Polymer 41 (2000) 8221–8229

polymer

www.elsevier.nl/locate/polymer

Quantitative analysis of bismaleimide-diamine thermosets using near infrared spectroscopy

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Received 16 April 1999; received in revised form 12 January 2000; accepted 15 March 2000

Abstract

A method is reported for studying the polymerisation kinetics of a commonly used bismaleimide monomer, 1,1′-(methylenedi-4,1-phenylene)bismaleimide (MDP-BMI) with aromatic diamines such as 4,4′-diaminodiphenylmethane (DDM). Fourier-transform near infrared (FT-NIR) spectroscopy was used to obtain quantitative data using an in-situ technique. The NIR technique was used to measure the concentration of the various functional groups in the BMI/diamine resins with respect to time during isothermal cure. Quantitative data were obtained for all the functional groups in the resins studied, either from direct measurement or from the mass balances involved in the reactions. In order to obtain truly quantitative data, Fourier self-deconvolution of the spectra was used to enhance peak separations and the determination of peak areas. A substantial difference in reactivity between primary and secondary amine was observed in the systems studied. This has significant implications for the modelling of the polymerisation kinetics where the conversions of primary and secondary amines have not been separately measured. Differences in the reactivities of different resin formulations where observed when the diamine was changed from DDM to 4,4′-diaminodiphenylsulphone (DDS). There is a strong suggestion that one of the initial reaction products has a catalytic effect on the reaction, at least when using DDS as the diamine. The most likely identity of the species involved in this self-catalysis is the secondary amine formed by reaction of the maleimide double bond with a primary amine. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Bismaleimides; Thermosets; Near infrared spectroscopy

1. Introduction

Bismaleimides are a class of monomers widely used to produce thermoset polymers. The maleimide moiety is a five-membered imide ring containing a carbon-carbon double bond, an aliphatic or aromatic spacer group is included between the maleimide functional groups. The maleimide double bond is highly electrophilic due to the two adjacent electron-withdrawing carbonyl groups. Aliphatic bismaleimides can be used to produce flexible polymers, while aromatic bismaleimides are used to produce polymers with higher thermal stability.

Copolymerisation is possible with a wide range of functional groups due to the variety of chemical reactions possible through the maleimide group. This study has concentrated on bismaleimide/diamine chemistry, which forms the basis of commercial resins, such as the successful Kerimid 601 resin manufactured by Rhone-Poulenc [1]. In this resin the primary components are the bismaleimide, 1,1′-(methylenedi-4,1-phenylene)bismaleimide (MDP-BMI) and the diamine, 4,4′-diaminodiphenylmethane (DDM). A second diamine, 4,4′-diaminodiphenylsulfone (DDS), was included in the study in order to investigate what effect other similar monomers have on the mechanism and kinetics of polymerisation.

With bismaleimides, reaction occurs through the double-bond of the maleimide ring. Bismaleimide homopolymerisation can occur by a free-radical mechanism [2] either with addition of a free-radical initiator or thermally without need of a catalyst [3]. In a previous paper, we elucidated the mechanism for the un-initiated homopolymerisation of aromatic maleimides [4].

Several reactions are known to be involved in the cure of BMI/diamine copolymers. These are: (i) the chain-extension reaction of maleimide with primary amine; (ii) the cross-linking reaction of maleimide with secondary amine;

