

# Comparison Between the Thermal and Microwave Curing of Bismaleimide Resin

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**ABSTRACT:** Microwave energy was used to cure Matrimid 5292A bismaleimide resin. The degree of cure at different cure times was determined with differential scanning calorimetry. A comparison was made with the same resin cured in a conventional oven. The resin cured faster in the microwave oven than in the conventional oven. The glass-transition temperature ( $T_g$ ) depended on the degree of cure. The samples cured with a conventional oven showed slightly higher  $T_g$ 's than the microwave-

cured samples at higher degrees of cure. At low degrees of cure, the two heating methods yielded materials with similar  $T_g$ 's. Fourier transform infrared spectroscopy and solid-state cross-polarity/magic-angle-spinning  $^{13}\text{C}$  NMR spectroscopy were used to investigate the cured structures. There was no difference in the chemical reactions taking place during the microwave cure and the thermal cure. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2764–2774, 2003

## INTRODUCTION

The microwave processing of thermosetting materials offers significant advantages over conventional heating, such as reduced cure cycles, more uniform curing, and improved physical and mechanical properties.<sup>1</sup> Microwave heating takes place through dipolar interactions between molecules and an alternating electric field rather than through thermal conduction or convection as in conventional heating. Microwave radiation penetrates materials, and the heat is generated internally. Studies on epoxy resin systems have shown that microwave processing significantly reduces the cure cycle without sacrificing the mechanical properties.<sup>2,3</sup>

Bismaleimide (BMI) resins are presently the best candidates to replace epoxy resins in high-performance composites because of their high temperature stability and resistance to hot and wet environments.<sup>4</sup> BMI resins contain reactive double bonds ( $\text{C}=\text{C}$ ) in the maleimide groups that can polymerize with or without the presence of a catalyst. Various curing reactions for BMI resin formulations have been suggested.<sup>5</sup> The main reaction proposed is homopolymerization via a free-radical mechanism.<sup>6</sup> Conventional curing processes involve heating in an oven, autoclave, or compression mold, in which heat transfer to

the material is accomplished through conduction or convection. Just as for other thermosetting materials, the low thermal conductivity of these resins leads to thermal gradients inside the resin, and the curing cycle becomes longer.

Initial studies of the microwave processing of BMI systems have been reported.<sup>7,8</sup> Researchers<sup>8</sup> found that the reaction kinetics in conventional and microwave ovens were identical under isothermal conditions. They concluded that no microwave effect could be observed. The term *microwave effect* implies the possibility of altering the rate and path of a chemical reaction to produce a different morphology and different physical and mechanical properties. The aforementioned researchers used *in situ* fiber-optic Fourier transform near-infrared spectroscopy to measure the extent of the reaction. Liptak et al.<sup>7</sup> however, found more rapid curing when microwave heating was used than when a conventional oven was used. They used extraction methods to determine the gel content in the cured resin. The apparent contradiction between these two reports is probably due to the different techniques used to cure and characterize the samples. Neither shows in detail the cure chemistry in microwave and conventional ovens. It is important to study the curing path because the final structure and mechanical properties of a network depend on the reaction path.

The objective of this study was to compare the cure chemistry of a BMI resin when conventional and microwave heating were used. The cure reactions were followed with spectroscopic techniques. The effect of

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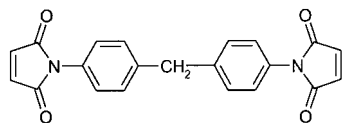


Figure 1 Chemical structure of Matrimid 5292A.

the sample size on the reaction rate in conventional and microwave ovens was also studied.

## EXPERIMENTAL

### Material

The BMI resin used was Matrimid 5292A (Ciba-Geigy). The chemical structure is shown in Figure 1.<sup>9</sup> The material was used as received.

### Curing procedures

#### Microwave processing

The sample was cured in a 60-mm-diameter, 10-mm-high Pyrex glass dish. A Moulinex Quickchef 1000QE microwave oven with a glass turntable and adjustable power settings was used. Initially, each sample was exposed to microwave radiation by being placed in the middle of the microwave cavity at the full-power setting (635 W). The samples were heated for different periods of time ranging from 6 to 11 min. Two different sample weights, 2.5 and 5.0 g, were used in this study. Part of each sample boiled after 10–12 min of heating. The curing procedure was then optimized to obtain a high degree of cure with few bubbles. This was achieved through the control of the microwave power setting and the placement of the sample where the microwave field was uniform.

The uniformity of the microwave power distribution within the cavity was determined by the heating of an epoxy slab and the observation of the variations in color from point to point. The microwave field was found to be uniform at the edge of the glass turntable. The optimized cure cycle for the microwave cure was as follows: first, each sample was heated at an average power of 473 W for 20 min, and then it was postcured at full power (635 W) for 3 min

#### Conventional oven processing

Conventional thermal curing was carried out in a circulating air oven (model 9-300, Townson and Mercer) at various times ranging from 15 min to 24 h. The samples were placed in the oven at room temperature before the oven was turned on and set to the required temperature. This step allowed the samples to heat up gradually and prevented exotherms and bubbles. The heating rates of the oven were as follows: from room temperature (25°C) to 190°C at 9°C min<sup>-1</sup> and from

190 to 210°C and from 210 to 250°C at 4°C min<sup>-1</sup>. For the study of the effect of the sample size, two different sample weights, 3.0 and 5.0 g, were cured isothermally at 190°C. For the study of the effect of the cure temperature, samples weighing 5 g were cured at 170, 180, or 190°C. Fully cured samples were prepared with the manufacturer's recommended procedure:<sup>10</sup> 2 h at 190°C, 5 h at 210°C, and 5 h at 250°C.

### Characterization techniques

#### Differential scanning calorimetry (DSC)

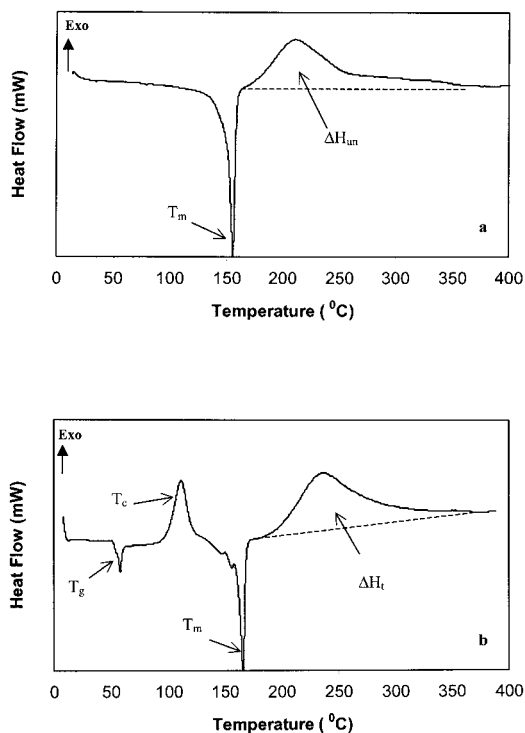
The thermal properties of the resins were investigated with a DuPont 900 instrument. The DSC cell was first calibrated with high-purity indium. The samples were heated from 25 to 400°C at a heating rate of 10°C min<sup>-1</sup> in flowing nitrogen at 40 mL min<sup>-1</sup>. The pans were closed but not hermetically sealed, and the sample weights were 8–12 mg. The samples were taken from the middle of the glass mold.

