

# Structure–Property Correlation for Thin Films of Semi-Interpenetrating Polyimide Networks. II. Anisotropy in Optical, Electrical, Thermal, and Mechanical Properties

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**ABSTRACT:** Three different semi-IPN polyimide systems were prepared through blending in solution by using two different polyimides, such as poly (p-phenylenebiphenyl tetracarboxyimide) (BPDA–PDA) and poly (4,4'-oxydiphenylene pyromellitimide) [PMDA–ODA(E)], and two different oligomers, such as bismaleimide (MDAB) and phenylthiyl-terminated BPDA–PDA (BPDA–PDA–PEPA) oligomers. These crosslinkable oligomers are used to modify the morphology of polyimides and, therefore, change the anisotropic properties of the resulting semi-IPN polyimide systems. The results show that the crosslinkable oligomers can disrupt the in-plane molecular arrangement which gives rise to an increase in lateral CTE and vertical CTE and a decrease in birefringence and the Young's modulus. The dielectric constant and water absorption increase with increasing MDAB content but decrease with increasing PEPA content. An empirical correlation between density and volume expansion is observed, indicating a correlation between the volume expansion and free volume expansion and free volume in the semi-IPN polyimide systems. The in-plane modulus decreases but the vertical moduli increases with increasing content of crosslinkable oligomers. In addition, the vertical modulus is affected by the free volume at low stress levels and can be enhanced by crosslinks or by a crystallinelike phase at higher stress levels. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 273–285, 1998

**Key words:** polyimide; semi-IPN; thin film; anisotropic properties

## INTRODUCTION

Polyimides are widely used in the semiconductor industry due to their excellent properties.<sup>1</sup> Usually, polyimides are spin-coated onto a flat substrate to form uniform films. This spin-coating

process introduces in-plane molecular orientation of polyimides because polyimide molecular chains are under a biaxial tensile stress caused by substrate confinement when the solvent evaporates and during the curing process.<sup>2,3</sup> This leads to a molecular ordering in properties that are isotropic in the film plane but anisotropic between in-plane and out-of-plane. Several investigations have shown that spin-coated polyimide thin films exhibit anisotropy in the refractive index, CTE, and modulus.<sup>4–9</sup> It has been found that the CTEs of polyimide thin films in the *z*-direction (out-of-

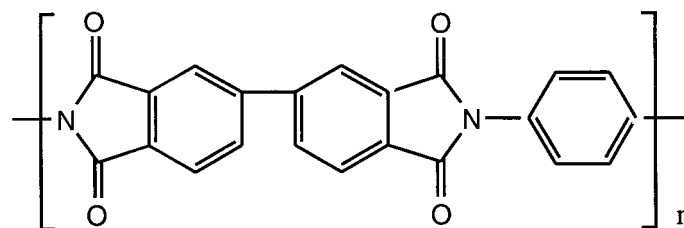
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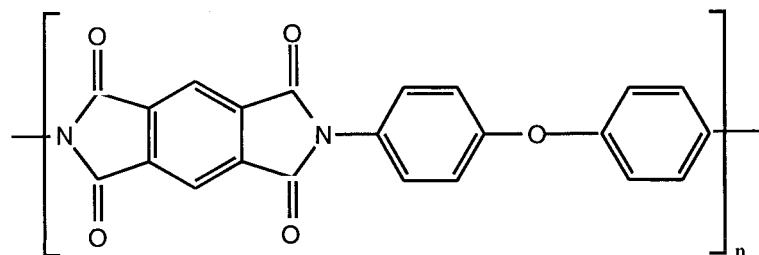
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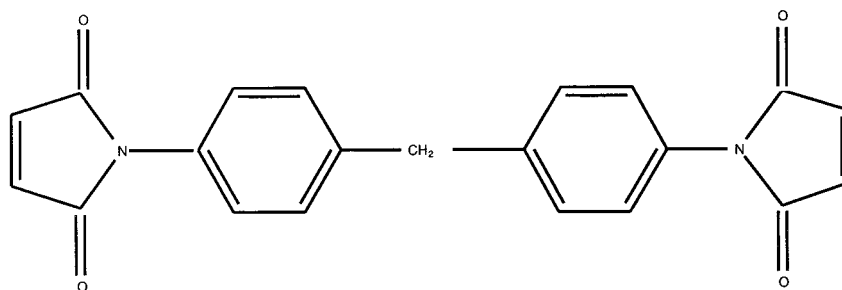
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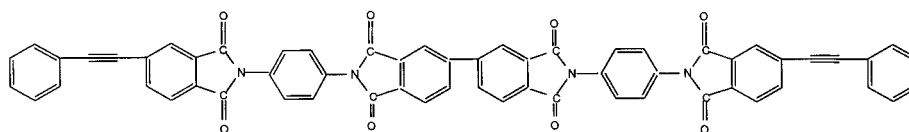
DuPont Pyralin 2611 (BPDA-PDA)



DuPont Pyralin 2801 (PMDA-ODA)



Shell Compimide (MDAB)



Imitec Inc. 4-PEPA-PDA-BPDA-PEA-4-PEPA (PEPA)

**Figure 1** Chemical structures of polymers used in this study.

plane or vertical direction) are 1–2 orders of magnitude larger than the CTE in the in-plane direction. For example, poly(*p*-phenylene biphenyltetracarboximide) (BPDA–PDA) with rigid rodlike chains has a higher anisotropy in the thermal expansion ( $CTE_{\text{lateral}} \sim 5 \text{ ppm}/^\circ\text{C}$  and  $CTE_{\text{vertical}} \sim 105 \text{ ppm}/^\circ\text{C}$ ) than that of poly(4,4'-oxydiphenylene pyromellitimide) (PMDA–ODA) with flexible chains ( $CTE_{\text{lateral}} \sim 27 \text{ ppm}/^\circ\text{C}$  and  $CTE_{\text{vertical}} \sim 145 \text{ ppm}/^\circ\text{C}$ ).<sup>8</sup> In contrast, the Young's modulus

in the *z*-direction for a polyimide, such as BPDA–PDA, is smaller than that in the in-plane-direction.<sup>7,9</sup> However, the high CTE in the *z*-direction of polyimide thin film may generate high stresses at the polymer/metal interface in the *z*-direction. In addition, if the product of the thermal expansion and modulus in the *z*-direction is too large, it will lead to delamination and/or cracking between layers. For example, the cracking of copper plated-through holes during thermal cycling of

**Table I** Composition of Semi-IPN Polyimide Systems

Semi-IPN System		
BPDA-PDA + MDAB	BPDA-PDA + BPDA-PDA-PEPA	PMDA-ODA(E) + MDAB
Composition		
80 : 20	80 : 20	80 : 20
60 : 40	60 : 40	60 : 40
40 : 60		

printed circuit boards is related to the thermal mismatch between the out-of-plane CTEs of the dielectric materials and the copper.<sup>10</sup>

Recently, multilayered structures combining polyimides as low dielectric interlayer materials with copper as an interconnect material to increase the signal propagation have become the leading-edge technology in the semiconductor industry.<sup>11</sup> To ensure the reliability of multilayered structure devices, there is a need to reduce the thermal and mechanical anisotropy of polyimide thin films. However, an understanding of the correlation between their chemical structure and their anisotropic properties, such as CTE and the Young's modulus, is still lacking. As the trends in microelectronics packaging lead to more complicated multilayered interconnect structures and multichip modules, it becomes increasingly important to understand the anisotropic properties of polyimide thin films.