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PII: S0032-3861(00)00198-1

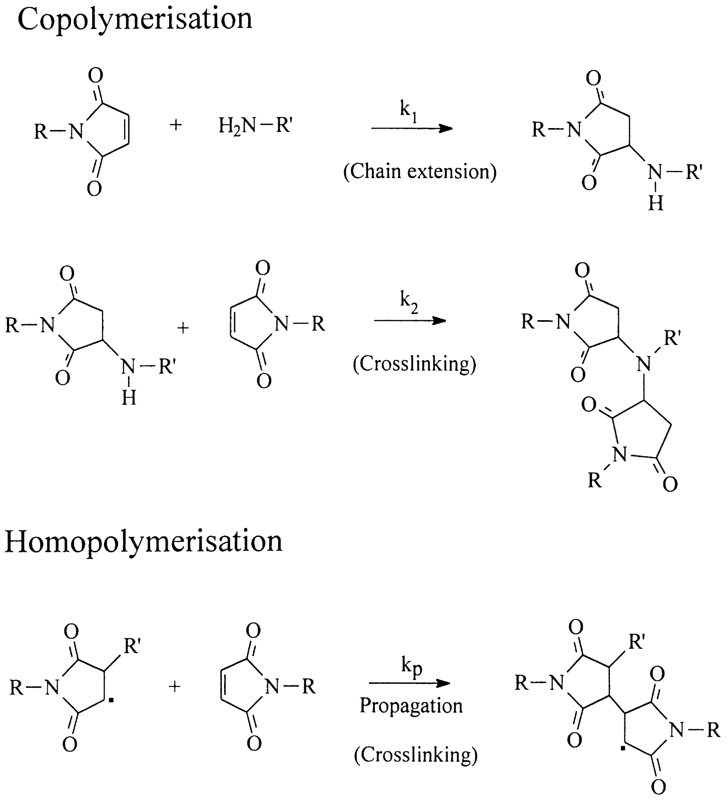

Fig. 1. General reaction scheme for BMI/diamine thermosetting resins.

and (iii) the free-radical homopolymerisation reaction. Fig. 1 summaries all three general reaction types that can occur in BMI/diamine resins. In the bismaleimide systems the copolymerisation with amine can occur as a step-growth polymerisation, as well as the chain-growth homo- polymerisation. Thus both chain-growth and step-growth polymerisation may occur simultaneously with the possibility of two different cross-linking reactions.

The final properties of a thermoset resin depend to a large extent on the chemical nature of the monomers utilised, but also depend on the actual kinetic pathway followed. This is because many thermoset properties depend on features of the network such as the cross-link density and residual monomer content. Therefore, knowledge of the polymerisation mechanism and kinetics allows optimisation of the polymerisation process and can possibly allow control of the structure of the resulting three-dimensional network.

Various spectroscopic techniques can be used to measure the time dependence of the functional group concentrations in the polymerising systems. However, part of the reason for the lack of fully quantitative kinetics of the BMI/diamine polymerisations has been the difficulty of analysing insoluble, intractable materials as thermosets. The traditional methods for characterising thermosets have been reviewed by Harrison [5]. Most of these techniques have limitations in regard to ease of use and accuracy. Advances in spectroscopic methods have opened up new possibilities for studying different aspects of thermoset materials. In recent years, several different forms of spectroscopy have been used to study the kinetics of epoxy and bismaleimide thermosets. These have included the techniques of Fourier-transform infrared (FT-IR) [6–8], Fourier-transform near infrared (FT-NIR) [9–12] and solid-state nuclear magnetic resonance spectroscopy [8,13,14].

In this study, a near infrared spectroscopic method was developed for obtaining quantitative data for the BMI/DDM and BMI/DDS thermoset systems. The infrared active bands in the NIR region between 4000 and 12,000 cm^{-1} are overtones and combinations of the fundamental vibrations [15]. An important feature of overtone and combination vibrational bands is that they have molar absorptivities orders of magnitude less than those of the associated fundamental vibrations. This allows the NIR path lengths to be very long compared with that possible in the mid-infrared (MIR) region and helps to ensure that the absorbance measurements are representative of the bulk samples. Because only vibrations between atoms of widely dissimilar mass have a high anharmonicity, and thus appreciable NIR absorptivity, NIR spectra are simplified compared with MIR spectra. However, the NIR bands are also much broader than those in the MIR, which can lead to more band overlap.

Despite the potential advantages outlined above, there have been remarkably few kinetic studies published concerning bismaleimide-based thermosets by NIR spectroscopy. However, recently a paper was reported in