#### Glass-transition temperature ( $T_g$ )

DSC was used to determine  $T_g$  for samples with degrees of cure ( $\alpha_{DSC}$ ) below 0.7. A Polymer Laboratories dynamic mechanical thermal analysis (DMTA) instrument was used to determine  $T_g$ 's for samples with  $\alpha_{DSC} > 0.7$ . For the latter measurements, the samples were cut into rectangular bars (1.3 mm × 6.2 mm × 12.0 mm) and clamped rigidly from the fixed clamp to the driven clamp in a single-cantilever mode. The sample was heated from 10 to 300°C at a heating rate of 5°C min<sup>-1</sup> and a frequency of 1 Hz.  $T_g$  was taken to be the maximum in  $\tan \delta$ .

#### Structural analysis

The chemical structures of the cured samples were investigated with Fourier transform infrared (FTIR) spectroscopy and solid-state <sup>13</sup>C NMR spectroscopy. FTIR spectra were obtained with a PerkinElmer 2000 spectrometer. Each sample was pressed into a disc with dried potassium bromide (KBr) powder at a concentration of 1 wt %. Each spectrum was scanned from 4000 to 450 cm<sup>-1</sup> 32 times at a 2-cm<sup>-1</sup> resolution, and the spectra were coadded. Solid-state cross-polarity/magic-angle-spinning (CP-MAS) <sup>13</sup>C NMR spectra were run on a Varian Associates Unity spectrometer operating at 75.4 MHz and equipped with a Doty Scientific 7-mm CP-MAS probe. Powdered samples were packed into 7-mm zirconia or alumina rotors fitted with Kel-F end caps. The contact time was 2.5 ms, and the recycle time was 3 s. Approximately 500 cycles were time-averaged.



**Figure 2** Typical DSC curves of Matrimid 5292A: (a) uncured and (b) partially cured ( $\alpha_{\text{DSC}} = 0.18$ ).

### Sol-gel analysis

Residual monomer and other low-molecular-weight noncrosslinked materials were studied with sol-gel analysis. The analysis was carried out by the soaking of powdered samples in dichloromethane in a hot water bath at 50°C for 2 weeks. The insoluble portion was filtered with a glass-fiber filter, dried, and weighed.

## RESULTS AND DISCUSSION

### DSC analysis of the resin

A DSC curve obtained from uncured Matrimid 5292A is shown in Figure 2(a). The DSC curve shows a strong and sharp endothermic peak at 157°C that is immediately followed by an exothermic peak. The endothermic peak is due to the melting of crystalline regions in the resin.<sup>11</sup> The exothermic region is due to the curing reaction during the heating process and has a maximum at about 202°C. The area under the exothermic peak [or the total enthalpy of the curing reaction for an uncured resin ( $\Delta H_{\text{unc}}$ )], between 160 and 280°C, is 183.3 J g<sup>-1</sup>. There is no  $T_g$  in the DSC curve for the uncured resin, and this can be attributed to the fact that the resin is a crystalline material.

$\alpha_{\text{DSC}}$  has been calculated with the following equation:<sup>12</sup>

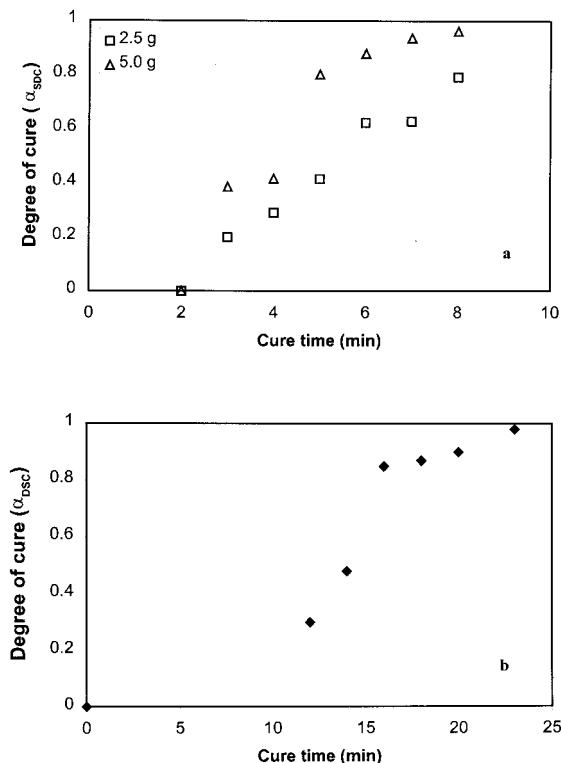
$$\alpha_{\text{DSC}} = 1 - \frac{\Delta H_t}{\Delta H_{\text{unc}}} \quad (1)$$

where  $\Delta H_t$  is the residual enthalpy of the reaction of a sample cured for time  $t$ .

Figure 2(a) shows the DSC curve of a partially cured sample ( $\alpha_{\text{DSC}} = 0.18$ ).  $T_g$  can be clearly observed at 55°C. An exothermic peak appears between 90 and 150°C as a result of cold crystallization during the DSC scan. Wang et al.<sup>13</sup> reported a similar observation when they studied another semicrystalline polyimide. This peak gradually decreases as curing proceeds and is not present in samples with  $\alpha_{\text{DSC}} > 0.45$ . The endothermic peak shifts from 157 (for the uncured resin) to 166°C.

