Variable Frequency Microwave Curing of 3,3’,4,4’-Biphenyltetracarboxylic Acid Dianhydride / P-Phenylenediamine (BPDA/PPD)

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Abstract

Variable frequency microwave (VFM) curing has been investigated as a rapid cure method for the polyimide 3,3’,4,4’-Biphenyltetracarboxylic acid dianhydride / P-Phenylenediamine (BPDA/PPD). Previous studies, involving curing of this polyimide using rapid thermal heating, have resulted in undesirable properties such as high residual stress. In this study, BPDA/PPD films produced using VFM curing (cure time ranging from 600-1800s) are compared with film produced via a conventional thermal cure (cure time of 18000s) and a rapid hotplate cure (cure time ranging from 1200-3600s). Properties, including dielectric constant, residual stress, modulus, solvent resistance, tensile strength, and coefficient of thermal expansion were measured for the films produced by each of the three techniques. The results of this study indicate that VFM curing can provide thin film properties similar to those achieved via lengthy, (conventional) thermal curing. In addition, for the first time, low residual stress BPDA/PPD polyimide has been created via a rapid cure process. Hence, it can be concluded that VFM curing is a viable method for more rapid production of BPDA/PPD polyimide film.

Key words:
3,3’,4,4’-Biphenyltetracarboxylic Acid Dianhydride / P-Phenylenediamine, BPDA/PPD, PI 2611, Polyimide, Rapid Cure, Variable Frequency Microwave Curing (VFM), and Residual Stress.

1. Introduction and Background

Polyimides have found many applications in the microelectronics industry due to their excellent mechanical, electrical, and chemical properties. A reduction in the processing time required to cure these polymers would result in increased throughput and reduced production costs. The process time needed for conventional thermal curing typically ranges from 4 to 6 hours due to slow temperature ramp rates and extended hold times at various temperatures which are necessary due to slow reaction rates, outgassing of reaction by-products and solvent, and orientation of polymer chains.

PI 2611 is a polyamic acid based polyimide manufactured by HD Microsystems. Its chemical structure includes 3, 3’, 4, 4’-biphenyltetracarboxylic acid dianhydride (BPDA) with p-phenylenediamine (PPD). This particular polymer system has been noted for electronic packaging applications where a low residual stress dielectric is essential. Many of the unique properties of this polymer are a result of the rigid nature of its backbone and the high degree of orientation, which occurs during cure. This orientation is critical to achieving the low coefficient of thermal expansion (CTE), resulting in a low stress film.

Previous studies have shown that the final properties of rapidly cured, rigid rod, polyamic acid polyimides differ significantly from the properties of conventionally cured films. Rapid heat-
ing typically results in a lower birefringence and a higher in-plane coefficient of thermal expansion (CTE). Lower birefringence indicates less in-plane molecular orientation. A decrease in the in-plane orientation leads to an increase in the in-plane CTE. The high in-plane CTE results in a higher CTE mismatch between the polymer and the silicon resulting in greater residual stress, possibly leading to delamination and cracking.

Another difference found in rapidly cured polyamic acid based films compared with those manufactured in a long oven cure is an increased amount of crystallization. This is attributed to the influence of heating rate on the effective glass transition temperature of the film. For films cured at slow heating rates, the effective glass transition temperature of the film is above the film temperature during much of the curing process. For films rapidly heated to the final cure temperature, the effective glass transition temperature of the film is below the film temperature during much of the curing process. Since the film temperature is above the glass transition temperature during most of the cure, crystallization can occur. Crystallinity is intimately connected with film properties and may cause changes in mechanical properties such as an increase in modulus.

