

Rapid Curing of Positive Tone Photosensitive Polybenzoxazole Based Dielectric Resin by Variable Frequency Microwave Processing

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Abstract—High performance polymer dielectrics such as polyimides and polybenzoxazoles are used for several applications in the semiconductor industry due to their excellent dielectric and thermomechanical properties. However, these materials require curing at high temperatures for long periods of time in order to achieve the desired properties. High temperature exposure for long periods of time can be detrimental to device characteristics and reliability. In this study, rapid low temperature curing of a positive tone photosensitive polybenzoxazole based dielectric resin by variable frequency microwave (VFM) processing was investigated. The chemical changes occurring in the film during the condensation reaction and the percent conversion achieved as a function of cure condition were monitored by Fourier transform infrared spectroscopy.

The effectiveness of rapid VFM curing was studied by characterizing the optical, electrical, and thermomechanical properties of VFM cured films with thermally cured films. The thermal stability of cured films was investigated by thermal gravimetric analysis (TGA) and mass spectrometry (MS) studies. The results showed that a higher percent conversion and higher thermal stability can be achieved by using VFM processing than can be obtained using conventional thermal curing at the same cure temperature. However, the complete removal of photopackage related residual products requires slow ramp rates and long cure times.

Index Terms—Dielectrics, infrared (IR), microwave curing, passivation, photosensitive polymer, polybenzoxazole.

I. INTRODUCTION

HIGH performance polymer dielectrics are used in the microelectronics industry for several applications such as interlevel dielectrics in multichip modules, redistribution layers for wafer level packaging, stress buffer passivation layers, and alpha-particle barriers for integrated circuits (ICs). Photosensitive polymers offer additional advantages by reducing the required number of processing steps. Traditionally, negative tone polyimides with organic solvent-based developers are used for these applications due to their high thermal stability and excellent mechanical properties [1]. Positive tone photosensitive polymers have distinct processing and performance advantages over negative tone systems [2]. Positive tone chemistries offer

the possibility of using an aqueous base developer which has environmental advantages. Also, positive tone polymers are less susceptible to mask defects because the masks used for interlevel via holes are dark-field.

One positive tone system of interest is polybenzoxazoles (PBO). PBOs have similar thermal stability and mechanical strength as polyimides and offer improved dielectric performance and chemical resistance [3]. In order to achieve the desired properties, these materials require a processing sequence, which typically involves a high temperature cure for long periods of time lasting several hours. Low coefficient of thermal expansion (CTE) dielectrics and low temperature processing techniques are essential for minimizing the stress arising due to the CTE mismatch between the silicon die and the packaging compounds.

In this study, rapid curing of positive tone photosensitive polybenzoxazole chemistry based dielectric resin, Sumiresin Excel CRC 8650 (Sumitomo Bakelite Co.), was investigated using variable frequency microwave (VFM) curing.

Microwave heating of materials occurs due to dielectric loss mechanisms. The dominant microwave heating mechanism of polymers is orientational or dipolar polarization. The amount of microwave energy per unit volume converted into heat is given by

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

where P_{absorbed} is the power absorbed per unit volume, E is the root mean square electric field strength, ϵ_0 is the permittivity of free space, ϵ'' is the relative loss factor, and f is the frequency. Variable frequency microwave offers significant advantages over traditional single frequency systems by allowing the processing of metals and other conducting materials [4]. VFM processing has been shown to be an effective rapid curing technique of dielectric polymers [5]. Previous studies have shown that VFM processing significantly reduces the cure times without a negative impact on the desired cured film properties. Low temperature curing of polyimides on silicon by variable frequency microwave processing has been demonstrated [6].

The chemistry of CRC 8650 used in this study is proprietary and generic structures are disclosed. The as-received resin was 25% to 40% by weight solids in γ -butyrolactone (GBL) solvent [7]. Typically, the polybenzoxazole cure reaction involves a ring-closing condensation (also referred to as cyclization or cyclo-dehydration) of a poly-hydroxy-amide (PHA) precursor obtained from polycondensation of bis-*o*-aminophenols and a

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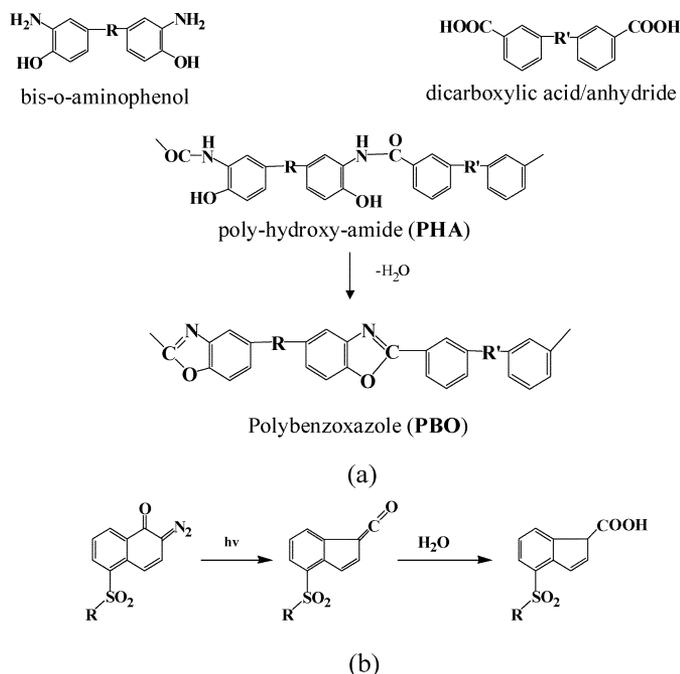


