Structure–Property Correlation for Thin Films of Semi-Interpenetrating Polyimide Networks. I. Miscibility, Curing, and Morphology Studies

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ABSTRACT: Three different semi-interpenetrating polymer network (semi-IPN) polyimide systems were prepared through blending in solution by using 2 different polyimides, BPDA–PDA and PMDA–ODA (E), and 2 different oligomers, bismaleimide (MDAB) and phenylthynyl-terminated BPDA–PDA (BPDA–PDA–PEPA) oligomers. The oligomers are used as crosslinkers to modify the morphology of polyimides. The results show that both MDAB and PEPA are miscible with BPDA–PDA, but MDAB is immiscible with PMDA–ODA (E). Fourier transform infrared spectrum, dynamic mechanical thermal analysis data, and calculated crosslinking density indicate that there are crosslinking networks in these semi-IPN polyimide systems. In addition, the density and wide-angle X-ray diffraction results confirm that the molecular ordering and packing order are reduced by the addition of oligomers for these semi-IPN polyimide systems. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 261–272, 1998

Key words: polyimide; semi-interpenetrating polymer networks; thin film; miscibility; curing; X-ray

INTRODUCTION

Polyimides have recently been used in the microelectronics industry either as insulation layers or as passivation layers due to their low dielectric constant, low coefficient of thermal expansion (CTE), desirable mechanical properties, good chemical stability, and high glass transition temperature.[1] Polyimide thin films have an in-plane molecular orientation introduced by the spin-coating process, and this orientation leads to the

properties to be isotropic in the film plane but anisotropic between in-plane and out-of-plane.[2–4] Several investigations have shown that spin-coated polyimide thin films exhibit anisotropy in the refractive index, CTE, and modulus.[5–10] It has been found that the CTEs of polyimide thin films in the z-direction are 1–2 orders of magnitude larger than the CTE in the in-plane direction.[9] In contrast, the Young's modulus in the z-direction for a polyimide, such as Poly (p-phenylene biphenyl tetracarboximide) (BPDA–PDA), is smaller than that in the film plane.[8,10]

Recently, multilayered structures combining polyimides as low dielectric interlayer materials with copper as interconnect material to increase the signal propagation have become the leading edge technology in the semiconductor industry.[11] However, the high CTE in the z-direction of poly-

imide thin film have shown to generate high stresses at the polymer–metal interface in the out-of-plane (z-direction) direction. In addition, if the product of thermal expansion and modulus in the out-of-plane direction is too large, it will lead to delamination and/or cracking between layers. It has been shown that cracking of copper plated-through holes during thermal cycling of printed circuit boards is related to the thermal mismatch between the out-of-plane CTEs of the dielectric materials and the copper.[12] 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 for the correlation between chemical structure and their anisotropic properties, such as CTE and Young's modulus, is still lacking.

Since the chemical structure and morphology of polymers have a profound effect on their properties, the anisotropic properties of polyimide thin films are also expected to be affected by its structure and morphology. Many efforts have been made to improve the thermal and mechanical properties by changing the chemical structure and/or the morphology of polyimides.[13,14] There are several approaches to modify the chemical structure. It has been reported that film obtained from crosslinkable oligomers, such as bisbenzocyclobutene (BCB) exhibit optical and CTE isotropy.[15] Polyimides with crosslinkable groups on the backbone or side chains also show less anisotropic behavior.[16] Meanwhile, noncoplanar polyimides with hex-fluoride molecules, such as poly(hexafluoroisopropylidene diphthalic anhydride 2,2-bis(4-aminophenoxy-p-phenylene) hexafluoropropane) (6FDA–BDAF), have shown optical isotropy.[17] However, BCB and 6FDA–BDAF have high lateral CTEs, and BCB has poor thermal stability. In addition, crosslinkable polyimides are brittle. All these disadvantages restrict their applications in the microelectronics industry. Other than the effect of chemical structure, the morphology of polyimides can be controlled by both molecular structure and processing conditions, such as curing temperature, curing rate, annealing, thickness, and coating processes.[3,4,18] In addition, the morphologies can also be modified by blending polyimide precursors with isomers or blending poly(amide ester) with poly(amic acid) to tailor thermal and mechanical properties.[19–22] Sachdev et al. tailored the properties of polyimide by disrupting the order along the chain and in the packing of polyimide chains through blends and copolymer approaches.[23,24]
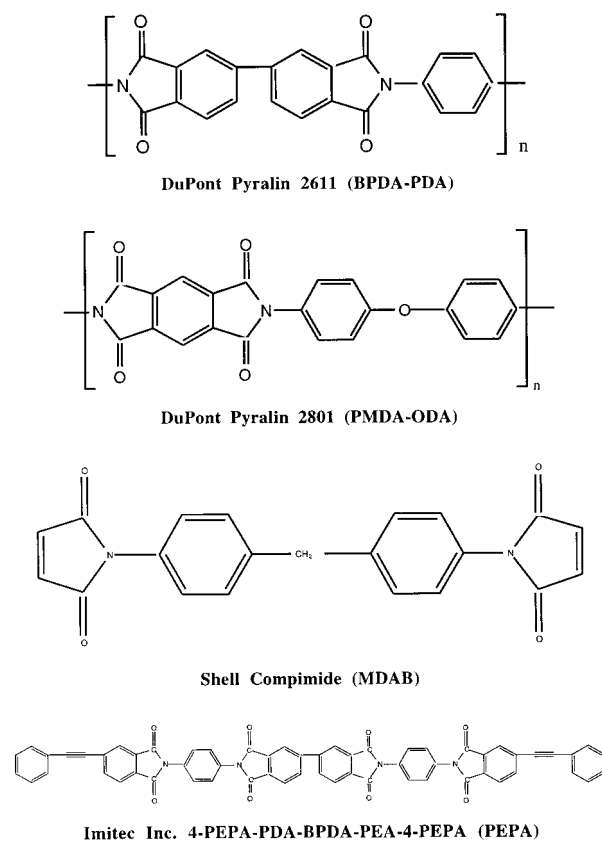
Figure 1   Chemical structures of polymers used in this studies.