In this study, variable frequency microwave (VFM) curing is investigated as an alternative rapid (< 30 minutes total cycle time) curing method. In order for VFM curing to be a viable option for the microelectronics industry, it must provide polymer properties that are comparable to, or superior to, those achieved via traditional, thermal curing. Evaluation of the quality of the films was based on the measured values of the following properties: residual in-plane stress on <100> silicon, coefficient of thermal expansion (CTE), biaxial modulus, Young’s modulus, elongation to break (ETB), tensile strength, adhesion, relative dielectric permittivity and dielectric loss, in-plane and through-plane refractive indices, degree of cure, percent moisture uptake, solvent resistance, and thermal stability. To provide an accurate comparison with VFM curing, films were also cured using a convection oven and a hotplate. Properties of these films are compared to those obtained via VFM curing.

2. Experimental Work

The polymer examined in this work is 3,3’,4,4’-Biphenyl tetracarboxylic acid dianhydride / P-Phenylenediamine (BPDA/PPD). It is a polyamic acid based polyimide manufactured by HD Microsystems and sold under the name PI 2611. At high temperatures (> 200°C), PI 2611 undergoes a conversion from its soluble, polyamic acid form, as received from HD Microsystems, to an insoluble, fully imidized polymer. This condensation reaction is shown in Figure 1 and as described later, can be monitored through FTIR spectroscopy. Many of the unique properties of the polymer are a result of the rigid nature of its backbone and the high degree of orientation, which occurs during cure.
temperature ramp during hotplate curing, several ceramic and metal plates were placed between the sample and the hotplate so as to provide a slow thermal ramp. It took approximately nine minutes for the sample to reach the desired curing temperature. The samples were held at 350°C for the remainder of the twenty minute cure cycle. The approximate temperature profile for these samples is shown in Figure 2. This temperature profile is similar to that experienced by some PI 2611 samples in the VFM and will be referred to as “Hotplate Ramp”.

To experimentally determine the CTE and biaxial modulus of a polymer film, it is necessary to determine the slopes of stress versus temperature curves (dσ/dT) for identically cured films on two different substrates. The two substrates used in this work were <100> silicon and <100> gallium arsenide. The stress versus temperature curves were generated using a temperature controlled fixture in the Flexus. These curves were not linear over the entire temperature range for which data was collected (25°C to 350°C). Therefore, the slope is determined in the temperature range between 40°C and 100°C. During the first ramp up, residual moisture, which significantly affects the residual stress level, was removed from the film. Therefore, the slope was calculated from data collected during the second ramp cycle which was reproducible. After dσ/dT was determined on the two substrates, Equation 2 was used to calculate the CTE and biaxial modulus of the films where [E/(1−ν)]sub is the biaxial modulus of the substrate (2.87 for silicon and 5.7 for gallium arsenide), and αsub is Poisson’s ratio, αfilm is the CTE of the substrate (2.87 for silicon and 5.7 for gallium arsenide), and αfilm is the CTE of the film.15

\[
\frac{d\sigma}{dT} = \left( \frac{E}{1-\nu} \right)_{\text{film}} \left( \alpha_{\text{substrate}} - \alpha_{\text{film}} \right)
\]  

(2)

Tensile properties were measured using film strips lifted off of silicon wafers. The strips were 1 cm in width and 4 cm in length. The strips were then lifted off the substrate by immersing the entire sample in hydrofluoric acid (HF) for 2-3 minutes. HF etches the native oxide on the silicon wafer and releases the polymer strips. Each strip was pulled to failure using an Instron. The Young’s modulus was calculated from the slope of the low strain region of each stress-strain curve. The elongation to break (ETB) and tensile strength are considered to be the maximum value that the test structure withstood prior to failure. It is important to note that the true ETB and tensile strength values will always be greater than or equal to the experimentally measured values. Defects or improper loading or handling of the film could produce fracture modes other than brittle, tensile fracture thereby significantly lowering the measured ETB. The values reported in this paper are the highest values obtained among all of the strips tested for a particular cure condition.