### Curing rate

Figure 3(a) shows  $\alpha_{\text{DSC}}$  for 2.5- and 5.0-g samples after microwave curing as a function of the curing time. The value of  $\alpha_{\text{DSC}}$  increases with the curing time. The 5.0-g samples cure rapidly between 7 and 8 min, the value of  $\alpha_{\text{DSC}}$  increasing from 0.40 to 0.80 over this time interval. The value of  $\alpha_{\text{DSC}}$  then increases gradually to 0.98 after an 11-min cure time. The 2.5-g sample shows a slower curing rate than the 5.0-g sample, and this suggests that the heating rate is affected by the sample weight. The reason may be that the amount of micro-



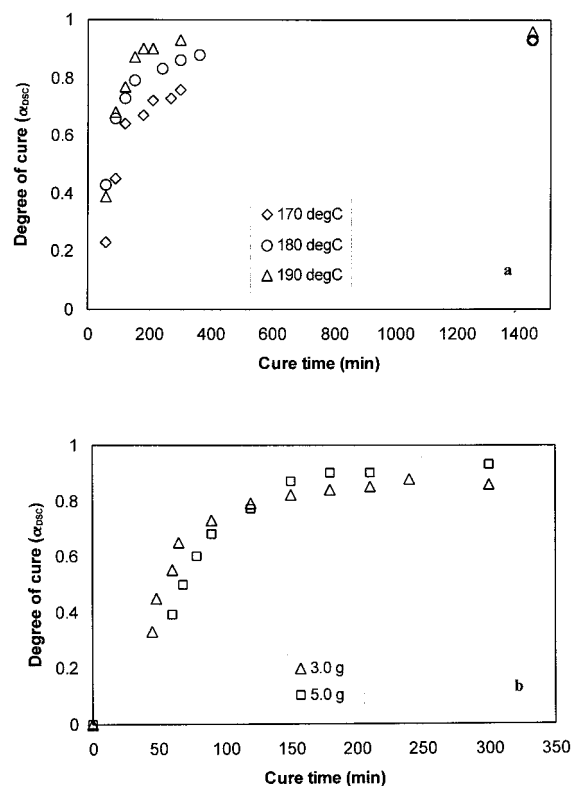
**Figure 3** Effect of the sample weight on  $\alpha_{\text{DSC}}$  as a function of time for the microwave curing of Matrimid 5292A after curing optimization.

wave radiation absorbed depends on the dielectric loss of a sample. The larger the sample volume is, the greater the absorption will be of microwave energy of the sample in comparison with the cavity, which has a fixed loss. Another reason is the slower rate of heat loss from the surface of a thick sample in comparison with a thin sample, particularly for BMI resins, which have very poor thermal conductivity.<sup>14</sup> Similar effects were observed by Demeuse and Johnson<sup>15</sup> when they studied the effect of the sample volume on the heating rate with variable-frequency microwave heating. They found that the thicker isocyanate/epoxy samples heated faster than the thinner samples. Theory also shows that the temperature at the center of a volumetrically heated slab will depend on the square of the thickness.

The value of  $\alpha_{DSC}$  as a function of time after cure cycle optimization is shown in Figure 3(b). Samples with high  $\alpha_{DSC}$  values (0.98) and few bubbles have been obtained. Some of each sample boils after 10–12 min of heating at full power because of the hot-spot effect. Nonuniform heating is common in multimode microwave cavities because of the variation of the microwave radiation with the position and because the outer layer cools more easily. Nightingale<sup>16</sup> used the same microwave oven for her studies and, using a sheet of partially cured epoxy resin, showed that the center part of the cavity was the area at which the microwave energy was most concentrated.

The value of  $\alpha_{DSC}$  as a function of time at 170, 180, and 190°C is presented in Figure 4(a). The rate of cure is highest at 190°C and lowest at 170°C, as expected. Matrimid 5292A resin contains only one type of monomer and thus undergoes homopolymerization after heat treatment.<sup>17</sup> The reactive species involved in the reaction are maleimide groups (C=C), and they react with one another through free-radical polymerization.<sup>18</sup> Generally, the curing process for the resin can be divided into four stages. The first stage is the melting process. In the microwave oven, the resin melts in only 6 min, whereas 15 min is needed in the conventional oven. As shown in the DSC curve [Fig. 2(a)], the as-received resin melts at 155°C.

The second stage is polymerization, which is shown as an exothermic peak in the DSC curve [Fig. 2(a)]. The resin starts to polymerize immediately after melting. The polymerization process involves free-radical addition reactions. According to Brown and Sandreczki,<sup>6</sup> in the initial step, biradicals are formed as a result of the thermal homolysis of the double bond in the maleimide groups. The biradicals then react with other maleimide groups to form propagation radicals. The propagation radicals are very reactive and will react with other maleimide units to form bigger molecules. The reaction rate depends on the mobility of these free radicals. The mobility of reactive sites is highly influenced by the viscosity of the medium and the degree

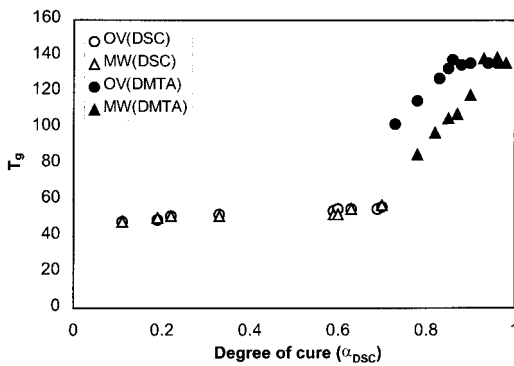


**Figure 4** (a) Effect of temperature on  $\alpha_{DSC}$  as a function of time for 5.0 g of Matrimid 5292A cured in a conventional oven at different temperatures and (b) the effect of the sample weight at 190°C.

of cure.<sup>11</sup> In microwave heating, a 5.0-g sample achieves a degree of cure of 0.6 after 7 min, whereas in the conventional oven, the resin does not reach this degree of cure until 15 min.

The third stage shows a slower curing rate than the second stage for both methods. The viscosity of the system increases very rapidly as the degree of cure increases. As a result, the cure reaction is slow because the mobility of the reactive sites is restricted.<sup>19</sup> In this stage, the microwave-cured samples achieve an  $\alpha_{DSC}$  value of 0.96 in 11 min, whereas in the conventional oven, it is only 0.87 after 420 min. The cure reactions in this stage depend on the temperature: the higher the temperature, the higher the degree of cure at a given time. Thus, a sample cured with conventional heating at 190°C shows a higher degree of cure than one cured at 170°C. This is expected because at higher temperatures, the reactive sites are more mobile than at lower temperatures, thus giving higher degrees of cure.

In the final stage, the cure reactions totally stop even though the heating is continued. This is because the network has become highly crosslinked; the mobility of reactive sites is totally restricted, and they are trapped in the matrix.<sup>20</sup> As shown in Figure 4(a), in the conventionally cured material, no further reaction can be observed even when the curing time is prolonged



**Figure 5**  $T_g$  as a function of  $\alpha_{DSC}$ , as determined by DSC and DMTA, for 5.0 g of Matrimid 5292A cured by a conventional oven (OV) at 190°C or a microwave oven (MW) at a 635-W power setting.