Since the chemical structure and morphology of polymers have a profound effect on their properties, the anisotropic properties of polyimide thin films will be affected by changing the polymer's structure and morphology. For this work, the morphology of the polyimides is changed by blending polyimide with a crosslinkable oligomer to form a semi-interpenetrating polymer network (semi-IPN). A semi-IPN is defined as a combination of two polymers in a network form: One component is crosslinked in

the presence of the other.<sup>12</sup> Three different semi-IPN polyimide systems were blended using two different polyimides, such as BPDA-PDA and PMDA-ODA(E), and two different oligomers, such as bis-maleimide (MDAB) and phenylthynyl-terminated BPDA-PDA (BPDA-PDA-PEPA) oligomers. The structure-property correlation in the anisotropic properties of these semi-IPN polyimide systems was investigated. The properties of interest include the refractive index, CTE, Young's modulus, stress-strain behavior, dielectric constant, and water absorption.

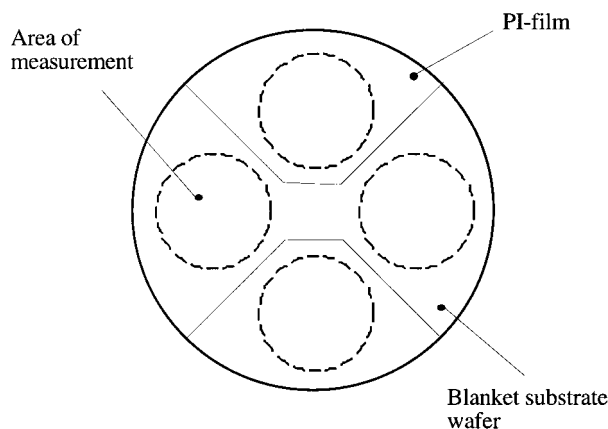
## EXPERIMENTAL

### Materials and Sample Preparations

The chemical structures of polyimides and oligomers used in this study are shown in Figure 1. DuPont 2611 is a polyimide made from biphenyl dianhydride (BPDA) and *para*-phenylenediamine (PDA); DuPont 2801 is a polyimide in ester form made from pyromellitic dianhydride (PMDA) and oxydianiline (ODA); the Shell MDAB bismaleimide oligomer is 4,4'-bismaleimido diphenylmethane; and Imitec PEPA is a phenylethynyl-terminated imide oligomer made from BPDA-PDA end-capped with 4-phenylethynylphthalic anhydride (4-PEPA). The Imitec copolymer is made

**Table II** Curing Profiles Used in this Study

Materials	Prebake (in Air)	Curing Conditions (in Nitrogen Environment)
Polyimide and polyimide semi-IPN system	80°C/15 min	RT to 150°C/30 min, ramp to 230°C/30 min at a 2°C/min. ramp to 300°C/30 min at a 2°C/min. ramp to 400°C/60 min at a 2°C/min.



**Figure 2** Sample configuration of vertical CTE measurement.

from BPDA, PDA, and bis (3-aminophenyl)acetylene (APA).

The three different semi-IPN polyimide systems are BPDA-PDA + MDAB, BPDA-PDA + BPDA-PDA-PEPA, and PMDA-ODA(E) + MDAB. The composition of these semi-IPN polyimide systems are listed in Table I. These semi-IPN polyimide systems were prepared by adding the specified components in the required ratios into 30-mL bottles and mixing in a rotary roller for 24 h. Some *N*-methylpyrrolidone (NMP) was added to these mixtures to increase the miscibility and control the viscosity for spin-coating. The solid content of these semi-IPN polyimide systems is about 10–15 wt %.

The polyimide precursors were spin-coated onto 3-in. Si wafers by using a spin coater (Headway Research Inc., Model #PWM101). Al/Si substrates were also used to prepare samples for dielectric constant measurements and quartz discs were used to prepare samples for water-absorption measurements. The spin time is 30 s and the spin speed is controlled so that the final film thickness is approximately 10  $\mu\text{m}$  after curing. The curing profile used in this study is shown in Table II.

After thermal curing, the films were cut into strips of  $2.5 \times 8.5$  mm for lateral CTE test samples,  $2.0 \times 40$  mm for microtensile test samples,  $5.0 \times 15$  mm for DMTA test samples,  $35 \times 35$  mm for WAXD test samples,  $10 \times 10$  mm for density test samples, and  $1 \times 1$  mm for vertical modulus test samples. The polyimide films were then removed from the substrate for the specified tests. The configuration of a vertical CTE sample is shown in Figure 2. After removing the unwanted

portion of the polyimide, a thin blanket layer of Cu is deposited onto the wafer for electronic contact. The sample configuration for the vertical modulus measurement is shown in Figure 3.

## Methods

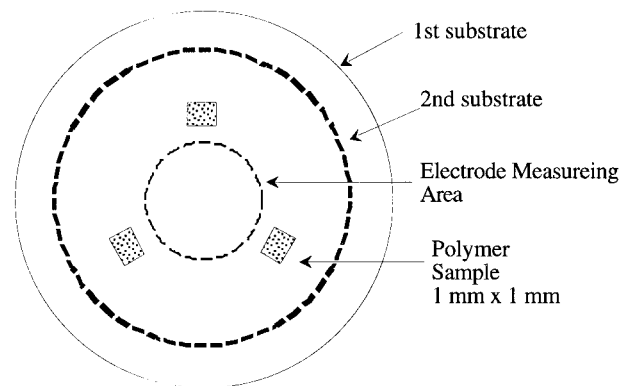
The refractive index and the thickness of the polyimide thin films were measured using a prism coupler (Metricron Inc., Model 2010) with a laser light ( $\lambda = 633$  nm) source. The laser light is polarized into the direction either parallel to the film plane (TE mode) or perpendicular to the film plane (TM mode). A combination of the TE mode and the TM mode is required for measuring the in-plane and the out-of-plane refractive indices. The difference between the in-plane refractive index and the out-of-plane the refractive index is the birefringence (see Table III).