Through-plane permittivity and loss measurements were made using parallel plate capacitor structures (metal insulator-metal) fabricated with the polymer film as the dielectric between the two parallel plates (ASTM D 150-95 16). Silicon wafers were thermally oxidized (3000 Å) and then metallized with titanium / gold / titanium (150 Å, 1000 Å, 150 Å). Polymer films were spin-cast onto the wafers and cured according to the desired cure schedule. After cure, another layer of metal was deposited and patterned to form the top electrodes. Each strip was pulled to failure using an Instron. The strips were ~ 1 cm in width and ~ 4 cm in length. The strips were then lifted off the substrate by immersing the entire sample in hydrofluoric acid (HF) for 2-3 minutes. HF etches the native oxide on the silicon wafer and releases the polymer strips. Each strip was pulled to failure using an Instron. The Young’s modulus was calculated from the slope of the low strain region of each stress-strain curve. The elongation to break (ETB) and tensile strength are considered to be the maximum value that the test structure withstood prior to failure. It is important to note that the true ETB and tensile strength values will always be greater than or equal to the experimentally measured values. Defects or improper loading or handling of the film could produce fracture modes other than brittle, tensile fracture thereby significantly lowering the measured ETB. The values reported in this paper are the highest values obtained among all of the strips tested for a particular cure condition.
Probable Assignment

Comments

infrared peaks for PI 2611 are outlined in Table 1.

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Table 1. Characteristics infrared peaks for PI 2611.

<table>
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<tbody>
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<td>Symmetric C=O stretch</td>
<td>Coupled stretch of the five membered imide ring</td>
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<tr>
<td>1717</td>
<td>Asymmetric C=O stretch</td>
<td>Same as above</td>
</tr>
<tr>
<td>1516</td>
<td>1,4 C₆H₄ substituted benzene</td>
<td>Ring breathing vibration associated with aromatic diamine; intensity does not change with cure hence used as internal reference</td>
</tr>
<tr>
<td>1359</td>
<td>C-N-C stretch of imide ring</td>
<td>Peak generally used for calculating extent of cure</td>
</tr>
<tr>
<td>736</td>
<td>Deformation of imide rings</td>
<td></td>
</tr>
<tr>
<td>1680</td>
<td>Solvent NMP</td>
<td></td>
</tr>
</tbody>
</table>

In-plane and through-plane refractive indices of the films were evaluated using a Metricon prism coupler. The difference in the in-plane and through-plane indices is known as the birefringence and is an indication of the degree of orientation in the film. It has been previously established that rigid rod polyimides undergo significant orientation during cure. This results in very different properties in and through the plane of the films and large positive birefringence values.

Fourier transform infrared spectroscopy (FTIR) was used to follow the chemical changes that occurred in the films during cure. The imidization reaction that occurs during cure in PI 2611 causes distinct changes in the FTIR spectra which can be correlated to the degree of imidization that has occurred in the film. Due to the high absorption coefficient of the C=O and other groups present in the polyimide films, it is necessary to have thin films (ca. 2 µm) for this analysis. Some of the key infrared peaks for PI 2611 are outlined in Table 1.

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The 1359 cm⁻¹ peak, corresponding to the C-N-C stretch of the imide ring, can be used as an indication of degree of cure. This peak is observed when the imide ring closes. The 1516 cm⁻¹ peak, corresponding to the “ring breathing vibrations” of the 1,4 substituted benzene, does not change during cure and can be used as an internal reference peak. The degree of imidization can be calculated using Equation (5) where A is the absorbance and the subscript indicates the wavenumber corresponding to the peak. The reference absorbances are determined from a film for which 100% imidization is assumed (standard thermal cure). Differences in film thickness or polymer orientation as well as uncertainty in determining the baseline may result in slight changes in peak heights. These changes can significantly influence the calculation of the degree of imidization, and thus this method of evaluating the extent of reaction is considered only semiquantitative. Therefore, the percent imidization for the films is presented as a range based on the peak heights from numerous spectra.

