

# Variable-Frequency Microwave Curing of Benzocyclobutene

RAVINDRA V. TANIKELLA, SUE A. BIDSTRUP ALLEN, PAUL A. KOHL

School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0100

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**ABSTRACT:** Polymer dielectrics are widely used in the microelectronics industry for several applications including interlevel dielectrics, encapsulants, and passivating layers. To attain the desired properties, these materials need to be processed via lengthy cure cycles. Variable frequency microwave (VFM) processing has been investigated as a rapid curing alternative for the processing of thin-film dielectrics. Previous studies on epoxies and polyimide-based materials have shown significant reduction in cure time and improvement in properties on VFM processing. In this study, VFM curing of Dow Chemical Cyclotene™ 3022 benzocyclobutene (BCB) was investigated. The kinetics of the cure reaction were studied by Fourier transform infrared (FTIR) spectroscopy. FTIR studies indicated no significant differences in chemical structure between VFM and thermally cured films. The electrical, optical, mechanical, and chemical properties of VFM-processed films were characterized and compared with thermally processed films to determine the effectiveness of microwave processing. The results showed that VFM curing of BCB is feasible, and properties comparable to thermally cured films can be attained. The residual stress of partially cured BCB was lower for VFM processing than for traditional thermal processing. The residual stress in fully cured BCB was similar. Improvements such as shorter cure times and lower processing temperatures than conventional thermal processing can be achieved. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 3055–3067, 2002; DOI 10.1002/app.10286

**Key words:** variable frequency microwave (VFM); benzocyclobutene (BCB); dielectric properties; cure kinetics; residual stress; curing of polymers; infrared spectroscopy

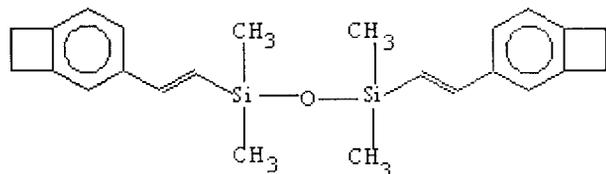
## INTRODUCTION

Polymer dielectrics are widely used in the microelectronics industry for a number of applications including interlevel dielectrics, passivation layers, encapsulants, and underfills due to their superior chemical, mechanical, and electrical properties. However, one of the key issues with the use of these materials is the lengthy processing time required to achieve the required properties. Novel, rapid-curing alternatives have been investigated to overcome this limitation.<sup>1,2</sup> Microwave

processing has been studied as an alternative curing technique for a number of polymeric materials. References 3, 4, and 5 and the references therein give a comprehensive review of research in the field of microwave processing of polymers. More recently, variable frequency microwave (VFM) processing has been studied for the synthesis<sup>6</sup> and processing<sup>7,8</sup> of materials and has shown to be an effective rapid-processing technique that results in a significant reduction in cure time with comparable or improved properties.<sup>9</sup> Previously, the feasibility of curing dielectric polymers in a VFM furnace and the effect of VFM processing on the physical and chemical properties of six different commercial dielectric materials was reported.<sup>1</sup> The objective of this

Correspondence to: P. A. Kohl (paul.kohl@che.gatech.edu).

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**Figure 1** Chemical structure of BCB monomer.

study was to investigate the effect of VFM processing on the properties of Cyclotene™ benzocyclobutene (BCB) 3022-63 from Dow Chemical Company (Midland, MI) and to determine if VFM processing caused any enhancement in the reaction kinetics.

Microwave heating of materials occurs because of dielectric loss mechanisms. When an external electric field is applied to a dielectric material, three types of polarization may occur. These are electronic, ionic or atomic, and orientational or dipolar polarization. The principal mechanism of coupling microwave radiation to polymer dielectrics is through dipole orientation by the electric field. The efficiency of coupling microwave energy into a material is dependent on a number of factors, including the dipole strength, the mobility of the dipole, and the mass of the dipole. The amount of microwave energy absorbed by a material is given by the following relation:

$$P_{\text{absorbed}} = 2\pi f E_{\text{rms}}^2 \epsilon_0 \epsilon'' \quad (1)$$

where  $P_{\text{absorbed}}$  is the dissipated or absorbed power per unit volume,  $E_{\text{rms}}$  is the root mean square electric field strength,  $\epsilon_0$  is the permittivity of free space,  $\epsilon''$  is the relative loss factor, and  $f$  is the frequency.

BCBs are a family of thermoset resins with a low dielectric constant (2.65) and good planarizability (>90%) and are used as interlevel dielectric materials in a variety of electronic packaging applications.<sup>10,11</sup> The resin, as received, is partially polymerized (B-staged) and dissolved in mesitylene. The structure of the monomer unit is shown in Figure 1. The polymerization (cure) of BCB proceeds through a two-step process: a thermally driven ring-opening mechanism followed by a Diels–Alder reaction that results in a crosslinked polymer matrix.<sup>12</sup> The degree of cure in the polymer is a function of the temperature and the time at that temperature. The final cure temperature used for curing this polymer varies between 200 and 350°C. The standard recom-

mended thermal cure process is a 1-h cure at 250°C.<sup>13</sup> The effect of VFM processing on the physical and chemical properties of BCB was investigated under different processing conditions and compared to the standard thermal cure.

## EXPERIMENTAL

All the VFM samples were processed in Microcure 2100™ VFM furnace from Lambda™ Technologies Inc. (Morrisville, NC). This system was described elsewhere.<sup>1</sup> Some of the important features include a central frequency ranging from 5.85 to 7.0 GHz, bandwidth varying from 0 to 10%, and variable sweep rates. One significant improvement in the system was the introduction of a feedback control system to control the temperature of the sample to be cured. The control system adjusted the power levels automatically to maintain the sample at the desired temperature. This allowed for control of ramp rates and hold temperatures of the samples. We processed all the samples in an inert (oxygen-free) atmosphere by purging the air inside the cavity using a mechanical pump and back-filling with nitrogen.

BCB samples were spin-cast onto silicon substrates and placed on a quartz disc supported by quartz mounts inside the microwave cavity. Three different temperature-sensing devices were used to monitor the temperature of the samples being processed. A thermocouple, a Nortech™ (Quebec, Canada) NoEMI-TS® family fiber optic probe, and a Raytek™ (Santa Cruz, CA) Thermoalert® T30 series IR pyrometer were used. The IR pyrometer was calibrated for emissivity of the sample and was used as the temperature-control device because it allowed better control of the sample temperature.

The extent of conversion in the cured films was monitored by Fourier transform infrared (FTIR) spectroscopy analysis. IR spectra were collected in both the transmission mode and the attenuated total reflection (ATR) mode with a Nicolet (Madison, WI) Magna-IR FTIR spectrometer. All spectra were recorded at a resolution of 4  $\text{cm}^{-1}$  and averaged over 512 scans.

