the heat flow ($\mathrm{d}H/\mathrm{d}t$) curve over the early stages of cure (before gelation at ~2100 s) using the relationship:

$$\mathrm{d}H/\mathrm{d}t=\Delta H_1\,\mathrm{d}[\mathrm{PA}]/\mathrm{d}t+\Delta H_2\,\mathrm{d}[\mathrm{TA}]/\mathrm{d}t+\Delta H_3\,\mathrm{d}[\mathrm{ET}]/\mathrm{d}t+C \qquad (4)$$

where [PA], [TA] and [ET] are concentrations of primary amine, tertiary amine and ether groups, respectively, H is enthalpy and C is a constant that represents the instrumental baseline. The parameters produced by the best fit correspond to $\Delta H_1=-83\pm2\,\mathrm{kJ\,mol^{-1}}$; $\Delta H_2=-131\pm9\,\mathrm{kJ\,mol^{-1}}$; $\Delta H_3=-65\pm6\,\mathrm{kJ\,mol^{-1}}$ and $C=-2.62\,\mathrm{mW}$. The value of C represents the asymmetry of sample with respect to the reference and for an isothermal experiment this is essentially due to the effect of the light that is focused through the sample. This effect has been observed to be constant in dynamic d.s.c. experiments and so is assumed to also produce a constant baseline shift in isothermal studies. A value for C of $-2.62\,\mathrm{mW}$ translates to a temperature shift of +0.84°C with respect to the reference. The heat flow curve calculated using these values with the instantaneous rates over the entire cure is shown in *Figure 9a* along with the d.s.c. measured heat flow data.

The fit of the data is now good over the region corresponding to the peak of the d.s.c. curve and up to gelation of the resin, but there is significant deviation at longer times and also a small deviation in the first 10 min. The anomaly at short cure time could represent an artifact due to thermal equilibration together with the assumed lack of secondary amine reactivity in the very early stages. Alternatively, it represents heat flow due to a reaction which involves species other than those described by reactions (1) to (3). It has been shown by near-i.r. and mid-i.r. analysis[12] and confirmed by *FT*-Raman studies[25] that at 160°C an impurity — *N*,*N*,*N*′-triglycidyl-*N*′-(2-hydroxy-3-chloropropyl)-4,4′-diaminodiphenylmethane — in the commercial resin MY721 undergoes a dehydrochlorination reaction to produce a cyclic product by backbiting on the aromatic ring. This cyclic product has also been reported in n.m.r. studies[24]. At 160°C this reaction occurs only in the first 40 min of cure[12] and could therefore explain the excess heat flow seen in the first 12 min at 170°C. The deviation at longer cure time is believed to be more fundamental in origin.

Heat capacity changes on cure

Figure 9b is the difference between the d.s.c. data and the calculated curve and, while the deviation at short time is seen as a peak, consistent with an excess reaction, the most significant anomaly is seen as a large baseline shift occurring from 2000 to 3800 s. The curve fit procedure made no assumptions regarding the baseline for the calculated heat flow curve other than a constant which was added to all the data. This is equivalent to assuming a flat baseline when analysing a d.s.c. curve, a procedure which assumes that there is no effect on the heat flow of the heat capacity changes occurring during the cure of the resin[7]. Changes in sample emissivity or