Percent imidization = \( \frac{(A_{1359}/A_{1516})}{(A_{1359}/A_{1516})_{Reference}} \times 100 \) (5)

A Quartz Crystal Nanobalance (QCN) was used to detect the change in mass of a film after exposure to a moist environment. The QCN works on the principle that characteristic frequency changes in a quartz crystal resonator can be related to mass changes that occur in material directly attached to it. The frequency change is related to the mass change by Equation 6 where \( \Delta f \) is the change in the frequency for a change in mass \( \Delta m \). \( f_r \) is the resonant frequency of the unloaded quartz crystal resonator, \( \rho_q \) is the density of the quartz crystal, and \( \mu_q \) is the elastic modulus of the resonator. In order to use the QCN for estimating moisture absorption, a thin layer of the polymer is spun onto the quartz crystal (diameter of the quartz crystal disc is 14 mm). The mass of the polymer deposited on the crystal can be estimated by measuring the change in the oscillation frequency of the crystal. Further, the mass change in the polymer when subjected to different environments can be tracked to give an estimate of the amount of moisture absorbed by the sample.

\[ \Delta f = -\frac{2f_r^2\Delta m}{\sqrt{\rho_q\mu_q}} \] (6)

Thermal stability of select films was evaluated using thermal gravimetric analysis (TGA). All data was collected using a Seiko TG/DTA 320. Films (without substrates) were investigated using a 10°C / minute ramp to 100°C (to remove moisture), a 30 minute hold at 100°C, a 10°C / minute ramp to 550°C, and a 60 minute hold at 550°C. The data was plotted as percent weight loss versus temperature. The degradation temperature is considered to be the temperature at which a polymer film begins rapidly losing mass.

3. Results and Conclusions

3.1. Thermally Cured Films

Polyimide PI 2611 was thermally cured using the manufacturer’s recommended process: 3°C/min to 350°C, hold at 350°C for 1 hour, and slow ramp back to room temperature. The measured properties of the films are reported in Table 2 along with the published values.
case and 6 MPa reported) are both low, compared to other polyimides. The moisture uptake here (0.5\%) was in 80\% relative humidity where as the condition for the previously reported are not stated.

### Table 2. Summary of properties for cured PI 2611 films

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Value</th>
<th>Value</th>
<th>Value</th>
<th>Value</th>
<th>Value</th>
<th>Value</th>
<th>Value</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Temperature (°C)</strong></td>
<td>350</td>
<td>350</td>
<td>350</td>
<td>350</td>
<td>350</td>
<td>350</td>
<td>350</td>
<td>350</td>
<td>350</td>
</tr>
<tr>
<td><strong>Residual Stress (MPa)</strong></td>
<td>0.350 GPa</td>
<td>&gt; 0.374 GPa</td>
<td>&gt; 0.325 GPa</td>
<td>&gt; 0.0841 GPa</td>
<td>&gt; 0.295 GPa</td>
<td>&gt; 0.232 GPa</td>
<td>&gt; 0.361 GPa</td>
<td>&gt; 0.339 GPa</td>
<td>&gt; 0.226 GPa</td>
</tr>
<tr>
<td><strong>Elongation to Break (ETB)</strong></td>
<td>25%</td>
<td>&gt; 24.7%</td>
<td>&gt; 9.8%</td>
<td>&gt; 1.9%</td>
<td>&gt; 5.1%</td>
<td>&gt; 6.25%</td>
<td>&gt; 21.7%</td>
<td>&gt; 10.0%</td>
<td>&gt; 7.64%</td>
</tr>
<tr>
<td><strong>Young’s Modulus (GPa)</strong></td>
<td>8.45 GPa</td>
<td>7.12 GPa</td>
<td>6.8 GPa</td>
<td>-</td>
<td>6.5 GPa</td>
<td>6.3 GPa</td>
<td>7.6 GPa</td>
<td>-</td>
<td>7.6 GPa</td>
</tr>
</tbody>
</table>

Low in-plane residual stress is one of the distinguishing properties of PI 2611 films. The slow ramp in temperature during the conventional thermal cure allows for orientation of the PI 2611 chains. The orientation of the film reduces the in-plane CTE of the PI2611 similar to that of <100> silicon substrates which results in very low residual stress. The experimentally measured values were approximately 0 MPa.

