Variable Frequency Microwave Curing of Amide-Epoxy Based Polymers

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***Abstract*—Irradiation of a dielectric material with microwave irradiation results in energy transfer due to rotational-vibrational transitions within the molecule. The energy transfer results in a local rise in temperature within the material. Microwave-induced reactions can occur at a lower average temperature than convective heating resulting in faster thermal curing of polymer dielectrics because the energy absorption is localized at particular sites. In this study, variable frequency microwave (VFM) curing of epoxy-based dielectric films was investigated. The microwave energy was swept through a range of frequencies to dissipate standing waves so that metallic conductors could be present with the dielectric films. The rate of reaction and film properties of polyamideimide (PAI) and bisphenol A epoxy resin (BPAEp) were studied. Benzanilide and BPAEp were used as model compounds for the reaction between the amide and epoxy. Compared to convective heating, the microwave reaction rates were higher at each isothermal cure temperature. The resulting mechanical properties of the films cured by microwave heated were superior to thermally cured materials. The elastic modulus of VFM cured PAI/BPAEp films was less than that of thermally cured films and the elongation to break was twice as high. Further, the adhesion to copper was improved with microwave processing. The chemical structure of the VFM cured polymer was different from the thermally cured polymer, based on Fourier transform infrared analysis, and is likely the origin of the improved properties.**

***Index Terms*—Chemical structure, cure of polymers, epoxy resin, fourier transform infrared (FT–IR) spectroscopy, model compounds, physical properties, polyamideimide (PAI), reaction schemes, variable frequency microwaves (VFM).**

I. Introduction

POLYMER dielectrics are used in many places in the microelectronics industry. The processing and curing conditions often require high temperature and extended heat treatments to fully cure thermoset polymers. It is highly desirable to develop curing methods which are rapid, lower temperature, and yield polymers with superior properties. Microwave processing has been studied as an alternative method of polymer curing [1]–[4]. The oscillating electric field in microwave radiation leads to dipole rotational-vibrational transitions in a dielectric material. This converts the electromagnetic irradiation to heat in the dielectric material. The fixed frequency, 2.45 GHz magnetron sources, have been used in many microwave processing studies [4]–[7]. However, it is difficult to uniformly heat materials due to standing waves.

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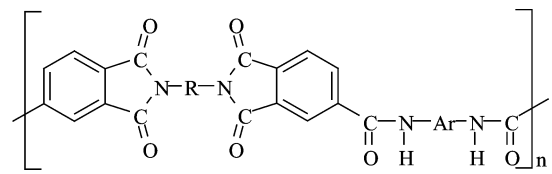

Fig. 1. Chemical structure of polyamideimide (PAI).

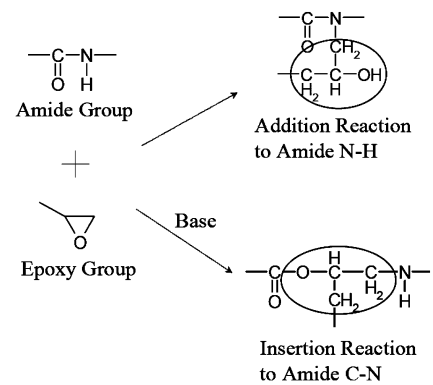

Fig. 2. Reaction of amide and epoxy.

In this study, a variable frequency microwave (VFM) source was used [1]–[3], [8]. The VFM source sweeps through a range of frequencies within milliseconds. So a time-averaged, uniform energy distribution is created throughout the cavity. Polyamideimide (PAI), Fig. 1, is an interesting material for specific applications in the electronics, aviation, and the space industry. PAI has excellent heat and chemical resistance, toughness, and electric properties. Moreover, functionalizing the PAI can improve specific properties. For example, PAI can used as a thermosetting polymer by added a multi-functional epoxy resin, such as bisphenol A epoxy (BPAEp) [9], [10]. In curing an epoxy functionalized PAI polymer, there are several reaction pathways that can occur between the base catalyzed amide and epoxy groups. The base catalyzed reactions, as shown in Fig. 2, are 1) the insertion of the epoxy into the amide C–N bond and 2) the addition of epoxy to the amide N–H bond [9], [10]. In the case of non-catalyzed mixtures, only the insertion reaction occurs. In this paper the properties and reaction pathway of VFM and thermally (in a convection oven) cured PAI/BPAEp films are compared.

