

# Variable Frequency Microwave Curing of Benzocyclobutene

Ravindra V. Tanikella, Sue A. Bidstrup Allen and Paul A. Kohl\*

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

## Abstract

Polymer dielectrics are widely used in the microelectronics industry for several applications such as interlevel dielectrics, encapsulants and passivating layers. In order 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 processing of thin-film dielectrics. Previous studies on epoxies and polyimide-based materials have shown significant reduction in cure time and improvement in properties upon 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 indicate 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 show 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

---

\* paul.kohl@che.gatech.edu

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.

Keywords: Variable Frequency Microwave (VFM), benzocyclobutene (BCB), polymer dielectrics, cure kinetics, residual stress.

## **Introduction:**

Polymer dielectrics are widely used in the microelectronics industry for a number of applications such as 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. Variable frequency microwave (VFM) processing has been shown to be an effective rapid processing technique resulting in significant reduction in cure time with comparable or improved properties<sup>1</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 has been reported<sup>2</sup>. The objective of the current work was to investigate the effect of VFM processing on the properties of Cyclotene™ benzocyclobutene (BCB) 3022-63 from Dow Chemical Company and to determine if VFM processing caused any enhancement in the reaction kinetics.

Microwave heating of materials occurs due to 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:

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

where  $P_{absorbed}$  is the dissipated or absorbed power per unit volume,  $E_{rms}$  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.

Benzocyclobutenes are a family of thermoset resins with a low dielectric constant (2.65) and good planarizability (>90%) and is used as an inter-level dielectric material in a variety of electronic packaging applications<sup>3,4</sup>. The resin, as received, is partially polymerized (B-staged) and dissolved in mesitylene. The structure of the monomer unit is shown in Fig. 1. The polymerization (cure) of BCB proceeds through a two step process: a thermally driven ring opening mechanism followed by a Diels Alder reaction resulting in a crosslinked polymer matrix<sup>5</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 can be varied between 200°C and 350°C. The standard recommended thermal cure process is a 1 hr cure at 250°C<sup>6</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. This system has been described elsewhere<sup>2</sup>. Some of the important features include: 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 adjusts the power levels automatically to maintain the sample at the desired temperature. This allows control of ramp rates and hold temperature of the samples. All the samples were processed 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™ NoEMI-TS® family fiber optic probe, and a Raytek™ Thermalert® T30 series infrared pyrometer were used. The infrared pyrometer was calibrated for emissivity of the sample and was used as the temperature control device as it allowed better control of sample temperature.

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

The index of refraction was measured using a Metricon™ thin film prism coupler at a wavelength of 632.8 nm. Measurements were taken in both the transverse electric (TE) and transverse magnetic modes (TM) in order 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 using a HP4263A LCR meter. Film thickness was measured using a Dektak™ profilometer.

Moisture absorption studies were performed using a quartz crystal nanobalance (Model EQCN-701 from Elchema Inc). BCB was spin coated onto 10 MHz quartz crystals and subsequently cured both in a thermal furnace and the VFM furnace. The cured films were subjected to an 85% relative humidity ambient, 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 thermo-gravimetric analysis (TGA) using a Seiko TG/DTA 320 analyzer. Samples of BCB films (about 30 mg) cured in a thermal convection oven and the VFM furnace were ramped at about 80°C/min to 330°C and held at that temperature for 1 hr. The weight loss after 1 hr at 330°C is recorded.

Residual stress in films cured on silicon due to film shrinkage and CTE mismatch can be estimated by measuring the change in the wafer curvature upon cure. The magnitude of residual stress of the processed BCB films was calculated by measuring the radius of curvature of the wafer before and after cure using a He-Ne laser based Flexus 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°C and 250°C, and the cure time was varied from 5 to 45 minutes. The effect of substrate heating was investigated

by curing samples on quartz, teflon and silicon substrates. The effect of VFM parameters such as central frequency, bandwidth, sweep rate and ramp rate was investigated.

To determine the influence of central frequency on the cure characteristics, films were cured on silicon substrate at different central frequencies between 5.8 GHz to 7.0 GHz with a narrow bandwidth at constant power. The heating characteristics of BCB films cured on silicon substrates at a constant power of 100 W and central frequencies 6.0, 6.4 and 6.8 GHz and a narrow bandwidth of 0.1 GHz are shown in Fig. 2. The gray line shows the heating rate at a central frequency of 6.425 GHz and full bandwidth of 1.15 GHz. As expected, the rate of heating increases with increasing central frequency. Moreover, the ultimate temperature reached by the samples also increases with increasing central frequency.

#### *FTIR studies on VFM cured films:*

FTIR analysis has been shown<sup>7</sup> to be an effective analytical tool in following the reaction progress of BCB. The infrared spectra of an uncured BCB film, a thermally cured film and a VFM cured film are shown in Fig. 3. As seen from this figure, there are distinct changes that occur in the spectrum upon cure. These changes include: increase in intensity of the peak at  $1500\text{ cm}^{-1}$ , representative of the tetrahydronaphthalene group being formed during cure<sup>7</sup> and decrease in intensity of peak at  $1475\text{ cm}^{-1}$ , which corresponds to reacting BCB group. The extent of cure may be estimated (Equation 2) from the ratio of the peak height at  $1500\text{ cm}^{-1}$  of the sample spectrum to the same peak in a control sample. After a one-hour cure at  $300^\circ\text{C}$  in a conventional thermal furnace, the absorbance at  $1475\text{ cm}^{-1}$  completely disappears. This sample is considered fully cured and the peak height at  $1500\text{ cm}^{-1}$  of this sample is taken as the control. Both the absorbances are normalized to

the absorbance at  $1253\text{ cm}^{-1}$ , which corresponds to the rocking mode of the methyl groups attached to the silicon atoms and remains unaffected by the polymerization and hence serves as an internal reference to account for thickness differences between samples.

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

From Fig. 3, it may be seen that the spectra of VFM and thermally cured films, are essentially identical with no significant differences indicating that the chemical structure of VFM cured films is similar to conventional thermally cured films. This analysis cannot account for any possible side reaction or oxidation during cure. However, there are no absorption peaks in the FTIR spectra in the range  $1700\text{-}1800\text{ cm}^{-1}$  indicating the absence of any oxidation during cure.

FTIR spectra were collected in both transmission and attenuated total reflection (ATR) mode. Transmission FTIR is a bulk sampling technique while the ATR mode samples only the top surface ( $< 1\text{ }\mu\text{m}$ ) of the cured films. Similar trends in 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 film. This shows the uniformity of VFM processing within the film thickness.

BCB films cured under identical conditions in the VFM furnace, a conventional thermal furnace and on a hot plate were compared to determine the effectiveness of VFM processing. Fig. 4 shows the percent conversion, as measured by FTIR, of films cured by these three methods at  $175$ ,  $200$  and  $225^\circ\text{C}$  for 30 minutes. All samples were ramped at

30°C per minute. For each cure condition, comparable or higher conversion was achieved by VFM processing.

In order to study the reaction kinetics of VFM processing, BCB films were cured for different times at final cure temperatures ranging from 175°C 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 second. All samples were ramped at 30°C per minute. Fig. 5 shows the infrared 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 cm<sup>-1</sup>. It can be seen that the absorbance at 1500 cm<sup>-1</sup> (indicative of the formation of the tetrahydronaphthalene functional group that forms during polymerization), and hence the extent of cure increases with increasing cure time.