The tensile properties were experimentally determined from stress versus strain data collected using an Instron. The data for several thermally cured PI2611 strips are shown in Figure 3. As noted previously, the true ETB values will always be greater than or equal to the experimentally measured values. The highest ETB measured for a thermally cured film was 24.7\%. Despite differences in ETB values among the thermally cured samples, the slopes in the low strain region are very consistent. The Young’s modulus, as determined from the slopes in the low strain region are very consistent. The Young’s modulus, as determined from the slopes in the low strain region are very consistent. The Young’s modulus, as determined from the slopes in the low strain region are very consistent. The Young’s modulus, as determined from the slopes in the low strain region are very consistent. The Young’s modulus, as determined from the slopes in the low strain region are very consistent.

### PI 2611 films.

The orientation in the cured PI 2611 films leads to differences in the in-plane and through-plane refractive indices. Softbaked films have an in-plane index of 1.6750 and a through-plane index of 1.6400 (that is, a birefringence of 0.0350). During cure, the in-plane index increase significantly resulting in a birefringence of 0.2249.

FTIR scans were collected on PI 2611 films both prior to and following cure. As shown in Figure 4, there are several changes which are clearly evident when comparing the spectra for softbaked and thermally cured films. The absence of the closed imide ring in the softbaked material is evident by the absence of the 1359 cm⁻¹ peak in the FTIR spectra. This peak increases as the imide ring closes and then continues to increase in intensity during cure. The degree of imidization can be estimated using the height of the 1359 cm⁻¹ and 1516 cm⁻¹ peak.

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The thermally cured films are assumed to be 100\% imidized and therefore used as the reference for all of the other samples.

### Figure 3. Complete stress-strain curves for thermally cured PI 2611 films.

A TGA scan showing the weight loss in a thermally cured film as a function of time and temperature is shown in Figure 5. Significant weight loss occurs above 300°C, and the total weight loss over the entire temperature cycle is approximately 12\%. It should be noted that isothermal TGA scans are a more appropriate method of measurement of long-term thermal stability. In this case, the dynamic TGA was used to investigate differences in materials.

### Figure 5. TGA scan of thermally cured PI 2611.
3.2. Hotplate Cured Films

A summary of the properties for films cured using the “Hotplate Ramp” and “Rapid Hotplate” cures is included in Table 2. A portion of the residual stress versus temperature data for both of these types of samples cured on silicon and gallium arsenide is shown in Figures 6. The slopes of these plots are used in calculating the CTEs and biaxial moduli of the films. A positive slope on gallium arsenide and a negative slope on silicon, as seen for the “Hotplate Ramp” sample, show that the CTE of the film is between the respective CTE value of the two substrates. In contrast, negative slopes on both types of substrates, as shown for the “Rapid Hotplate” films indicate that the CTE of the film is greater than that of both substrates (> 5.7 ppm/°C).

\[ y = -0.0974x + 44.228 \]
\[ y = -0.0169x + 19.806 \]
\[ y = -0.038x + 15.15 \]
\[ y = 0.0539x - 4.913 \]

Figure 6. Residual stress versus temperature for PI 2611 “hotplate ramp” and “ramp hotplate” films.

Other properties, which show that the two types of hotplate cures result in different films, include the ETB, tensile strength, and refractive indices. The “Rapid Hotplate” films have two distinct sets of refractive indices. This is probably caused by crystalline and amorphous regions within the polymer films. Rigid-rod polyimides are known to crystallize when cured rapidly because the polymer is subjected to temperatures above its glass transition temperature (T_g). “Rapid Hotplate” films are the only films studied in this work that have two sets of refractive indices, indicating a mixture of two phases or materials.