The out-of-plane dielectric constant was measured using a mercury probe (Materials Development Corp., Model #811-150) at 1 MHz. The diameter of the contact is  $0.399 \times 10^{-6}$  m<sup>2</sup>. The dielectric constant can be calculated by using eq. (1):

$$\varepsilon = \frac{dC}{\varepsilon_0 A} \quad (1)$$

Where  $\varepsilon$  is the dielectric constant;  $\varepsilon_0$ , the permittivity of the vacuum;  $C$ , the capacitance;  $A$ , the area for which capacitance is measured; and  $d$ , the thickness of the polymer film measured using the prism coupler.

The density of polyimide was measured by the method described in ASTM D1505 using a density gradient column made by Techne Co. The liquid



**Figure 3** Sample configuration for vertical modulus measurement.

**Table III Refractive Index of Polyimides and Oligomers**

	Sample			
	BPDA-PDA	PMDA-ODA(E)	MDAB	BPDA-PDA-PEPA
In-plane (TE mode)	1.864	1.715	1.609	1.832
Out-of-plane (TM mode)	1.615	1.621	1.602	1.621
Birefringence	0.231	0.071	0.007	0.211

systems are toluene and carbon tetrachloride. The densities of toluene and carbon tetrachloride are 0.87 and 1.59 g/cm<sup>3</sup>, respectively. The density range in the column is about 1.3–1.5 g/cm<sup>3</sup> and the density–position correlation was calibrated using five standard density floats. The temperature of the density gradient column was kept at 23 ± 1°C using a temperature-controlled circulating bath. When a polymer sample is put into the density column, it sinks until it reaches a position along the gradient where the liquid density equals its own density. The density of the polymer sample can be calculated from the interpolation of the density–position correlation.

The lateral CTE was measured by a TMA machine (TA Instruments, Model 2940) in the extension mode. The polymer sample was loaded with a 0.1g force and preheated from room temperature to 200°C at a ramp rate of 20°C/min. A nitrogen purge (120 mL/min) was used to remove the water absorbed and then cooled to –25°C at 10°C/min. The lateral CTE data was recorded from –25 to 200°C at a heating rate of 5°C/min after the preheating cycle. The lateral CTE was obtained from the total displacement between 0 and 200°C and then divided by the temperature difference. The vertical CTE of the polymer samples was measured by using the differential capacitance technique.<sup>13</sup> The data were recorded from 30 to 200°C

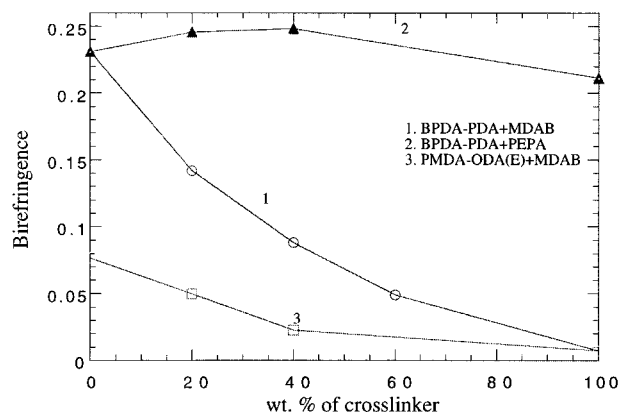
at a ramp rate of 0.5°C/min. By combining a high-resolution capacitance bridge with a differential method, systematic errors can be eliminated and a resolution of 2 Å in displacement can be achieved. Such a resolution is sufficient for monitoring the vertical thermal expansion of 2-μm-thick polyimide films.

The thermomechanical behavior of polyimides and semi-IPN polyimide systems was measured by using a Rheometric Scientific DMTA Mark III with the accessories in the tensile mode. The data were taken from room temperature (RT) to 500°C at a frequency of 10 Hz and a heating rate of 5°C/min. The stress–strain relationship for the polymers in this study was measured using a homemade microtensile tester. Such a test enables the determination of the mechanical strength and the elongation at break of the polymer film in the lateral direction. The Young's modulus can be calculated from the slope of the stress–strain curve during the initial 1% deformation, which is in the linear elastic range. The elastic constant of the polymers in the *z*-direction was measured using a precision capacitance dilatometry developed in our lab.<sup>14</sup> It consists of a precision capacitance sensor and a load cell to record the stress–strain relationship in the *z*-direction. Since polymers are viscoelastic materials, their properties are time–temperature-depen-

**Table IV Measured Density, Calculated Density, Free Volume, and Volumetric CTE of BPDA-PDA and PMDA-ODA**

Polymer	Measured Density (g/cm <sup>3</sup> )	Calculated Density <sup>a</sup> (g/cm <sup>3</sup> )	Free Volume (cm <sup>3</sup> /mol)	Volumetric CTE (ppm/°C)
PMDA-ODA	1.396	1.56	34	208
BPDA-PDA	1.454	1.58	20	114

<sup>a</sup> Calculated crystalline density.<sup>32</sup>



**Figure 4** Birefringence of semi-IPN polyimide systems.

dent. Therefore, the dc zigzag method was used to obtain the mechanical properties in the  $z$ -direction. The elastic modulus can be calculated from the initial slopes of the unloading curves.

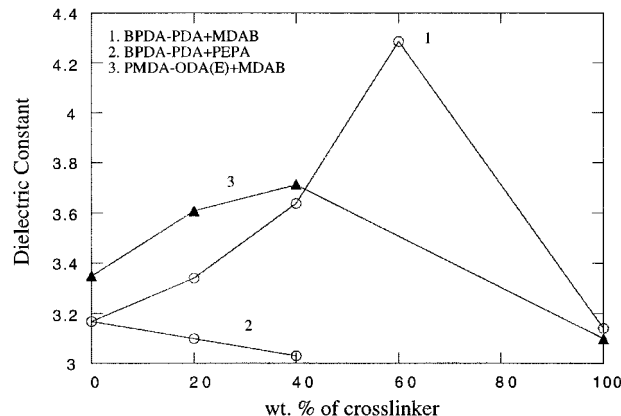
The water-absorption behavior of these semi-IPN polyimide systems was characterized by using a quartz crystal microbalance in the moisture chamber. The water measurements were performed under a 100% humidity environment at 25°C. Since the frequency change is proportional to the mass change of quartz crystal, a frequency counter was used to record the frequency change as polyimide absorbs water.