Fig. 1. Schematic representation of (a) cure reaction of polybenzoxazole (PBO) formation and (b) DNQ reaction-Wolff rearrangement.

dicarboxylic acid chloride or anhydride [2], [8]–[10]. The cure reaction and the photoreaction in PBO are schematically shown in Fig. 1. The photoreaction in PBO is based on diazonaphthoquinone (DNQ) chemistry. The DNQ moiety is included as part of the main chain or as part of a photoactive compound (PAC), typically a multifunctional phenol or a benzophenone [11]. The DNQ acts as a dissolution inhibitor of the base resin in developer solution in the unexposed regions. Upon UV exposure the DNQ undergoes Wolff rearrangement forming indene carboxylic acid, which causes the base solubility (Fig. 1). The manufacturer recommended cure schedule for CRC 8650 (standard thermal cure) is a 30 min hold at 150 °C followed by an additional 30 min hold at 320 °C. The effect of VFM processing conditions on the properties of PBO films was characterized and compared to thermally cured films.

II. EXPERIMENTAL

All VFM samples were processed in a Microcure 2100 VFM furnace from Lambda Technologies Inc. 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. The VFM furnace consists of a feedback control system, which controls the temperature of the sample to be cured. The control system automatically adjusts the power levels to maintain the sample at the desired temperature. This allows control of ramp rates and hold temperature of the samples. All 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.

Thin films of PBO (5 to 20 μm) were spin cast onto 4-in diameter $\langle 100 \rangle$ silicon wafers and placed on a quartz disc supported

by quartz mounts inside the microwave cavity. A Raytek Thermalert T30 series infrared (IR) pyrometer was used for temperature measurements. The IR pyrometer was calibrated for emissivity of the sample using a hot plate. The films coated on silicon were cured in the dark without any UV exposure.

The chemical changes occurring in the films during curing and the degree of ring closure of the cured films were monitored by Fourier transform infrared spectroscopy (FTIR) analysis. IR spectra were collected in the attenuated total reflection (ATR) mode using a Nicolet Magna-IR Fourier transform IR spectrometer. All spectra were recorded at a resolution of 4 cm^{-1} and averaged over 128 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. Film thickness was measured using a Dektak profilometer.

Thermal stability was determined by thermogravimetric analysis (TGA) using a Seiko TG/DTA 320 analyzer. Samples of cured PBO films were lifted off silicon substrates using dilute aqueous hydrofluoric (HF) acid and dried for 12 to 18 h in a vacuum oven to remove moisture from the HF-dip process. About 10 to 15 mg of dried sample was placed in a TGA pan and ramped at 10 °C/min to 550 °C in a nitrogen atmosphere (~ 100 sccm). The weight loss during this temperature ramp was recorded. Thermal stability is reported as: a) temperature for 1% weight loss ($T_{1\%}$) and b) temperature for 5% weight loss ($T_{5\%}$).

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 (σ) of the processed polyimide 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) by the following equation:

$$\sigma = \left(\frac{E}{1 - \nu} \right)_{\text{substrate}} \frac{h^2}{6t} \left(\frac{1}{R_{\text{coated}}} - \frac{1}{R_{\text{uncoated}}} \right) \quad (2)$$

where $(E/1 - \nu)$ is the biaxial elastic modulus of the substrate (1.805×10^{11} Pa for $\langle 100 \rangle$ silicon) h is the substrate thickness, t is the film thickness, R_{coated} is the radius of curvature of the substrate with coated with a polymer film, and R_{uncoated} is the radius of curvature of the bare substrate.

The Young's modulus of cured polyimide samples was determined by Instron tensile tester (Model 5640). Rectangular strips of the polyimide films 40 to 60 mm in length and 5 to 8 mm wide were cut while the sample was on the silicon substrate and lifted off using the HF dip, as explained earlier. The films were then dried in a vacuum oven for 12 to 18 h and allowed to equilibrate to the humidity and temperature of the ambient before they were tested. Samples were tested under a constant strain rate, typically 5 mm/min, and the Young's modulus was estimated from the load versus extension data.

III. RESULTS

Fig. 2 shows a differential scanning calorimetry (DSC) scan of an as-received PHA sample under a constant ramp rate of

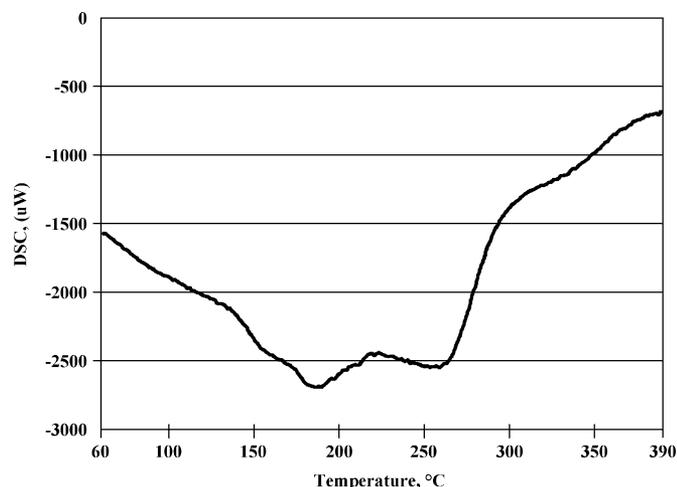


Fig. 2. DSC scan of a PBO sample under a constant ramp rate of 3 °C/min.