II. Experimental

A Microcure 2100 system from Lambda Technologies was used for the microwave curing experiments. The central frequency of VFM sweep was 6.425 GHz. The sweeping band-

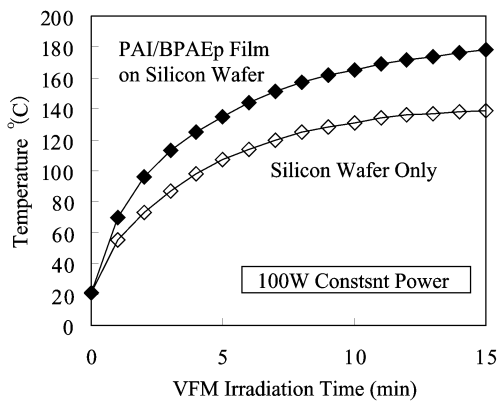

Fig. 3. Heating rate of PAI/BPAEp films on Silicon at 100 W microwave power.

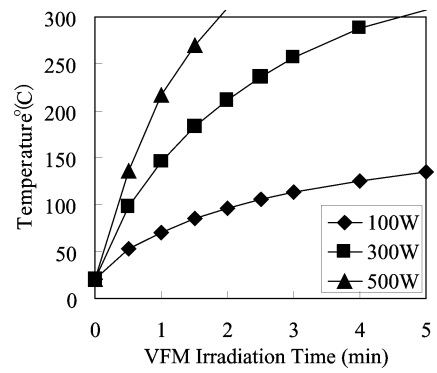

Fig. 4. Heating rate of PAI/BPAEp on silicon as a function of VFM power.

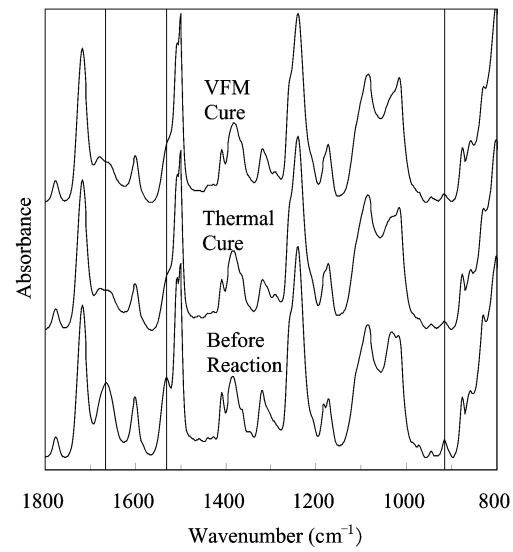

Fig. 5. Comparison of the FT-IR spectra of before reaction, VFM cured, and thermally cured PAI/BPAEp films.

width was 1.15 GHz and the sweep rate was 0.1 s. An infrared pyrometer was used to monitor the temperature within the VFM. An Isotemp Vacuum Oven Model 281A was used for the conventional (thermal) curing experiments.

The PAI (from Hitachi Chemical Co., Ltd.) and BPAEp (DER-331L from Dow Chemical Company) composite films (PAI:BPAEp ratio of 4: 1) were made by solvent casting the solution onto 18-μm thick copper foil (F0-WS-18 from Furukawa Circuit Foil) at a thickness of 40 μm. These polymer mixtures included 1 wt% 2-ethyl-4-methylimidazole (2E4MZ), with respect to the epoxy, as the catalyst. These films or those with Cu foil were irradiated with microwave on the silicon wafer in the VFM furnace.

Model compounds were chosen to study the reaction between the amide and epoxy groups. Bisphenol A epoxy resin (Dow Chemical Company) was used as the epoxy polymer and benzanilide (Aldrich Chemical) was used as amide compound. Equi-molar mixtures were used. 2E4MZ was added as the catalyst at 0.25 wt% with respect to epoxy. The polymer mixtures were dissolved in methyl ethyl ketone for spin coating onto silicon wafers. The thickness of the films made from these model compounds was 40 to 50 μm. Duplicate films were made for VFM and thermal curing.