Another way to change the morphology of polyimide is to blend polyimide with a crosslinkable polymer and form a semi-interpenetrating polymer network (semi-IPN). A semi-IPN is defined as a combination of 2 polymers in a network form; one of them is crosslinked in the presence of the other.[25] Therefore, 3 different semi-IPN polyimide systems were blended using 2 different polyimides, such as poly(p-phenylene biphenyl tetracarboximide) (BPDA–PDA) and poly(4,4′-oxydiphenylene pyromellitimide) (PMDA–ODA(E)), and 2 different oligomers, such as bismaleimide (MDAB) and phenylthynyl-terminated BPDA–PDA (BPDA–PDA–PEPA) oligomers. In this article, the investigations of miscibility, curing, and morphology of these semi-IPN polyimide systems will be discussed.

EXPERIMENTAL DETAILS

Experimental Materials and Sample Preparations

The chemical structures of polyimides and oligomers used in this study are shown in Figure 1.

Table I   The Semi-IPN Polyimide Systems and Compositions

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		

DuPont Pyralin 2611 is a polyimide made from biphenyl dianhydride (BPDA) and para-phenylene diamine (PDA); DuPont Pyralin 2801 is a polyimide made from pyromellitic dianhydride (PMDA) and 4,4′-oxydianiline (ODA); Shell MDAB bismaleimide oligomer is 4,4′-Bismaleimido diphenyl methane; Imitec PEPA is a phenylethynyl-terminated imide oligomer made from BPDA–PDA and end-capped with 4-phenylethynylphthalic anhydride (4-PEPA). Three different semi-IPN polyimide systems, BPDA–PDA + MDAB, BPDA–PDA + BPDA–PDA–PEPA, and PMDA–ODA (E) + MDAB, have been blended. The species and composition for these semi-IPN polyimide systems are listed in Table I. Semi-IPN polyimide systems were prepared by adding 2 materials in the required ratio with different compositions into 30-mL bottles and mixing on a rotary roller for 24 h. Some N-methyl-pyrrolidone (NMP) was added to these blends to increase the miscibility and control the viscosity for spin-coating. The solid content of the semi-IPN polyimide systems is about 10–15 wt %.

These poly(amic acid) solutions were spin-coated onto 3-in. Si wafers and glass slides by using a spin-coater (Headway Research Inc., Model #PWM101). In addition, Al/Si substrates were used to prepare the samples for dielectric constant measurements, and quartz discs were used to prepare the samples for water absorption measurements. The spin time is 30 s, and the spin speed is controlled so that the final film thickness is about 10 μm after curing. The curing recipes used in this study are shown in Table II.

EXPERIMENTAL METHODS

In order to verify the miscibility of these blends, a Leitz polarized optical microscope (Model Orthoplan-Pol) was used to examine the phase domain or phase separation in the semi-IPN polyimide systems, which was spin-coated on glass slide. The resolution of Leitz microscope is about 0.25 μm with a crossed polarizer.[26] The miscibility of semi-IPN polyimide systems can be determined by looking at the contrast in the brightness of the domains in these systems.