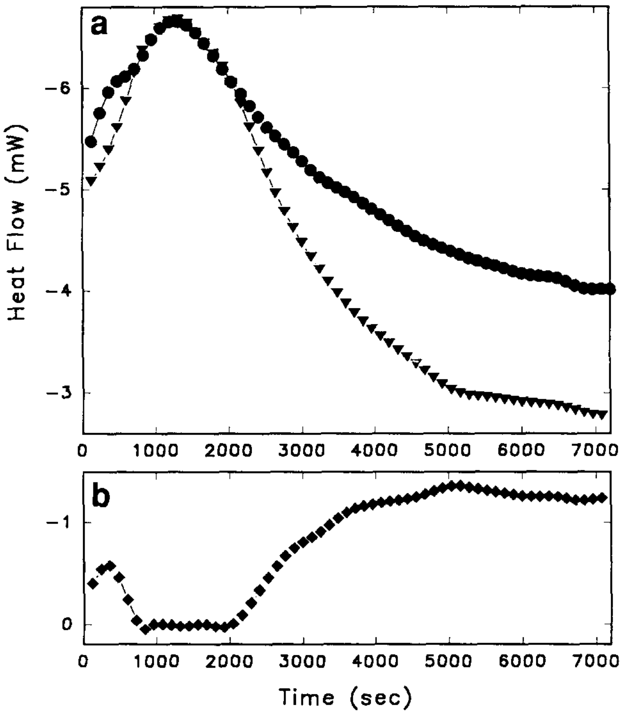

Figure 9 (a) Plot of heat flow *versus* cure time at 170°C from isothermal d.s.c. (●) and calculated using 'best fit' values with instantaneous reaction rate data from near-i.r. (▼). (b) Plot of measured minus calculated curves in (a) *versus* cure time at 170°C (◆)

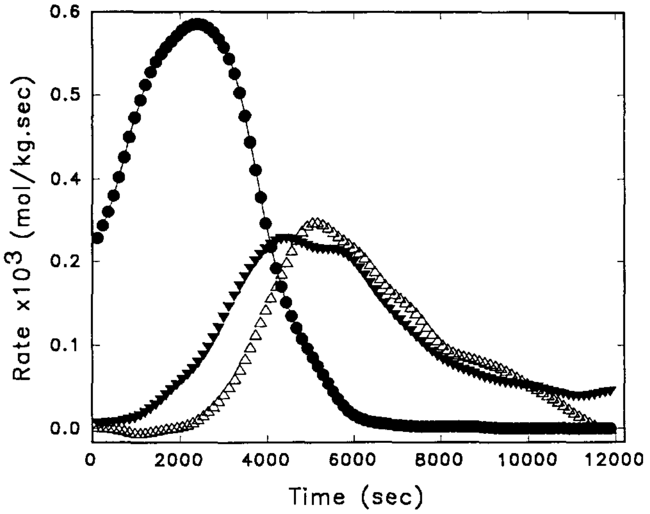

Figure 10 Plot of instantaneous reaction rates, d[PA]/d*t* (●), d[TA]/d*t* (▼) and d[ET]/d*t* (△) *versus* cure time at 150°C calculated from near-i.r.

increase in light absorption due to darkening of the sample during cure would be small effects compared to the large shift observed. Any effect of heat capacity change on calorimetric measurement during an isothermal experiment would not be expected with conventional symmetric heat flux or power compensation type d.s.c.; however, with the experimental arrangement used with the FP84 this may not be the case. It is therefore believed that the difference curve from 1000 to 7000 s in *Figure 9b* reflects the change[26] in heat capacity of the resin during isothermal cure at 170°C. This effect could not have been determined without the simultaneous spectral data.

Rheological studies may be used to determine the time of isothermal reaction at which the rubber-to-glass transition occurs. At 160°C this is reported[12] to occur in MY721 containing 27% DDS from 4800 s after the commencement of cure and the resin reaches a constant modulus after approximately 7500 s. It is therefore considered that the anomaly in the measured and calculated heat flow curves is consistent with a heat capacity change as the resin gels and then vitrifies. In quantitative analysis of the d.s.c. curve, such as the determination of the total enthalpy change for the isothermal cure reaction, it is necessary to subtract this baseline to obtain meaningful data. Comparison of *Figure 9b* with the individual reaction rate data in *Figure 8* shows that the significant chemical reactions of epoxide with secondary amine and hydroxyl groups are still occurring at a low rate even though vitrification of the resin has occurred. The reactions at this stage would be expected to be possible only over localized regions, and cyclization would therefore be expected to be dominant.