The extent of cure data (from FTIR) of the processed films for different processing conditions is summarized in Fig. 6. From Fig. 6, it is observed that the extent of cure increases with both temperature and cure time. At any given temperature, the rate of reaction levels off which suggests vitrification of the polymer matrix. This phenomenon is commonly seen in thermally cured thermosetting polymer systems<sup>8</sup>.

From Fig. 6, it is also observed that a 5-minute cure at 240°C and a 15-minute cure at 225°C give the same extent of cure as the prescribed standard cure of one hour at 250°C. (Note: A one-hour cure at 250°C gives 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, comparable extent of cure can be achieved at shorter cure times at any given temperature and at lower temperatures for the same cure time.

Fig. 7 shows plots of  $-\ln(1-x)$  as a function of cure time for different temperatures. The cure times used for this analysis correspond to the time before the onset of vitrification (as may be inferred from Fig. 6). The linearity of these plots indicates that the reaction follows 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,  $\ln(k)$  Vs  $1/T$  is plotted in Fig. 8. This plot shows an Arrhenius-type relationship between temperature and rate constants. The slope of this plot yields an apparent activation energy  $E_a$ , of  $25.722 \pm 4.427$  kcal/mol which is about 30% lower than the activation energy reported for thermally cured samples<sup>5,9</sup>.

*Comparison of properties of thermal and VFM cured films:*

The optical and electrical properties of VFM were characterized and compared to thermally cured films. Fig. 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 the VFM furnace under similar conditions. The index of refraction decreases from 1.59 for a soft baked sample to about 1.55 for a fully cured sample. It is observed that at each of these conditions, the VFM cured samples show comparable or lower index of refraction than the thermally cured films. This is consistent with the higher extent of cure attained in these samples as compared to the thermally cured samples.

Similar trends are also seen on comparing the electrical properties of films processed in the VFM furnace and the thermal furnace. Fig. 10 compares the dielectric constant of BCB films processed under different conditions by both these methods. The dielectric constant decreases with increasing extent of cure and VFM cured films show comparable dielectric constant to thermally cures 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 results from the CTE (coefficient of thermal expansion) mis-match between BCB and silicon. The magnitude of the residual stress has been shown to be dependent on the extent of cure<sup>10,11</sup>. The residual stress of a soft baked film and a cured film at its cure temperature (maximum temperature) is nearly zero. Upon cooling to room temperature, the residual stress increases to ~33 MPa (tensile) for a fully cured film. Fig. 11 compares the room temperature residual stress of BCB films cured in the VFM and thermal furnace at different temperatures as a function of percent 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. It may be seen that the residual stress in films depends on the extent of cure and the cure method. For any partially cured condition, VFM processed films show significantly lower residual stress than the corresponding thermally cured films.

Further, there is a significant difference in the rate of increase of stress in the VFM cured films as compared to the thermally cured films. As seen from Fig. 11, the residual stress of thermally cured films increases linearly with percentage conversion and gradually levels off at high conversions. However, VFM cured films show 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 comparing the properties of VFM cured films with thermally cured films. Table 1 compares the optical,

electrical, mechanical and chemical properties of VFM and thermally cured films. Table 1 indicates that a 5-minute VFM cure at 250°C gives properties comparable to films cured at 250°C for one hour in a conventional thermal oven. The in-plane and out of plane index of refraction measurements of cured films were performed using a Metricon™ prism coupler. The optical birefringence of VFM cured BCB films is as low as 0.003 indicating the isotropy of the cured films. The dielectric properties of VFM cured films are comparable to thermally cured films. VFM cured films have a moisture uptake of < 0.2% by weight at 85% relative humidity as determined by quartz crystal microbalance measurements. VFM cured films show thermal stability comparable to thermally cured films with < 1% weight loss after 1 hr 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>12</sup>. Microwave processing differs from thermal processing in that heat is produced within the material by dielectric loss mechanisms unlike thermal processing where heat is transferred from the ambient.

Fig. 2 shows that the heating rate and the ultimate temperature reached by films cured at a constant power increase 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 (Equation 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 the statistical thermal motion of the polar groups in the material. Previous studies<sup>13</sup> on high frequency dielectric characterization of dielectric materials indicate that the dielectric loss of BCB increases with frequency in the range 2.4 to 8.1 GHz. Hence, with increasing central frequency we would expect to see greater absorption and dissipation of microwave energy, which results in higher heating rates and higher ultimate temperature.

Previous studies with hot plate<sup>14</sup> and infrared radiation<sup>15</sup> demonstrated the feasibility of rapid thermal curing of BCB dielectric polymer. No significant differences were observed in the properties of cured films such as residual stress and adhesion. No enhancement in chemical reaction kinetics was reported by the absorption of infrared radiation. From Fig. 3, the FTIR spectra of VFM and thermally cured films are identical. This suggests that the chemical structure of VFM cured BCB films is 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 is 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 has been studied<sup>16</sup> and many promising property improvements along with a reduction in cure time were shown. Thermoset resin systems are characterized by gelation and vitrification phenomenon. For BCB, gelation has been shown<sup>7</sup> to have negligible effect on reaction rate indicating that local mobilities are 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. Fig. 6 clearly shows a drop in 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 apparent activation energy for the cure reaction by VFM processing,  $\sim 25$  kcal/mol is about 30% lower than the reported value of 36 kcal/mole which is not as significant an enhancement in kinetics as other systems studied<sup>17</sup>. This is 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 lower temperatures. Similar results of enhancement in reaction kinetics by microwave processing have been reported by a number of previous studies<sup>18</sup> on thermoset systems. A proposed mechanism for enhanced kinetics suggests<sup>19</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-minute 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 five minutes giving a conversion of about 90% and in the next 55 min of the prescribed standard cure, reaction advances to only about 95%. Microwave processing thus shows a significant improvement in the post-vitrification reaction rates. Alternately, it is likely that due to high local temperatures, the transition to the glassy phase occurs at a higher percent conversion for any given bulk temperature over a shorter 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 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 as compared to thermally cured films. The resulting solvent-induced plasticization could lead to a lower effective modulus and hence lower residual stress. However, this is probably not a significant factor since the index of refraction and dielectric constant of VFM 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 hrs 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, 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 was 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.

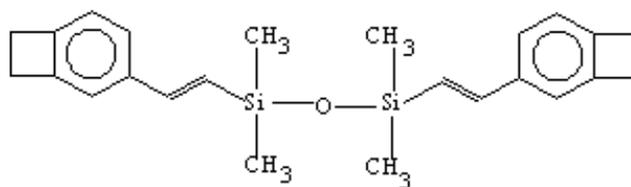
Residual stress is set in a film, upon cooling from the highest  $T_g$  that has been reached<sup>15</sup> independent of the maximum temperature excursion the film experiences in reaching this degree of cure. If curing occurs at a temperature greater than the  $T_g$ , the

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., 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 post-vitrification 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 minutes give a conversion of ~95% and a residual stress of about 22 MPa which is 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.