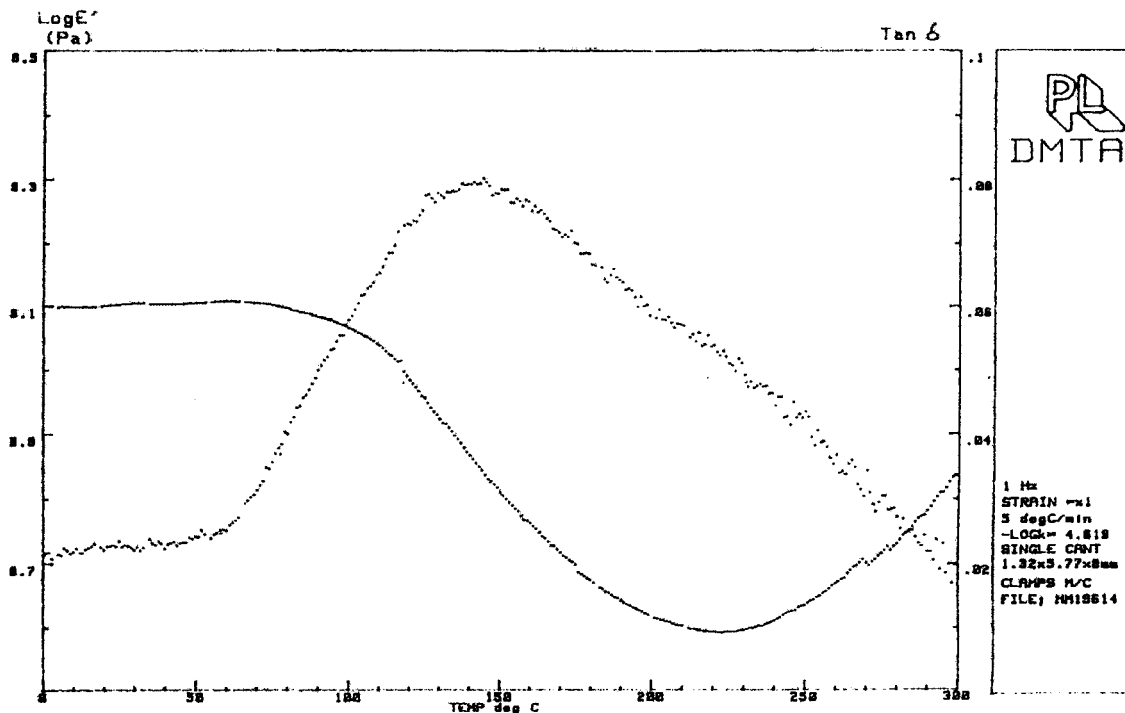
to 24 h. The temperature at this stage is known as the vitrification temperature.

Figure 4(b) shows the effect of the sample weight on the degree of cure as a function of time when samples are heated conventionally at 190°C. This figure shows a slower reaction rate in a 5.0-g sample than in a 3.0-g sample in the initial stages up to a 120-min heating time. This is because a longer time is required to melt a bigger sample (5.0 g) in the first stage on account of slow heat transfer from the oven into the material. The curing rate is higher after 120 min in the second stage for a 5.0-g sample than for 3.0-g sample. In this stage, the curing rate is affected by the exothermic heat from the polymerization process. The magnitude of heat

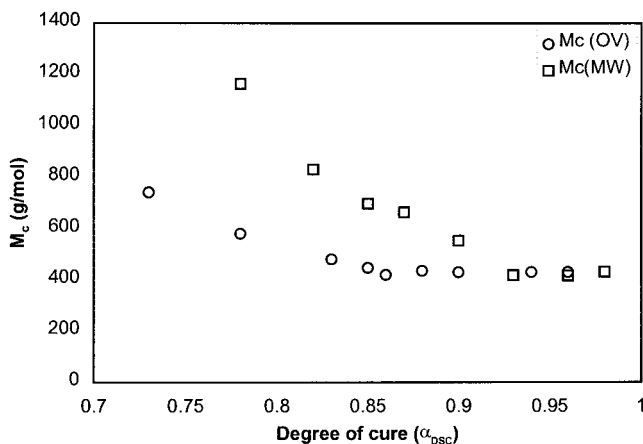
released is proportional to the size of the sample. More heat is produced in a 5.0-g sample than in a 3.0-g sample, and so the reaction rate is higher in a 5.0-g sample because the heat is lost from this more slowly.

### $T_g$

Figure 5 shows  $T_g$  as a function of  $\alpha_{DSC}$  for both microwave-cured and conventionally cured samples. There is only a small increase in  $T_g$  from 48 to 57°C as the degree of cure increases from 0 to 0.7. This is probably because the molecular segments begin to polymerize<sup>19</sup> and there is little crosslinking.  $T_g$  of a polymer is very much influenced by its molecular weight and increases proportionally with increasing molecular weight.<sup>21</sup> There is no significant difference in  $T_g$  at this stage for the microwave-cured and conventionally cured samples, and this indicates that the morphology of samples at this stage is similar with both curing methods. This suggests that the cure reaction is the same in this region. After the degree of cure reaches 0.70, DMTA must be used because the DSC technique is not sufficiently sensitive to detect  $T_g$ . A typical DMTA curve is shown in Figure 6.  $T_g$  rises rapidly when  $\alpha_{DSC}$  is greater than 0.70 in both curing methods. The increase in  $T_g$  suggests that the molecules become more crosslinked and that the movement of the polymer chains is restricted as the curing progresses.<sup>11</sup> Microwave-cured samples show lower  $T_g$ 's than conventionally cured samples for values of  $\alpha_{DSC}$  between 0.7 and 0.9. The difference in  $T_g$  may be



**Figure 6** Typical DMTA curves for microwave-cured Matrimid 5292A ( $\alpha_{DSC} = 0.93$ ).



**Figure 7** Calculated  $M_c$  values as a function of  $\alpha_{DSC}$  ( $>0.7$ ) for samples cured with a conventional oven (OV) or a microwave oven (MW).

attributed to the variation of the crosslinking network formed at higher degrees of cure. Alternatively, the different values may be a result of different cooling rates. When the degree of cure approaches 100%, however, both cure methods show similar  $T_g$ 's.  $T_g$  is known to be strongly dependent on the crosslink density.<sup>20</sup> To estimate the structural variation of samples cured in conventional and microwave ovens, the molecular weight between crosslinks ( $M_c$ ) can be calculated from the corresponding  $T_g$  according to the following empirical equation:<sup>22</sup>

$$M_c = \frac{3.9 \times 10^4}{T_g - T_{g0}} \quad (2)$$

where  $T_{g0}$  is the glass-transition temperature of the noncrosslinked polymer.  $T_{g0}$  is 48°C, according to a DSC curve of a resolidified sample. From this equation,  $M_c$  has been calculated for conventionally cured and microwave-cured samples for  $\alpha_{DSC} > 0.7$ ; the results are presented in Figure 7. The values of  $M_c$  for the microwave-cured samples are generally higher than those for the conventionally cured samples, but the values merge as the degree of cure approaches 100%. These results show that samples cured in a

conventional oven have a higher crosslink density than the microwave-cured samples in the region  $\alpha_{DSC} = 0.7-0.9$ , but the fully cured samples are similar. It is very important to confirm the cure reactions because the two heating methods give different values of  $T_g$  and  $M_c$  below  $\alpha_{DSC} = 1$ , and this gives the impression that the reaction scheme might be different. This has been done by the determination of the structures of samples as the curing progresses with spectroscopic techniques.