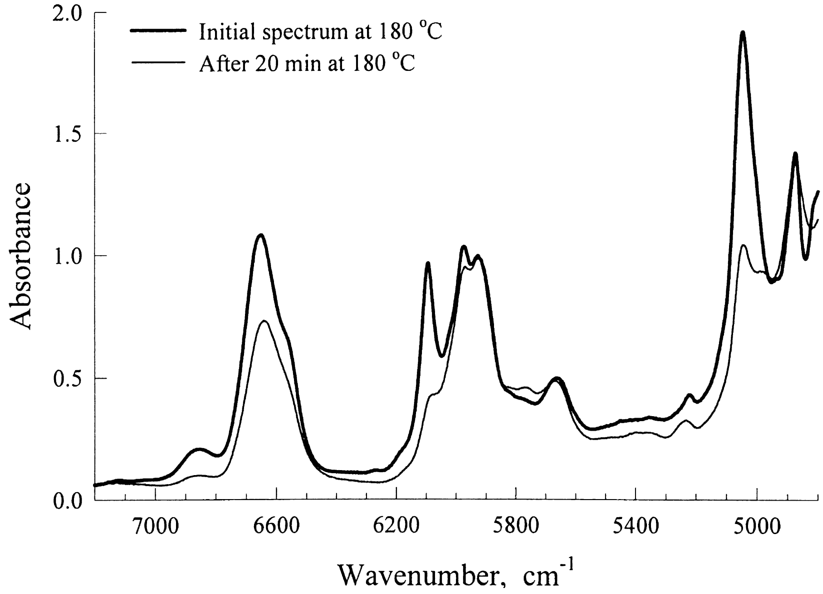

Fig. 2. NIR spectra for a 1:1 mixture of MDP-BMI and DDM, the initial spectrum and the spectrum after curing for 20 min at 180°C.

which FT-NIR was used to study a bismaleimide/diallyl system [12]. By contrast, NIR spectroscopy has found more use in studies of the cure of other network polymers, such as epoxy resins [9–11] and multi-functional acrylates like CR-39 [16].

In this paper a method is presented in which FT-NIR spectroscopy is used to quantitatively measure in-situ in real time the conversion of functional groups in two BMI/diamine resin systems.

2. Materials and methods

1,1′-(methylenedi-4,1-phenylene)bismaleimide (MDP-BMI) from Aldrich was purified by column chromatography using silica gel as the column support and eluting with chloroform. The elutant was reduced in volume on a rotary evaporator and the bismaleimide was then precipitated using methanol as the non-solvent. 4,4′-diaminodiphenylmethane (DDM) and 4,4′-diaminodiphenylsulfone (DDS), both obtained from Aldrich, were twice recrystallised from distilled water or an 80:20 water/methanol mixture, respectively.

The purified monomers were dried in a vacuum oven at 60–70°C for at least 24 h, before being weighed into a sample vial in the required amounts. The fine crystalline powders were then mechanically mixed. The mixtures were transferred into 5 mm external diameter Pyrex NMR tubes. All samples were degassed under high vacuum (<0.1 Pa) for 12 h and sealed either under high vacuum or after back filling to approximately 50 kPa with nitrogen.

Table 1
Assignment of band regions in the NIR for BMI/diamine resins

Peak region	Assignments
4800–5150 cm^{-1}	Primary amine combination bands ($\upsilon_{N-H} + \delta_{NH_2}$)
5350–5750 cm^{-1}	Aliphatic 1st overtones (υ_{C-H})
5750–6000 cm^{-1}	Aromatic 1st overtones (υ_{C-H})
6100 cm^{-1}	Double bond 1st overtone ($\upsilon_{C=C-H}$)
6400–7000 cm^{-1}	Primary amine 1st overtones (υ_{N-H})

A Mattson Instruments FT-IR spectrometer fitted with a tungsten lamp, a quartz beam splitter and a liquid nitrogen cooled mercury–cadmium–telluride (MCT) detector was used and spectra were acquired in the NIR region from 8000 to 4000 cm^{-1} with a resolution of 8 cm^{-1} and triangular apodisation. Usually 32 scans were co-added to give a good signal to noise ratio, but with particularly fast or slowly reacting samples, 16 or 64 scans respectively were co-added to give the final spectrum. NIR spectra were acquired at regular intervals under computer control.

For kinetic experiments, the sample tubes were inserted into a pre-heated aluminium block, with the temperature controlled by a Eurotherm thermostat. The temperature of the block was constant to within ±0.2°C of the set temperature over several hours.

3. Results and discussion

The near-Infrared spectra of the 1:1 MDP-BMI/DDM system initially and near full cure are shown in Fig. 2 The observed initial spectrum is a direct addition of the spectra of the two individual components, except for some minor changes due to hydrogen bonding effects. Identification of the various peaks was made by comparison with the literature [4,17]. Assignments were verified by calculating the expected peak positions for overtone and combination