The index of refraction was measured with a Metricon™ (Pennington, NJ) thin-film prism coupler at a wavelength of 632.8 nm. Measurements were taken in both the transverse electric and transverse magnetic modes to obtain the in-plane and the through-plane refractive indices of the cured films. For dielectric measurements, parallel

plate capacitors were fabricated with Ti/Cu/Ti metal electrodes. Capacitance and conductance measurements were performed at a frequency of 10 kHz with a HP4263A (Palo Alto, CA) LCR meter. Film thickness was measured with a Dek-tak™ (Plainview, NY) profilometer.

Moisture absorption studies were performed with a quartz crystal nanobalance (model EQCN-701 from Elchema Inc., Pottsdam, NY). BCB was spin-coated onto 10-MHz quartz crystals and subsequently cured both in a thermal furnace and in the VFM furnace. The cured films were subjected to an ambient 85% relative humidity, and the change in the resonant frequency of the crystals was monitored to estimate the moisture uptake of the cured films.

Thermal stability was determined by thermogravimetric analysis with a Seiko (Paramus, NJ) TG/DTA 320 analyzer. Samples of BCB films (about 30 mg) cured in a thermal convection oven and in the VFM furnace were ramped at about 80°C/min to 330°C and held at that temperature for 1 h. The weight loss after 1 h at 330°C was recorded.

Residual stress in films cured on silicon due to film shrinkage and coefficient of thermal expansion (CTE) mismatch can be estimated by measurement of the change in the wafer curvature on cure. We calculated the magnitude of residual stress of the processed BCB films by measuring the radius of curvature of the wafer before and after cure using a He-Ne laser based Flexus (Sunnyvale, CA) stress analyzer™ (model F2320).

## RESULTS

The effect of VFM processing on the physical and chemical properties of BCB was investigated under different processing conditions and compared to the standard thermal cure. The cure temperature was varied between 175 and 250°C, and the cure time was varied from 5 to 45 min. We investigated the effect of substrate heating by curing samples on quartz, teflon, and silicon substrates. The effects of VFM parameters such as central frequency, bandwidth, sweep rate, and ramp rate were investigated.

To determine the influence of central frequency on the cure characteristics, films were cured on a silicon substrate at different central frequencies between 5.8 and 7.0 GHz with a narrow bandwidth at a constant power. The heating characteristics of BCB films cured on silicon substrates

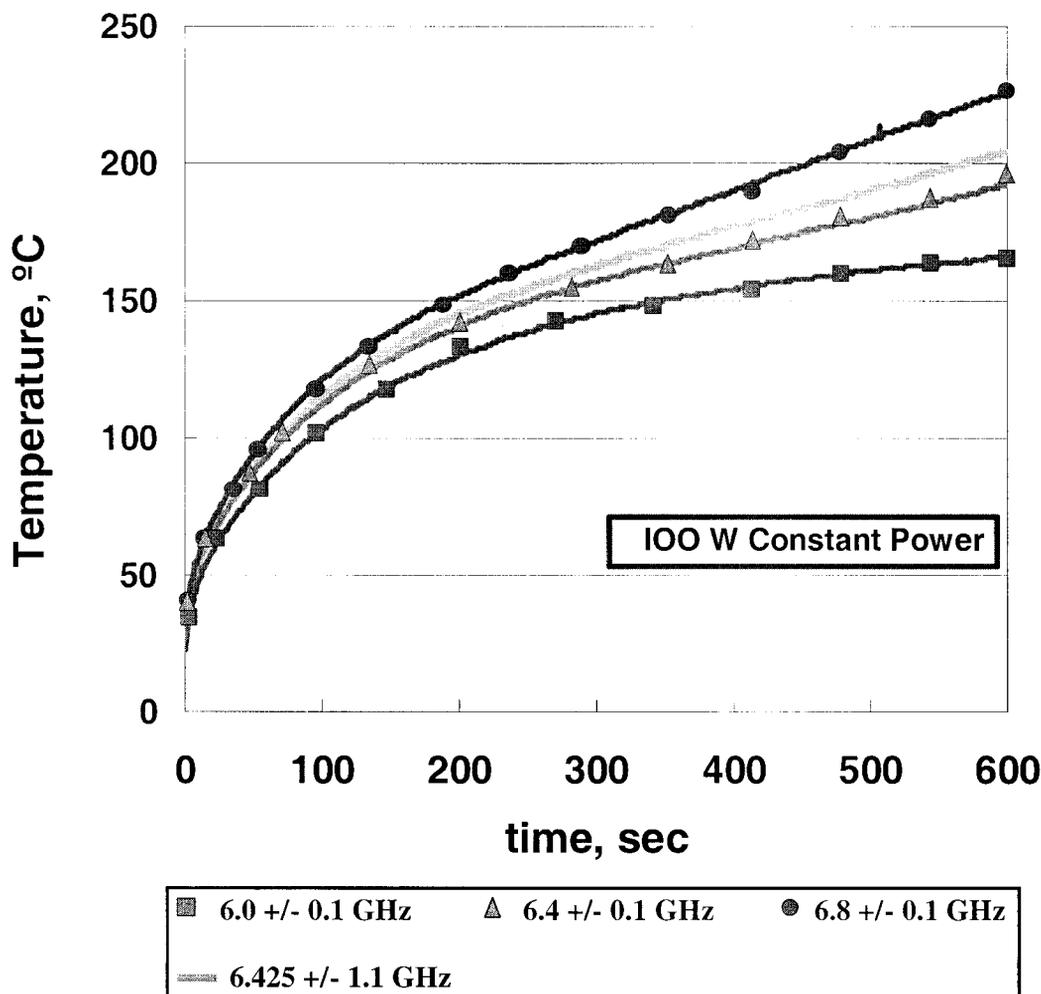
at a constant power of 100 W; central frequencies of 6.0, 6.4, and 6.8 GHz; and a narrow bandwidth of 0.1 GHz are shown in Figure 2. The gray line shows the heating rate at a central frequency of 6.425 GHz and a full bandwidth of 1.15 GHz. As expected, the rate of heating increased with increasing central frequency. Moreover, the ultimate temperature reached by the samples also increased with increasing central frequency.

### FTIR Studies on VFM-Cured Films

FTIR analysis has been shown<sup>14</sup> to be an effective analytical tool for following the reaction progress of BCB. The IR spectra of an uncured BCB film, a thermally cured film, and a VFM-cured film are shown in Figure 3. As shown in this figure, there were distinct changes that occurred in the spectrum on cure. These changes included an increase in the intensity of the peak at 1500 cm<sup>-1</sup> representative of the tetrahydronaphthalene group formed during cure<sup>14</sup> and a decrease in intensity of peak at 1475 cm<sup>-1</sup>, which corresponds to the reacting BCB group. The extent of cure may be estimated from the ratio of the peak height at 1500 cm<sup>-1</sup> of the sample spectrum to the same peak in a control sample. After a 1-h cure at 300°C in a conventional thermal furnace, the absorbance at 1475 cm<sup>-1</sup> completely disappeared. This sample was considered fully cured, and the peak height at 1500 cm<sup>-1</sup> of this sample was taken as the control. Both the absorbances were normalized to the absorbance at 1253 cm<sup>-1</sup>, which corresponds to the rocking mode of the methyl groups attached to the silicon atoms and remained unaffected by the polymerization and, hence, served as an internal reference to account for thickness differences between samples:

$$\text{Extent of Cure} = \frac{(A_{1500}/A_{1253})_{\text{sample}}}{(A_{1500}/A_{1253})_{\text{full cure}}} \quad (2)$$

In Figure 3, it is shown that the spectra of VFM-cured and thermally cured films were essentially identical with no significant differences, which indicates that the chemical structure of VFM-cured films was similar to conventional thermally cured films. This analysis cannot account for any possible side reactions or oxidation during cure. However, there were no absorption peaks in the FTIR spectra in the range 1700–1800 cm<sup>-1</sup> indicating the absence of any oxidation during cure.