## RESULTS AND DISCUSSION

### Birefringence and Dielectric Constant

The birefringence of the three semi-IPN polyimide systems studied is shown in Figure 4. The birefringence decreases with increasing content of MDAB for the BPDA-PDA and PMDA-ODA(E) semi-IPN systems.

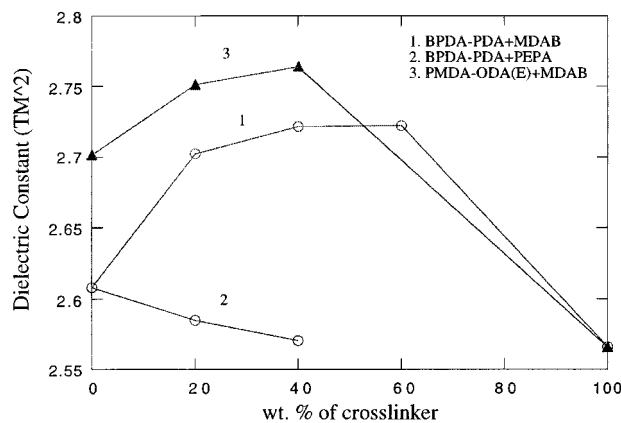
Usually, the birefringence is correlated to the in-plane molecular ordering of polyimides.<sup>4,8,15-18</sup> The birefringence increases with increasing the in-plane molecular ordering. This indicates that the in-plane orientation of the BPDA-PDA and PMDA-ODA(E) semi-IPN systems is reduced by the addition of MDAB oligomers.<sup>19</sup> This is consistent with the WAXD data which suggest that the molecular ordering decreases with increasing content of the crosslinkable oligomer. However, the birefringence increases with increasing content of PEPA for the BPDA-PDA + PEPA semi-IPN



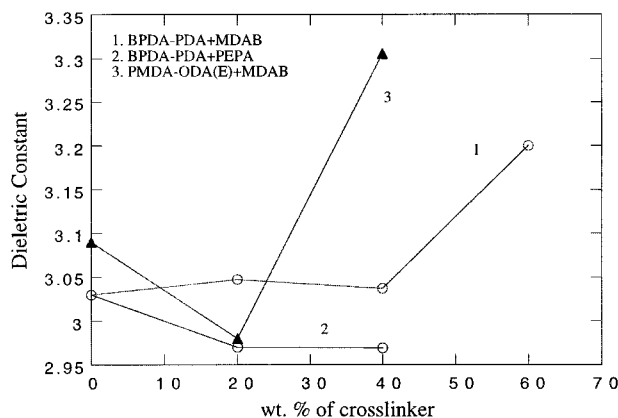
**Figure 5** Out-of-plane dielectric constants of semi-IPN polyimide systems at 1 MHz.

systems because the rigid rodlike structure of PEPA is a nonpolar oligomer and it contributes to this decreasing of the out-of-plane polarizability.

The out-of-plane dielectric constant of semi-IPN polyimide systems was measured at 1 MHz using a mercury probe as shown in Figure 5. The data show that the dielectric constant increases with increasing MDAB content for the BPDA-PDA + MDAB and PMDA-ODA(E) + MDAB semi-IPN systems. In contrast, the dielectric constant of the BPDA-PDA + PEPA semi-IPN systems decreases with increasing PEPA content. The dielectric constant is proportional to the total polarizability of the material including electronic, atomic, and dipolar polarizabilities.<sup>20</sup> The dielectric constant equals the square of the refractive index at an optical frequency according to the Maxwell relationship.<sup>21</sup> The dielectric constant



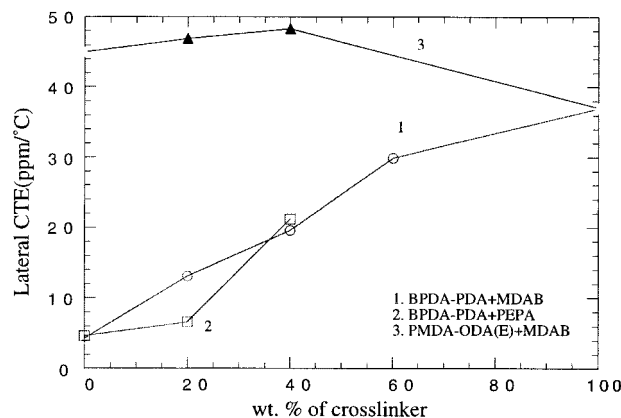
**Figure 6** Out-of-plane dielectric constants of semi-IPN polyimide systems at  $6 \times 10^{14}$  Hz.



**Figure 7** Out-of-plane dielectric constants of semi-IPN polyimide systems after subtracting the effect of water absorbed in the films.

calculated from the square of the out-of-plane refractive index follows the same trend as that of the dielectric constant at 1 MHz as shown in Figure 6. Accordingly, the MDAB oligomers increase the out-of-plane dielectric constant and out-of-plane refractive index of the semi-IPN systems while PEPA decreases the out-of-plane dielectric constant and out-of-plane refractive index of the semi-IPN systems. This may explain why the birefringence decreases for the semi-IPN systems containing MDAB but increases for the semi-IPN systems containing PEPA. The results are consistent with the WAXD data and the birefringence and dielectric constant are correlated to the degree of molecular order.<sup>19</sup>

Since semi-IPN polyimide systems absorb water, the water molecules may have an impact on the dielectric constant. Melcher et al. reported that the dielectric constant of polyimide film increases as the water absorption increases.<sup>22</sup> The experimental setup was exposed to the air environment and it was hard to eliminate the water effects during the dielectric constant measurement resulting in the absorption of moisture on to the polyimide thin films from the air environment. Therefore, the dielectric constant is calculated without the contribution of the water molecules by subtracting the dielectric constant that was contributed by the amount of water absorbed in the films. The effect of water molecules on the dielectric constant for the semi-IPN polyimide systems similar to that indicated by Melcher et al.'s data is assumed. The corrected dielectric constants of the semi-IPN polyimide systems are shown in Figure 7. These data still show the same trend similar to Figure 5, but the scale is differ-