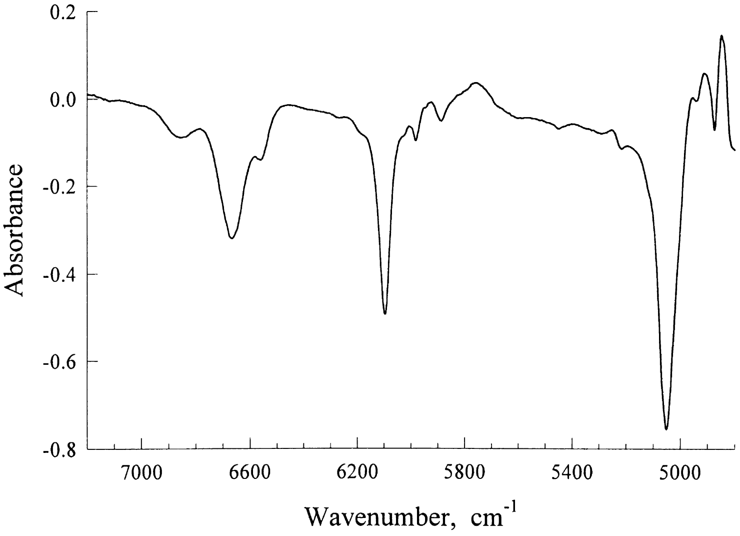

Fig. 3. Subtraction of the initial spectrum from that after 20 min of cure at 180°C for a 1:1 mixture of MDP-BMI/DDM.

bands from the peak wavenumbers in the mid-infrared [18–20]. These peak assignments are outlined in Table 1.

Fig. 2 shows the effect of cure on the overall NIR spectrum. The bands due to the reactive double bonds and primary amine groups are seen to decrease in intensity, while the aromatic overtone band stays constant and there is an increase in the region for aliphatic overtones. The overall line shape of the amine band envelope near 6700 cm^{-1} also changes during the cure.

Changes in the NIR spectra on curing can be seen more clearly by performing a subtraction of the spectrum of a neat, unreacted resin from that of a partially cured sample. In Fig. 3 there are three regions where the absorbance decreases during cure due to consumption of the maleimide double bonds (6100 cm^{-1}) and primary amine groups (5005 and 6700 cm^{-1}). Growing peaks are observed at around 5750 cm^{-1} due to formation of new methylene groups and at around 4800 cm^{-1} due to the formation of secondary amines.

Table 2
Peak assignment in neat resins of MDP-BMI and DDM

Peak (cm^{-1})	Assignment	
6920	Primary amine (υ_{asym})	
∽ 6750	(H-bonded)	
6670	Primary amine (υ_{sym})	Secondary amine peaks
6580	(H-bonded)	Co-incident
6095	Maleimide double bond overtone	
6020, 5980	Aromatic overtone peaks (several)	
5800–5650	Aliphatic overtone peaks (several)	
5065	Primary amine combination band ($\upsilon_{asym} + \delta_{NH_2}$)	
4990	(H-bonded)	
4940	Primary amine combination band ($\upsilon_{sym} + \delta_{NH_2}$)	
4860	(H-bonded)	Secondary amine peak(s) co-incident

There are several peaks within the band profile due to the primary amine functional group but only a single peak due to the maleimide double bond. This arises because primary amines have two fundamental stretching vibrations, in which the nitrogen-hydrogen stretch is either symmetrical or anti-symmetrical. The symmetric vibrational mode has a longer average bond length and therefore a lower wave number than the anti-symmetric vibrational mode. Both of these vibrational modes can be affected by hydrogen bonding.

3.1. Hydrogen bonding effects

Hydrogen bonding adds additional complications to the near-infrared spectra of amines. In a bismaleimide/diamine resin there are several potential sites for hydrogen bonding. The most common hydrogen bonds are expected to be those between the hydrogens of the primary amines and the oxygens of the carbonyl groups. Hydrogen bonding increases the bond length and therefore decreases the frequency of vibration, thus shifting the absorption to a lower wave number.

The NIR spectra of DDM diluted in diphenylmethane, DPM, where minimal hydrogen bonding would be expected, and of a neat 2:1 MDP-BMI/DDM resin mixture, where strong hydrogen bonding would be expected, were examined to observe the effect of hydrogen bonding on the amine band overtone. The spectra for the MDP-BMI/DDM mixture showed a slight shift in the amine peak at 6670 cm^{-1} and the shoulder at 6580 cm^{-1} increased in the intensity compared with these peaks for the DPM/DDM