3 °C/min to 400 °C in a nitrogen atmosphere. As seen in Fig. 2, two prominent endothermic peaks are observed during the cure cycle. The initial peak starting at ~ 150 °C corresponds to the evolution of solvent and photoproducts from the DNQ based PAC. The broad endotherm at higher temperatures is due to solvent evaporation and evolution of residual higher molecular weight photoproducts. The peak at ~ 275 °C is associated with an increase in the benzoxazole ring-closing reaction, which is completed at a temperature of ~ 320 °C. The DSC scan shows that a temperature greater than 275 °C is essential to achieve significant ring-closing reaction in a short cure time in the PBO films cured thermally. These results are typical of DNQ based PACs [12] and PBOs [10], [13]–[15]. Long cure times are required to achieve significant conversions at low temperature for conventional thermal curing [10].

The chemical changes occurring in the PBO films during the cure process were monitored using FTIR analysis. The formation of the benzoxazole ring-structure from the PHA precursor can be followed by IR spectroscopy. The IR spectra of a) softbaked (unexposed), b) standard thermally cured (30 in at 320 °C), and c) VFM cured PBO films (5 min at 320 °C) are shown in Fig. 3. The changes in the FTIR spectrum can be correlated to the chemical or structural changes occurring within the film. Table I summarizes some of the peak assignments [9], [10], [13], [14], [16]–[22]. As seen in Fig. 3, comparing the spectra (a) and (b) several distinct changes occur during the curing process. The softbaked film shows the characteristic absorption peaks of the poly-hydroxy-amide precursor which include: a broad absorption in the range 3000 to 3500 cm^{-1} corresponding to the $-\text{N}-\text{H}$ and $-\text{O}-\text{H}$ stretch, a carbonyl ($-\text{C}=\text{O}$) stretch at 1650 cm^{-1} and an $-\text{N}-\text{H}$ bending mode vibration at wavenumber 1527 cm^{-1} . As seen from spectrum Fig. 3(b), all of these absorbencies disappear after the standard thermal cure.

The formation of the benzoxazole ring during the cure reaction is characterized by the appearance of a distinct peak at wavenumber 1054 cm^{-1} representative of the $-\text{C}-\text{O}-\text{C}$ stretch of the benzoxazole ring in the standard thermally cured film. This peak is absent in the softbaked film and increases (Fig. 4) with the cyclization reaction by condensation of water as

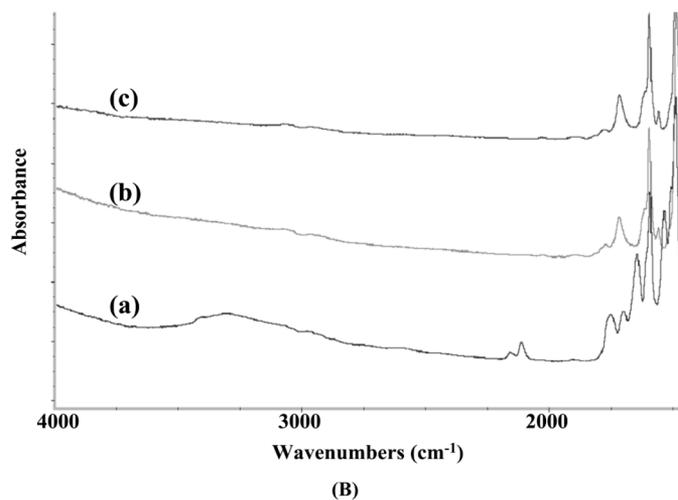
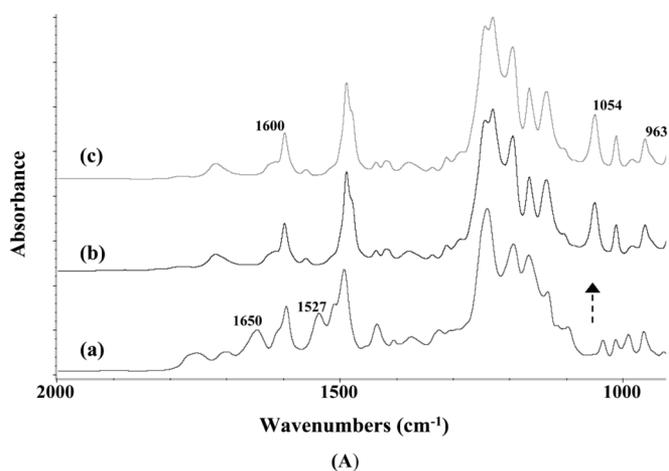


Fig. 3. FTIR spectra of (a) softbaked, (b) standard thermal cured, and (c) VFM cured films: (A) 900–2000 cm^{-1} and (B) 2000–4000 cm^{-1} .

TABLE I
PEAK ASSIGNMENTS OF PBO AND THE CORRESPONDING
CHANGES OCCURRING DURING THE CURE REACTION

Wavenumbers cm^{-1}	Probable Peak Assignment	Changes with cure
3000–3500	$-\text{N}-\text{H}$ stretching	(↓) Disappears completely after cure
3000–3400	$-\text{O}-\text{H}$ stretching	(↓) Disappears completely after cure
1650	amide $-\text{C}=\text{O}$ stretching	(↓) Disappears completely after cure
1616	benzoxazole ring $-\text{C}=\text{N}-$ stretching	(↑) Increases with cure: Indicative of cyclization
1479	benzoxazole ring $-\text{C}=\text{N}-$	(↑) Increases with cure: Indicative of cyclization
1054	benzoxazole ring $-\text{C}-\text{O}-\text{C}$ stretching	(↑) Increases with cure: Indicative of cyclization
963	deformation of aromatic $-\text{C}-\text{H}$ $-\text{C}-\text{F}$ bending	Remains unchanged during curing: Internal standard
1527	$-\text{N}-\text{H}$ bending	(↓) Disappears completely after cure
1600	$-\text{C}=\text{C}-$ from aromatic group	Internal standard

shown in Fig. 1. The benzoxazole ring also shows an absorbance at 1479 cm^{-1} and 1616 cm^{-1} ($-\text{C}=\text{N}-$ stretch). Both these