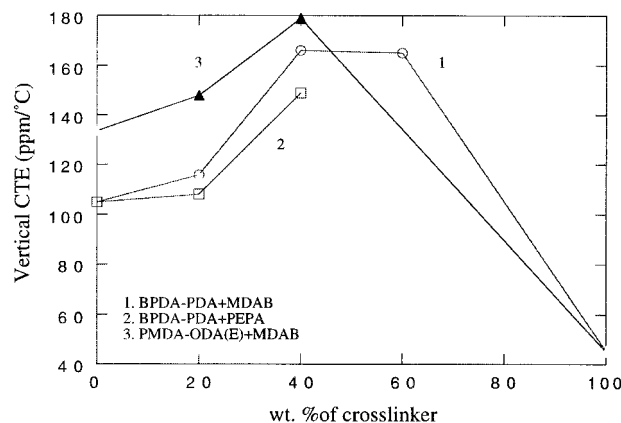


**Figure 8** Lateral CTEs of semi-IPN polyimide systems.

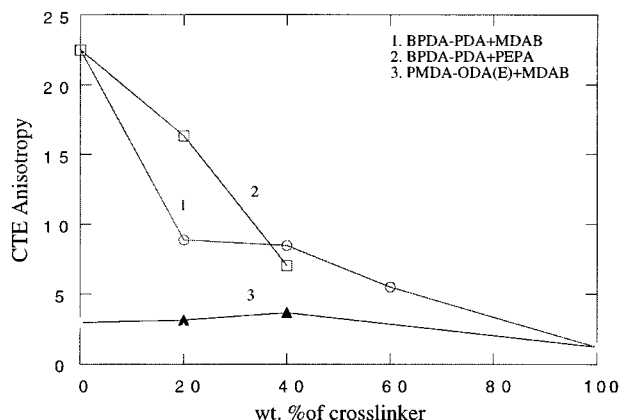
ent. This trend indicates that the dielectric constant increases with increasing content of the crosslinkable oligomers. Since PEPA is nonpolar, the dielectric constants of the BPDA-PDA + PEPA semi-IPN systems decrease with increasing PEPA content.

### Thermal-Expansion Properties

The lateral CTEs of the three semi-IPN polyimide systems, BPDA-PDA + MDAB, BPDA-PDA + PEPA, and PMDA-ODA(E) + MDAB, are shown in Figure 8. The lateral CTE increases with increasing content of the crosslinkable oligomers for these semi-IPN polyimide systems. This implies that the addition of crosslinkable oligomers reduces the in-plane ordering. In a previous study, Ree and Yoon indicated that for the lateral CTE to increase as the content of crosslinkable oligomer increases is ex-



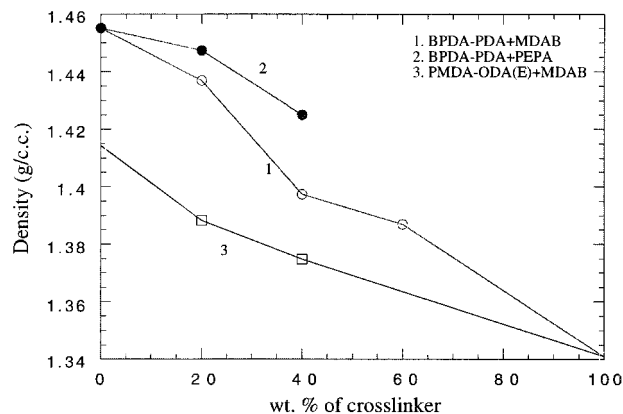
**Figure 9** Vertical CTEs of semi-IPN polyimide systems.



**Figure 10** CTE anisotropy of semi-IPN polyimide systems.

pected.<sup>23</sup> The vertical CTE of these semi-IPN polyimide systems was found to be about 1–2 orders of magnitude greater than the lateral CTE as shown in Figure 9. In addition, the vertical CTE increases with increasing content of crosslinkable oligomers. This indicates that incorporating crosslinkable oligomers into polyimide not only increases the lateral CTE but also increases the vertical CTE of these semi-IPN polyimide systems.

There are several possible ways to explain the results obtained in this study. First, crosslinkable oligomers may serve as plasticizers during the curing process and disorder the molecular chains in the film plane and, hence, cause an increase in the lateral CTE. In addition, the disordered molecular structure gives rise to an increase in the vertical CTE. That means that the vertical CTE is not only controlled by interchain forces but also by the molecular morphology. For example, a polyimide with flexible chains, such as PMDA-ODA, has a higher lateral as well as a higher vertical CTE.<sup>8</sup> Second, the content of crosslinkable oligomers may still be low when compared with a pure thermosetting polymer. The reaction of crosslinkable oligomers may occur in the chain propagation of oligomers instead of crosslinking with itself. Third, the crosslinking density may not be large enough unless the matrix of these semi-IPN polyimide systems is a crosslinked material. In addition, the vertical CTE of MDAB itself is much smaller than that of semi-IPN polyimide systems and the vertical CTE seems to be higher at 40 to 60 wt % content of the crosslinkable oligomers. Therefore, the crosslinks in polyimide semi-IPN systems cannot effectively reduce the vertical CTE. If there is a large content of

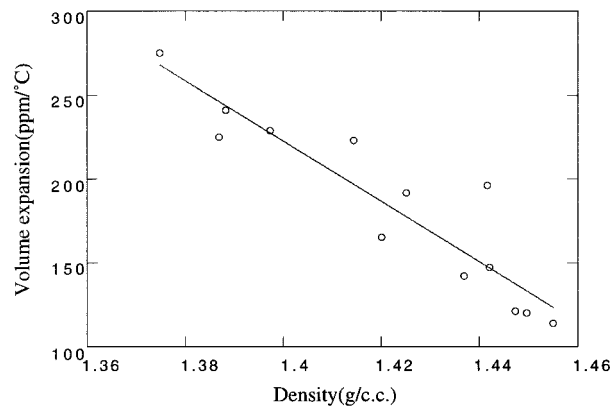


**Figure 11** Densities for semi-IPN polyimide systems.

crosslinkable oligomers in these semi-IPN polyimide systems, that is, crosslinkable oligomer is the matrix, the vertical CTE will likely be reduced.