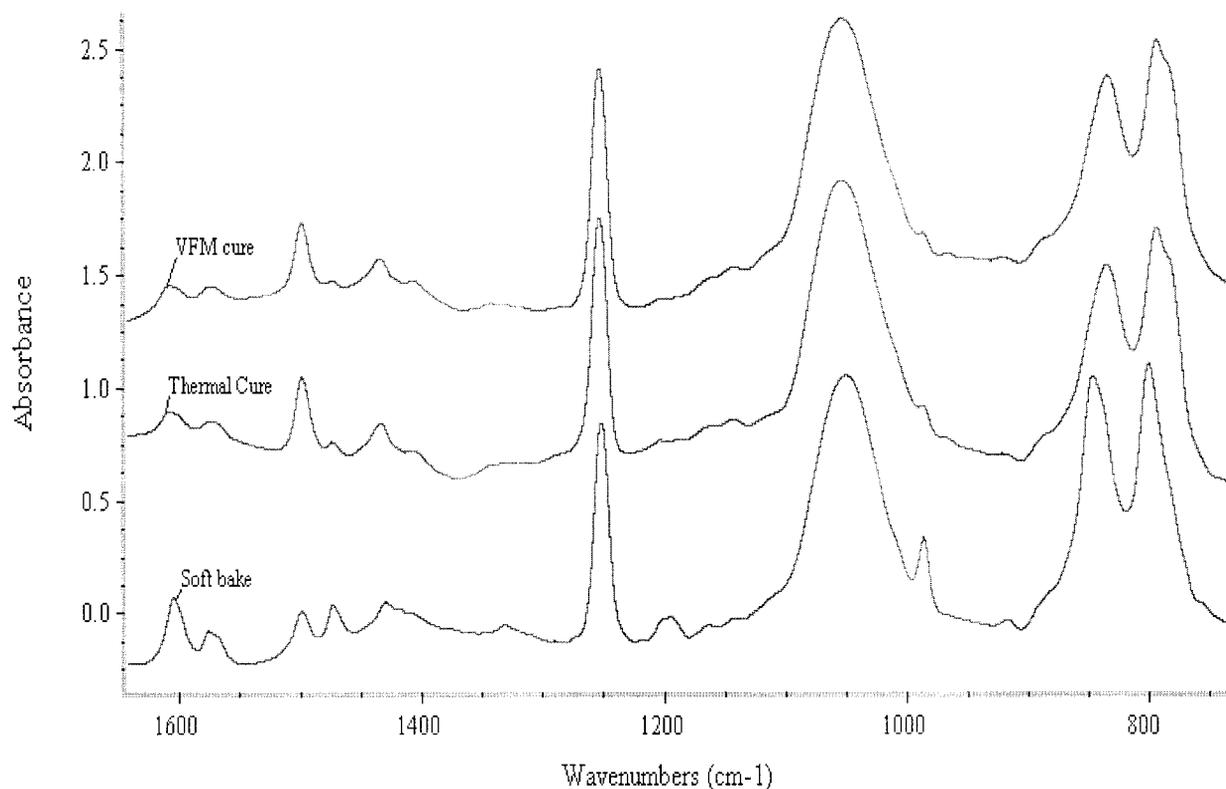
**Figure 2** Effect of central frequency on the heating characteristics of BCB on silicon at a constant power of 100 W.

FTIR spectra were collected in both transmission and ATR mode. Transmission FTIR is a bulk sampling technique, whereas the ATR mode samples only the top surface ( $<1 \mu\text{m}$ ) of the cured films. Similar trends in the extent of cure with cure conditions were observed by both these techniques, indicating that the chemical structure of the cured films was identical at the surface and in the bulk of the films. This shows the uniformity of VFM processing within the film thickness.

BCB films cured under identical conditions in the VFM furnace, in a conventional thermal furnace, and on a hot plate were compared to determine the effectiveness of VFM processing. Figure 4 shows the percentage conversion, as measured by FTIR, of films cured by these three methods at 175, 200, and 225°C for 30 min. All samples were

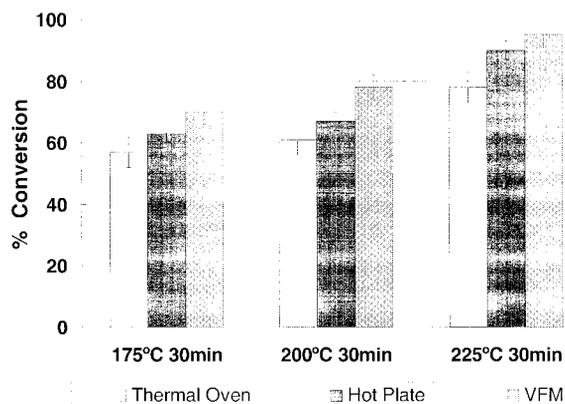
ramped at 30°C/min. For each cure condition, a comparable or higher conversion was achieved by VFM processing.

To study the reaction kinetics of VFM processing, BCB films were cured for different times at final cure temperatures ranging from 175 to 250°C. Samples were processed at a central frequency of 6.425 GHz with full bandwidth of 1.15 GHz and a sweep time of 0.1 s. All samples were ramped at 30°C/min. Figure 5 shows the IR spectra of BCB films cured in the VFM furnace at 225°C for different hold times. The progress of the cure reaction can be studied by monitoring the absorbance at  $1500 \text{ cm}^{-1}$ . The absorbance at  $1500 \text{ cm}^{-1}$  is indicative of the formation of the tetrahydronaphthalene functional group that forms during polymerization, and hence, the extent of cure increased with increasing cure time.