The refractive index and the thickness of polyimide thin films were measured using a Prism Coupler (Metricon Inc., Model 2010) with a laser light (λ = 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 TE mode and TM mode are 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.

A dynamic thermal mechanical analyzer (DMTA) has been used for advanced examination since DMTA can distinguish the dimension resolution in several hundred Å range in polymer blends.[27] The miscibility of blends can be determined by looking at the variation in T_gs of these blends. In this study, the T_gs of polyimide and semi-IPN polyimide systems were measured by using Rheometric Scientific DMTA Mark III with accessories in tensile mode. The data was taken

Table II   The Curing Recipes Used in This Study

Materials	Prebake (in Air)	Curing Conditions (in Nitrogen Environment)
Polyimides and polyimide; Semi-IPN systems	80°C/15 min	Room temp (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

Table III   The 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	0.249	0.094	0.007	0.211

from room temperature (RT) to 500°C at a frequency of 10 Hz and with a heating rate of 5°C/min.

Fourier transform infrared (FTIR) spectroscopy has been widely used to study the kinetics of the thermal imidization of poly(amic acid) because it is very sensitive to the changes in the molecular environmental of functional groups.[28,29] IBM IR/98 with an attenuated total reflection (ATR) accessory was used for these studies. The infrared (IR) source is a globar mid IR (MIR) range from 700 to 4000 cm^{-1} at a resolution of 4 cm^{-1}. Each IR spectrum was collected with 300 scans.

The density of semi-IPN polyimide systems was measured by the method described in ASTM D1505 using a density gradient column made by Techne Co. The liquid systems are toluene and carbon tetrachloride. The densities of toluene and carbon tetrachloride are 0.87 and 1.59 g/cm^3, respectively. The density range in the column is about 1.3 to 1.5 g/cm^3, and the density–position correlation was calibrated using 5 standard density floats. The temperature of the density gradient column was kept at 23 ± 1°C by keeping the column immersed in 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 density–position correlation.

The morphology of semi-IPN polyimide systems can be obtained by wide-angle X-Ray diffraction (WAXD) measurements. The WAXD patterns were obtained by using a Phillips automatic powder diffractometer equipped with CuKα source (λ = 1.5418 Å) operated at 40 kV and 40 mA. The diffraction data were recorded from $2\theta = 2°$ to $2\theta = 60°$ with a step size of 0.05°.

## RESULTS AND DISCUSSIONS

Miscibility Study

The phase separation behavior of semi-IPN polyimide systems is similar to polymer blends. Under a cross-polarized optical microscope, no phase separation could be detected in these semi-IPN polyimide systems neither before nor after cure. We notice that there are cases in which phase separation may not be detectable by cross-polarized optical microscopy due to the similarity in refractive index for polymers. The refractive index of these polyimides and oligomers were measured using the prism-coupler are listed in Table III. The refractive indices of these polyimides and oligomers are different. Consequently, we rule out the possibility that similarity of refractive indices among phases may cause the phase separation to be unobservable.

The advanced determination of miscibility relies on the glass transition (T_g) method. The tan δ versus temperature plots of these semi-IPN polyimide systems measured by DMTA are shown in Figures 2–4. The DMTA data for BPDA–PDA show that its α and β transitions are around 360 and 214°C, respectively. In addition, another transition known as the α_c transition, which is due to melting of the crystalline-like phase in the polymers, appears around 415°C.[29] The DMTA data for PMDA–ODA (E) show an obvious T_g (α transition) around 430°C but do not show a clear β transition. However, PMDA–ODA (E) doesn't show any α_c transition because PMDA–ODA is almost amorphous. A similar T_g for PMDA–ODA
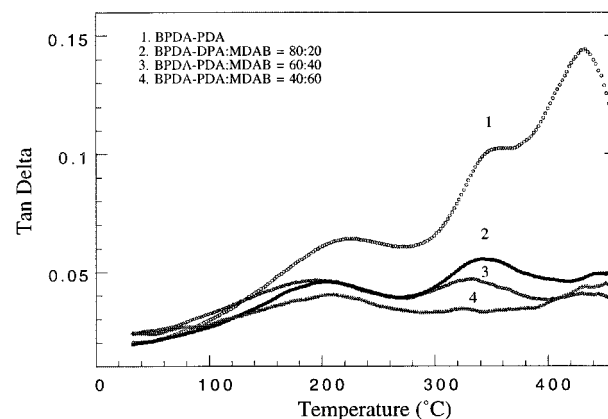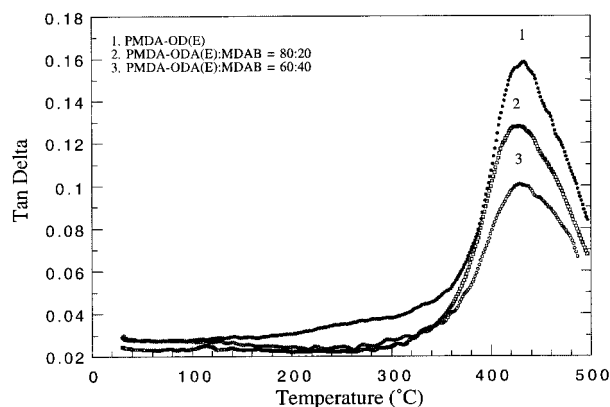