Reaction rates and heat flow during cure at 150°C

At 150°C the isothermal experiments are subject to greater error since both the heat flow and measured changes in reactant and product concentration are much lower than at 170°C. However, if the previous data analysis and interpretation are valid, the reaction enthalpies previously derived should produce agreement between the calculated and measured heat flow data at 150°C, and there should also be a discernible change in heat capacity through gelation and vitrification.

Figure 10 shows the instantaneous rate of reactions (1), (2) and (3) calculated from the near-i.r. concentration data in *Figures 5* and *6*. It can be seen that at the lower temperature the rate of reaction of secondary amine is initially greater but then becomes comparable to the etherification reaction through gelation and vitrification. When these reaction rates are converted to heat flow by using the reaction enthalpies obtained at 170°C ($\Delta H_1 = -83\,\mathrm{kJ\,mol^{-1}}$; $\Delta H_2 = -131\,\mathrm{kJ\,mol^{-1}}$; $\Delta H_3 = -65\,\mathrm{kJ\,mol^{-1}}$) and a best fit baseline value of $-2.75\,\mathrm{mW}$ (equation (4)), the curve shown in *Figure 11a* is obtained. It is seen that there is agreement with the measured d.s.c. heat flow up to approximately 6000 s, except for the initial higher heat flow attributed to an impurity cyclization reaction[12] and a difference around the maximum, possibly an artifact due to poorer quality data at 150°C.

Figure 11b shows the difference between the measured and calculated heat flow curves and there is again a step change (in this case from 6000 to 8000 s) followed by a constant difference up to 12 000 s. This step change is similar to that from the resin at 170°C (*Figure 9b*) except that it is occurring at longer time, which is consistent with the longer gel time at the lower temperature. This new baseline may be used to determine the total enthalpy change for isothermal cure at 150°C.

Comparison with 'conventional' d.s.c. analysis of cure

The previous sections have shown that the simultaneous technique can achieve a level of information on the enthalpy changes for the epoxy–amine reactions and the heat capacity changes under isothermal conditions which was not possible by d.s.c. alone. One of the most common experiments previously used to determine the extent of

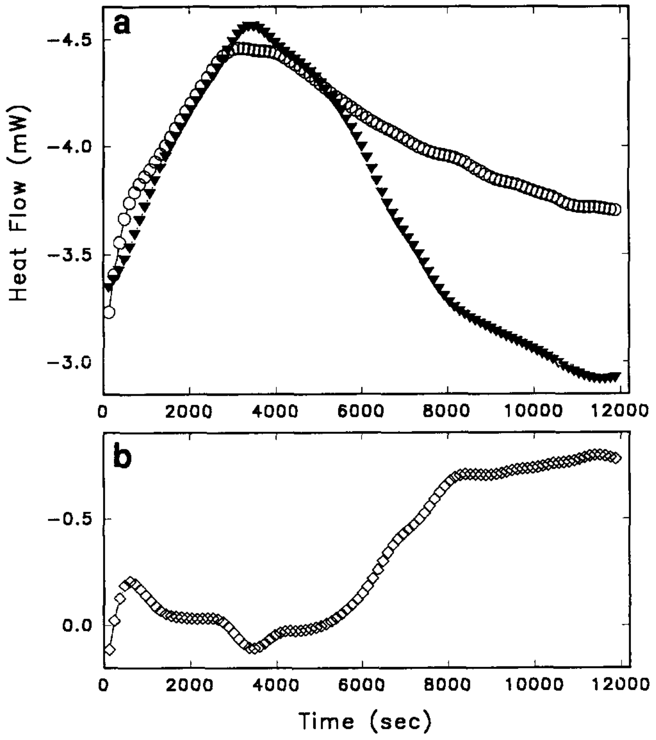

Figure 11 (a) Plot of heat flow *versus* cure time at 150°C from isothermal d.s.c. (○) and calculated using 'best fit' values calculated at 170°C with instantaneous reaction rate data from near-i.r. (▼). (b) Plot of measured minus calculated curves in (a) *versus* cure time at 150°C (◇)