**Figure 3** Comparison of the FTIR spectra of soft-baked, VFM-cured, and thermally cured BCB samples.

The extent of cure data (from FTIR) of the processed films for different processing conditions is summarized in Figure 6. The extent of cure increased with both temperature and cure time. At any given temperature, the rate of reaction leveled off, which suggests vitrification of the polymer matrix. This phenomenon is commonly

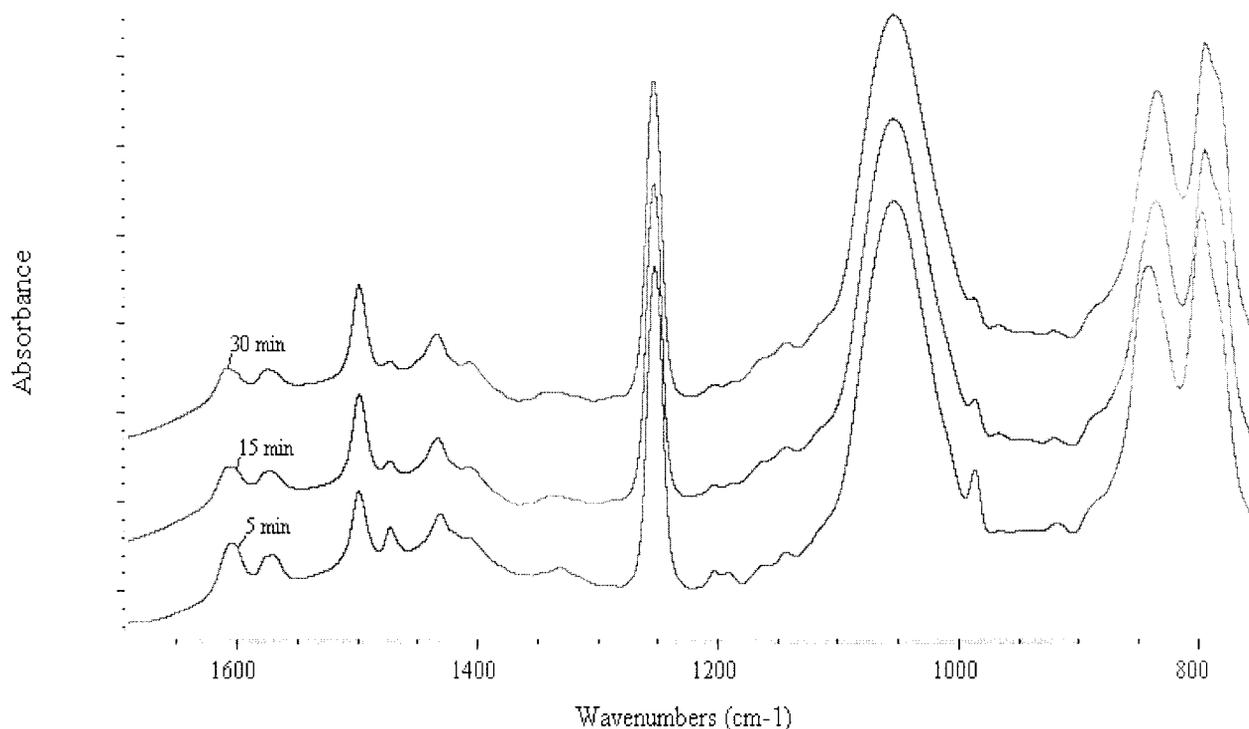


**Figure 4** Comparison of percentage conversion of films cured in the thermal oven, on the hot plate, and in the VFM furnace under identical conditions.

seen in thermally cured thermosetting polymer systems.<sup>15</sup>

As shown in Figure 6, a 5-min cure at 240°C and a 15-min cure at 225°C gave the same extent of cure as the prescribed standard cure of 1 h at 250°C. (Note, a 1-h cure at 250°C gave a conversion of about 0.97 relative to the same control full cure sample.) This shows the efficacy of VFM processing in driving reactions to completion. Moreover, a comparable extent of cure could be achieved at shorter cure times at any given temperature and at lower temperatures for the same cure time.

Figure 7 shows plots of  $-\ln(1 - x)$  as a function of cure time for different temperatures. The cure times used for this analysis corresponded to the time before the onset of vitrification (as may be inferred from Fig. 6). The linearity of these plots indicates that the reaction followed first-order kinetics. The slope of each of these plots gives the kinetic rate constant,  $k$ , at that temperature. From the rate constants so derived,  $\ln k$  versus  $1/T$  is plotted in Figure 8. This plot shows an Arrhenius-type relationship between temper-



**Figure 5** FTIR spectra of BCB films cured in the VFM furnace for different times at 225°C.

ature and the rate constants. The slope of this plot yields an apparent activation energy ( $E_a$ ) of  $25.7 \pm 4.4$  kcal/mol, which is about 30% lower than the  $E_a$  reported for thermally cured samples.<sup>12,16</sup>

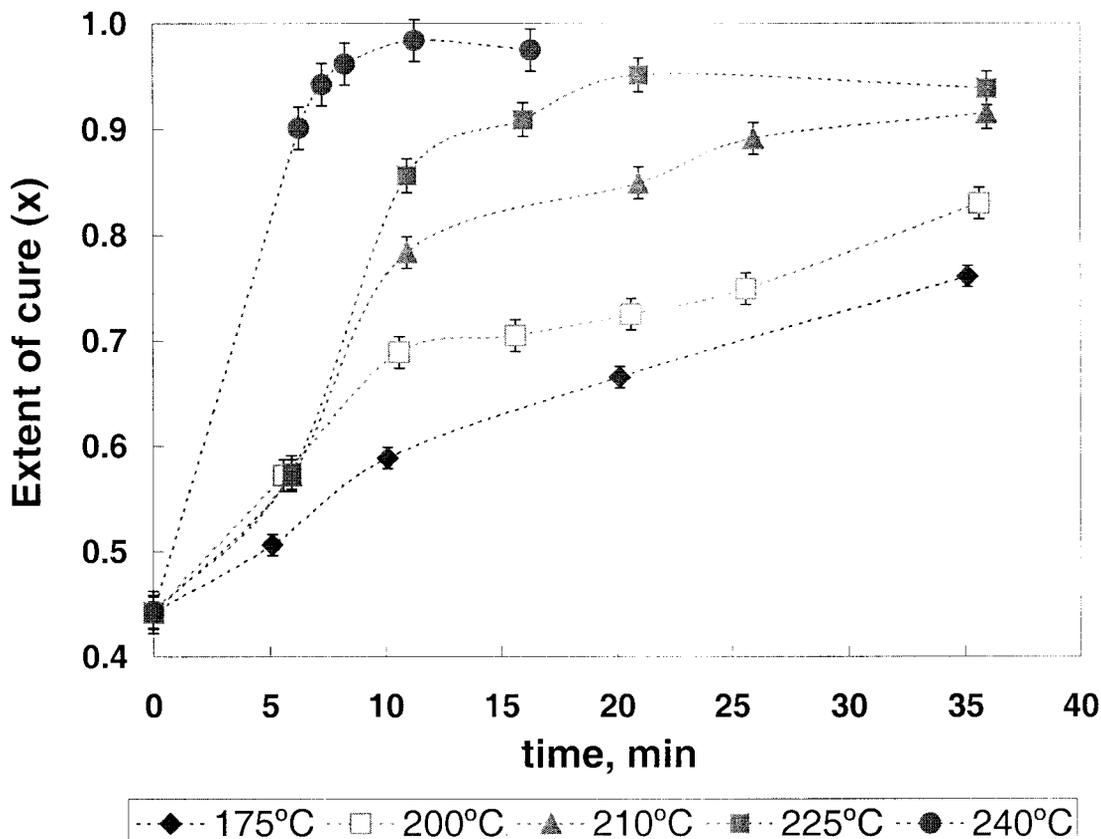
#### Comparison of Properties of Thermal and VFM-cured Films

The optical and electrical properties of VFM-cured films were characterized and compared to thermally cured films. Figure 9 compares the index of refraction (at a wavelength of 632.8 nm) of BCB samples cured by different methods: hot plate, thermal furnace, and VFM furnace under similar conditions. The index of refraction decreased from 1.59 for a soft-baked sample to about 1.55 for a fully cured sample. At each of these conditions, the VFM-cured samples showed comparable or lower indices of refraction than the thermally cured films. This was consistent with the higher extent of cure attained in these samples compared to the thermally cured samples.