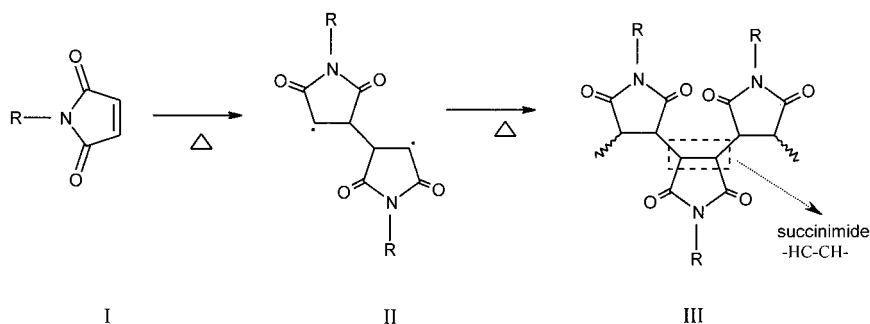
### Structure of the cured resin

BMI resins contain a reactive double bond (H—C=C—H) in the maleimide groups that can undergo homopolymerization via a free-radical addition reaction.<sup>5</sup> The proposed reaction scheme is shown in Figure 8.<sup>6</sup> The reactions show that the maleimide group (I) is converted into the succinimide group (III) as a final product via an intermediate (II). FTIR<sup>11</sup> and NMR<sup>23</sup> spectroscopy have been used to follow this reaction in conventional and the microwave ovens.

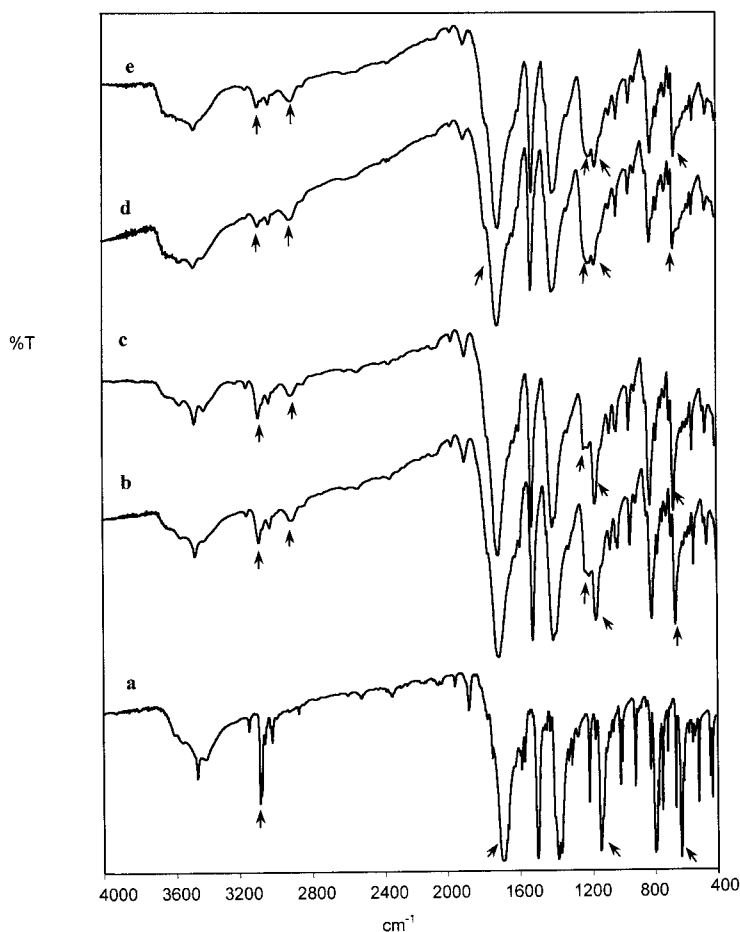
### FTIR spectroscopy

Figure 9 shows the overlaid FTIR spectra of uncured samples and conventionally cured and microwave-cured samples at different degrees of cure. The details of the uncured spectrum interpretation have been reported.<sup>24</sup> Several spectral changes can be observed after polymerization:

- The disappearance of the peak at 3100  $\text{cm}^{-1}$  characteristic of the C—H stretch in maleimide groups (H—C=C—H). These groups have been converted into succinimide groups (H—C—C—H), the C—H stretch of which shows as a broad peak centered at 2915  $\text{cm}^{-1}$ . This peak overlaps with that of the C—H stretch in methylene groups.
- The disappearance of the peak centered at 1150  $\text{cm}^{-1}$  (C—N—C, maleimide) and the growth of a peak centered at 1185  $\text{cm}^{-1}$  (C—N—C, succinimide).



**Figure 8** Homopolymerization reaction scheme of Matrimid 5292A.



**Figure 9** FTIR spectra of Matrimid 5292A: (a) uncured, (b,d) conventionally cured ( $\alpha_{\text{DSC}} = 0.3$  or  $1.0$ , respectively), and (c,e) microwave-cured ( $\alpha_{\text{DSC}} = 0.35$  or  $0.98$ , respectively).

ide). These peaks strongly overlap, but the doublet structure is perceptible.