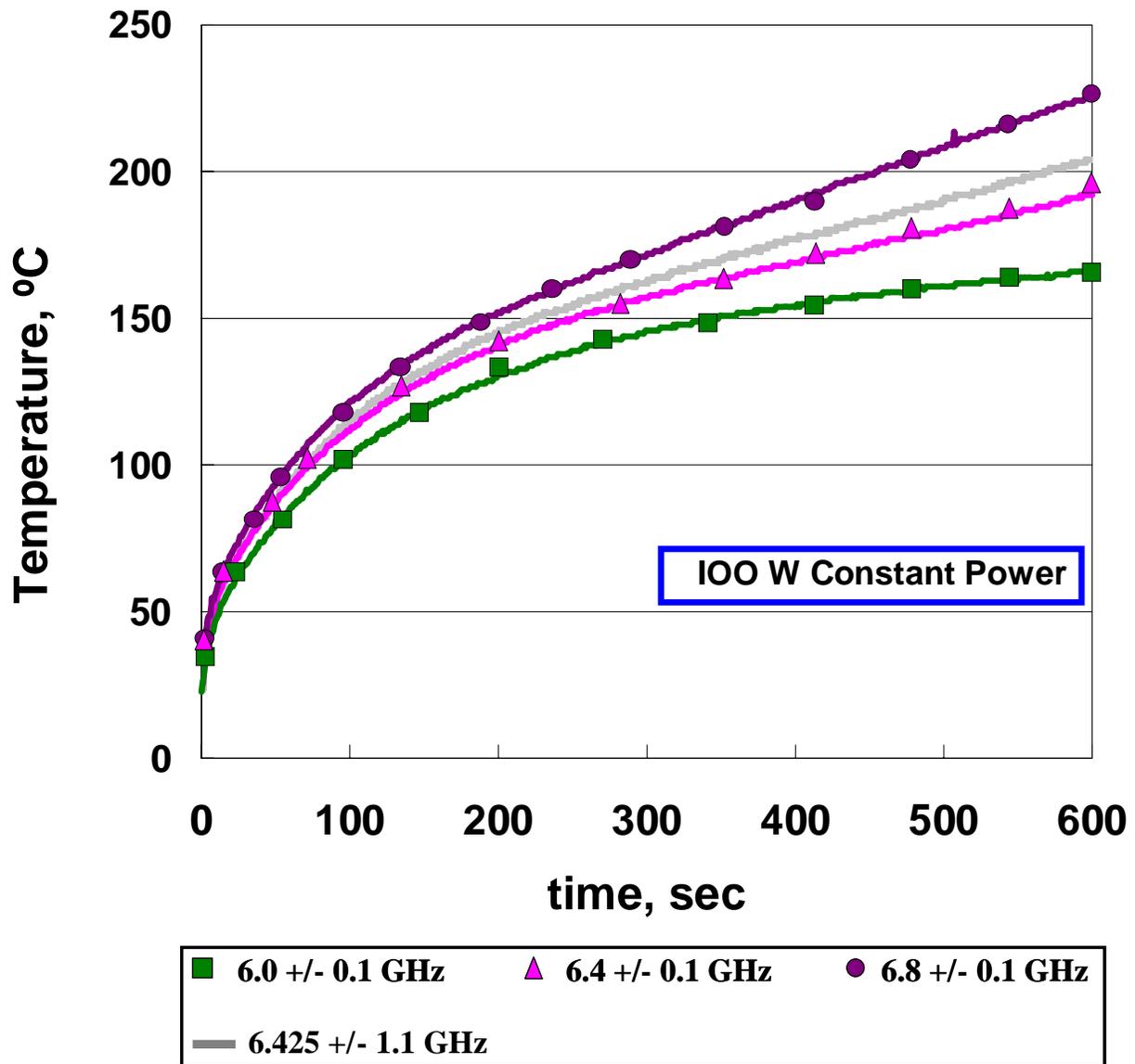
Lastly, possible differences in the intrinsic modulus and CTE of the cured films could contribute to differences in residual stress. Although IR spectra did not show any significant differences in chemical structure, subtle differences in bonding or crosslinked network structure and the nature of crosslinks could exist, which can affect the bulk properties of films. A lower intrinsic modulus and/or CTE results in lower residual stress. It was not possible to verify this hypothesis as 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:**

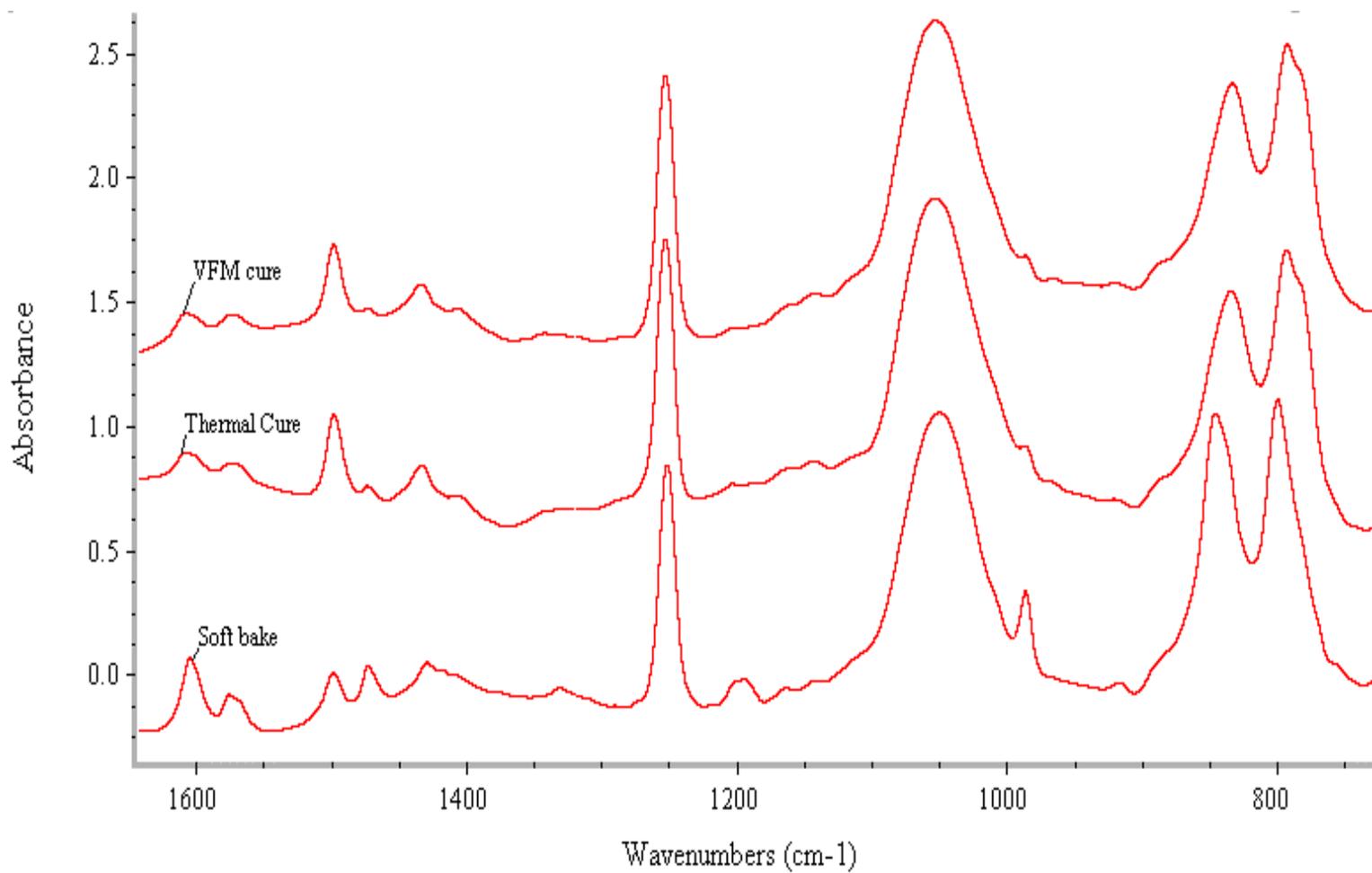
Variable frequency microwave processing of benzocyclobutene was investigated. Results from this study show that VFM processing of BCB is feasible. The chemical structure of VFM cured films is the same as thermally processed films. Ring opening followed by Diels-Alder crosslinking is the primary reaction mechanism for VFM curing of BCB. Study of reaction kinetics shows that the cure reaction follows first order kinetics before vitrification. The rate constants show an Arrhenius-type relationship with temperature with an apparent activation energy of  $25.722 \pm 4.427$  kcal/mol, which is about 30% lower than the reported thermal activation energy. 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 than thermally cured films. Processing improvements such as shorter cure time or lower processing temperature can be achieved. The residual stress of VFM cured films was lower than thermally cured films especially 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.