cure as a function of time at a constant temperature was to measure the isothermal d.s.c. curve until there was no further heat flow, and then to measure the residual heat of reaction by scanning until no further heat was evolved[6,9]. In aliphatic amine cured systems this generally occurred at temperatures below 130°C but in aromatic amine cured systems the higher temperatures of cure of the weaker base generally required post-cure above 200°C, so that degradation reactions may have contributed to the total heat flow thus falsifying the total heat of reaction[11,27]. This limitation may be overcome by measuring the concentration of functional groups (epoxide and amine) present at the end of isothermal cure and so determining the extent of conversion and the reaction enthalpy directly[7]. This has been demonstrated for the model system, phenylglycidylether and n-butylamine, where the reaction product was soluble and could be determined by titration after d.s.c. It was determined that the heat of reaction of $102 \pm 2.5\,\mathrm{kJ\,mol^{-1}}$ epoxide was independent of extent of conversion or stoichiometry. However, the insolubility of the difunctional (and higher functionality) commercial epoxy resins after cure has limited this approach and most studies have been carried out by using scanning d.s.c. to high temperatures to determine either the excess heat of reaction in isothermal experiments or, more frequently, to study the entire cure reaction. In the latter experiments on TGDDM/DDS, heating up to 280°C was required for total reaction and it is extremely likely that at these temperatures a variety of reactions, including epoxide homopolymerization and degradation, are contributing to the total heat of reaction[11].

As the simultaneous technique can provide the concentration of the epoxide at any stage of the isothermal cure, it is of interest to compare the values obtained for the reaction enthalpy per mole of epoxide after isothermal cure at 170°C and after determining the residual heat by scanning to 300°C. If the prevailing view that the contributing reactions, for example (1) to (3) described before, have equal enthalpies is correct, then it would be expected that the overall enthalpy change would be independent of the extent of conversion. After isothermal cure at 170°C for a longer time than shown in *Figure 9*, the near-i.r. analysis of epoxide shows an extent of conversion of 0.92. The dynamic d.s.c. scan after this to 300°C resulted in total consumption of epoxide and an average reaction enthalpy of $-132\,\mathrm{kJ\,mol^{-1}}$ epoxide. This is to be contrasted with the isothermal value of $-60\,\mathrm{kJ\,mol^{-1}}$ epoxide obtained using the usual flat extrapolated baseline construction[7] on the d.s.c. data shown in *Figure 9a*. If the change in baseline demonstrated in *Figure 9b* is taken into account in the enthalpy calculation, an average isothermal enthalpy of reaction at 170°C of $-91\,\mathrm{kJ\,mol^{-1}}$ epoxide is obtained. This value is much lower than the $-132\,\mathrm{kJ\,mol^{-1}}$ epoxide obtained for the residual reaction from the dynamic d.s.c. scan to 300°C and probably results from the difference in reaction enthalpies for reactions (1) to (3) as opposed to that previously proposed. The primary amine–epoxide reaction dominates the early stage of cure, as shown in *Figure 7*, with an enthalpy of $-83\,\mathrm{kJ\,mol^{-1}}$. The secondary amine and etherification reactions dominate the later stages of cure with calculated enthalpies of $-131\,\mathrm{kJ\,mol^{-1}}$ and $-65\,\mathrm{kJ\,mol^{-1}}$, respectively.

The use of dynamic d.s.c. scans in the determination of accurate heats of reaction and extent of epoxide reaction must be open to question for the TGDDM/DDS system when one considers these results. The change in favoured reactions and thus heat flow at the higher temperatures used in dynamic d.s.c., suggested by our observations, has been noted for other high functionality, high temperature curing systems[27]. Mid-i.r. *FT*i.r. analysis[11] has shown that both degradation and cure reactions other than (1) to (3) occur in TGDDM/DDS to a significant degree at temperatures higher than 200°C.