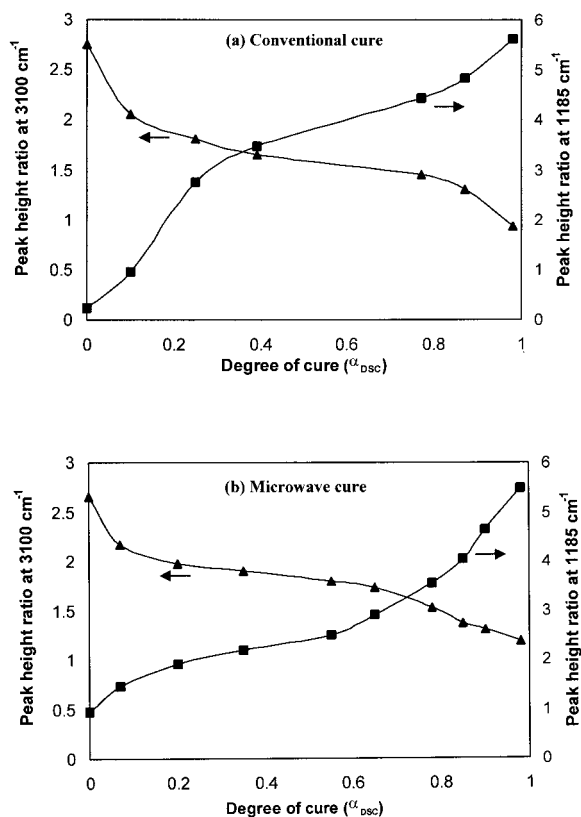
- The disappearance of the peak at  $690\text{ cm}^{-1}$  characteristic of maleimide groups ( $\text{C}=\text{C}-\text{H}$ ).

The peak at  $1709\text{ cm}^{-1}$  (maleimide  $\text{C}=\text{O}$ ) is broadened as a result of overlap with a slightly different peak due to the formation of succinimide  $\text{C}=\text{O}$ .

The peak changes at  $3100$ ,  $1150$ , and  $690\text{ cm}^{-1}$  have been used by several workers to follow the cure reaction in BMI polymerization.<sup>23,24</sup> Here, the peak height changes at  $3100$  and  $1185\text{ cm}^{-1}$  have been used to follow the cure reaction. The peak at  $3100\text{ cm}^{-1}$  has been chosen as it is well resolved from other peaks and suitable for quantitative analysis. It is difficult to analyze this peak in the spectrum of the uncured resin because it is split on account of the high crystallinity of the resin. This problem was overcome by the remelting of the resin at a temperature low enough to avoid curing before the spectrum was obtained. The formation of succinimide molecules was followed by an examination of the peak changes at  $1185\text{ cm}^{-1}$ . Even though this peak overlaps with the peak at  $1150\text{ cm}^{-1}$ ,

this is acceptable for the purpose of comparative analysis. The peaks at  $3038$  and  $831\text{ cm}^{-1}$ , characteristic of  $\text{C}-\text{H}$  in benzene, are unchanged throughout the process. The peak at  $3038\text{ cm}^{-1}$  has been chosen as an internal reference.

Figure 10(a,b) shows the peak height changes at  $3100$  and  $1185\text{ cm}^{-1}$  for conventionally cured and microwave-cured samples as a function of  $\alpha_{\text{DSC}}$ . The peak heights have been normalized to the peak height at  $3038\text{ cm}^{-1}$  ( $\text{C}-\text{H}$ , benzene ring) to eliminate variations in the sample thickness and concentration. Both figures show that as the curing progresses, the peak decrease at  $3100\text{ cm}^{-1}$  is proportional to the peak increase at  $1185\text{ cm}^{-1}$ . This suggests that a similar reaction occurs in both curing methods. Close observation shows that the patterns of the peak changes at  $3100$  and  $1185\text{ cm}^{-1}$  are slightly different for the two cure methods. The peak height at  $3100\text{ cm}^{-1}$  is slightly lower in a conventionally cured sample than in a microwave-cured sample at the same degree of cure. This shows that the concentration of the maleimide groups is higher in the microwave-cured sample. This is probably due to residual reactive groups trapped in



**Figure 10** Peak height changes as a function of  $\alpha_{\text{DSC}}$  for IR peaks at 3100 ( $\text{C}=\text{C}$ , maleimide) and 1181  $\text{cm}^{-1}$  ( $\text{C}-\text{N}-\text{C}$ , succinimide): (a) conventionally cured samples (5.0 g at 190°C) and (b) microwave-cured samples (5.0 g at a 635-W power setting).

the microwave-cured sample, which cannot be detected by DSC.

The peak changes at 1185  $\text{cm}^{-1}$  are significantly different in the two curing methods. Initially ( $\alpha_{\text{DSC}} < 0.2$ ), conventionally cured samples show a lower peak height than microwave-cured samples, but the heights are higher when  $\alpha_{\text{DSC}}$  is greater than 0.2. The peak height difference is maximum when  $\alpha_{\text{DSC}}$  is between 0.4 and 0.7. This indicates that lower succinimide groups are present in the microwave-cured samples with this cure state. This suggests that a larger amount of intermediate species (structure II in Fig. 8) remains in the matrix of the microwave-cured samples. Fast microwave heating results in immediate changes of maleimide moieties into radicals (II); however, because of the comparatively low temperature, this species does not immediately transform into succinimide molecules. As the curing proceeds, the temperature increases, and more succinimide groups are formed. This is shown in Figure 10(b): the peak height at 1185  $\text{cm}^{-1}$  increases rapidly when  $\alpha_{\text{DSC}}$  is greater than 0.7. Figure 10(a) also shows that microwave-cured samples have a slightly higher number of residual maleimide groups than conventionally cured samples. This is due to more reactive groups being

trapped in the network during microwave heating as a result of fast curing at an earlier stage. The details of the chemical structure have also been studied with NMR.

FTIR spectroscopy has been used to study the extent of the reaction.<sup>25</sup> The peak height ratios from Figure 10(a,b) have been used to calculate the degree of cure with the following formula:

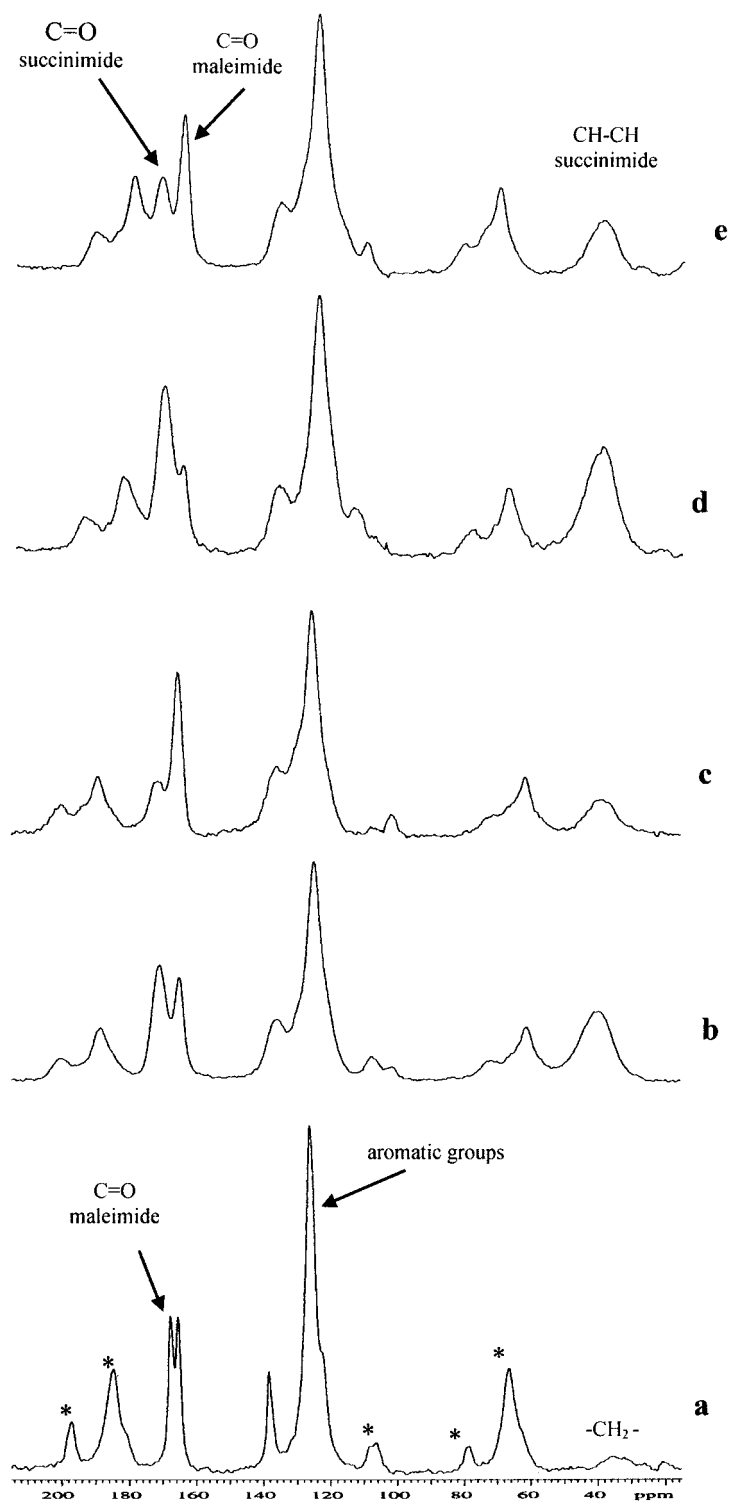
$$\alpha_{\text{FTIR}} = 1 - \frac{R_t}{R_{\text{unc}}} \quad (3)$$

where  $R_{\text{unc}}$  and  $R_t$  are the peak height ratios at 3100  $\text{cm}^{-1}$  of an uncured sample and a sample cured for time  $t$ , respectively.

#### NMR analysis

Solid-state  $^{13}\text{C}$ -NMR is a technique complementary to infrared spectroscopy in the determination of the chemical structures of materials. Figure 11(a) shows the NMR spectra of a sample of the uncured resin obtained with solid-state  $^{13}\text{C}$ -NMR. Resonance signals between 30 and 40 ppm are characteristic of  $\text{CH}_2$  groups of the methylene bridge between the two aromatic rings.<sup>23</sup> Between 112 and 144 ppm, the signal can be attributed to unsaturated carbons in aromatic rings and in alkene groups in the maleimide ring. The signal between 160 and 180 ppm is due to the carbon of the carbonyl groups of the two maleimide rings. NMR spectra from conventionally cured samples with  $\alpha_{\text{DSC}} = 0.56$  and  $\alpha_{\text{DSC}} = 1.0$  are shown in Figure 11(b,c), respectively, and spectra of microwave-cured samples with  $\alpha_{\text{DSC}} = 0.50$  and  $\alpha_{\text{DSC}} = 0.95$  are shown in Figures 11(d,e), respectively. Two peaks at 30–50 and 170 ppm appear as the curing progresses. The 30–50 ppm peak is attributed to the  $\text{sp}^3$  carbon of succinimide groups ( $-\text{CH}-\text{CH}-$ ), and the peak at 170 ppm is characteristic of carbonyl groups from the succinimide environment<sup>23</sup> (Fig. 8). The intensity of these peaks increases as the curing proceeds in both cure methods. Basically, both conventionally cured and microwave-cured samples show similar NMR spectra, and this suggests that the same curing reactions take place in each case. The NMR results are in agreement with the FTIR data, which show that the chemical structures of both conventionally cured and microwave-cured samples are the same. The difference in the peak intensity in the NMR spectra is due to the residual monomer present in the polymer matrix. The peak area at 160 ppm ( $\text{C}=\text{O}$  maleimide) is larger in the microwave-cured sample than in the conventionally cured sample. This may be because more residual monomer is trapped in the polymer matrix in the microwave-cured sample.





**Figure 11** Solid-state CP-MAS  $^{13}\text{C}$  NMR spectra of Matrimid 5292A: (a) uncured, (b,c) conventionally cured ( $\alpha_{\text{DSC}} = 0.56$  or  $0.98$ , respectively), and (d,e) microwave-cured ( $\alpha_{\text{DSC}} = 0.50$  or  $0.95$ , respectively). Asterisks denotes sidebands from chemical shielding anisotropy.

In addition to structural identification, NMR has also been used to calculate the extent of the reaction through a comparison of the peak areas at 166 (C=O maleimide) and 172 ppm (C=O succinimide) with a component analysis technique; an example of this analysis is shown

in Figure 12. The degree of cure from NMR ( $\alpha_{\text{NMR}}$ ) can be calculated with the following equation:

$$\alpha_{\text{NMR}} = \frac{A_{172}}{A_{172} + A_{166}} \quad (4)$$

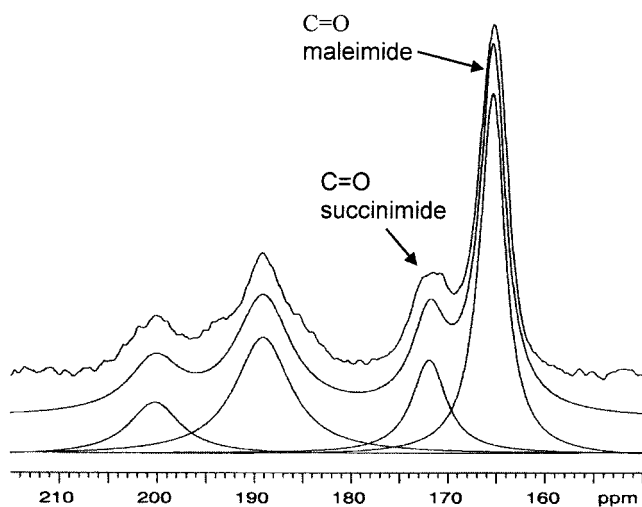


Figure 12 Component analysis of the NMR spectrum.

where  $A_{166}$  is the peak area at 166 ppm and  $A_{172}$  is the peak area at 172 ppm.