A comparison of the FTIR spectra for the two types of hotplate cured films and a thermally cured PI 2611 film is shown in Figure 7. There are slight peak shifts which occur between the standard thermal and the “Rapid Hotplate” films. The 1717 cm⁻¹ peak (asymmetric C=O stretch) shifts to 1710 cm⁻¹ and the 1359 cm⁻¹ peak (C-N-C stretch of the imide ring) shifts to 1364 cm⁻¹. No shifts from the standard thermal sample were detected in the “Hotplate Ramp” sample. The slight shifts in the “Rapid Hotplate” films have previously been associated with crystallization (crystallization confirmed through x-ray diffraction). Spectral shifts occur upon crystallization as a result of intermolecular rotations and intermolecular chain packing of certain molecular groups at specific sites along the chain backbone.

3.3. VFM Cured Films

Properties from five films cured using multiple VFM conditions are summarized in Table 2. The ramp rates, intermediate hold temperatures and times, final cure temperatures, and total cure times for each condition are also included in this table.

Residual stress levels in VFM cured PI 2611 films are very dependent on the cure condition. The highest residual stress of 18.8 MPa is present in the VFM film which was cured with extremely fast, uncontrolled ramp rates and no intermediate hold step. With controlled ramp rates and an intermediate hold step at 200°C, several films were produced with residual stress levels under 5 MPa (Conditions II-V). This is significantly lower than the stress levels in the “Rapid Hotplate” and “Hotplate Ramp” films (35.3 MPa and 9.1MPa, respectively).

The stress versus temperature data used in calculating the CTE and biaxial modulus for Condition V (Table 2) is shown in Figure 8. The negative slope on silicon and positive slope on gallium arsenide shows that the CTE of the VFM cured films are between those of silicon (2.9 ppm/°C) and gallium arsenide (5.7 ppm/°C).

Figure 7. FTIR scans of thermal, “hotplate ramp”, and “rapid hotplate” PI 2611 samples.

Figure 8. Residual stress versus temperature for VFM cured PI 2611 (VFM condition V).
As noted in Table 2, the tensile properties of VFM cured films depend on the cure conditions. Condition III produced films with the highest ETB and tensile strength. The stress versus strain curves generated for samples cured using this condition are shown in Figure 9. The Young’s modulus, as determined from the slopes in the low strain region, is 6.29 GPa with a standard deviation of 0.215 GPa.

![Stress-strain curves from VFM cured PI 2611 (VFM condition III)](image)

**Figure 9. Complete stress-strain curves from VFM cured PI 2611 (VFM condition III).**

The FTIR spectra for a thermally cured film and a film cured using VFM Condition III are compared in Figure 10. Using the standard thermal film as a reference, the degree of imidization on the VFM film was calculated to be between 82% and 102%. No FTIR shifts, indicating crystallization, were present in any of the VFM samples. Spectroscopic analysis of the thermal, VFM, “Hotplate Ramp,” and “Rapid Hotplate” samples indicates that all of the films have the same bulk chemical structures. A direct comparison of these four spectra is provided in Figure 11.

![FTIR spectra for VFM (condition III) and thermally cured PI 2611 films](image)

**Figure 10. FTIR spectra for VFM (condition III) and thermally cured PI 2611 films.**

Thermal gravimetric analysis data was collected for PI 2611 films cured using VFM Conditions II, III, and V. These three VFM conditions all involved similar ramp rates and intermediate hold steps but had different total cure times (12, 20, and 30 minutes, respectively). All three conditions yielded similar TGA scans with a small weight loss around 350°C and a major weight loss beginning near 540°C. A representative scan (Condition III) is shown in Figure 12. The largest weight loss at 350°C (approximately 3%) occurred for Condition II samples which had the shortest total time in the VFM.