Notwithstanding these limitations, the combined isothermal/dynamic d.s.c. technique has been widely employed in fundamental studies of TGDDM/DDS reaction kinetics. This produces deviations in the extent of reaction plots for isothermal cure, since the ultimate extent of cure is underestimated because of the larger contribution of the enthalpy calculated from the dynamic scan to the estimated residual epoxy concentration. *Figure 12* shows the actual epoxide conversion *versus* time plot at 170°C derived from near-i.r. analysis compared with that obtained using 'conventional' d.s.c. analysis of the same sample at the same time (i.e. integrating the isothermal heat flow curve with a flat baseline and correcting using the residual reaction enthalpy from a dynamic scan). While the two curves seem qualitatively similar and, if collected on separate samples, would probably be regarded as the same, there are noticeable differences between the *FT*i.r. and d.s.c. analysis. The error in overall conversion due to the high residual reaction enthalpy is seen and also the rate of reaction of epoxide in the region prior to gelation is also in error. In this region there is a positive deviation which, as previously discussed, is probably due to enthalpy of an impurity cyclization reaction.

While the differences shown in *Figure 12* are not significant in studies of the effect of temperature and stoichiometry on the overall extent of reaction or for qualitative comparisons between different curing agents, they become critical when d.s.c. data are used to determine possible reaction mechanisms[8–10]. There has also been widespread use of d.s.c. for chemorheological modelling of the process cycle of composite prepregs[3]. The incorrect estimation of the reaction rate prior to gelation will lead to the adoption of rate parameters which, while internally consistent for d.s.c. analysis, do

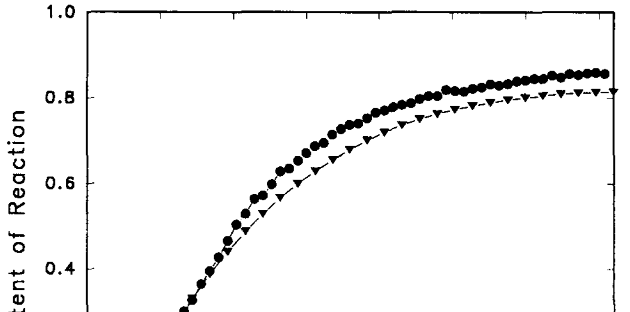

Figure 12 Plot of extent of reaction for epoxide *versus* cure time at 170°C calculated using group concentration data from near-i.r. (●) and 'conventional' analysis of isothermal d.s.c. data (▼)

not accurately reflect the development of the crosslinked network which produces the observed changes in rheology in a curing system.

Perhaps the greatest divergence between the data generated in the simultaneous technique and conventional d.s.c. analysis lies in the values attributed to the individual enthalpies of reaction. The near-i.r. data analysis, when combined with the d.s.c., has shown that reactions (1) to (3) cannot have equal enthalpies as believed from model studies and scanning experiments. However, while it is not surprising that the overall isothermal reaction enthalpy ($-92 \pm 1\,\mathrm{kJ\,mol^{-1}}$ epoxide) is lower than that obtained by scanning to high temperatures ($-110\,\mathrm{kJ\,mol^{-1}}$ epoxide) it is surprising that when the individual values for reactions (1) and (2) are determined, ΔH_1 is $-83\,\mathrm{kJ\,mol^{-1}}$ compared to $-131\,\mathrm{kJ\,mol^{-1}}$ for ΔH_2. A simple thermochemical bond enthalpy calculation would lead to values for ΔH_1 and ΔH_2 which were similar. One possible explanation for the lower ΔH for the primary amine–epoxide reaction is the formation of a stable donor–acceptor complex when the reagents are mixed at temperatures lower than that for appreciable reaction to occur. Rozenberg[23] has considered the thermodynamics of such complexes, and enthalpies of formation of $-20\,\mathrm{kJ\,mol^{-1}}$ are possible in model systems. The most relevant recent study concerns the dielectric properties of a diglycidyl ether of bisphenol A/DDS epoxy resin system when heated to the cure temperature[28]. It was found that the dielectric properties could only be explained by the formation of a polar entity as an intermediate between the mixing of the two reagents and the commencement of the chain-extending reaction. Below 125°C the formation of the entity was reversible, but above this temperature the polar species disappeared due to reaction. While the formation of such complexes has been considered in detail[23] their importance has been dismissed because of the apparent constant reaction enthalpy found for a wide range of different epoxy resin–amine systems throughout the cure[23]. It has therefore been believed that there was some 'compensation effect' of the various donor–acceptor interactions such that the contribution to the overall reaction enthalpy cancelled out. It has been shown in our investigations that the assumption of equal reaction enthalpy in the TGDDM/DDS system at the stoichiometry and temperature investigated cannot be supported, and indeed, the lower enthalpy change for the primary amine–epoxy reaction is consistent with reaction taking place from a preformed complex between the two reactants. Further research using the simultaneous d.s.c.–*FT*i.r.–near-i.r. technique and model systems may help to elucidate the role of such complexes.