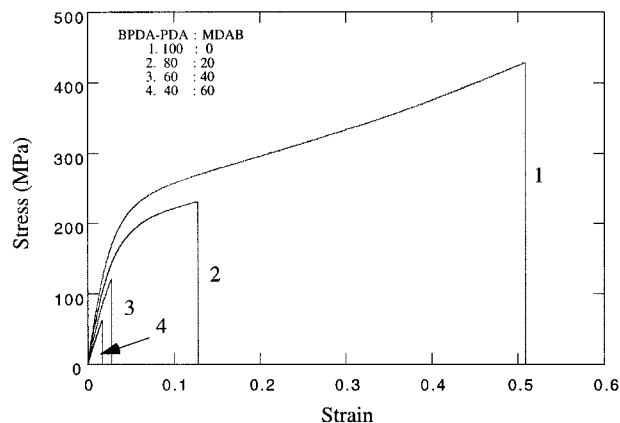
The disordering of the molecular chains by the crosslinkable oligomers strongly influences the CTE anisotropy as shown in Figure 10. The CTE anisotropy of BPDA-PDA + MDAB and BPDA-PDA + PEPA are reduced by adding crosslinkable oligomers. However, the CTE anisotropy of PMDA-ODA(E) + MDAB is slightly different and reaches a higher value at 40 wt % MDAB.

As mentioned earlier, the  $T_g$  of semi-IPN polyimide systems decreases with increasing the content of crosslinkable oligomers and, therefore, the interchain forces between two polymers become weaker and, hence, increase the free volume.<sup>19</sup> The density of these semi-IPN polyimide systems decreases with increasing crosslinking concentration as shown in Figure 11. Since density is a



**Figure 12** Correlation between volume CTE and density for semi-IPN polyimide systems.



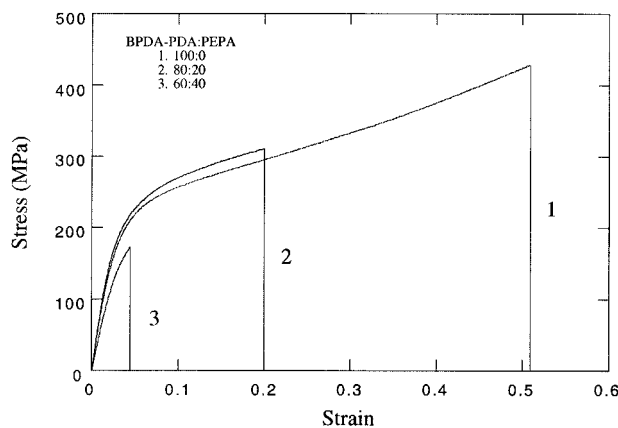


**Figure 13** Stress-strain curves of BPDA-PDA + MDAB semi-IPN systems.

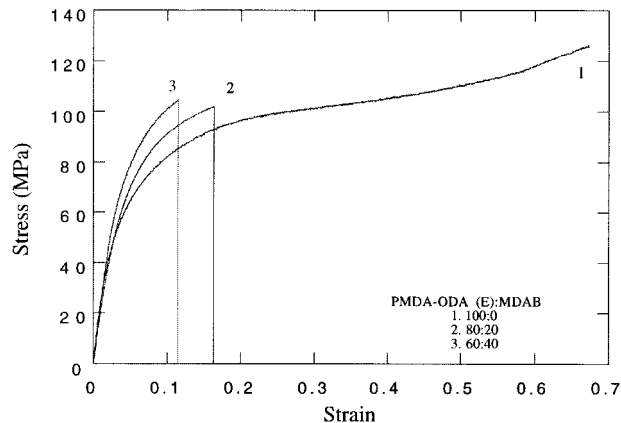
property for the entire polymer, an empirical correlation between density and volumetric expansion is observed as shown in Figure 12. The volumetric CTE is the sum of the CTE in the  $x$ ,  $y$ , and  $z$  directions. This result suggests that the volumetric CTE of polyimides is proportional to its free volume in the film. Again, BPDA-PDA and PMDA-ODA are taken as the examples. The measured density, calculated density, free volume, and volumetric CTE of these two polyimides are listed in Table IV.

### Mechanical Properties

The stress-strain relationship of these semi-IPN polyimide systems was measured using a microtensile tester as shown in Figures 13-15. The elongation at break of these semi-IPN polyimide systems decreased with increasing content of the crosslink-

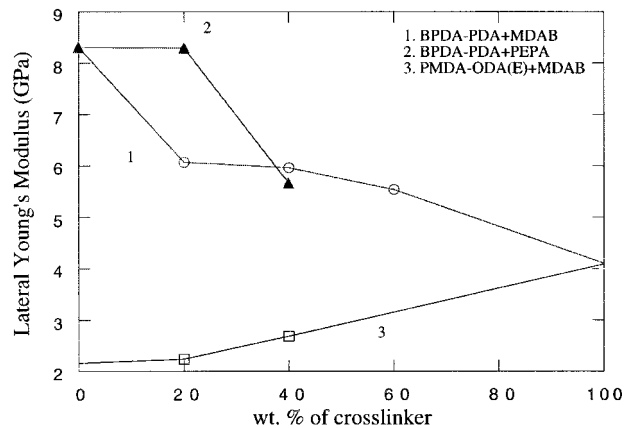


**Figure 14** Stress-strain curves of BPDA-PDA + PEPA semi-IPN systems.

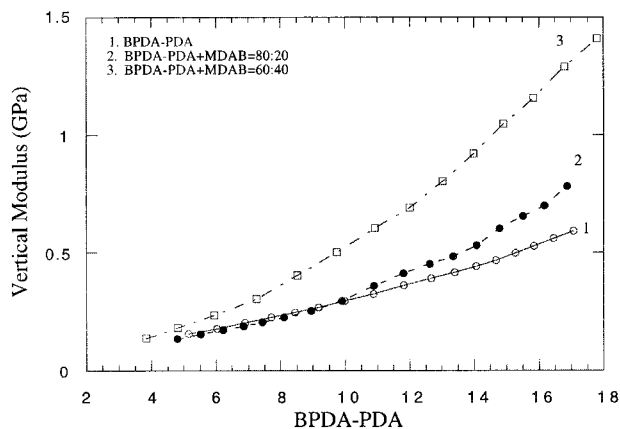


**Figure 15** Stress-strain curves of PMDA-ODA(E) + MDAB semi-IPN systems.

able oligomers. The elongation of PMDA-ODA(E) is larger than 70% strain. It is very common to observe a shorter elongation at break for crosslinked polymers or semi-IPN systems than for thermoplastic polymers because crosslinks restrict the molecular motion.<sup>22-25</sup> The lateral Young's modulus of these semi-IPN polyimide systems is shown in Figure 16. The data show that the lateral Young's modulus decreases with increasing content of oligomers for the BPDA-PDA + MDAB and BPDA-PDA + PEPA semi-IPN systems. This is most likely due to the decrease in the in-plane ordering caused by the addition of MDAB and PEPA to BPDA-PDA. However, the Young's modulus of the PMDA-ODA(E) + MDAB semi-IPN systems increases with increasing MDAB content. Since MDAB has a smaller lateral CTE than that of PMDA-ODA(E), the chain rigidity of MDAB is better than that of PMDA-ODA(E). Therefore, the lateral Young's