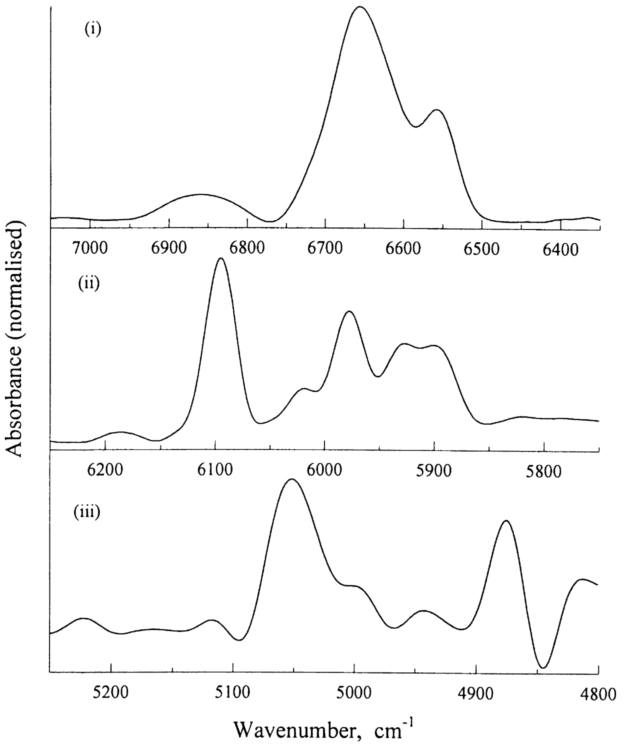

Fig. 4. Deconvolution of the NIR spectrum of 1:1 MDP-BMI/DDM: (i) 1° and 2° amine overtone band region; (ii) Maleimide double bond overtone; and (iii) 1° and 2° amine combination band region.

mixture, confirming the presence of significant hydrogen bonding interactions in the MDP-BMI/DDM system.

There are therefore four peaks expected in the NIR due to primary amine overtones; namely those from symmetric and anti-symmetric vibrations with and without hydrogen bonding. Four peaks are therefore also expected for the primary amine combination modes. The maleimide double bond gives a single peak. The complete peak assignments for the MDP-BMI/DDM resins are given in Table 2.

3.2. Quantification of NIR data

In this work, quantitative results from the NIR spectra were obtained for the concentration dependence of the three different reactive functional groups: maleimide double bonds, primary amines and secondary amines. The maleimide double bond gives rise to a peak at 6096 cm^{-1} in MDP-BMI that is not completely separated from the adjacent aromatic peaks. As a result, a simple measure of the peak height will not be proportional to the double bond concentration. In addition, some of the primary amine combination and overtone bands are co-incident with peaks arising from secondary amine groups formed in the same reaction. Fourier self-deconvolution (FSD) provides a means for separating the overlapping peaks and was used in this work. Details of the FSD technique have been described extensively in the literature [21–24].

Table 3
Deconvolution parameters used for BMI/diamine resins. All other decovolution parameters were the same for each region

Range (cm^{-1})	K	FWHH (cm^{-1})	Comments
5300–4750	1.6	56.0	1° amine combination peaks ($\upsilon_{\mathrm{asym}} + \delta_{\mathrm{NH2}}$) separated from 2° amine peaks.
6300–5300	1.6	44.0	Reasonable separation of maleimide peak achieved
7200–6300	1.4	80.0	1° amine υ_{asym} peak well separated from the rest 1° υ_{sym} and 2° amine peaks overlap

The spectra were analysed over three wavelength regions: (i) 7200–6300 cm^{-1}, which contains the primary and secondary amine overtone bands; (ii) 6300–5300 cm^{-1}, which contains all the aromatic, aliphatic and double-bond overtone bands; and (iii) 5300–4750 cm^{-1}, which covers the combination bands of primary and secondary amines as well as some other minor peaks. The reason for this is that each functional group peak requires a different set of deconvolution parameters to achieve the best results. Examples of the above deconvolutions are displayed in Fig. 4 for a sample of 1:1 MDP-BMI/DDM resin. Suitable deconvolution parameters were determined, and are given in Table 3. The peak areas of the deconvolved spectra were shown to obey the Beer–Lambert law, thus providing a means for obtaining the functional group concentrations.

3.3. Concentration of maleimide and primary amine

Fig. 5 shows a plot of the time dependence of the concentration of the functional groups (double bond and primary amine) for a 1:1 stoichiometric MDP-BMI/DDM resin cured at 170°C. The concentration of the double bonds is less than the concentration of the primary amine, as additional double bonds are consumed through the reaction with secondary amine to form tertiary amine cross-links, and also through maleimide homopolymerisation.