Similar trends were also seen on comparison of the electrical properties of films processed in the VFM furnace and the thermal furnace. Figure 10

compares the dielectric constant of BCB films processed under different conditions by both these methods. The dielectric constant decreased with increasing extent of cure, and VFM-cured films showed a comparable dielectric constant to thermally cured films for all the cure conditions studied. The dielectric constant of (VFM processed) fully cured BCB films was 2.69, and the loss tangent was 0.0011.

The residual stress within the polymer films cured on silicon resulted from the CTE mismatch between BCB and silicon. The magnitude of the residual stress has been shown to be dependent on the extent of cure.<sup>17,18</sup> The residual stresses of a soft-baked film and a cured film at its cure temperature (maximum temperature) were nearly zero. On cooling to room temperature, the residual stress increased to about 33 MPa (tensile) for a fully cured film. Figure 11 compares the room-temperature residual stress of BCB films cured in the VFM and thermal furnaces at different temperatures as a function of percentage conversion (degree of cure). At each temperature, VFM samples were cured for 5 min, whereas the thermal samples were cured for much longer times to reach about the same conversion. The



**Figure 6** Progress of the VFM cure reaction with time at different temperatures (from FTIR data).

residual stress in films depended on the extent of cure and the cure method. For any partially cured condition, VFM-processed films showed significantly lower residual stress than the corresponding thermally cured films.

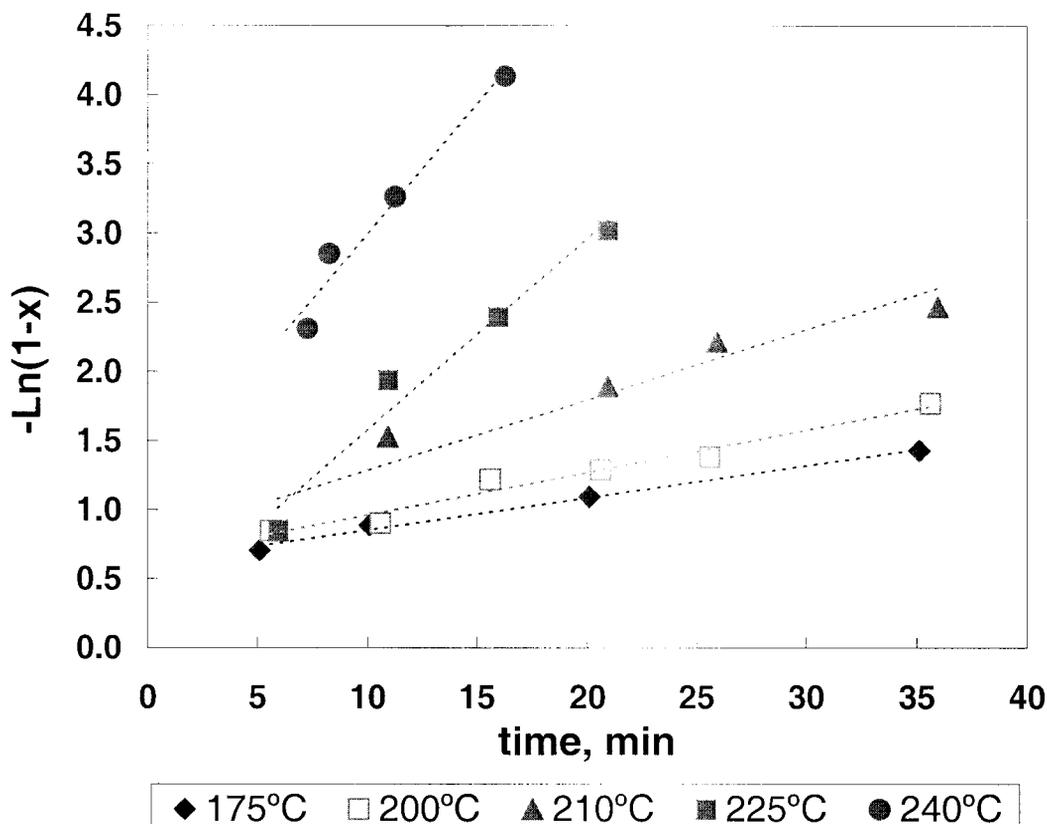
Further, there was a significant difference in the rate of increase of stress in the VFM-cured films as compared to the thermally cured films. As shown in Figure 11, the residual stress of thermally cured films increased linearly with percentage conversion and gradually leveled off at high conversions. However, VFM-cured films showed very low stress until about 70% conversion and, thereafter, a final residual stress close to that of the thermally cured films.

The effect of VFM processing on film properties was studied by comparison of the properties of VFM-cured films with thermally cured films. Table I compares the optical, electrical, mechanical, and chemical properties of VFM-cured and thermally cured films. Table I indicates that a 5-min VFM cure at 250°C gave properties comparable to films cured at 250°C for 1 h in a conventional

thermal oven. The in-plane and out-of-plane index of refraction measurements of cured films were performed with a Metricon™ prism coupler. The optical birefringence of VFM-cured BCB films was as low as 0.003, indicating the isotropy of the cured films. The dielectric properties of VFM-cured films were comparable to thermally cured films. VFM-cured films had a moisture uptake of less than 0.2% by weight at 85% relative humidity as determined by quartz crystal microbalance measurements. VFM-cured films showed thermal stability comparable to thermally cured films with less than 1% weight loss after 1 h at 330°C.

## DISCUSSION

Microwave processing of polymers has been shown to be an efficient, rapid processing technique offering potential advantages over conventional thermal processing.<sup>3</sup> Microwave processing differs from thermal processing in that heat is



**Figure 7** Plots of  $-\ln(1 - x)$  versus time at different cure temperatures for the determination of the rate constants.

produced within the material by dielectric loss mechanisms unlike thermal processing where heat is transferred from the ambient.

Figure 2 shows that the heating rate and the ultimate temperature reached by films cured at a constant power increased with increasing central frequency. The amount of microwave energy absorbed by a material at a given power depends on the applied frequency and the dielectric behavior of the material [eq. (1)]. The dielectric loss primarily determines the relative electromagnetic dissipation or the rate of conversion of electrical energy into thermal energy. The dielectric loss of a material varies with both temperature and frequency. This depends on the charge distribution within bonds, chain conformations, bulk morphology, and statistical thermal motion of the polar groups in the material. Previous studies<sup>19</sup> on high-frequency dielectric characterization of dielectric materials indicated that the dielectric loss of BCB increases with frequency in the range 2.4–8.1 GHz. Hence, with increasing central frequency, we would expect to see greater absorption and dissipation of microwave energy, which

would result in higher heating rates and higher ultimate temperature.