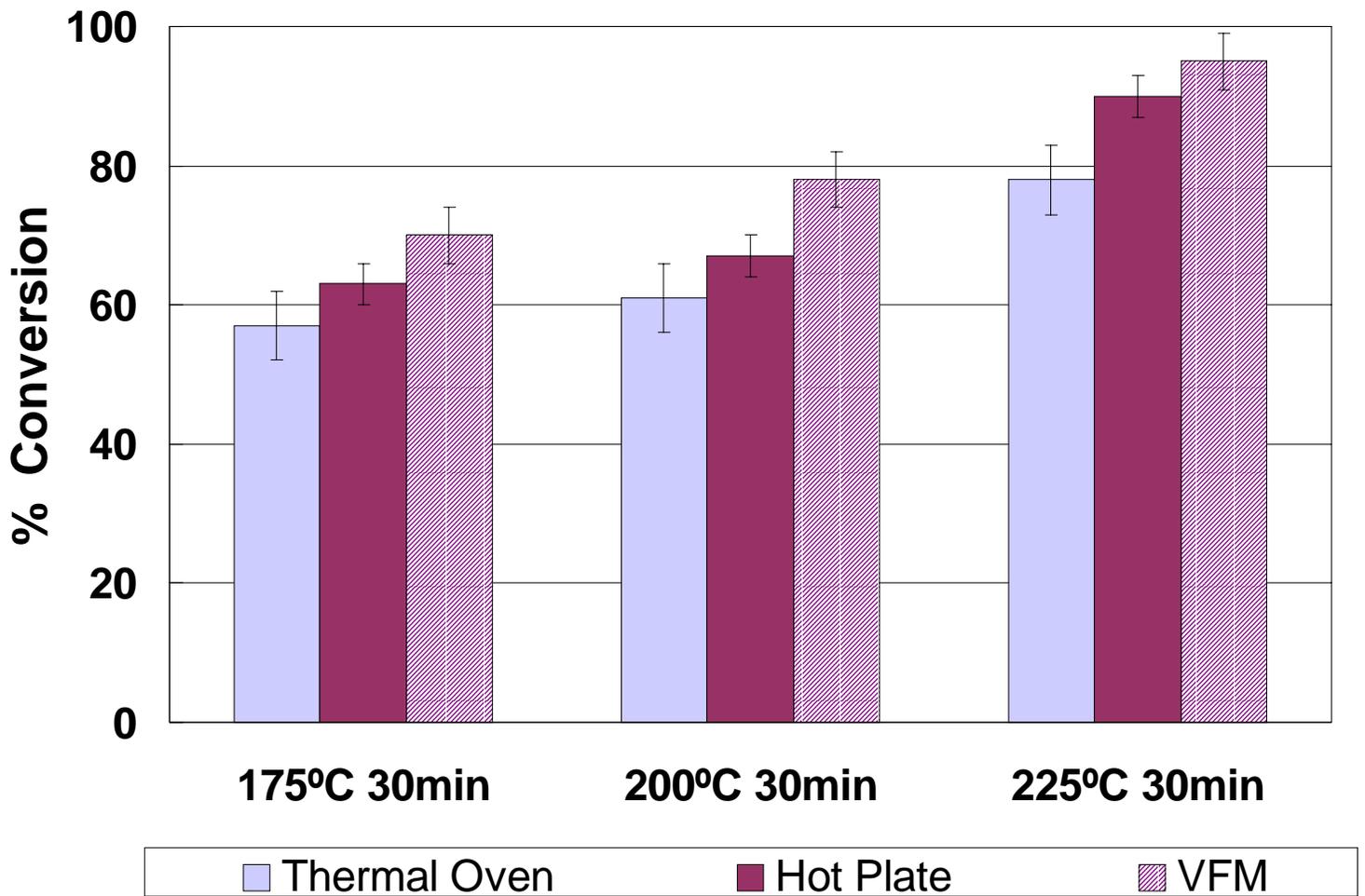
**Figure 1. Chemical structure of benzocyclobutene (BCB) monomer.**



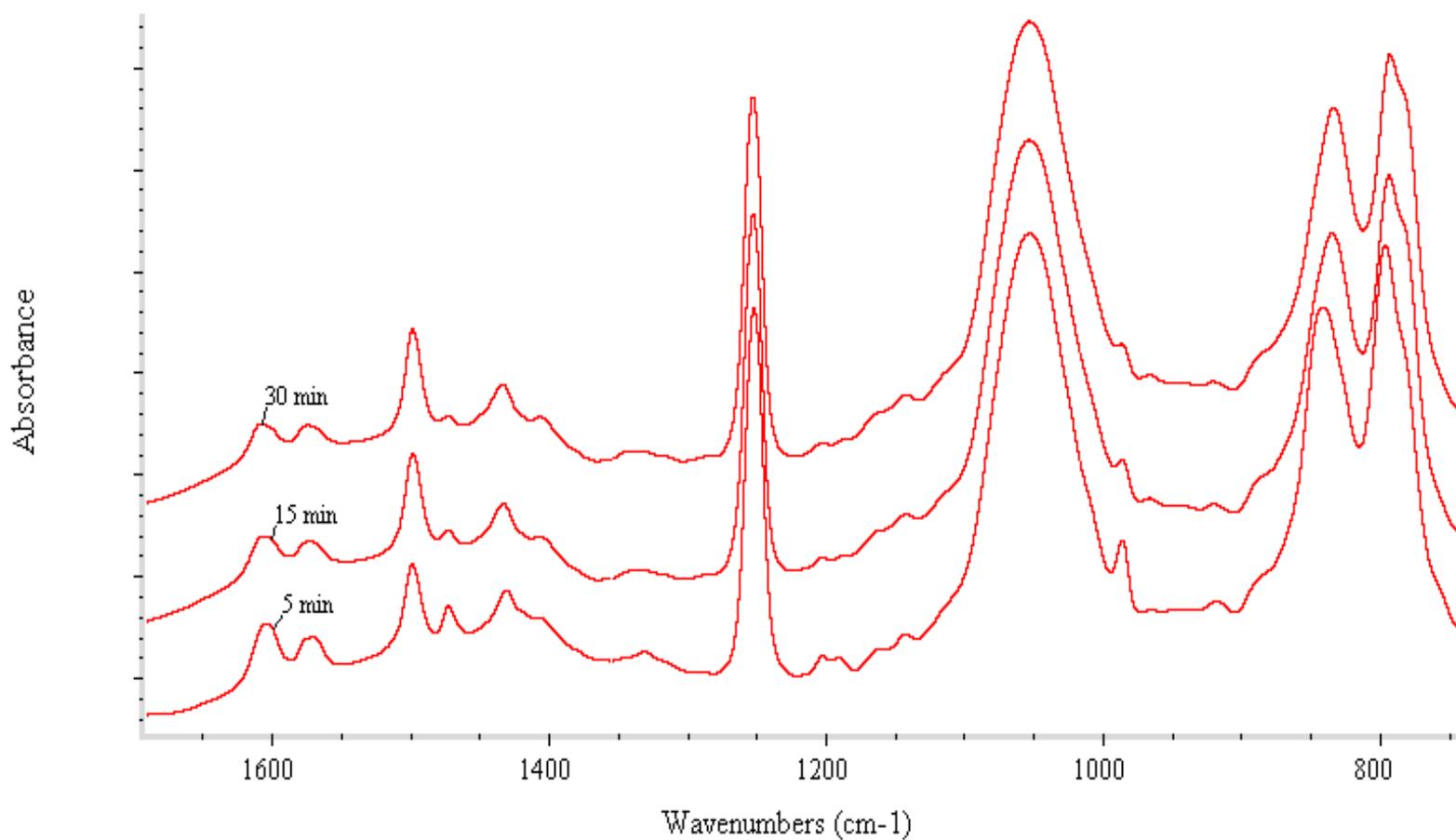
**Figure 2.** The effect of central frequency on the heating characteristics of BCB on silicon at a constant power of 100 W.