The extent of reaction in the PAI/BPAEp films and model compound films (epoxy and amide) were obtained by fourier transform infrared (FT–IR) spectroscopy analysis. The FT–IR spectra were collected in both the transmission and the attenuated total reflectance (ATR) mode using a Nicolet Magna-IR FTIR spectrometer. The physical properties of the cured PAI/BPAEp films were measured with an Instron tensile tester (Model 5842). The Instron films were 10-mm wide, 60-mm long, and 40-μm thick. The films were pulled at rate of 5 mm/min rate until failure. The peel strength of the Cu foil from the cured PAI/BPAEp films was measured in the Instron tester by pulling the Cu foil at 90° at a rate of 50 mm/min.

III. Results

The heating rate, temperature vs. time profile, for the polymer films when exposed to VFM irradiation is an important parameter because the polymer reacts during the heating cycle even though it is not at the final cure temperature. Fig. 3 shows the wafer temperature as a function of time during exposure to 100 W VFM irradiation. The temperature of an uncoated wafer is compared to a PAI/BPAEp coated wafer. The PAI/BPAEp film on the silicon wafer is highly absorbing at microwave frequencies resulting in the higher temperature of the coated wafer.

The temperature rise is more rapid at higher VFM powers, as shown in Fig. 4 for constant power irradiation from 100 to 500 W. The rate of heating and the temperature of sample increase with applied power. This shows that a minimum power level is required to achieve a particular cure temperature and compensate for wafer cooling.

The reactivity of the PAI/BPAEp films was evaluated by use of FT-IR. The spectra for an uncured film, VFM cured film, and thermally cured film are shown in Fig. 5. The height of the amide $C=O$ stretch (1664 cm^{-1}), amide N–H bending (1531 cm^{-1}), and epoxy deformation (916 cm^{-1}) peaks decreased as a result of the curing reaction. The spectra of VFM cured and thermally cured films were essentially identical. The extent of reaction between the amide and epoxy groups was calculated from the ratio of the peak heights at 916 cm^{-1}. The absorbance at 916 cm^{-1} was normalized to the absorbance at 1776 cm^{-1} for each sample as an internal standard. The 1776 cm^{-1} absorbance corresponds to the symmetric $C=O$ stretching of the five-membered imide ring. The extent of reaction between the amide and epoxy groups

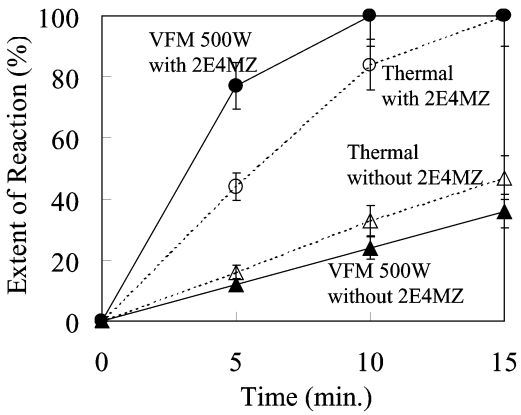

Fig. 6. Extent of cure for PAI/BPAEp films at 180 °C in a convectively heated oven and VFM at 500 W, with and without 2E4MZ.

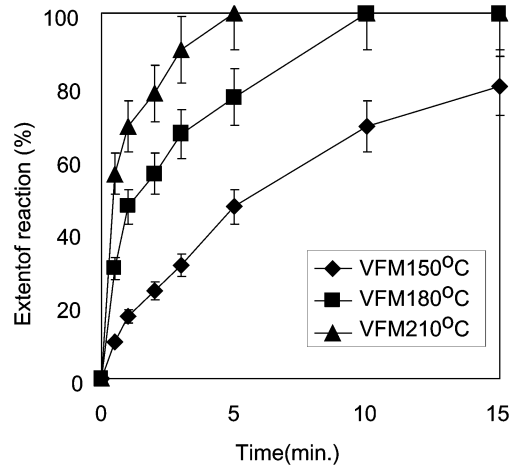

Fig. 7. Extent of VFM cure for PAI/BPAEp films with 2E4MZ held at 150 °C, 180 °C, and 210 °C.