Previous studies with a hot plate<sup>20</sup> and with IR radiation<sup>21</sup> demonstrated the feasibility of rapid thermal curing of a BCB dielectric polymer. No significant differences were observed in the properties, such as residual stress and adhesion, of cured films. No enhancement in chemical reaction kinetics was reported by the absorption of IR radiation. As shown in Figure 3, the FTIR spectra of VFM-cured and thermally cured films were identical. This suggests that the chemical structure of VFM-cured BCB films was similar to that of thermally cured films within the sensitivity of FTIR. Furthermore, the absence of any distinct peaks in the entire range studied other than those seen in the thermally cured films indicates that a ring-opening mechanism followed by a Diels–Alder crosslinking reaction was the primary reaction mechanism for BCB curing by VFM processing with no significant alternative reaction pathways.

Microwave processing of thermosetting resins such as epoxies, polyesters, and polyurethanes were studied,<sup>4</sup> and many promising property im-

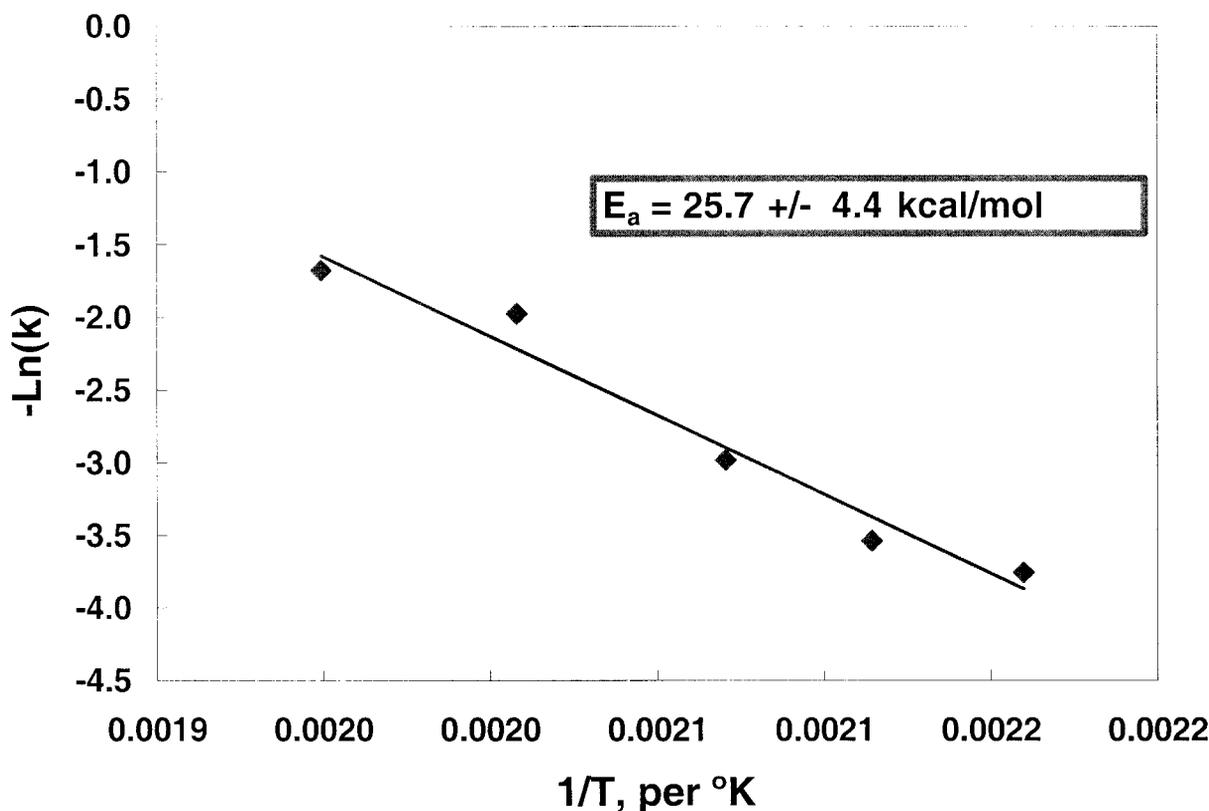


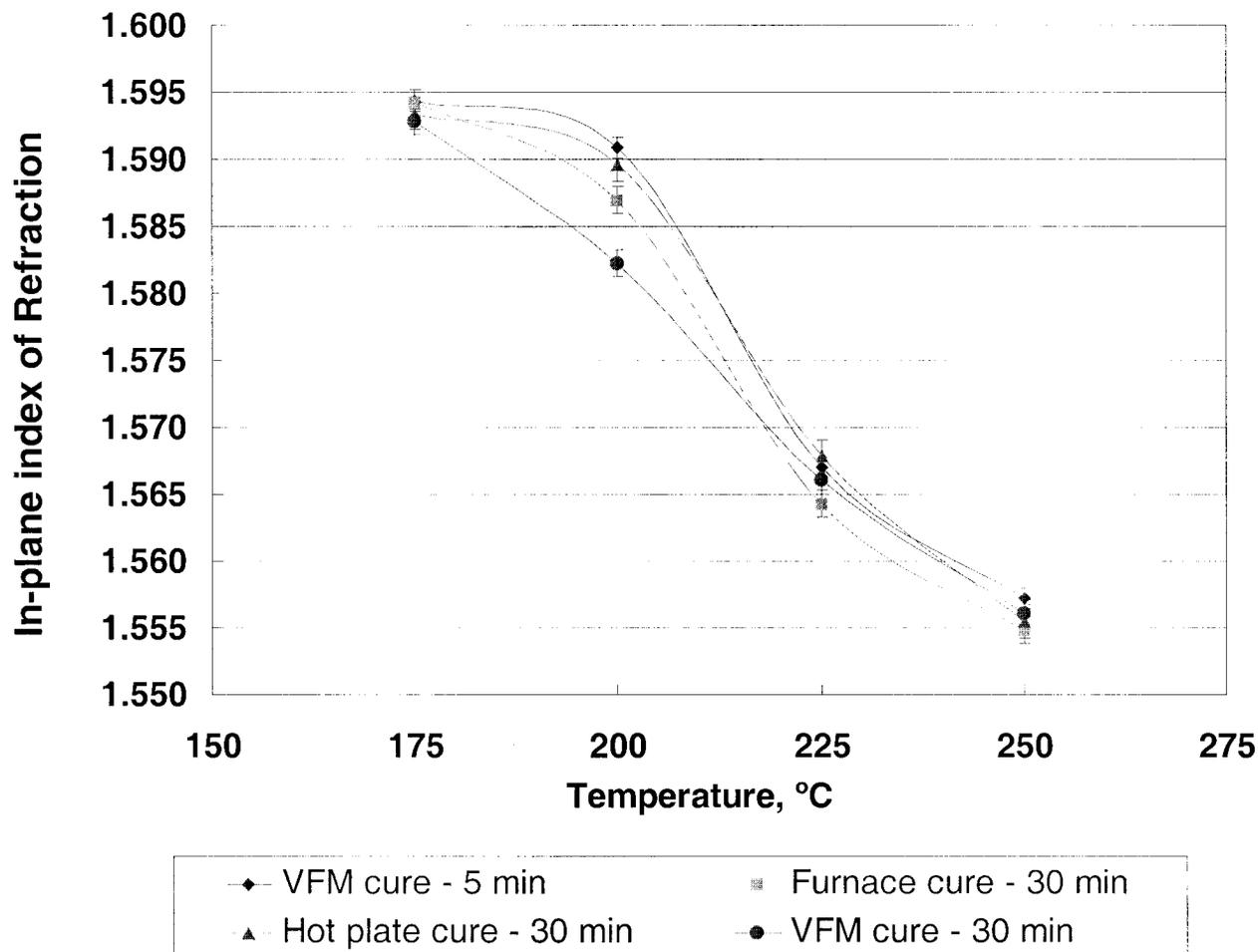
Figure 8 Plot of  $-\ln(k)$  versus  $1/T$  for the determination of  $E_a$  for the cure reaction.