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



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



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

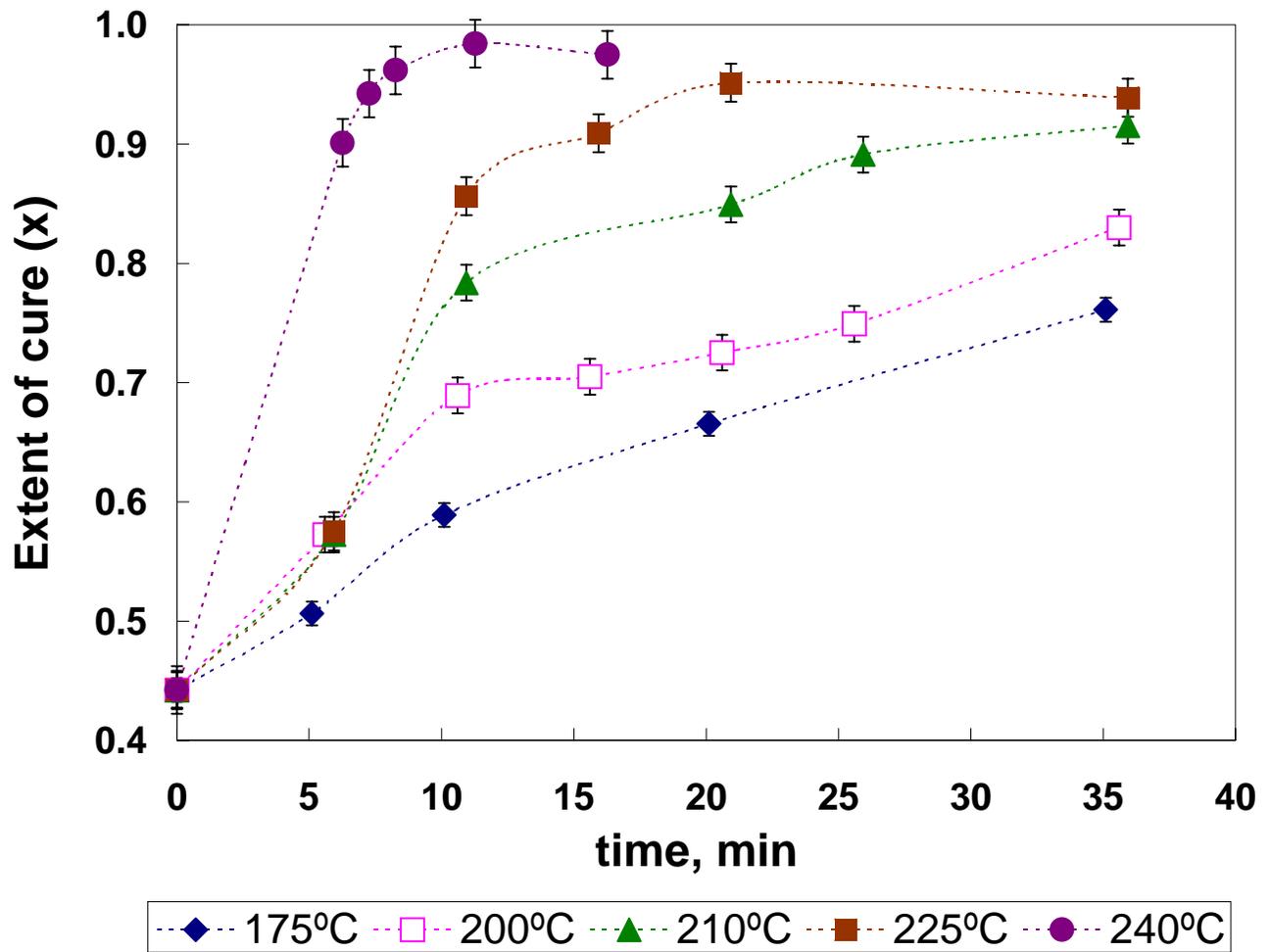


Figure 6. Progress of VFM cure reaction with time at different temperatures (from FTIR data).