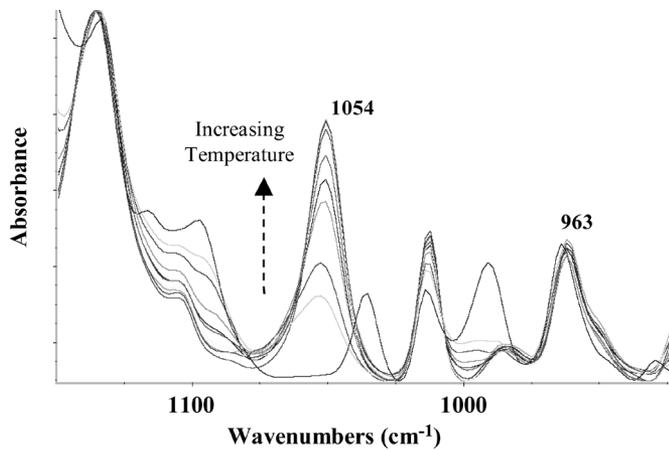


Fig. 4. FTIR spectra of thermally cured PBO films showing an increasing absorbance at 1054 cm^{-1} with cure temperature.

peaks however interfere with the $-\text{C}=\text{C}$ absorption bands of the aromatic ring at 1500 and 1600 cm^{-1} respectively. Further, from Fig. 3, (comparing (b) and (c)) the FTIR spectra of the standard thermal cured film and the VFM cured film are essentially identical with no significant differences in the range 400 to 4000 cm^{-1} . This shows that the chemical structure of VFM cured PBO is similar to that of the standard thermal cured film.

The percent conversion (cyclization or percent ring closure) achieved in cured PBO films was estimated by FTIR analysis using (3).

$$\% \text{Conversion} = \frac{(A_{1054}/A_{\text{Internal Standard}})_{\text{Sample}}}{(A_{1054}/A_{\text{Internal Standard}})_{\text{Std. Thermal}}} \times 100 \quad (3)$$

The absorbance at 1054 cm^{-1} is attributed to the benzoxazole ring formation. The peak height corresponding to the standard thermal cured film was considered fully cured (100% conversion). The peak at 1054 cm^{-1} was normalized by an internal standard. The absorbencies at 1600 cm^{-1} and 963 cm^{-1} ($-\text{C}-\text{H}$ deformation/bending of the aromatic ring/ $-\text{C}-\text{F}$ bending) were relatively unaffected by the cure process (remained constant) and were used as the internal standard. All other peaks were either affected by the cure reaction or interfered with the nearby peaks for e.g., with the broad $-\text{C}-\text{F}$ stretching peaks between 1000 – 1400 cm^{-1} . The estimates of percent conversion in the cured films based on either internal standard were in good agreement and within 1% of each other (as discussed below).

Fig. 4 shows the FTIR spectra of PBO films cured in a conventional thermal oven in the temperature range between 225 and $350\text{ }^{\circ}\text{C}$. Each film was ramped at $3^{\circ}\text{C}/\text{min}$ and held at that temperature for one hour. As seen in Fig. 4, the absorbance at wavenumber 1054 cm^{-1} increases with the cure temperature indicating increasing ring closure while the absorbance at 963 cm^{-1} remains constant. The results from the estimation of percent conversion [from (3)] in the thermally cured films are shown in Fig. 5. As seen in Fig. 5, negligible reaction occurs at temperatures less than $275\text{ }^{\circ}\text{C}$, and complete conversion is possible only at a temperature of $320\text{ }^{\circ}\text{C}$ or greater. These results are consistent with the DSC results discussed earlier, which show that significant reaction occurs only at temperatures greater than

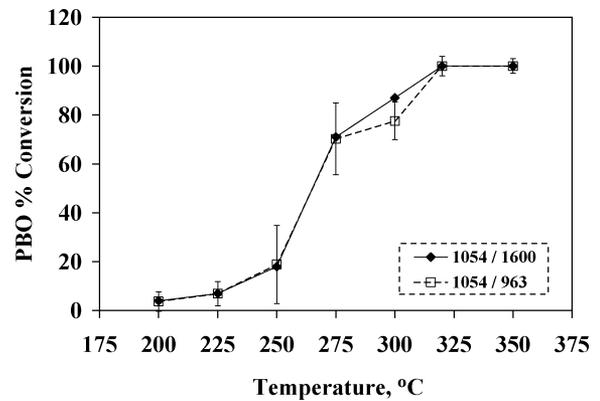


Fig. 5. Percent conversion achieved in thermally cured PBO films as a function of cure temperature estimated from FTIR analysis with peak height at 1054 cm^{-1} and (a) 1600 cm^{-1} and (b) 963 cm^{-1} as an internal standard.