improvements along with a reduction in cure time were shown. Thermoset resin systems are characterized by gelation and vitrification phenomena. For BCB, gelation has been shown<sup>14</sup> to have a negligible effect on reaction rate, indicating that local mobilities were virtually unaffected. Vitrification, however, has a significant impact on the reaction rate. Vitrification occurs when the glass-transition temperature ( $T_g$ ) equals the cure temperature. Loss of free volume associated with a glass transition reduces mobility locally.

Prior to vitrification, the crosslinking reaction is kinetically or chemically controlled and after vitrification (i.e., once the polymer is in its glassy state), mobility is limited, and the rate of reaction slows down and tends to become diffusion controlled. This phenomenon is very common in most thermosetting systems like epoxies. In the case of microwave processing, the dielectric loss in the microwave frequency range is primarily due to dipolar polarization. Before vitrification, due to high dipolar mobility, which can have translational apart from rotational contributions, the reaction rates are high. After vitrification, the mobility of the dipoles is rather constrained, and the

mechanism of loss has primarily electronic and vibrational contributions. Figure 6 clearly shows a drop in the reaction rate after a certain time and conversion at a given temperature indicating vitrification.

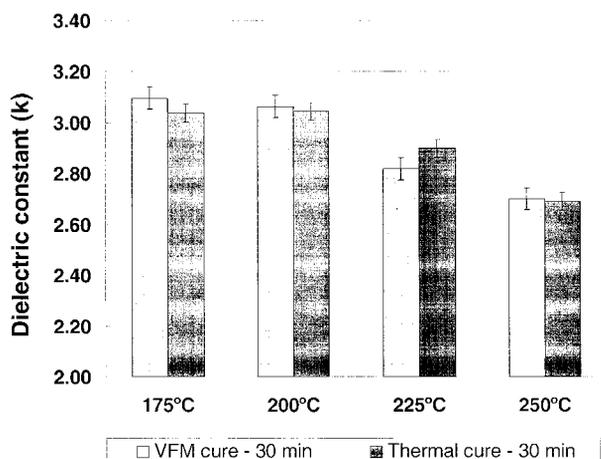
Both chemical-reaction-controlled kinetics and diffusion-controlled kinetics are favored by higher temperatures. It is possible that even though the bulk temperature of the material is lower, the local temperature resulting from localized loss mechanisms (relaxation of polarization) is higher. This would result in reaction rates that are higher than those expected at the bulk temperature. A higher conversion or shorter cure time would result for any given processing temperature. Alternately, one would require a lower processing temperature for the same cure time. The  $E_a$  for the cure reaction by VFM processing ( $\sim 25$  kcal/mol) was about 30% lower than the reported value of 36 kcal/mol, which was not as significant an enhancement in kinetics as other systems studied.<sup>22</sup> This was not surprising as microwave-induced acceleration of reaction kinetics is known to be significant in slower reacting systems, and the magnitude of the observed effect is greater at



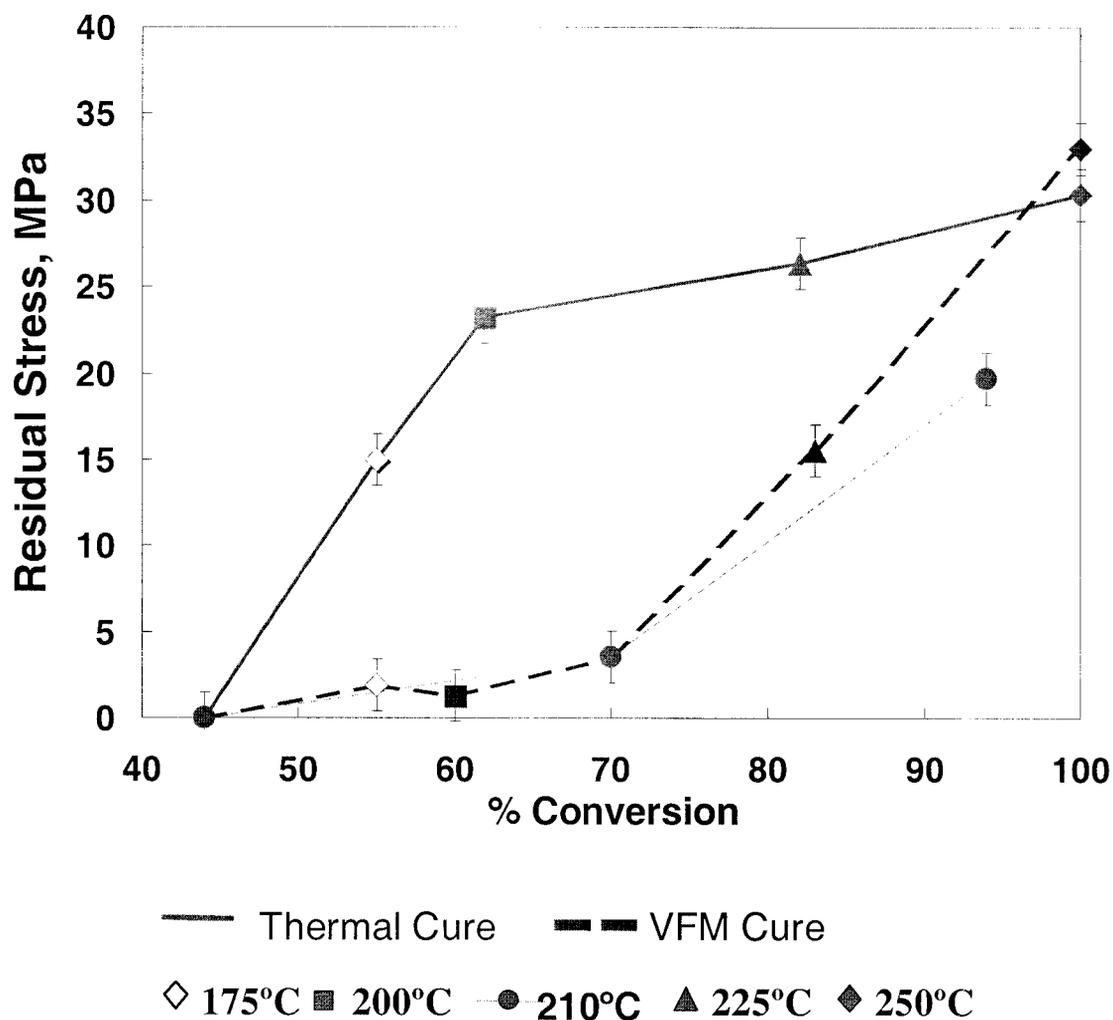
**Figure 9** Comparison of the in-plane indexes of refraction of BCB films cured in a furnace, on a hot plate, and in a VFM furnace under different processing conditions.