in the PAI/BPAEp film is given by the (1). A sample cured for 1-h at 200 °C in a conventional thermal furnace was used as the fully cured sample (100% cure)

$$\text{Extent of Reaction}(\%) = \frac{\left(\frac{A_{916}}{A_{1776}}\right)_0 - \left(\frac{A_{916}}{A_{1776}}\right)_{\text{sample}}}{\left(\frac{A_{916}}{A_{1776}}\right)_0 - \left(\frac{A_{916}}{A_{1776}}\right)_{100}} \times 100 \tag{1}$$

where A is the absorbance at a particular wavenumber (given by the subscript, e.g., 916 cm^{-1}), at different cure states (0% cure, 100% cure, or the unknown state). The extent of the curing reaction, (1), was measure as a function of time for samples cured at constant temperature in a traditional, thermal oven and samples cured at different VFM conditions. In the VFM system, the samples can be cured at constant power, where the temperature will depend on the absorbance of energy and cooling rate, or at constant temperature where the power is adjusted to maintain isothermal conditions. Further, the effect of the catalyst was investigated by curing polymer films with and without catalyst. Fig. 6 shows the extent of reaction for PAI/BPAEp films with and without catalyst heated in the VFM system at 500 W (constant power) and in a thermal oven at 180 °C. The catalyst clearly accelerates the rate of the reaction. With the catalyst present, the VFM heating is very effective in curing the polymer film. However, as shown earlier in Fig. 4, the temperature changes in the film when exposed to a constant power of 500 W. Thus, a series of isothermal VFM curing experiments for polymer films with 2E4MZ were undertaken. Fig. 7 shows the extent of reaction for VFM for PAI/BPAEp films with 2E4MZ at three temperatures. In each case the reaction rate is rapid. Fig. 8 shows the extent of reaction for the same PAI/BPAEp films (with 2E4MZ) thermally cured at the same temperature as the VFM films in Fig. 7.

The relationship of the resulting physical properties between the thermal and VFM cured films are very important in determining the usefulness of the films. Table I shows three physical properties, maximum strength, percent elongation prior to brittle fracture (stretch rate), and elastic modulus for the cured PAI/BPAEp films. The values listed in Table I are the highest ones obtained among all of the strips tested for a particular cure condition. Lower values can be obtained due to defects and improper loading or handling of the films. Defects can lead to film fracture which does not reflect the intrinsic property of the film. If unintentional defects are not present, then the true mechanical properties (especially elongation and strength) are reflected in the maximum value of that test. The strength of all the VFM and thermally cured films were essentially the same. Significant differences were found in the percent elongation (stretch rate) and modulus of the films. The elastic modulus of the VFM cured films was less than that of thermally cured films. Moreover, elongation to break was much higher for the 150 °C VFM

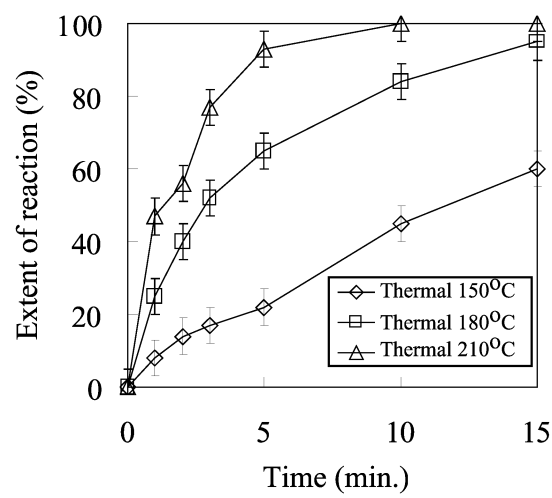

Fig. 8. Extent of thermal cure for PAI/BPAEp films with 2E4MZ held at 150 °C, 180 °C, and 210 °C.