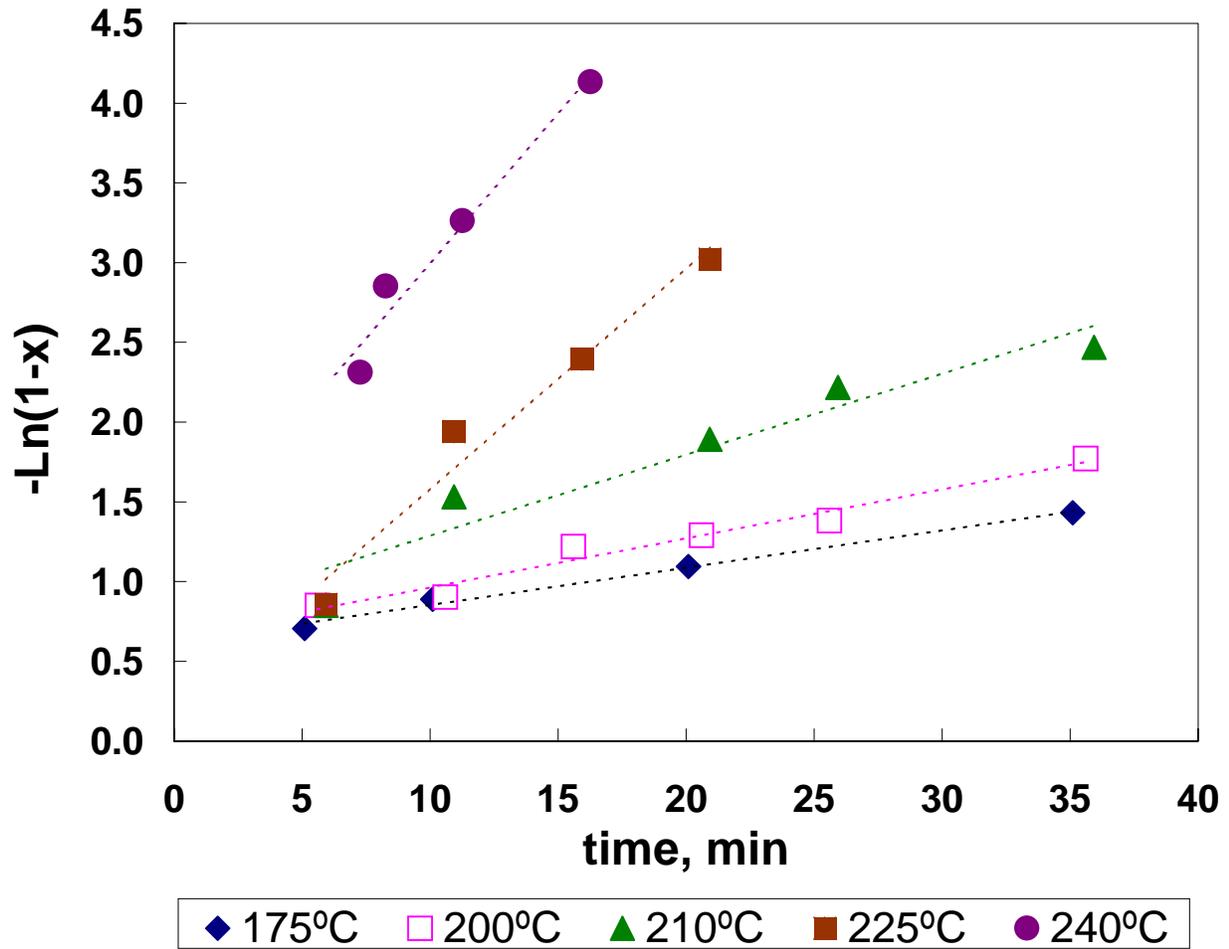
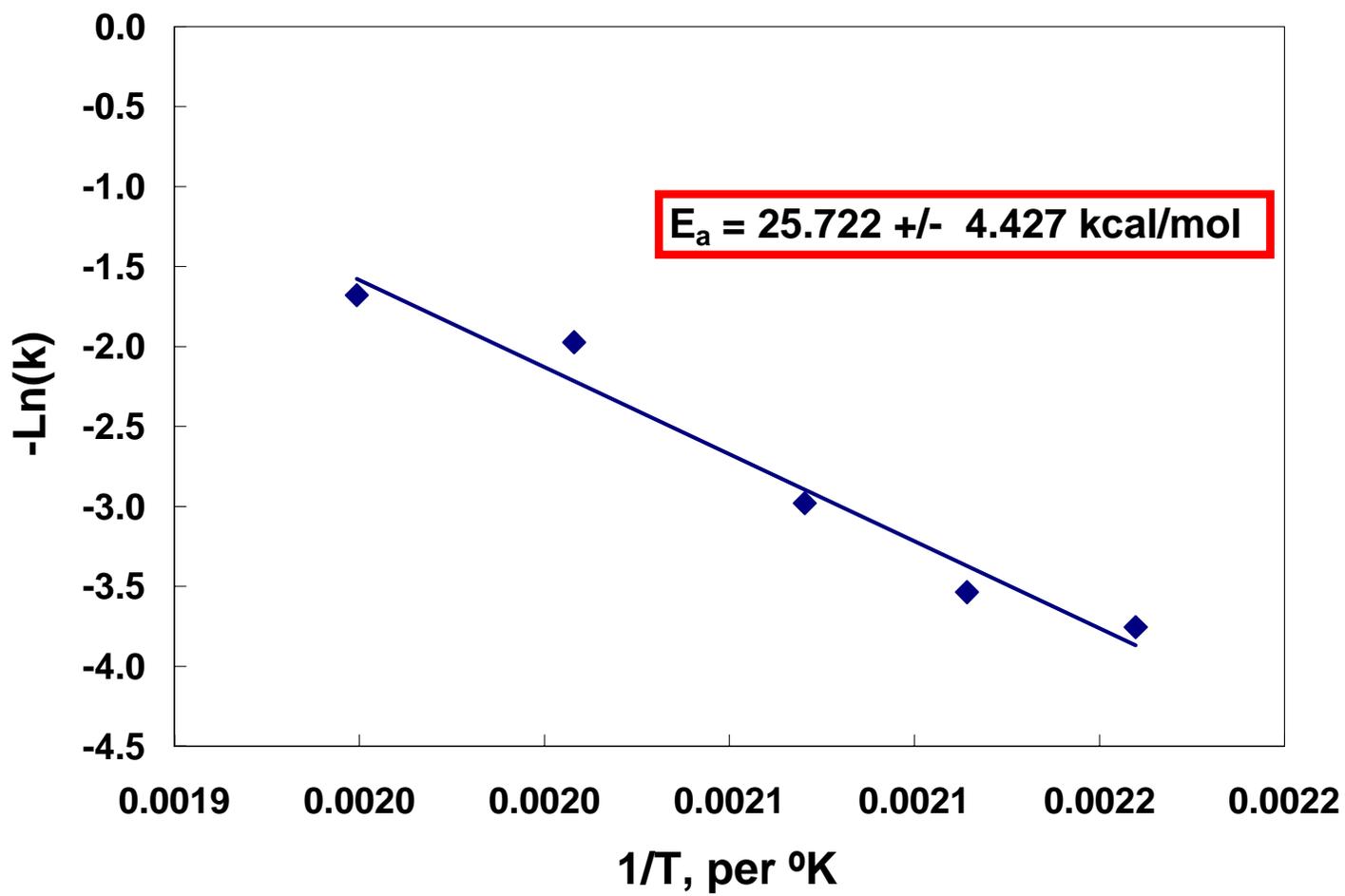


Figure 7. Plots of  $-\ln(1-x)$  Vs time at different cure temperatures to determine the rate constants.