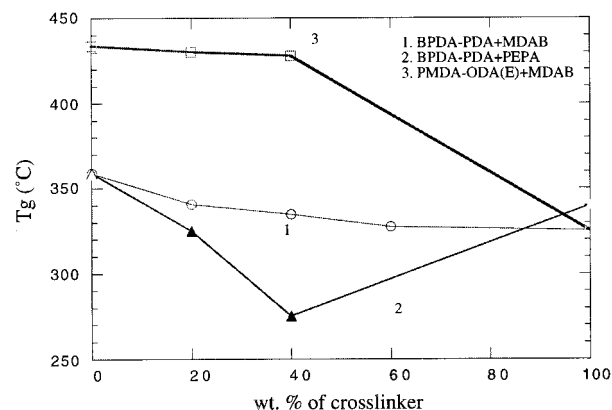**Figure 2**   DMTA data for BPDA–PDA and MDAB semi-IPN systems.
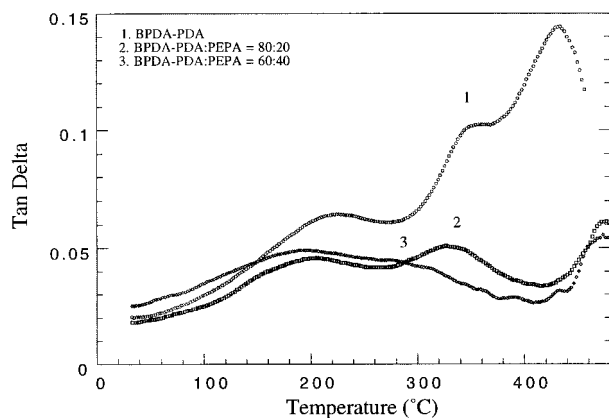
Figure 3 DMTA data for BPDA–PDA and PEPA semi-IPN systems.

Figure 5 Glass transition temperatures for semi-IPN polyimide systems.

has been reported in the literature.[3] The T_gs for bulk MDAB and PEPA are 325 and 345°C, respectively, as determined using differential scanning calorimetry (DSC).[30] The DMTA data show that BPDA–PDA + MDAB and BPDA–PDA + PEPA semi-IPN systems have only one T_g, which changes with an increasing weight percentage of crosslinkable oligomers, as shown in Figure 5.

These observations indicate that these BPDA–PDA + MDAB and BPDA–PDA + PEPA semi-IPN systems are miscible at these compositions. There is only one T_g at the vicinity of 430°C for PMDA–ODA (E) + MDAB semi-IPN systems, as shown in Figure 5. This observation donates that PMDA–ODA (E) and MDAB are immiscible. Since there is no observable phase separation under the optical microscope for PMDA–ODA (E) + MDAB semi-IPN systems, the domain size are likely between several hundred Å and 0.25 μm. Crosslinks in polymers are known

to increase their T_gs.[31] Sometimes, the T_gs of semi-IPN polyimide systems are smaller than the T_gs of pure polymers because the interactions between the 2 polymers in semi-IPN polyimide systems may weaker than the interchain forces in the individual polymers.[32] In addition, since polyimides, such as BPDA–PDA and PMDA–ODA (E), form the matrix in these semi-IPN polyimide systems, the crosslinking density caused by the crosslinkable oligomers in semi-IPN polyimide systems should be smaller than in the case of polymers obtained from only crosslinkable oligomers. Therefore, the T_gs of BPDA–PDA + PEPA semi-IPN systems are lower than the T_g of PEPA. However, the α_c transition of BPDA–PDA + PEPA semi-IPN systems is larger than 415°C. This indicates that there may be more crystalline-like phases in BPDA–PDA + PEPA semi-IPN systems than those in BPDA–PDA + MDAB semi-IPN systems.