TABLE I
PHYSICAL PROPERTIES OF CURED PAI/BPAEP FILMS

Item	Hold at 210°C		Hold at 180°C		Hold at 150°C	
	VFM	Thermal	VFM	Thermal	VFM	Thermal
Max. Strength (MPa)	60.1	62.0	57.3	61.0	62.5	61.4
Stretch Rate (%)	15.5	14.2	13.3	15.5	28.2	13.4
Initial Elastic Modulus (MPa)	1430	1830	1640	1910	1530	1750

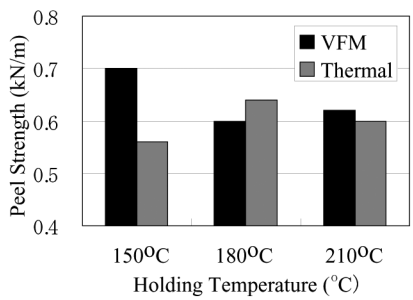

Fig. 9. Peel strength of Cu foil from cured PAI/BPAEp films.

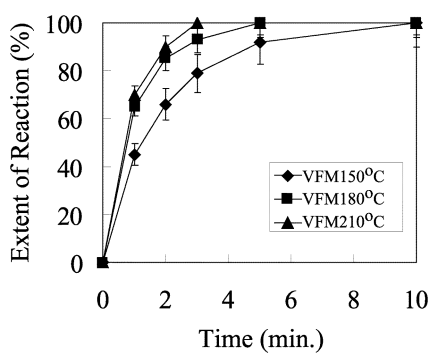

Fig. 10. Extent of VFM cure for model epoxy compounds with 2E4MZ at three temperatures.

sample than the thermally cured film at the same temperature, or VFM films at higher temperature.

The adhesive strength between copper foil and the cured PAI/BPAEp films was measured by pulling a copper strip from the polymer at a 90° angle. Fig. 9 shows data for VFM and thermally cured films at three curing temperatures. There was no significant difference between the thermally cured and VFM films when cured 210 °C and 180 °C. The films cured at 150 °C (VFM and thermal) both deviated from the higher temperature samples. The VFM sample exhibited higher peel strength while the thermally cured sample exhibited a lower peel strength. This is an important observation because copper/insulator adhesion is an important parameter in the lifetime of epoxy boards and substrates.

The extent of reaction between the amide and epoxy for the model compounds was estimated from the ratio of the peak heights at 916 cm^{-1}, as shown in (2). The absorbance at 916 cm^{-1} was normalized to the absorbance at 1600 cm^{-1}, which corresponds to the aromatic $C{=}C$ stretch

$$\text{Extent of Reaction}(\%) = \frac{\left(\frac{A_{916}}{A_{1600}}\right) - \left(\frac{A_{916}}{A_{1600}}\right)_{\text{sample}}}{\left(\frac{A_{916}}{A_{1600}}\right) - \left(\frac{A_{916}}{A_{1600}}\right)_{100}} \times 100. \tag{2}$$

The extent of reaction for the model compounds with 2E4MZ at three temperatures is shown in Fig. 10 for VFM curing and Fig. 11 for thermal curing. The reaction proceeds considerably faster through VFM processing compared to thermal curing, at the same temperature.

The nature of the chemical reactions and origin of the mechanical property differences between VFM and thermal curing was investigated. The FT–IR spectra of the VFM and thermally

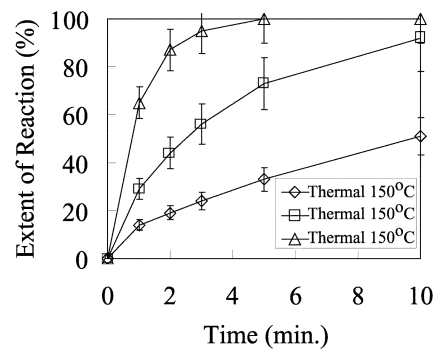

Fig. 11. Extent of reaction for thermally cured model compounds with 2E4MZ three temperatures.

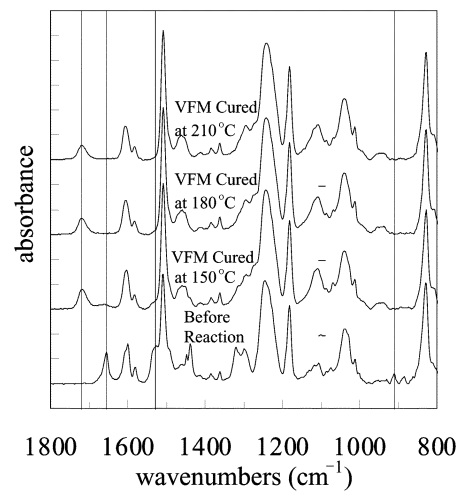

Fig. 12. FT–IR spectra for fully cured model compounds via VFM heating.