**Figure 8. Plot of  $-\ln(k)$  Vs  $1/T$  to determine the apparent activation energy  $E_a$ , for the cure reaction.**

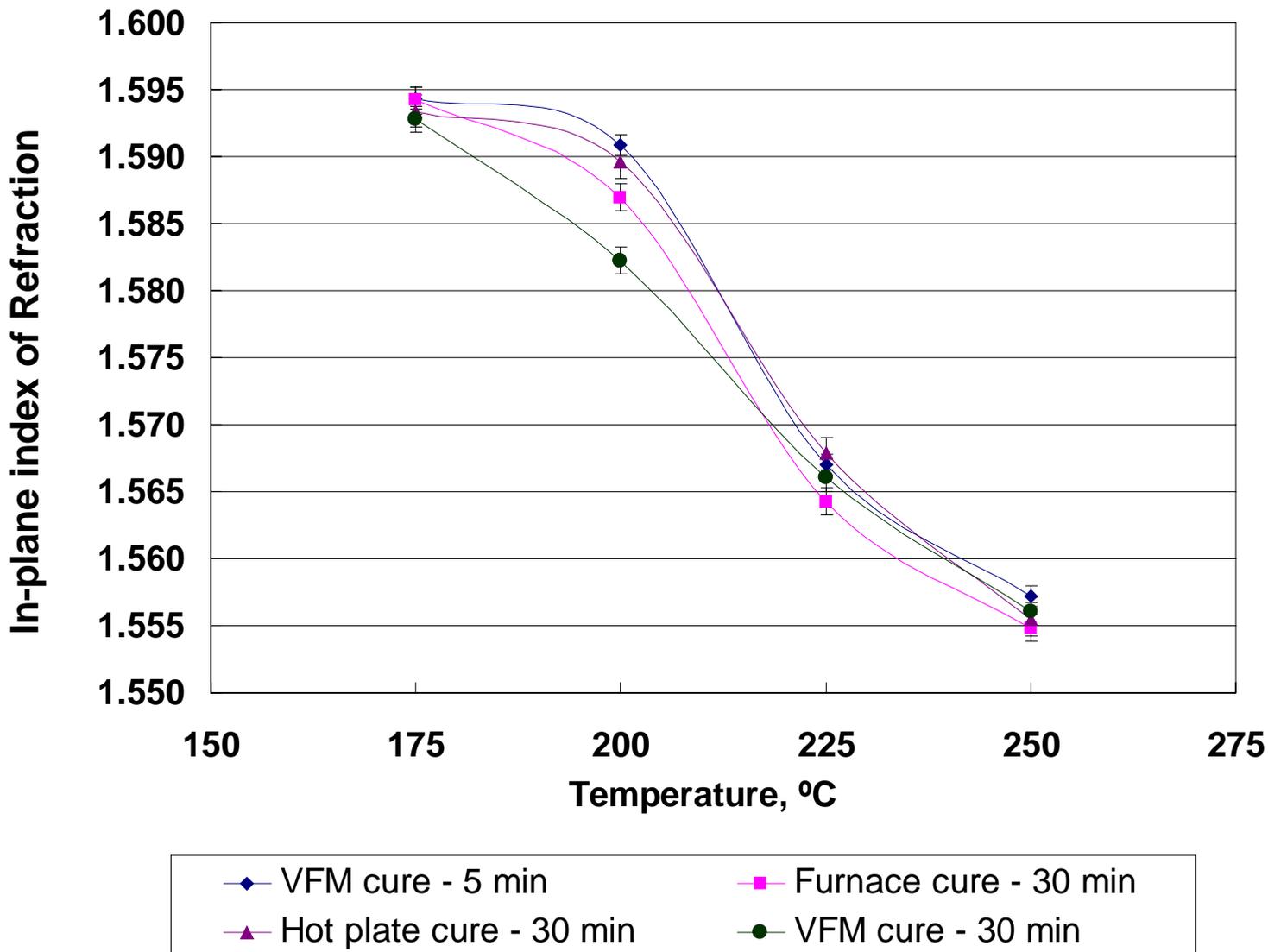


Figure 9. Comparison of in-plane index of refraction of BCB films cured in a furnace, hot plate and VFM under different processing conditions.

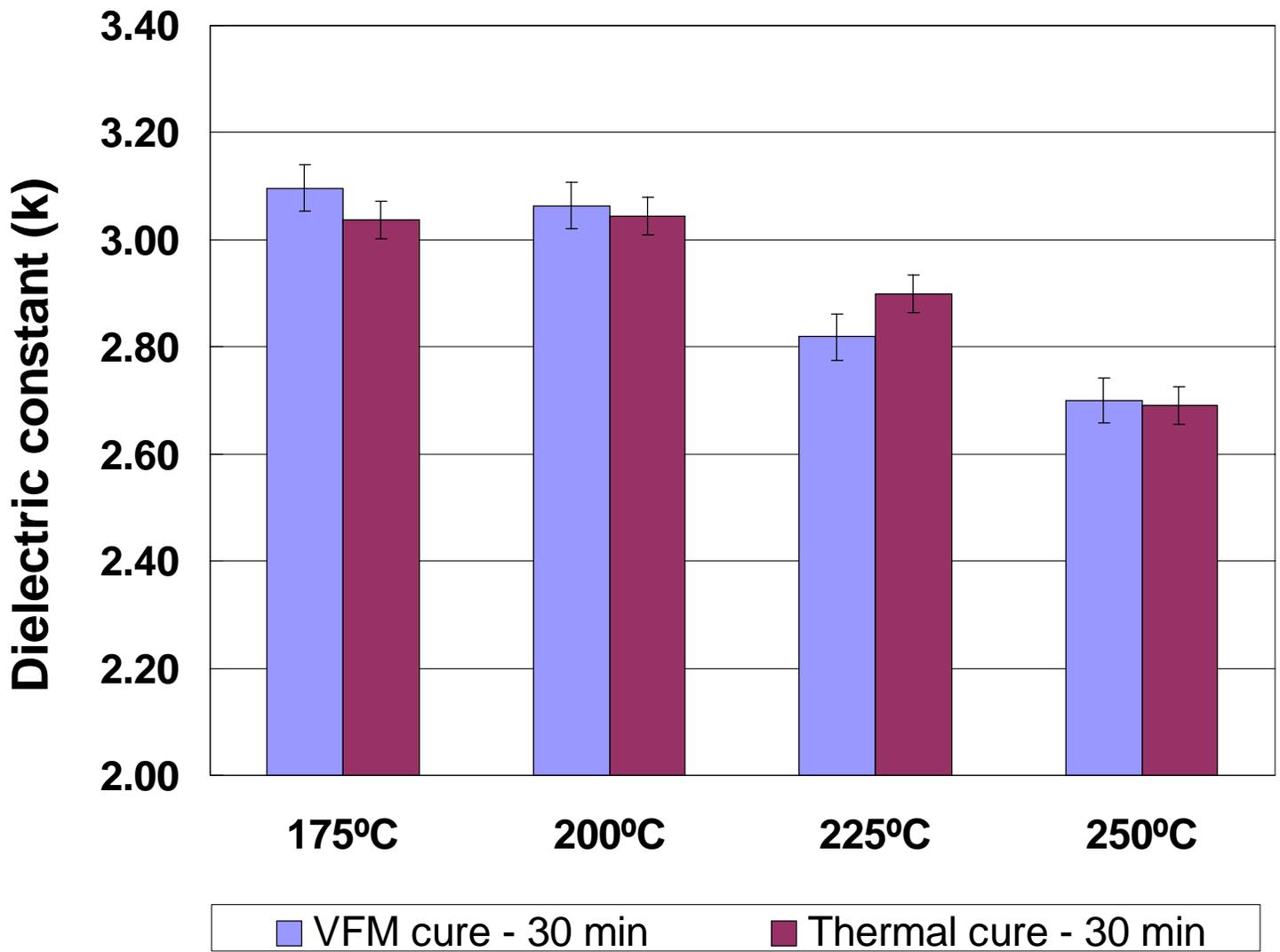


Figure 10. Dielectric constant of VFM and thermally cured BCB films processed under different conditions.