There have been few studies of the reaction enthalpies for epoxy–hydroxyl reactions which may be compared with the value of $\Delta H_3 = -65\,\mathrm{kJ\,mol^{-1}}$ from this study. Apicella *et al.*[18] studied the reaction of MY720 with isopropanol and from their calorimetric data a reaction enthalpy of $-85\,\mathrm{kJ\,mol^{-1}}$ epoxide has been estimated (assuming an epoxy equivalent weight of 120 for MY720). Though higher than our value, it supports the finding of a lower reaction enthalpy for etherification than for secondary amine reaction.

CONCLUSIONS

An instrumental method has been described for obtaining the absolute concentration of reactive groups by near-i.r. spectroscopy while measuring the heat flow by isothermal d.s.c. during the cure of a commercial tetraglycidyldiaminodiphenylmethane epoxy resin (MY721) with DDS. Analysis of the reaction rates of epoxide groups with primary amine, secondary amine and hydroxyl groups at 170°C allowed the heat flow during the cure to be calculated using the generally accepted equal reaction enthalpies for all epoxide reactions. It was found that there was poor agreement between the measured and calculated heat flows.

Curve fitting of the reaction rate data from near-i.r. analysis to the heat flow data from d.s.c. at extents of conversion before gelation yielded the reaction enthalpy values $\Delta H_1 = -83\,\mathrm{kJ\,mol^{-1}}$, $\Delta H_2 = -131\,\mathrm{kJ\,mol^{-1}}$ and $\Delta H_3 = -65\,\mathrm{kJ\,mol^{-1}}$ for primary amine, secondary amine and hydroxyl reactions with epoxide, respectively. The lower value of $-\Delta H$ for primary amine–epoxide reaction would be consistent with the formation of a stable donor–acceptor complex preceding reaction. When these values were used in turn to calculate a heat flow curve for the entire cure, a significant deviation was observed from the measured heat flow curve, which was consistent with the effect of a decrease in the heat capacity of the resin on vitrification. This enabled a 'true' baseline to be calculated for the isothermal cure as studied by d.s.c. The enthalpy values obtained at 170°C were also found to be in agreement with the near-i.r. and d.s.c. data obtained at 150°C, suggesting consistency in both the reaction enthalpy values and heat capacity effects determined.

An average enthalpy of reaction for epoxide of $-92 \pm 1\,\mathrm{kJ\,mol^{-1}}$ was calculated from the isothermal d.s.c. at 170°C and 150°C using the determined baselines. This is lower than the value of $-105\,\mathrm{kJ\,mol^{-1}}$ reported from dynamic d.s.c. results, suggesting a contribution of highly exothermic homopolymerization and degradation reactions at the high temperatures used in the scanning experiments. It was found that using scanning d.s.c. to determine the residual epoxide content after isothermal runs caused the final extent of reaction to be underestimated. These results indicate a limitation to the use of scanning d.s.c. experiments alone to obtain precise kinetic information on the cure of epoxy resins such as the TGDDM/DDS system.

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