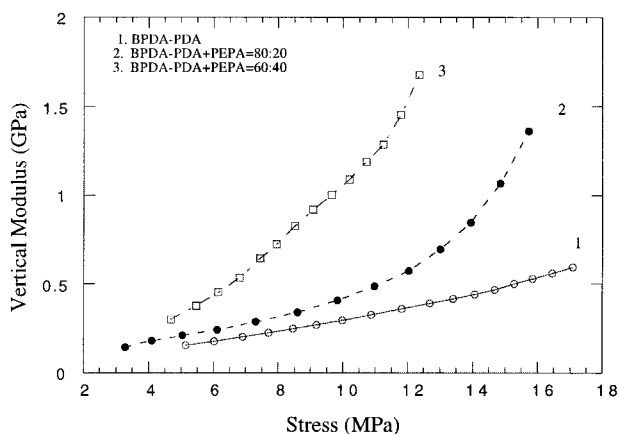
**Figure 16** Lateral Young's moduli of semi-IPN polyimide systems.



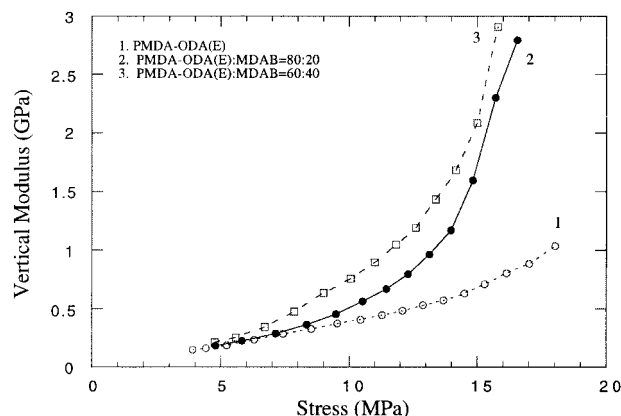
**Figure 17** Vertical elastic moduli of BPDA-PDA + MDAB semi-IPN systems.

modulus of the PMDA-ODA(E) + MDAB semi-IPN systems is improved by the addition of MDAB.

The vertical elastic moduli of the BPDA-PDA + MDAB, BPDA-PDA + PEPA, and PMDA-ODA(E) + MDAB semi-IPN systems are shown in Figures 17–19. It was found that the vertical modulus of these semi-IPN systems increased with increasing stress levels. As mentioned earlier, the free volume in the film decreased with increasing stress level. Since spin-coated polyimide thin films exhibit preferred in-plane ordering, polyimide molecules may stack like laminates in the  $z$ -direction as shown in Figure 20(a). The intermolecular forces between them are weak van der Waals forces and there may be some free volume (void) between them. As the compression force is applied, the free volume decreased as shown in Figure 20(b). The decrease in free vol-



**Figure 18** Vertical elastic moduli of BPDA-PDA + PEPA semi-IPN systems.

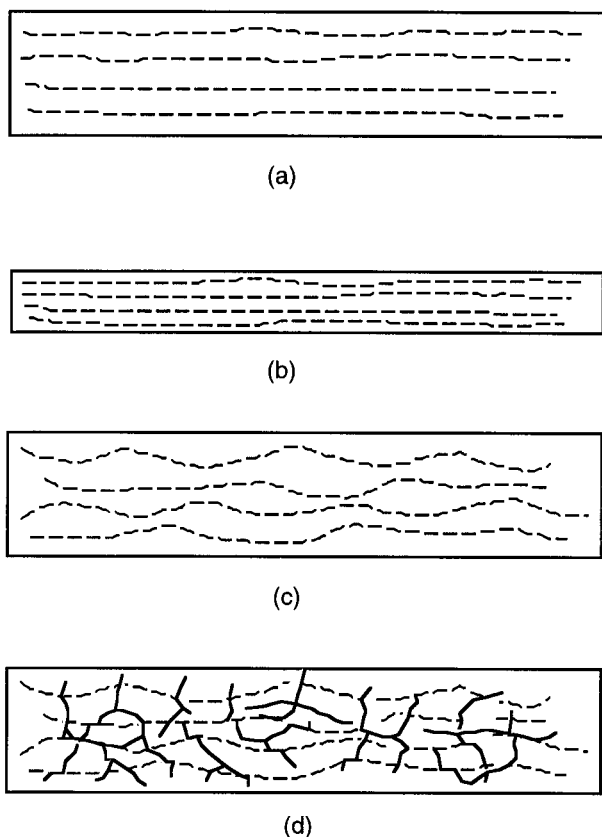


**Figure 19** Vertical elastic modulus of PMDA-ODA(E) + MDAB semi-IPN systems.

ume restricts the molecular motion and, hence, increases the elastic modulus in the  $z$ -direction.

The friction between the polymer and substrate can also lead to a similar effect. The friction increases as the compressing force increases and this restricts the free expansion of the film in the lateral direction and, therefore, may contribute to the modulus increase in the vertical direction. Since a very thin layer of oil between the polymer-substrate interfaces was applied, the effect of friction is expected to be minimum. Liou et al. studied the vertical elastic moduli of BPDA-PDA and PMDA-ODA thin films at different thicknesses and found that the vertical elastic modulus increases with increasing the film thickness for polyimides.<sup>9</sup> Since the in-plane ordering in spin-coated films decreases with increasing film thickness, more molecules orient away from the in-plane direction as film thickness increases. Therefore, as the number of strong intrachain covalent bonds with components along the  $z$ -direction increases, the vertical elastic modulus increases as the film thickness increases. The morphology of polyimide molecules can be represented as shown in Figure 20(c).