Curing Study

The imidization temperatures for poly(amic acid) precursors and the crosslinking temperatures of crosslinkable group are listed in Table IV.[33–36] The FTIR spectra of BPDA–PDA + MDAB, BPDA–PDA + PEPA, and PMDA–ODA (E) + MDAB semi-IPN systems are shown in Figures 6–8. The FTIR assignment of functional group is listed in Table V.[28,37–40] The imidization reactions was monitored by following the appearance of imide bands around 1780 cm^{-1} (symmetric stretch of carbonyl groups), 1720 cm^{-1} (asymmetric stretch of carbonyl groups), 1370 cm^{-1} (C—N stretch), and 730 cm^{-1} (deformation of imide ring).[28,34,37,41,42] The crosslinking reaction of MDAB was monitored by the disappearance of maleimide C=C band at 1150 cm^{-1}.[38] The

Figure 4 DMTA data for BPDA–PDA and PEPA semi-IPN systems.

Table IV The Imidization Temperature and Crosslinking Temperature of Semi-IPN Systems

Polyimide	Crosslinker	Crosslinking Agent

BPDA–PDA
  curing temperature:
  135–250°C
	MDAB curing temperature: 208–332°C
	PEPA curing temperature: 330–400°C
		Maleimide group (C=C)
		Phenylethynyl (C≡C)

PMDA–ODA (E)
  curing temperature:
  190–310°C
	MDAB curing temperature: 208–332°C	Maleimide group (C=C)