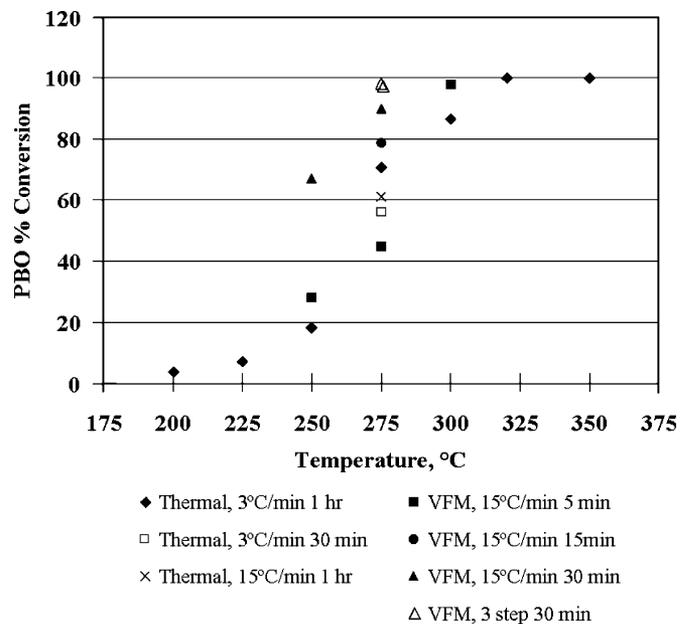


Fig. 6. Comparison of percent conversion achieved in VFM and thermally cured PBO films from FTIR analysis. (VFM 3-Step: $30\text{ }^{\circ}\text{C}$ to $150\text{ }^{\circ}\text{C}$ 5 min, $30\text{ }^{\circ}\text{C}$ to $250\text{ }^{\circ}\text{C}$ 10 min, $10^{\circ}\text{C}/\text{min}$ to $275\text{ }^{\circ}\text{C}$ 30 min).

$275\text{ }^{\circ}\text{C}$. Furthermore, as seen in Fig. 5, the percent conversion of PBO estimated (3) using both 963 cm^{-1} and 1600 cm^{-1} as the internal standard was in good agreement and within 1% of each other (within the sensitivity of the IR spectrometer). FTIR analysis thus provided a semi-quantitative estimate of the percent conversion (effectiveness of the curing) in the PBO films as a function of cure conditions.

VFM curing of PBO under various processing conditions was performed to investigate the feasibility of rapid and low-temperature curing. The percent conversion achieved under different VFM cure conditions from FTIR results is shown in Fig. 6 and compared with the thermally cured samples at corresponding conditions. At least three samples were made at each condition and the results were self-consistent. The solid squares in Fig. 6 represent VFM cured PBO films each ramped at $15^{\circ}\text{C}/\text{min}$ to a given temperature and held at that temperature for 5 min. As seen with the polymer films processed using the standard thermal cure, the percent conversion achieved in VFM cured

films increases with increasing cure temperature. For example, at 275 °C, increasing the VFM cure time from 5 min to 30 min at increased the % conversion from ~42% to ~85%. Complete conversion is achieved even after a 5 min VFM cure at a temperature of 300 °C or higher. Increasing the cure time at lower temperatures (250 °C and 275 °C) for the VFM cured samples shows a significant increase in the percent conversion achieved (solid circles and solid triangles of Fig. 6). Also, a much higher percent conversion can be achieved by a 30-min VFM cure at 250 °C as compared to a slow ramp 1-hour long cure in the thermal oven at the same cure temperature. In addition, increasing the ramp rate or decreasing the cure time at 275 °C in the thermal oven reduces the percent conversion. Considering that significant imidization occurred only at temperatures above 250 °C and residual solvent photoproduct evolution occurred significantly only at temperatures above 250 °C, a three-step VFM cure (30 °C/min to 150 °C 5 min, 30 °C/min to 250 °C 10 min, 10 °C/min to 275 °C 30 min) with a slow intermediate ramp and hold time was developed. The three-step VFM cure gives a significantly higher percent conversion than a 1-h thermal cure at 275 °C. These results are consistent with other studies, which have shown acceleration in cure kinetics by VFM processing [26] and demonstrate the effectiveness of VFM curing as a rapid curing alternative to conventional thermal curing. This acceleration of the cure kinetic is consistent with the acceleration in kinetics observed previously [5], [6]. It has been described as a local heating effect where the reactive moiety is responsible for absorbing the microwave energy and is at a higher average temperature than the remainder of the molecule.

The photoreaction in the PBO films was monitored using FTIR and UV-visible spectroscopy. Fig. 7(a) and (b) show the FTIR and UV-visible spectra, respectively, of PBO precursor (PHA) films before and after exposure. As discussed earlier, PBO is based on a DNQ photochemistry. The unexposed PBO film shows a distinct IR absorbance in the region 2000 to 2220 cm^{-1} ; 2118 cm^{-1} attributed to the $-\text{C}-\text{N}$ stretch [11], [23], [24] and 2164 cm^{-1} ($-\text{N}=\text{N}$ stretch) [24] of the diazo group of the DNQ moiety. This absorbance is seen in the softbaked and unexposed film (Fig. 7) and disappears when fully exposed to UV-radiation. The UV-visible spectra of PBO films as a function of increasing UV exposure dose (g-line) are also shown in Fig. 7. The doses were increased from zero to 1150 mJ/cm^2 (0, 250, 500, 750, 1000, 1150 mJ/cm^2). As seen in Fig. 7(b), the characteristic UV absorbance band in the wavelength range 350 to 450 nm decreases with increasing dose. Further, the fully bleached film (~ 1150 mJ/cm^2 for a 25- μm -thick film) has a negligible absorbance in range 350 to 450 nm, which enables patterning of relatively thick films. The PAG used in PBO is also heat sensitive. Even without any UV exposure the fully cured films did not show an IR absorbance in the range 2000 to 2220 cm^{-1} indicating the disappearance of the $-\text{N}=\text{N}$ moiety. Increasing bake temperatures reduced the IR and UV absorbance of the photosensitive species. The FTIR absorbance of the $-\text{N}=\text{N}$ moiety disappeared completely after a 10-min bake at 150 °C. High temperature bakes are known to have similar reaction mechanisms as those induced photolytically [25].