3.4. Concentration of secondary and tertiary amine

The concentration of tertiary amine cross-links can be calculated from the mass balance relationship

$$[\mathrm{PA}]_0 = [\mathrm{PA}]_t + [\mathrm{SA}]_t + [\mathrm{TA}]_t,$$

provided the concentration of the primary and secondary amines are known. Although secondary amines absorb in the near-infrared region, there is no way to directly measure the concentration of secondary amines from the NIR spectrum, because the secondary amine peaks overlap with primary amine peaks. This problem was address by utilising the methods reported by St John [25] and by Kozielski [11].

3.5. Extent of maleimide homopolymerisation

As well as the copolymerisation with amine, the

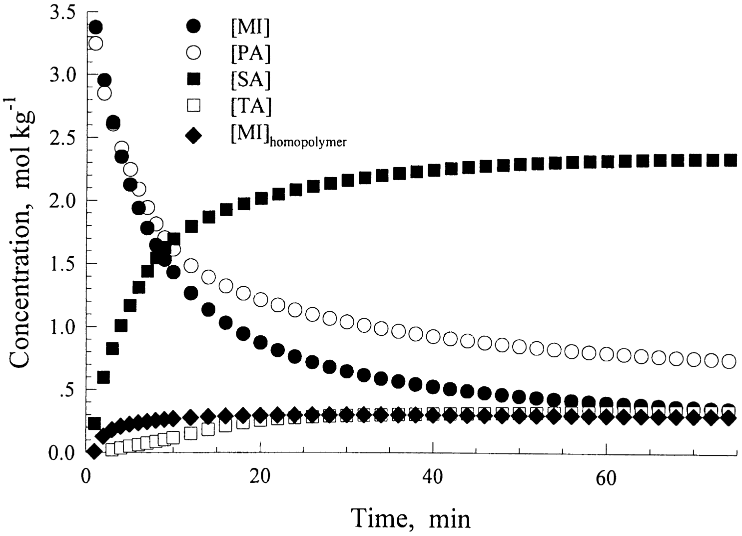

Fig. 5. Concentration of the various functional groups as a function of time for 1:1 MDP-BMI/DDM polymerised at 170°C.

homopolymerisation reaction of maleimides can occur in BMI/diamine resins at higher temperatures. As the copolymerisation reactions involve the consumption of maleimide double bonds through the reaction with amines, the amount of double bonds unaccounted for by reaction with primary or secondary amines was taken to provide a measure of the amount of double bonds consumed by the homopolymerisation reaction. The following equation was used to calculate the concentration of maleimide double bonds involved in homopolymerisation at any polymerisation time t:

$$[\mathrm{MI}]_{\mathrm{homopolymerization}} = ([\mathrm{MI}]_0 - [\mathrm{MI}]_t) - ([\mathrm{SA}]_t + [\mathrm{TA}]_t)$$

where the subscript '0' indicates the initial concentration.

Fig. 5 shows the concentrations of each of the functional groups plotted as a function of the cure time for a representative experiment and Fig. 6 shows similar data at 180°C. In both cases, a small amount of tertiary amine is formed. For MDP-BMI/DDM resins, the secondary amine is clearly less reactive than that of the primary amine in the nucleophilic addition reaction with maleimide double bonds. Thus, similar to the nucleophilic addition reaction of aromatic amines with epoxides [25], it is found that primary and secondary amines are of unequal reactivity.

The Figs. 5 and 6 show that maleimide homopolymerisation is comparatively rapid during the early stages of the reaction, but slows dramatically at longer times due to the decreased mobility in the network. These changes in the kinetics are caused by gelation and/or vitrification.

The cross-linking reactions associated with formation of tertiary amine and maleimide homopolymerisation are very important to determination of the final properties of the resins. The total amount of cross-linking can be calculated