![TGA scan of VFM cured PI 2611 (VFM condition III)](image)

**Figure 12. TGA scan of VFM cured PI 2611 (VFM condition III).**

To confirm that the weight loss at 350°C represented a true irreversible weight loss, one sample was ramped to 350°C and held for one hour before being cooled and then run under the TGA testing conditions described in the experimental section. As expected, a small weight loss occurred when the sample was heated to 350°C during the first cycle but none occurred at this temperature when the sample was rerun under “normal” TGA conditions.

The majority of VFM films have higher relative permittivities than films cured according to the standard thermal process. One explanation for these higher relative permittivities is a lesser degree of orientation of the polymer chains in the plane of the film. Oriented PI 2611 is known to have significantly different electri-
cal properties parallel and perpendicular to the direction of the polymer chains. In a thermally cured (oriented) film, the in-plane relative permittivity is higher than the through-plane value. The through-plane permittivity in the VFM films are slightly higher than that in the thermal film while the in-plane permittivity are slightly lower. This result is an indication that the VFM film may have a lesser degree of orientation. This agrees very well with the previously presented residual stress results indicating that VFM cured films have residual stress levels slightly higher than thermally cured films. The residual stress, birefringence, and relative permittivity all indicate that the level of orientation in VFM films is slightly lower than that in thermally cured films but much higher than that in the “Rapid Hotplate” films.

The experimental results presented here indicate that among the VFM conditions used in this work, Condition III produced the best overall film properties. The temperature profile for this condition involved a 60°C/min ramp to 200°C, a 2 minute hold at 200°C, a 36°C/min ramp to 350°C, and a final hold at 350°C for the remainder of the twenty minute VFM cure cycle. The residual stress levels in these films are very low and nearly identical to the best thermal cure conditions. The major difference in residual stress levels in VFM films is noted between Condition I and the other VFM conditions. Condition I showed higher residual stress levels than the other VFM conditions. The tensile properties of films produced using VFM Condition III are much higher than those for other VFM conditions. All of the mechanical properties for VFM Condition III are within experimental error of the values for thermally cured films. The dielectric permittivity and loss tangent of films cured using VFM Condition III are slightly higher than those for thermally cured films. However, a direct comparison of the results for Conditions II, III and V (all with identical ramp rates) indicates that total cure times greater than that for Condition III (1200 seconds) will not significantly improve the dielectric properties.

Based on the results from VFM cured films, the two minute hold at 200°C was experimentally found to be important for achieving the low residual stress levels desired in this polymer. The stress was monitored in-situ during the curing and during the temperature ramp. The stress as a function of temperature for two samples is shown in Figures 13 and 14. The heating and cooling rates for each sample are stated in the figure captions. The cure (imidization) occurred during the first ramp up and subsequent 350°C hold for 1 hour. Therefore, no changes in the stress profile occurred during the second temperature cycle. As is evident from the two stress profiles shown, the heating rate has a dramatic effect on the stress development.

In Figure 13 (3°C/minute heating ramp), the initial decrease in stress is a result of thermal expansion of the polymer. In the temperature range between 100°C and 200°C, the solvent slowly evaporates and the film shrinks. N-methyl pyrrolidone has a boiling point of 205°C, but its vapor pressure allows the bulk of the solvent to be removed before the sample reaches that temperature. The shrinkage as a result of solvent loss would be expected to result in an increase in tensile stress in the film, but the effect of the thermal expansion of the polymer (resulting in a compressive stress in the film) continues to dominate and the stress level continues a steady decrease up to 200°C. Above 200°C, imidization begins to play an important role and counterbalances the effect of thermal expansion of the polymer. The stress level up to 350°C remains relatively unchanged from its position at 200°C. Upon further temperature cycling, the slope of the stress versus temperature curve is very close to zero. This indicates that the CTE of the film is similar to that of the silicon substrate, due to the polymer orientation that occurs during the long thermal soak at 350°C.