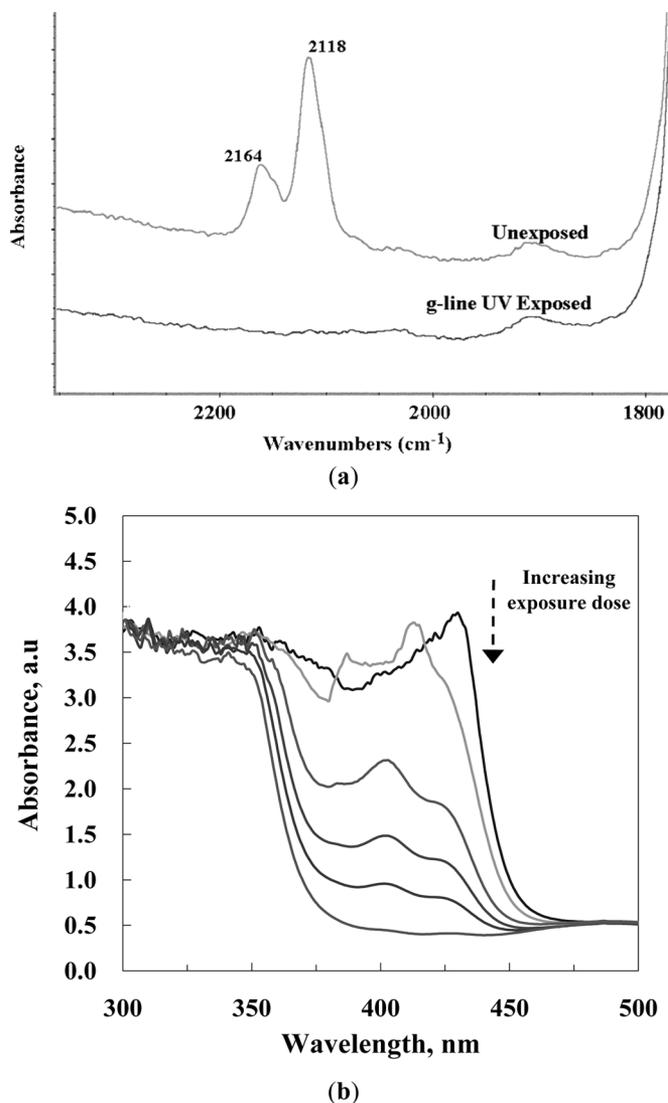


Fig. 7. Photoreaction of PBO precursor films: (a) FTIR spectra and (b) UV-visible spectra.

To investigate the effect of rapid VFM curing on the physical properties of the cured films, PBO properties for films cured at 320 °C and 275 °C were characterized and compared to thermally cured films. The cure conditions used and the properties measured are summarized in Table II.

As seen from Table II, PBO films cured under all four conditions show a low birefringence indicating that the films are essentially isotropic in nature. Further, no significant differences were observed in the index of refraction and birefringence of films cured under the four conditions. However, significant differences in the electrical properties between the standard thermal cured films (A) and low temperature cured films (B and D) can be observed. The standard thermally cured film has a dielectric constant of 2.97 measured at 10 kHz, whereas the low temperature thermal and VFM cured films show a dielectric constant of 3.24 and 3.29, respectively. Similarly, the loss tangents of the low temperature thermal and VFM cured films measured at 10 kHz are significantly higher than the standard thermal cured films. Residual solvent and photoproducts are

TABLE II
COMPARISON OF PROPERTIES OF VFM AND THERMALLY CURED FILMS CURED AT 320 °C AND 275 °C

Cure Condition →	Thermal		VFM	
	A	B	C	D
Property ↓	320°C	275°C	320°C	275°C
Degree of Cure	100%	78%	100%	98%
Optical				
In-plane Refractive Index	1.6179	1.6185	1.6202	1.6172
Through-plane Refractive Index	1.6097	1.6098	1.6096	1.6082
Birefringence	0.0082	0.0087	0.0106	0.0089
Electrical				
Dielectric Constant (@ 10 kHz, 50 % RH)	2.97	3.24	3.04 @	3.29
Loss Tangent (@ 10 kHz, 50 % RH)	0.0043	0.0938	0.0047	0.0199
Mechanical				
Residual Stress, MPa	31.49	28.88	36.47	31.54
Tensile Modulus, GPa	2.59	2.48	2.26	2.48
Thermal				
Coeff. Of Thermal Expansion, ppm/°C	60.91	69.5	57.9	55.7
Glass transition, T _g , °C	284	259	286	254
Temp. for 5 % wt. loss (°C)	433	400	422	420
Temp. for 1 % wt. loss (°C)	361	323	352	351

@ 10 min at 320°C

Cure Conditions:

A: 3°C/min to 150°C 30 min + 3°C/min to 320°C 30 min

C: 15°C/min to 150°C 5 min + 15°C/min to 320°C 5 min

B: 3°C/min to 150°C 30 min + 3°C/min to 275°C 60 min

D: 30°C/min to 150°C 5 min + 30°C/min to 250°C 10 min + 10°C/min to 275°C 30 min

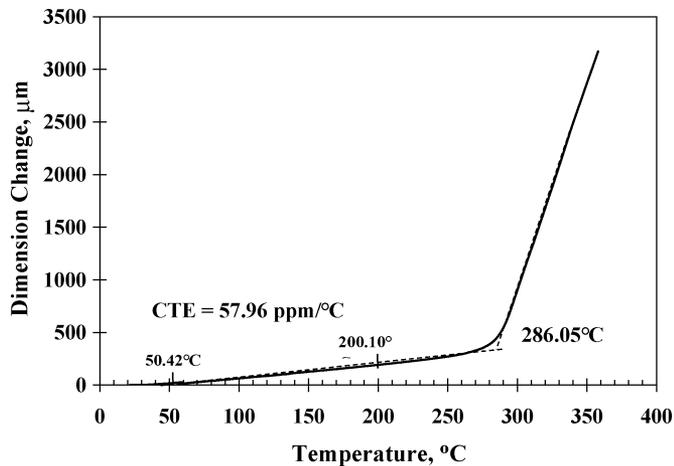


Fig. 8. TMA plot of VFM cured PBO film cured at 320 °C for 5 min. TMA ramp rate: 5 °C/min. Load: 0.05 N.

believed to be responsible for the increased dielectric constant and dielectric loss in the low temperature cured films.

The thermomechanical properties of cured films are also shown in Table II. As described in the experimental section, residual stress in cured films was estimated from wafer curvature measurements and the Young's modulus was determined from Instron pull tests. The residual stress in a standard thermal cured film was ~32 MPa. No significant difference in the Young's modulus of the films was observed for the four cure conditions studied. The CTE and T_g of cured films were determined by TMA measurements. Fig. 8 shows a typical TMA plot of a cured PBO film (C) ramped at 5 °C/min in

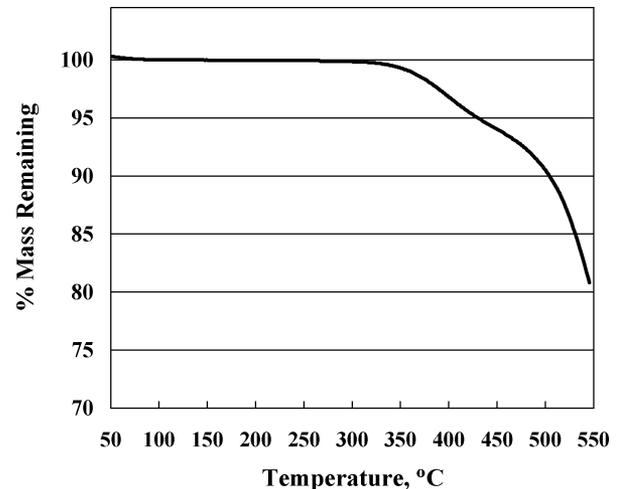


Fig. 9. TGA scan of a standard thermal cured PBO film ramped at 10 °C/min to 550 °C.

the TMA. As seen from Table II, the T_g of low temperature cured films was lower than the T_g for standard thermal cured films (condition A of Table II). Further, the CTE of the low temperature thermally cured film (condition B of Table II) is higher than the standard thermally cured film.

Thermo gravimetric analysis (TGA) was performed on VFM and thermally cured PBO films to evaluate the effect of rapid low-temperature VFM curing on the thermal stability of cured films. About 5 to 10 mg samples of the cured films were ramped to a temperature of 550 °C at 10 °C/min in a nitrogen atmosphere. Fig. 9 shows the TGA scan of a standard thermal cured

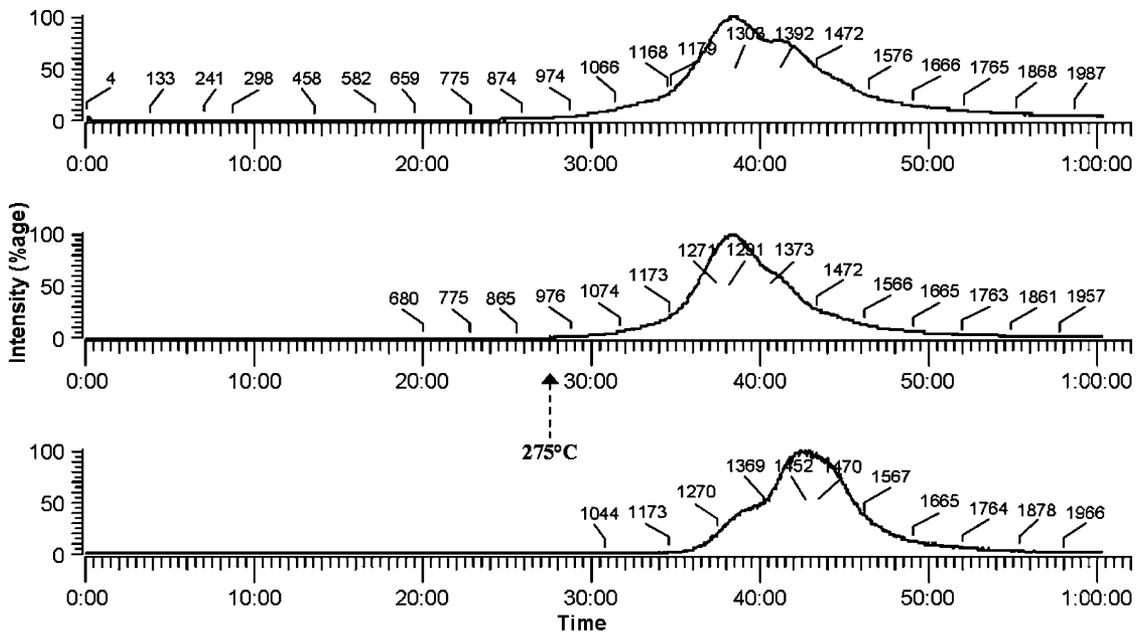


Fig. 10. Mass spectroscopy results of PBO films ramped at 10 °C/min to 450 °C.