#### Comparison of $\alpha_{\text{DSC}}$ , $\alpha_{\text{FTIR}}$ (the degree of cure from FTIR), and $\alpha_{\text{NMR}}$

The degrees of cure calculated with eqs. (2)–(4) are summarized in Table I. The results show that the degrees of cure by the DSC, FTIR, and NMR techniques are in poor agreement with one another. The DSC analysis gives the highest degree of cure, whereas the FTIR analysis shows the lowest. The discrepancies in the results are probably due to different methods being used to measure the concentrations of unreacted groups. For example, in DSC, a sample is heated in a small oven or DSC cell, and the area under the exothermic peak ( $\Delta H$ ), characteristic of the polymerization process, is measured. The magnitude of  $\Delta H$  relies on the ability of DSC to record all the heat released from the remaining reactive groups of the monomer during polymerization. This assumes that all unreacted groups are totally reacted after the DSC scan. However, some of the reactive species actually remain trapped and are unable to react. As a result, the measured  $\Delta H$  value becomes smaller than the actual value, and this gives a larger degree of cure when applied to eq. (1). Prime<sup>26</sup> reported that the sensitivity of DSC decreases as the degree of cure increases.

In FTIR analysis, the concentration of H—C=C of maleimide groups is directly measured in the polymer matrix on the basis of Beer's law. The peak height at  $3100\text{ cm}^{-1}$  is proportional to the concentration of maleimide groups (H—C=C). The  $\alpha_{\text{FTIR}}$  results are lower than  $\alpha_{\text{DSC}}$  because more H—C=C groups are detected by FTIR than by DSC. FTIR spectra show the presence of H—C=C groups even for a sample with  $\alpha_{\text{DSC}} = 1$ . This is probably due to residual monomers or end

groups of polymer chains. In FTIR analysis, however, there are several sources of error. Scattered infrared radiation makes the direct application of Beer's law inaccurate. Another source of error is the difficulty of choosing the correct base line, and this affects the accuracy of the data.

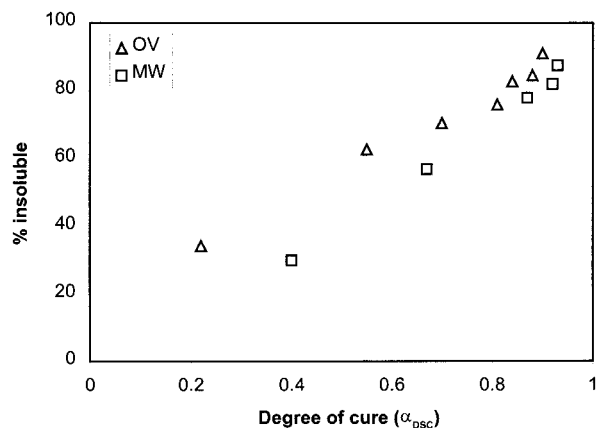
In the solid-state  $^{13}\text{C}$ -NMR technique, the actual number of maleimide and succinimide carbonyl groups (C=O) is measured directly, similarly to FTIR, but it does not depend on Beer's law. Even though these peaks overlap one another, the peak area is calculated separately with the component analysis technique. The results are expected to be more accurate than those of FTIR. They show that the degree of cure calculated with NMR is closer to that found with the DSC technique. As shown in the NMR spectra in Figure 11(c), the amount of C=O, maleimide is much greater in the microwave-cured sample. It is proposed that this carbonyl group is probably from a residual monomer trapped in the matrix or end groups of the polymeric chain. To investigate this assumption, we have conducted a sol-gel analysis.

#### Sol-gel analysis

The results of a sol-gel analysis for conventionally cured and microwave-cured samples are shown in Figure 13. The conventionally cured samples weigh 5.0 g and are cured at  $190^\circ\text{C}$ , whereas the microwave-cured samples weigh 5.0 g and are cured at the full-power setting (635 W). Interestingly, the results show a linear relation between the insoluble percentage and  $\alpha_{\text{DSC}}$ . Microwave-cured samples display slightly higher amounts of the soluble monomer than the conventionally cured samples, and this means that more residual monomer is trapped in microwave-cured samples. This result agrees with NMR results but does not support the  $T_g$  results at a lower value of  $\alpha_{\text{DSC}}$  ( $<0.7$ ). This is probably because the amount of the residual monomer present in the polymer matrix does not significantly affect the  $T_g$  value at lower degrees of cure for both curing methods. When  $\alpha_{\text{DSC}}$  is greater than 0.7, the microwave-cured samples show slightly greater amounts of soluble material. This supports the

TABLE I  
Comparison of the Degree of Cure Determined by DSC, FTIR, and NMR

Conventional oven (5.0 g at $190^\circ\text{C}$ )			Microwave oven (5.0 g at 635 W)		
$\alpha_{\text{DSC}}$	$\alpha_{\text{FTIR}}$	$\alpha_{\text{NMR}}$	$\alpha_{\text{DSC}}$	$\alpha_{\text{FTIR}}$	$\alpha_{\text{NMR}}$
0.56		0.47	0.50		0.33
0.66	0.39		0.65	0.37	
0.81	0.47		0.85	0.50	
0.98		0.86	0.95		0.77
1.0	0.66		0.98	0.67	



**Figure 13** Sol-gel analysis results for samples cured with a conventional oven (OV) or a microwave oven (MW) as a function of  $\alpha_{DSC}$ .

argument that the lower  $T_g$  value in microwave-cured samples is due to more residual monomer and a lower crosslink density. It has been reported<sup>20</sup> that fast curing when microwave heating is used can result in unreacted monomer being trapped in the matrix of an epoxy system. However, when  $\alpha_{DSC}$  approaches 1.0, the percentage of insoluble material in samples cured by both heating methods becomes similar. This suggests that the trapped monomer eventually reacts as the heating proceeds in the microwave oven. This explains why the  $T_g$  values for both methods converge at 100% cure.

## CONCLUSIONS

Microwave processing significantly reduces the cure cycle for Matrimid 5292A. Spectroscopy has revealed that the cure chemistry of both conventional oven and microwave processing is basically the same. Rapid curing in a microwave oven does not occur because the reactions that take place have been altered. This is probably due to volumetric heating that takes place when microwave heating is used. It is important to control the microwave power, as it affects the sample

temperature and subsequently the morphology of the final sample. Through control of the microwave power, samples with high degrees of cure and few bubbles can be obtained. Samples cured with a conventional oven have a higher crosslink density than microwave-cured samples up to  $\alpha_{DSC} = 0.95$ , but  $M_c$  converges at 100% cure. The fast curing that occurs during microwave heating leads to some monomers being initially trapped in the matrix, but these react later in the cure cycle.

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