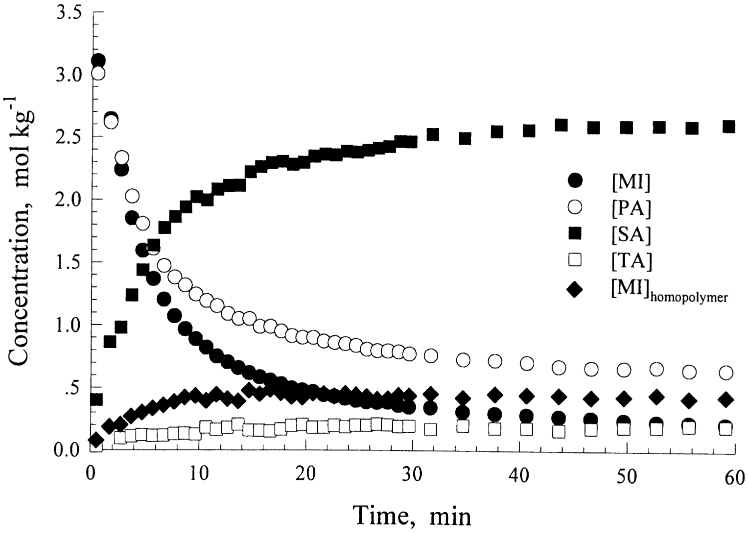

Fig. 6. Concentration of the various functional groups as a function of time for 1:1 MDP-BMI/DDM polymerised at 180°C.

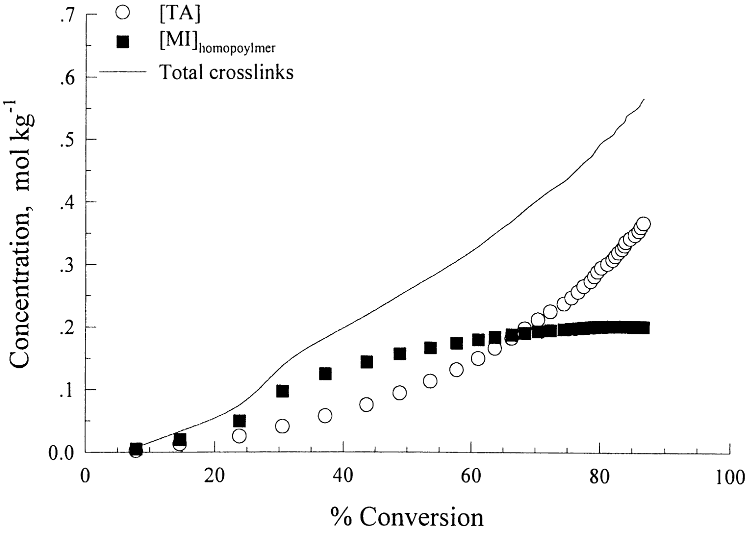

Fig. 7. Concentration of tertiary amine and homopolymerised maleimide cross-link sites for 1:1 MDP-BMI/DDM reacted at 170°C.

from the experimental FT-NIR data throughout the cure process. Fig. 7 shows how the concentration of cross-link sites, from both maleimide homopolymerisation and tertiary amine formation, increase with increasing conversion of the double bonds.

Interestingly, during the early stages of cure the concentration of tertiary amine cross-links is very low, while the amount of homopolymerisation is relatively high. At higher conversion, the amount of homopolymerisation almost becomes constant (that is, the reaction rate slows dramatically) while the concentration of tertiary amine cross-links continues to increase. Therefore, for a resin of a particular stoichiometry at a certain cure temperature, the relative importance of the two cross-linking reactions will vary during the cure.

For cure at a particular polymerisation temperature, changing the stoichiometry will have a large effect on the extent of the cross-linking reactions. Fig. 8 shows a plot of the extent of tertiary amine formation and maleimide homopolymerisation plotted as a function of the conversion of the maleimide double bonds at 160°C. Increasing the BMI content from a ratio of 1:1 to 2:1 ratio greatly increases the amount of homopolymerisation that occurs. This is a consequence of the maleimide homopolymerisation being dependent only on the concentration of one component - the maleimide functional groups. As a result, for the same overall extent of reaction, a resin with high BMI content is expected to be more highly cross-linked than one of lower BMI content.

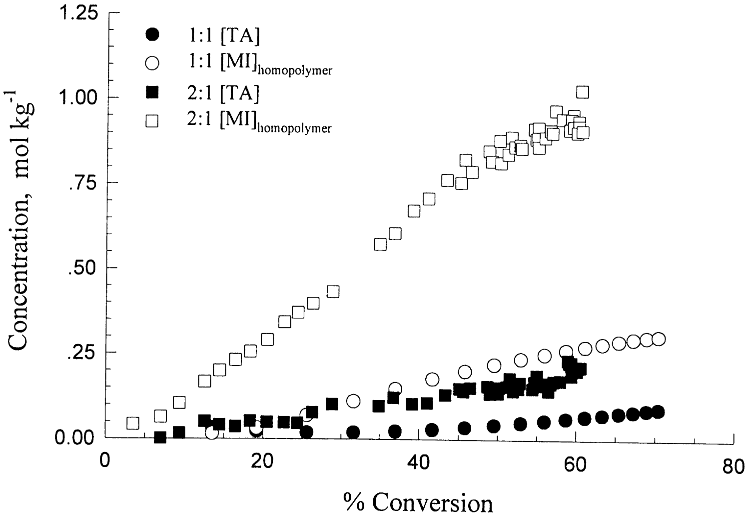

Fig. 8. Concentration of cross-linking sites as a function of the conversion of maleimide for two different stoichiometries of MDP-BMI/DDM during cure at 160°C.