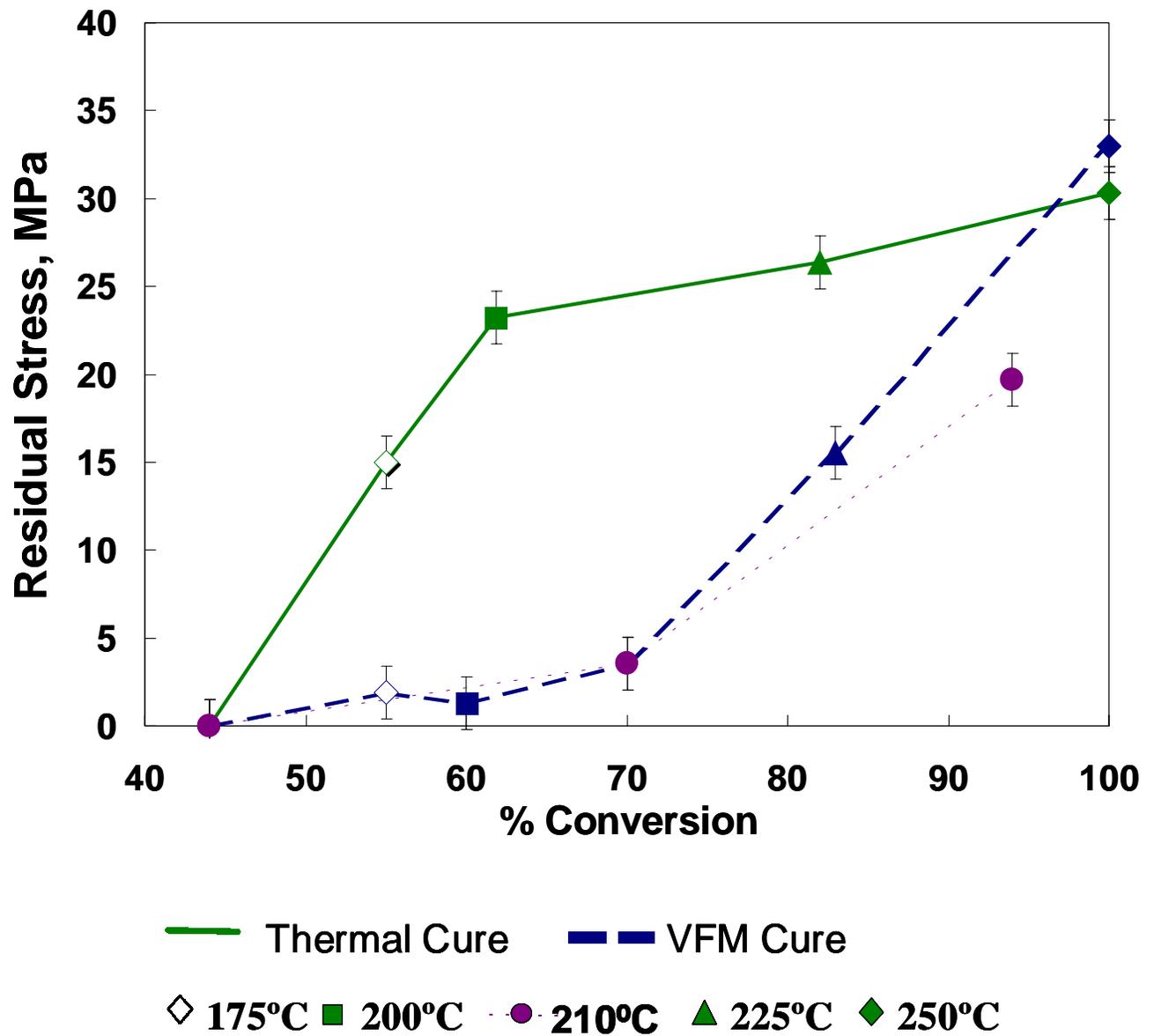


Figure 11. Residual stress of VFM and thermally cured films as a function of percent conversion.

<b>Property</b>	<b>Standard Thermal Cure</b>	<b>VFM Cure</b>
	<b>1 hr at 250°C</b>	<b>5 min at 250°C</b>
<b>In-plane index of Refraction (at 632.8 nm)</b>	<b>1.55</b>	<b>1.55</b>
<b>Birefringence</b>	<b>0.002</b>	<b>0.003</b>
<b>Dielectric constant (at 10 kHz)</b>	<b>2.69</b>	<b>2.70</b>
<b>Loss tangent (at 10 kHz)</b>	<b>0.0009</b>	<b>0.0011</b>
<b>Thermal stability (wt. loss after 1 hr at 330°C)</b>	<b>&lt; 1 %</b>	<b>&lt; 1 %</b>
<b>Moisture uptake (wt% absorbed at 85% RH)</b>	<b>0.194</b>	<b>0.197</b>
<b>Residual Stress (MPa)</b>	<b>30</b>	<b>33</b>

**Table 1. Comparison of properties of BCB films cured by the standard thermal cure, 1 hr at 250°C and VFM cure of 5 min at 250°C.**

## References:

- 
- <sup>1</sup> B. Panchapakesan et al, Variable Frequency Microwave, *Advanced Packaging*, p.60, September / October 1997.
- <sup>2</sup> Kimberley Farnsworth, PhD dissertation, Georgia Institute of Technology, 1999.
- <sup>3</sup> Philip Garrou, "Polymer Dielectrics for Multi-chip module Packaging", Proceedings of IEEE, Vol. 80, No. 1, Dec. 1992.
- <sup>4</sup> Philip Garrou, *Semiconductor International*, Vol. 23, No. 12, pp 119-128.
- <sup>5</sup> BCB Technical Data Sheets, Dow Chemical Company, Midland, MI, 48642.
- <sup>6</sup> Cyclotene processing guidelines and data sheets, Dow Chemical Company, Midland, MI 48642.
- <sup>7</sup> Ted Stokich et al, "Real-time FT-IR studies of the reaction kinetics for the polymerization of divinyl siloxane bis-benzocyclobutane monomers" Material Science of High Temperature polymers Symposium, Proceedings, MRS, vol. 227, pp 103-114, 1991.
- <sup>8</sup> Gillham, J.K, *Polym. Eng. Sci.* vol. 26 (20), pp 1429-1433 , 1986.
- <sup>9</sup> Bair H.E and C.A. Pryde pp 1550-1553 , Proceedings., Soc. Plastic Engineers, ANTEC Montreal, 1991.
- <sup>10</sup> Mechanical properties of BCB films on silicon substrates, Townsend P.H. Stokich T.M. and Huber B.S Material research society symposium proceedings, pp 215-223, vol. 226, 1991.
- <sup>11</sup> Advances in MCM fabrication with BCB dielectric, Heistand R.H et al, *The International Journal of Microcircuits and Electronic Packaging*, Vol. 15, Number 4, 1992.

---

<sup>12</sup> David A. Lewis, Microwave processing of polymers-an Overview, Materials Research Society Symposium Proceedings, vol. 269, pp 21.

<sup>13</sup> Kirk Laursen et al, Examination of High Frequency Dielectric Properties of Thin Film Polymers using an In-situ Resonant technique, Multi-Chip Module Conference, 1995, MCMC-95, Proceedings. 1995 IEEE, 1994, pp 229-231.

<sup>14</sup> Thomas C. Hodge et al, Rapid Thermal Curing of Polymer Interlayer Dielectrics, The international Journal of microcircuits and Electronic Packaging, Vol. 17, Number 1, 1994.

<sup>15</sup> Philip E. Garrou et al, "Rapid thermal curing of BCB dielectric", IEEE transactions on Components, Hybrids and Manufacturing Technology, pp 46-52, Vol. 16, No. 1, Feb. 1993.

<sup>16</sup> Microwave Processing of Materials, National Research Council, National Academy Press, 1991.

<sup>17</sup> Farnsworth, K.D., Manepalli, R.N., Bidstrup Allen, S. A., and Kohl, P. A., "Variable Frequency Microwave Curing Of 3,3', 4,4'-Biphenyltetracarboxylic acid dianhydride/ P-phenylenediamine (BPDA/PPD)", International Journal of Microcircuits and Electronic Packaging, 23, pp 162-171 (2000).

<sup>18</sup> Alazard et al, Materials Research Society Symposium Proceedings, vol.430, pp 593, 1996.

<sup>19</sup> D.A. Lewis et al, J.Polym. Sci., Polym. Chem. Ed. Vol. 23, pp 1647-1653, 1992.