An initial decrease in stress as a result of thermal expansion of the polymer and plasticization by the decomposed solvent is also evident in Figure 14 (30°C / min ramp). The sudden increase in stress near 80°C reflects the rapid evaporation of solvent beginning near that temperature. Due to the faster heating rate, the polymer is given less time to reorient and compensate
for the loss of the solvent. Around 125°C, the stress level begins to drop again. It has been suggested that this may be because the temperature of the film is near or above the glass transition temperature (Tg) of the only partially (< 20%) imidized polyamic acid. Above the Tg, the polymer can more easily reorient into a lower stress conformation. Above 200°C, rapid imidization occurs. A large portion of the orientation in PI 2611 occurs as a result of the shrinkage which occurs upon solvent loss. If the film is heated so quickly that imidization begins before all of the solvent is removed, the polymer chains may be locked in their non-oriented positions. After imidization, the polymer chains are not able to significantly reorient even with additional solvent loss. The mobility of the imidized chains is restricted because imidization significantly elevates the glass transition temperature of the polymer. Thus, the rapidly heated film is less oriented, and has a higher in-plane CTE and residual stress level than the film cured with a 3°C/min ramp as shown by the higher residual stress for VFM samples II, III, and IV.

200°C is an important intermediate hold temperature in the stress build-up in PI 2611 films. The 200°C hold in the VFM allows most of the solvent to be removed before imidization occurs. Thus, low orientation is observed. Since microwaves are absorbed directly by the polymer of interest, this method of heating provides the unique ability to quickly heat the film and then hold it at 200°C without a significant temperature overshoot. This allows for maximum solvent removal and shrinkage prior to imidization.

In addition to providing an intermediate hold temperature for solvent evaporation, VFM provides a different means of energy transfer than conventional convective heating. Microwave energy interacts with the molecular dipoles causing rotational-translational changes. This molecular movement is thought to assist in the orientation of the PI 2611 polymer.

A comparison of the properties achieved via VFM curing (specifically Condition III) and the two different types of hotplate curing demonstrates that for PI 2611, VFM curing provides film properties not achievable via conventional rapid heating methods. The most significant differences are noted in the mechanical properties of these films. The residual stress in the VFM films is 4.2 MPa while that in the “Rapid Hotplate” and “Hotplate Ramp” films is 35.5 MPa and 9.1 MPa, respectively. The elongation to break is greater than 21.7% for VFM and only > 1.9% and > 9.8% for the “Rapid Hotplate” and “Hotplate Ramp” films is, respectively, but that in VFM films is > 21.7%. The biaxial moduli of both of the hotplate cured films, 26 GPa for “Rapid Hotplate” and 30 MPa for “Hotplate Ramp”, are higher than that of the VFM films, 12.1 GPa.

The differences in these and other properties (see Table 2) indicate that for rigid rod polymers, such as PI 2611, VFM heating is capable of providing better values for some critical film properties (including low film stress) than those achievable via conventional rapid heating methods. The in-plane orientation, which occurs during the standard lengthy thermal cure, is very important in creating the low residual stress and high mechanical strength found in conventionally cured PI 2611 films.

4. Summary

Mechanical, electrical and chemical properties of VFM cured BPDA/PPD films were compared with films produced using long conventional thermal cures and rapid hotplate cures. The results of this work show that VFM curing can provide BPDA/PPD thin film properties similar to those achieved via lengthy conventional thermal cure, with a significant reduction in processing time. During the conventional lengthy thermal cure, PI 2611 undergoes a significant level of orientation in the plane of the film. This orientation results in some unique and very desirable film properties. Rapid, hotplate curing of BPDA/PPD does not create a low residual stress film. However, we have demonstrated that VFM curing has enabled the formation of oriented and low stress, BPDA/PPD polyimide films via rapid curing.
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References


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