lower temperatures. Similar results of enhancement in reaction kinetics by microwave processing have been reported by a number of previous studies<sup>23</sup> on thermoset systems. A proposed mechanism for enhanced kinetics suggests<sup>24</sup> a nonequilibrium, nonuniform energy distribution on the molecular level, which results in certain dipoles having a greater energy than the average energy of adjacent dipoles. This increased energy was shown to correspond to a 50°C increase in effective temperature for solution imidization studies.

A 10-min VFM cure at 250°C gave the same conversion as the reference/control full-cure sample. At this temperature, for conventional thermal curing, vitrification is known to occur in about 5 min, giving a conversion of about 90%, and in the next 55 min of the prescribed standard cure, the reaction advances to only about 95%.



**Figure 10** Dielectric constants of VFM-cured and thermally cured BCB films processed under different conditions.



**Figure 11** Residual stress of VFM-cured and thermally cured films as a function of percentage conversion.

Microwave processing, thus, shows a significant improvement in the postvitrification reaction rates. Alternately, it is likely that due to high

local temperatures, the transition to the glassy phase occurs at a higher percentage conversion for any given bulk temperature over a shorter

**Table I** Comparison of Properties of BCB Films Cured by the Standard Thermal Cure of 1 h at 250°C and the VFM Cure of 5 min at 250°C

Property	Standard Thermal Cure (1 h at 250°C)	VFM Cure (5 min at 250°C)
In-plane index of refraction (at 632.8 nm)	1.55	1.55
Birefringence	0.002	0.003
Dielectric constant (at 10 kHz)	2.69	2.70
Loss tangent (at 10 kHz)	0.0009	0.0011
Thermal stability (weight loss after 1 h at 330°C)	<1%	<1%
Moisture uptake (wt % absorbed at 85% relative humidity)	0.194	0.197
Residual stress (MPa)	30	33

time. As a result of higher reaction rates, the reaction proceeds farther to completion before vitrification for microwave processing as compared to thermal processing.

Residual stress in thin-film dielectrics arises due to CTE mismatch between the films and the substrate. The polymer film is at nearly zero stress at its cure temperature, and when it cools, it contracts more than the silicon substrate due to its higher CTE. This contributes to tensile stress within the film.

The origin of the lower residual stress of partially cured VFM cured films is not known. Several factors may contribute to the lower residual stress in VFM cured films. First, the residual solvent in VFM-cured and thermally cured films may be different. The short cure times of VFM-processed films (especially at low temperatures) may result in higher residual solvent compared to thermally cured films. The resulting solvent-induced plasticization could lead to a lower effective modulus and, hence, to lower residual stress. However, this is probably not a significant factor because the index of refraction and dielectric constant of VFM-cured and thermally cured films, at the same conversion, are similar. Moreover, VFM-cured samples did not show a significant change in residual stress even after vacuum treatment for 24 h to remove any residual solvent.

Second, there may be an apparent lower CTE mismatch penalty. In a thermal furnace, the bulk of the film and the substrate are at the same temperature as the furnace temperature. On the other hand, in VFM processing, the bulk temperature of the film and the substrate and the local temperatures could be different. The higher local temperatures at the reaction sites could result in enhanced crosslinking reaction as the mobility of the reacting species increases with increasing temperature. However, if the bulk of the film is at a lower temperature, the associated CTE mismatch penalty is due to the bulk temperature rather than the local temperature. This could result in a lower residual stress. Indeed, if the modulus of films cured by both the techniques is the same, the lower residual stress corroborates the hypothesis of high local temperatures.

Residual stress is set in a film, on cooling from the highest  $T_g$  that has been reached,<sup>21</sup> independent of the maximum temperature excursion the film experiences in reaching this degree of cure. If curing occurs at a temperature greater than the  $T_g$ , the film becomes plastic, and stress is reset at the  $T_g$  corresponding to the higher conversion

reached. However, if the cure temperature is always below the  $T_g$  (i.e., the reaction proceeds in the solid or glassy state), the stress will not increase. Hence, if the  $T_g$  of microwave cured films were to be higher, enhanced postvitrification reaction rates could lead to lower residual stress. From the results, films cured in the VFM at a temperature as low as 210°C for 30 min gave a conversion of about 95% and a residual stress of about 22 MPa, which was lower than the residual stress for thermally cured films of the same conversion. Further, it would take a longer time to reach the same conversion in a thermal oven at that temperature.

Lastly, possible differences in the intrinsic modulus and CTE of the cured films could contribute to differences in residual stress. Although IR spectra did not show any significant differences in chemical structure, subtle differences in bonding or crosslinked network structure and the nature of crosslinks could have existed, which could have affected bulk properties of the films. A lower intrinsic modulus and/or CTE results in lower residual stress. It was not possible to verify this hypothesis because measurement of modulus and CTE of BCB films are very challenging. Free thin films of BCB are brittle, and heating characteristics on any other substrate could be significantly different. Hardness and modulus measurements from indentation techniques could validate this hypothesis.

## CONCLUSIONS

VFM processing of BCB was investigated. Results from this study show that VFM processing of BCB is feasible. The chemical structure of VFM-cured films is the same as thermally processed films. Ring opening followed by Diels–Alder crosslinking is the primary reaction mechanism for VFM curing of BCB. Study of reaction kinetics showed that the cure reaction follows first-order kinetics before vitrification. The rate constants showed an Arrhenius-type relationship with temperature with an apparent activation energy of  $25.7 \pm 4.4$  kcal/mol, which is about 30% lower than the reported thermal  $E_a$ . The optical, electrical, mechanical, and chemical properties of VFM-cured films were characterized and compared with thermally cured films to determine the effectiveness of VFM processing. VFM-cured films showed comparable or improved properties compared to thermally cured films. Processing improvements, such

as shorter cure times or lower processing temperatures, could be achieved. The residual stress of VFM-cured films was lower than thermally cured films, for partially cured films. Property measurements, such as  $T_g$ , elastic modulus, and CTE, could explain the lower residual stress in partially cured (VFM) BCB films.

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