Crosslinks in the semi-IPN polyimide systems under study occur by the formation of covalent bonds. This type of network in the film can inhibit molecular motion. The in-plane ordering decreases and the crosslinking density increases with increasing content of crosslinkable oligomers.<sup>19</sup> The morphology of semi-IPN polyimide systems can be represented as shown in Figure 20(d). Thus, the vertical elastic moduli of the BPDA-PDA + MDAB semi-IPN systems and the BPDA-PDA + PEPA semi-IPN



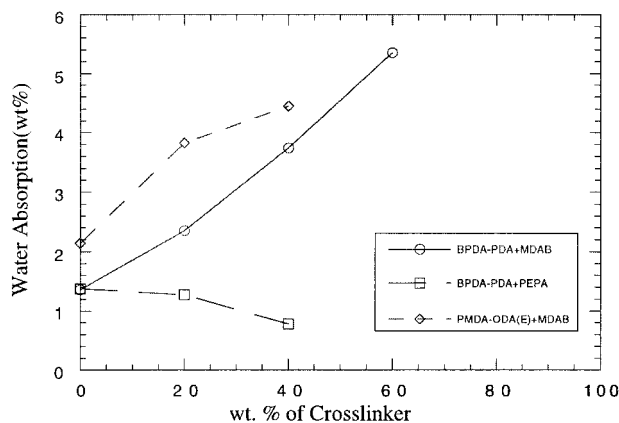
**Figure 20** Schematic description of molecular arrangement of polyimide thin films: (a) spin-coated polyimide with high in-plane ordering; (b) spin-coated polyimide with high in-plane ordering under compression force; (c) spin-coated polyimide with less in-plane ordering; (d) spin-coated semi-IPN polyimide systems with less in-plane ordering and crosslinks.

systems increase with increasing MDAB or PEPA content. In addition, the BPDA-PDA + PEPA semi-IPN systems were found to have a higher modulus than that of the BPDA-PDA + MDAB semi-IPN systems in the  $z$ -direction. This may be due to a higher crystalline-like phase in the BPDA-PDA + PEPA semi-IPN systems because the crystalline-like phase is characterized by a higher packing order and modulus than those of the amorphous phase. Although the crystalline-like phase in the BPDA-PDA + MDAB semi-IPN systems decreases with increasing MDAB content, the vertical elastic modulus increases with MDAB content. This implies that preventing molecular motion in a polymer is better achieved by higher crosslinking than by higher crystalline-like phase in the polymer.

### Water Absorption

The amount of moisture uptake for these semi-IPN systems is shown in Figure 21. The water absorption of BPDA-PDA and PMDA-ODA(E) increased with increasing MDAB content. However, the water absorption of the BPDA-PDA + PEPA semi-IPN systems decreased with increasing PEPA content.

Researchers have suspected that the water absorption of a polymer is related to the free volume in the polymer.<sup>24-27</sup> Generally, the molecular chains are randomly tangled, with less ordering in amorphous regions allowing for more free volume than in the crystalline regions where molecular chains are more ordered and well packed in crystalline repeat units, leading to a reduced free volume. Amorphous PMDA-ODA is reported to have a higher water absorption than that of the partial crystalline BPDA-PDA.<sup>28</sup> It has also been reported that there are two water absorption sites,  $\gamma_1$  and  $\gamma_2$ , in polyimides.<sup>25,28</sup> The absorption site  $\gamma_1$  is relatively homogeneously distributed throughout the polymer and may be bonded to oxygen sites along the polymer chains. The absorption site  $\gamma_2$  occurs in the form of small clusters which give rise to large dipole moments due to the orientation correlation. A comparison of the WAXD data of these polyimide semi-IPN systems showed that the water absorption in the BPDA-PDA and PMDA-ODA(E) semi-IPN systems increases with increasing MDAB content, which can be correlated to the increase of the amorphous phase for the semi-IPN polyimide systems. Matsuguchi et al. reported that the shorter the chain length of the oligomer the lower is the molecular packing density for acetylene-terminated polyim-



**Figure 21** Water absorption in polyimide semi-IPN systems.

ides.<sup>26</sup> The decrease in molecular packing density gives rise to an increase in free volume and, hence, an increase in water absorption. Since polymerized MDAB is an amorphous polymer according to the WAXD data, the morphologies of the BPDA-PDA + MDAB and PMDA-ODA(E) + MDAB semi-IPN systems become more amorphous with the addition of MDAB. As a result, the MDAB oligomer disturbs the packing density and increases the free volume of the BPDA-PDA + MDAB and PMDA-ODA(E) + MDAB semi-IPN systems. Therefore, it is reasonable to observe a higher amount of water absorption in these semi-IPN polyimide systems. In contrast, PEPA enhances the crystalline-like phase of the BPDA-PDA + PEPA semi-IPN systems and results in a reduction in the amount of water absorption. This may be caused by (1) the rigid structure leading to a reduction in the number of sorption sites (the space around the polar group),<sup>26</sup> (2) higher crystalline-like regions (better packing density) in the BPDA-PDA + PEPA semi-IPN systems, and (3) PEPA being nonpolar. Therefore, the effect of oligomers on water absorption depends on the change in the amount of crystalline-like and the polarizability of oligomers.

## CONCLUSIONS

The structure-property correlations of the BPDA-PDA + MDAB, BPDA-PDA + PEPA, and PMDA-ODA(E) + MDAB semi-IPN systems were investigated. The in-plane molecular arrangement becomes disordered which gives rise to an increase in the lateral CTE and a decrease in the birefringence and Young's modulus. In the same way, the small molecules of MDAB and PEPA disturb the in-plane molecular ordering of semi-IPN polyimide systems. This results in a reduction in the birefringence and Young's modulus and an increase in the lateral and vertical CTE. This implies that MDAB and PEPA also act like plasticizers during the curing process in their respective semi-IPN systems. In addition, the free volume increases as a result of the decrease in density. The crosslinks in the semi-IPN polyimide systems can increase the atomic and dipolar polarizabilities and, hence, increase the dielectric constant at 1 MHz. However, the reduction in water absorption and the dielectric constant and the increase in birefringence of the BPDA-PDA + PEPA semi-IPN systems come from the contribution of the nonpolar PEPA. The properties of

semi-IPN systems change with increasing oligomer content because there is a crosslinking network forming in these systems and the amount of the crosslinkable oligomers does affect the final properties of semi-IPN polyimide systems.

The CTE anisotropy of polyimides is reduced by adding the crosslinkable oligomers. This is caused mainly by the disordering of the in-plane molecular arrangements although the crosslinking density in semi-IPN polyimide systems is not large enough to reduce the vertical CTE. However, an empirical correlation between density and volume expansion is observed, indicating a correlation between the volume expansion and free volume in polyimides.

We found that the vertical moduli of these semi-IPN polyimide systems increase with increasing stress level because of the effect of stress in decreasing the free volume. The vertical elastic moduli also change with the content of crosslinkable oligomer because crosslinking restricts the molecular motion in polymers. Consequently, the vertical modulus is affected by the free volume at low stress levels and can be increased by crosslinking or by a crystalline-like phase at higher stress levels.

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