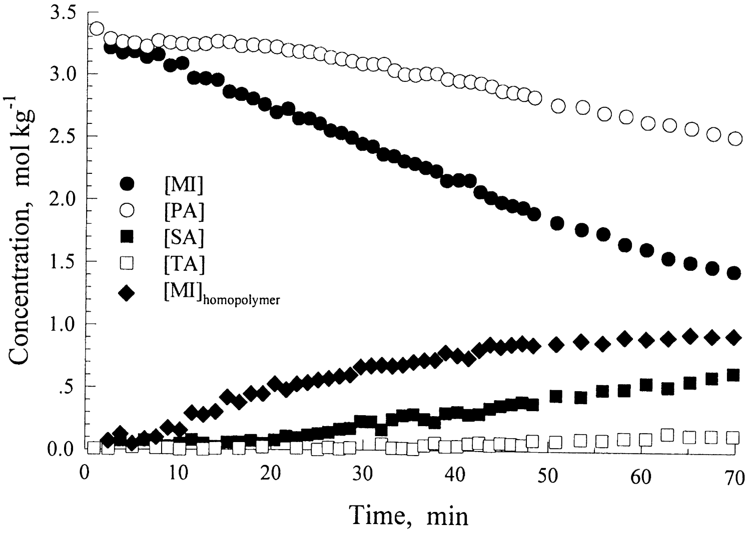

Fig. 9. Concentration of functional groups for 1:1 MDP-BMI/DDS reacted at 200°C.

3.6. Copolymerisation with DDS

To draw a comparison of another MDP-BMI/amine comonomer system with MDP-BMI/DDM, data were also obtained using DDS as the diamine instead of DDM. Fig. 9 shows the concentration of each of the functional groups for an equimolar mixture of MDP-BMI/DDS cured at 200°C. It can be seen that the DDS has much lower reactivity than DDM. There is also clear evidence of autocatalysis, because the rate of the primary amine reaction increases with time despite a concurrent decrease in the maleimide concentration.

The higher temperature of 200°C necessary to enable the Michael addition reaction with the weaker nucleophile DDS results in a much higher extent of homopolymerisation than found for the MDP-BMI/DDS copolymerisation.

4. Conclusions

NIR transmission spectroscopy is a powerful technique when used in conjunction with Fourier self-deconvolution to gather in-situ data on the cure of bismaleimides with diamines. The Beer-Lambert law was shown to apply in this system, allowing quantitative data to be obtained throughout the cure process. The concentration of maleimide double bonds and primary amines were measured in real time from the NIR spectra. The concentration of secondary amine could be determined by analysis of an overlapping band region in the NIR arising from both primary and secondary amines. Finally, the concentrations of the tertiary amines formed by reaction of the secondary amine, and of maleimide double bonds consumed by homopolymerisation could also be calculated.

For MDP-BMI/DDM resins the secondary amine was found to be less reactive than the primary amine in the nucleophilic addition reaction with maleimide double bonds. This contradicts the assumption made in a number of papers of equal reactivity of primary and secondary amines, when the concentrations of the individual amines were not measured.

The degree of maleimide homopolymerisation could be determined, but only occurs to a relatively small extent at the cure temperatures studied. It is however moderately rapid in the early stages of cure in maleimide-rich formulations. In all cases, the rate of homopolymerisation slows dramatically at higher conversion, presumably due to gelation or vitrification of the network.

Primary amines from DDS exhibited much lower reactivity with the maleimide double bonds than those in DDM, due to their decreased nucleophilicity. Plots of concentration against time show clear signs of autocatalysis in the MDP-BMI/DDS system.

A detailed discussion of the kinetics of the MDP-BMI/DDM resin system is presented in an accompanying paper.

Acknowledgements

The authors wish to acknowledge the financial support of the Australian Research Council for this work.

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