PBO film ramped at 10 °C/min to 550 °C in a nitrogen atmosphere. As seen in the Fig. 9, there is no significant weight loss in the cured film at temperatures below 300 °C. However, at higher temperatures there is a gradual drop in mass starting at 300 °C. This is followed by a sharper drop in mass at temperatures greater than 500 °C. As seen from Fig. 9 and Table II, (Sample B) the standard thermal cured film shows a $T_{5\%}$ (temperature at which 5% weight loss occurred) of ~ 433 °C. Low-temperature thermal curing significantly lowered the $T_{5\%}$ of cured film. The thermal stability of low-temperature VFM cured films (Sample D) is however greater than the low-temperature thermally cured films (Sample B). Thus, it is possible to essentially fully cure a material by VFM (Sample D) at low temperature, and yet not achieve all the desired mechanical properties because the chemical reaction of curing, is different from the evolution of the products.

In order to identify the species responsible for weight loss in the TGA, mass spectroscopy (MS) studies were conducted on the cured films. Fig. 10 shows the total ion-trace and that of the primary species detected from a PBO film cured at 250 °C. As seen in Fig. 10, at temperatures greater than 250 °C, the primary species evolved correspond to molecular weights 200 and 292 and their fragments, which could be attributed to the photo-package associated with the PBO film.

IV. DISCUSSION

Polybenzoxazole based dielectric resins are known for their exceptional mechanical properties, high thermal stability, and good chemical resistance. Microwave processing has been shown to provide significant reduction in the processing times of several thin films polymers [26]. Unlike polyimides where the imide-ring closure is completed at ~ 240 °C, the benzoxazole ring formation typically occurs at much higher temperatures. Several studies have reported the PBO ring cyclization reaction at temperatures from 240 to 350 °C [13]–[15], [17]. Significant

ring closure is possible only at high temperatures or very long times at low temperatures [9]. Increased chain mobility and high local temperatures resulting from localized relaxation of polarization in microwave-processed films could enhance the reaction rates at relatively lower temperatures. Indeed, as seen from Fig. 6, FTIR results show significantly higher percent conversion in a shorter cure time by microwave processing, especially at low processing temperatures (250 °C and 275 °C). This is consistent with observations by other researchers that microwave processing improvements are more pronounced in slower reacting systems and particularly at lower temperatures [27].

The characterization of the electrical properties of cured PBO films showed that films cured at low temperatures had a higher dielectric constant and a higher dielectric loss which is likely due to residual solvent and photoproducts. These observations are consistent with other reports in literature that report increased relative permittivity and loss tangent for rapid cured photosensitive dielectric films [28].

TMA studies show that lowering of the cure temperature also lowered the T_g of the cured PBO films. This may be attributed to a) incomplete reaction (ring closure), b) residual solvent or photoproducts which could act as plasticizers, and c) differences in the packing density and associated free volume as a result of low temperature cure. No significant difference in the Young's modulus of PBO films was observed under the cured conditions studied. As discussed earlier, the low birefringence of PBO films suggests that they are isotropic in nature. The residual stress in VFM cured films at 320 °C and 275 °C is slightly higher than that of films cured thermally at the corresponding temperature. The residual stress in the cured films depends on several factors. Differences in processing methodology can significantly impact the evolution of intrinsic stress in the film depending on the inherent chain rigidity [29], [30]. For example, the rate of solvent and photoproduct evolution relative to the rate of ring-closing

reaction could be different in VFM cured films as compared to thermally cured films.

Weight loss in TGA for the low-temperature thermal cured films (Table II, Sample B) could also be due to the evolution of ring-closure condensation products (water). This is evident by the much lower $T_{1\%}$ for the low temperature thermally cured film, which is only 78% cured. At higher temperatures, the films begin to lose mass and this may be attributed to the residual photoproducts. These may result from the initial DNQ based PAC or its reaction byproducts. The PAC is usually functionalized to improve the lithographic and processing performance and is typically a higher molecular weight species [8], [11] as compared to the solvent, making it difficult to remove from the film during the cure process. Further, reaction byproducts of the PAC may also be responsible for TGA weight loss.

The thermal reactions of DNQ based PACs have been studied [11], [25], [31]. The PAC typically has $\sim 2\text{--}3$ DNQ moieties [8], [11], and their reaction with neighboring backbone chains forming ester-type species (which also affects the percent conversion achieved) could make the PAC act as a crosslinking agent [31]. These crosslinks are reasonably stable even up to temperatures of $\sim 200^\circ\text{C}$ [32] (or higher based on the actual PAC composition). This could affect the percent conversion achieved as well as the thermal stability of the PBO films especially at low cure temperatures.

V. CONCLUSION

Rapid curing of a positive tone photosensitive polybenzoxazole dielectric resin was investigated by VFM processing. The feasibility of low temperature curing on silicon was also studied. The chemical changes occurring during the cure reaction and the effect on processing conditions on the percent conversion achieved in cured films were monitored by FTIR spectroscopy. FTIR studies show that the chemical structure of VFM cured PBO films is identical to standard thermal cured films. These studies also show that rapid curing of PBO by VFM processing is feasible and significantly higher conversion can be achieved by microwave processing at low temperatures as compared to conventional thermal curing. The effectiveness of rapid VFM curing was studied by characterizing the optical, electrical, and thermomechanical properties of VFM cured films with thermally cured films. The thermal stability of cured films was investigated by TGA and MS studies. The results show that while higher percent conversion and thermal stability than thermal curing can be achieved by VFM processing at lower temperatures, complete removal of photopackage related residual products requires slower ramp rates and longer cure times.

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