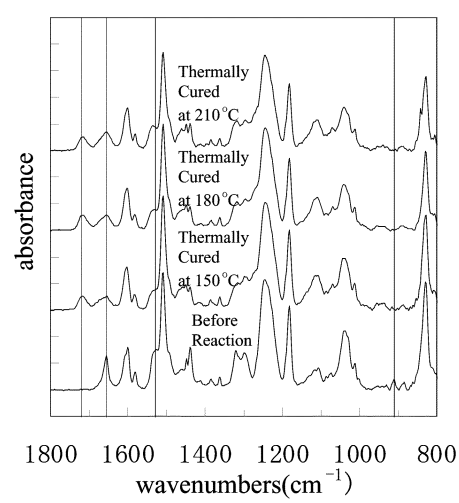

Fig. 13. FT–IR spectra of thermally full cured model compounds.

cured films (model compounds) are shown in Figs. 12 and 13, respectively. As shown in these two FT–IR figures (Figs. 12 and 13), the intensity of the peaks of the amide $C{=}O$ stretching (1654 cm^{-1}), amide $N{-}H$ bending (1531 cm^{-1}), and epoxy group (916 cm^{-1}) all decrease as the films cure. Each of the three peak heights are smaller in the cured samples, for both VFM and thermal curing. Also, both the VFM cured and

thermally cured films showed a new IR peak 1716 cm^{-1}. This new peak corresponds to a $C=O$ stretch from an ester group. An ester linkage is formed through the 'insertion reaction' of the epoxy to the amide C–N bond, as shown in Fig. 2. The 1654 cm^{-1} and 1531 cm^{-1} peaks disappeared in the VFM samples cured at of 210 °C and 180 °C. When the samples were VFM cured at 150 °C, only small peaks were observed at 1654 cm^{-1} and 1531 cm^{-1}.

The FT-IR spectra of the thermally cured film, Fig. 13, also showed the new peak at 1716 cm^{-1}, corresponding to the ester $C=O$ from the insertion reaction of epoxy into the amide C–N bond. However, in contrast to the VFM cured samples the peaks at 1654 cm^{-1} and 1531 cm^{-1} reminded, even after the film was fully cured at the highest temperature.

IV. Discussion

Microwave curing of polymer dielectrics has been shown to occur at lower temperature or at higher isothermal rates than traditional thermal curing. [2]–[4] Electromagnetic irradiation in the microwave region interacts with dipoles and translational-vibrational transitions are activated resulting in a rise in temperature. The absorbed energy is proportional to the dielectric loss, as given by

$$P = 2\pi f E_{rms}^2 \varepsilon_o \varepsilon'' \tag{3}$$

where P is the power per unit volume, f is the frequency of the microwave irradiation, E_{rms} is the microwave electric field intensity, ε_o is the permittivity of free space, and ϵ'' is the dielectric loss.

The selective absorption of microwave energy by the higher loss uncured polymer can be seen in Fig. 3 for PAI/BPAEp on silicon. Although the mass of the polymer is less than 5% of the mass of the silicon, the heating rate of the composite is more than 20% higher than the blank wafer. Fig. 3 shows the temperature of wafer was higher than blank silicon wafer. This means that the uncured PAI/BPAEp film is highly absorbing. Further, the microwave energy is absorbed by the polar groups with the polymer and not by the nonpolar part of the polymer backbone. The nonuniform absorbance of energy leads to a local temperature gradient on the nanometer scale throughout the polymer film. The measured temperature is the average or bulk temperature and not the temperature on the local scale. The structures with the higher absorbance are also the ones responsible for the chemical curing of the polymer. Thus, one view of the "apparent" acceleration in the rate of reaction is because the reactive groups are at a higher local temperature than the bulk. The effect of the selective absorption of microwave energy on the overall reaction rate and mechanistic pathway is likely complex. Consider the role of the catalyst in accelerating the reaction in microwave irradiation. It was shown in Fig. 6 that the PAI/BPAEp film without the 2E4MZ catalyst did not react faster in VFM than in a conventional oven. However, with the catalyst, the VFM curing was accelerated, compared to conventional heating at the same temperature.

The FT-IR analysis of the VFM and thermally cured PAI/BPAEp films shows that the films are very similar, Fig. 5. The intensity of the amide $C=O$ stretching peak (1664 cm^{-1}), N–H bending peak (1531 cm^{-1}), and epoxy absorbance (916 cm^{-1}) all decrease in a similar way upon curing, regardless of the curing method. The insertion reaction of epoxy into the amide C–N bond, making the ester functionality, is difficult to detect at 1710–1720 cm^{-1} because of the asymmetric $C=O$ stretching of the five membered imide ring peak at the same energy. Thus, it is difficult to compare the spectra because of the complex background. However, the mechanical properties, Table I, show that there is a difference between films cured by VFM and conventional heating. The elastic modulus of the VFM cured PAI/BPAEp film was less than that of thermally cured films, and the elongation to break of the film VFM cured at 150 °C was more than twice that of the thermally cured film at 150 °C. Moreover, Fig. 9 shows that the peel strength of the Cu foil from the VFM cured film was greater than that from the thermally cured film (150 °C cures). These two observations (modulus and elongation to break) suggest that the crosslinking structure of the VFM cured film is different from that of the thermally cured film. The bisphenol-A epoxy and benzanilide amide 'model compound' was used to study the reaction between the amide and epoxy. The VFM reaction rate for the model compounds is also faster than the thermal reaction at each temperature. The FT-IR spectra for the cured model compounds clearly showed that the VFM cured samples where structurally different from the thermally cured samples. An additional peak corresponding to the ester $C=O$ stretch due to the insertion reaction of the epoxy into the amide C–N bond was observed (1716 cm^{-1}) at the same time that the 916 cm^{-1} epoxy peak disappeared. In the 210 °C and 180 °C VFM cured samples, the 1654 cm^{-1} peak (amide $C=O$ stretching) and 1531 cm^{-1} peak (amide N–H bending) were not observed showing that that all epoxy groups were inserted to the amide C–N bond. The effect of catalyst concentration was evaluated. The selectivity of the epoxy insertion over the amide C–N bond, as observed by FT-IR, occurred with higher concentrations of catalyst (2E4MZ). When the amount of catalyst was changed 0.25 wt% to 0.5 wt% with respect to epoxy, the FT–IR spectra of its VFM cured samples were essentially identical to each other. However, for the 150 °C VFM sample small 1654 cm^{-1} and 1531 cm^{-1} peaks were observed even though the epoxy peak was not present. This appears to suggest that some of the epoxy groups may co-react at 150 °C. This co-polymerization of the epoxy groups could be responsible for the exceptional elongation to break values for the 150 °C VFM cured film (Table I). It appears that the elongation-to-break of the PAI/BPAEp film cured by VFM at 150 °C was higher due to the slight increase in the distance between closslinking points because of the homopolymerization of the epoxy resin. The increase in adhesion to the surface may reflect both the improved mechanical properties and bonding to the surface.

V. Conclusion

VFM curing of PAI/BPAEp films and model epoxy-amide compositions were investigated. VFM curing proceeded faster than the thermal curing at all temperatures for both PAI/BPAEp and the model compounds. It appears that the local absorbance of microwave energy activates the 2E4MZ catalyst. The VFM

cured PAI/BPAEp samples exhibited lower elastic modulus, and significantly higher elongation to break compared to thermally cured films. The VFM samples also exhibited greater copper peel strength. The FT–IR analysis of the model compounds suggest that the 210 °C and 180 °C VFM samples reacted by insertion of the epoxy into the amide C–N. At lower VFM temperatures, it appears that some epoxy groups copolymerized.

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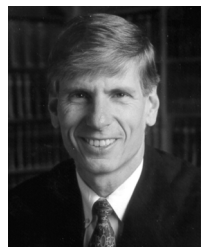

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