maleimide C=C at 1150 cm^{-1} disappeared after cure for BPDA–PDA + MDAB semi-IPN and PMDA–ODA (E) + MDAB semi-IPN systems are shown in Figures 9–10. This evidence indicates that the MDAB is fully reacted during the curing process. The crosslinking mechanism for MDAB was shown in Figure 11.[43] This mechanism involves the thermal initiation to form free radicals, which then react with the maleimide double bonds to form a crosslinking network. The crosslinking reaction of PEPA was monitored by the disappearance of phenylethynyl group (C≡C bond) at 2215 cm^{-1}.[44–48]
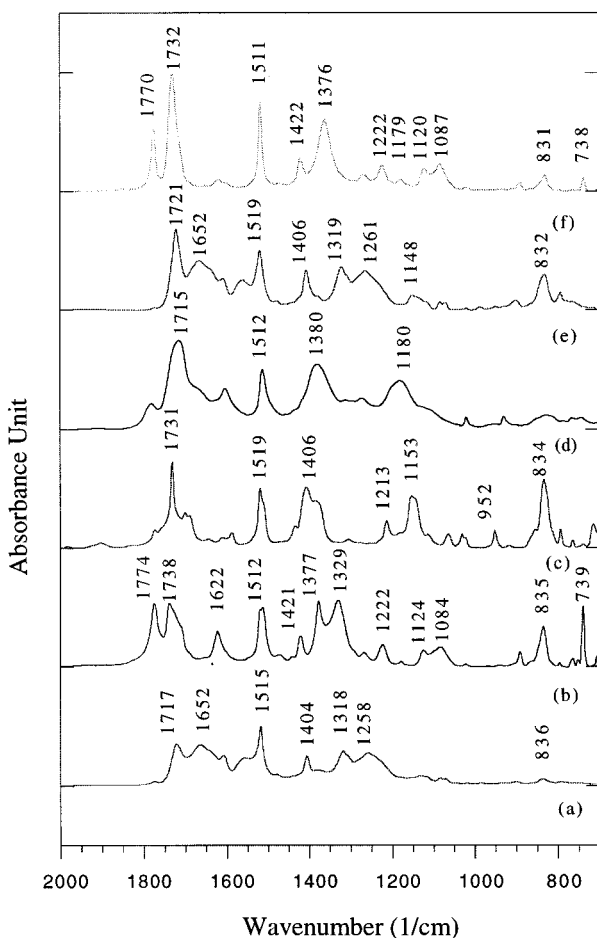
Figure 6 FTIR spectra for (a) prebaked BPDA–PDA, (b) cured BPDA–PDA, (c) precured MDAB, (d) cured MDAB, (e) precured BPDA–PDA + MDAB (80 : 20) semi-IPN systems, and (f) cured BPDA–PDA + MDAB (80 : 20) semi-IPN systems.
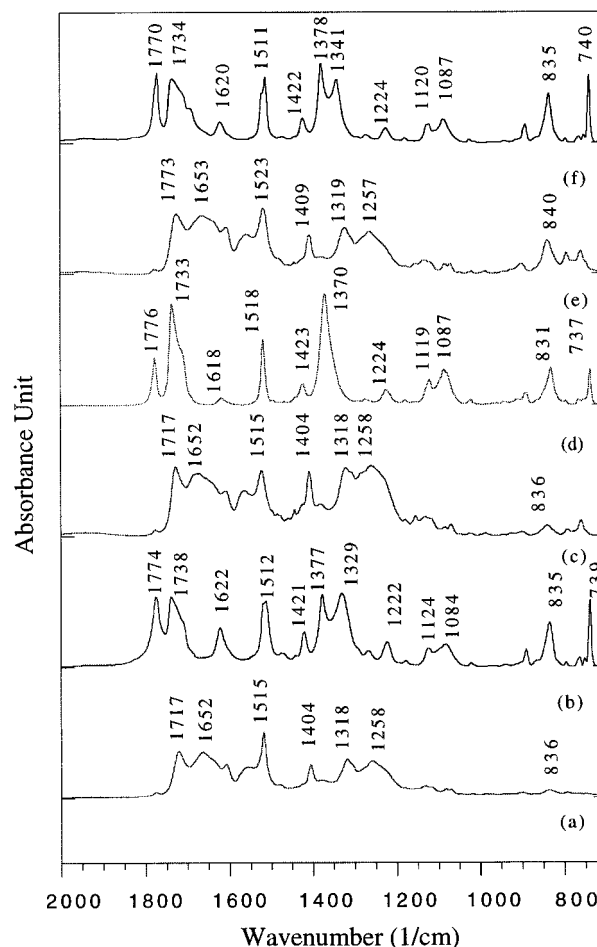
Figure 7 FTIR spectra for (a) prebaked BPDA–PDA, (b) cured BPDA–PDA, (c) precured PEPA, (d) cured PEPA, (e) precured BPDA–PDA + PEPA (80 : 20) semi-IPN systems, and (f) cured BPDA–PDA + PEPA (80 : 20) semi-IPN systems.
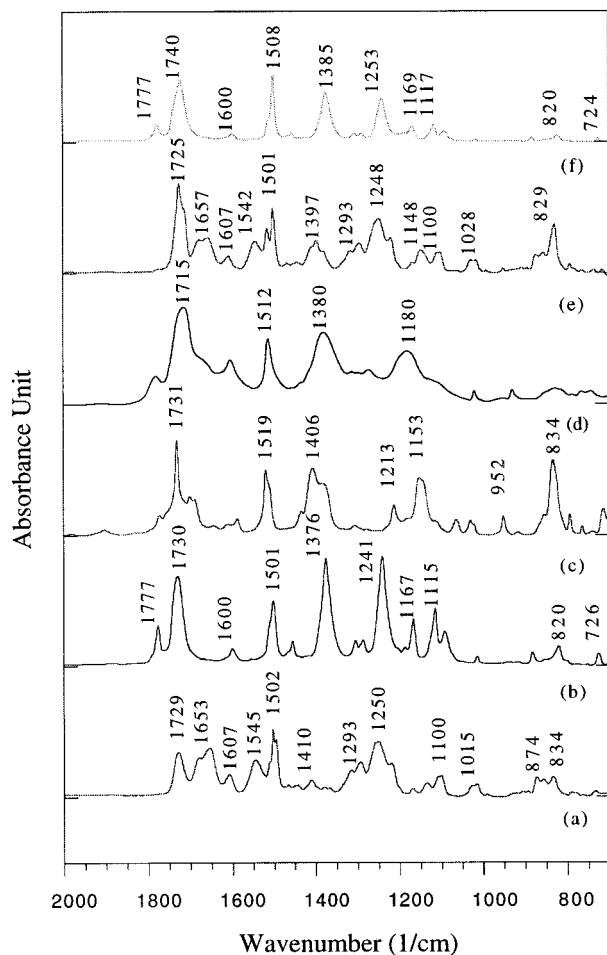
Figure 8 FTIR Spectra for (a) prebaked PMDA–ODA (E), (b) cured PMDA–ODA (E), (c) precured MDAB, (d) cured MDAB, (e) prebaked PMDA–ODA (E) + MDAB (80 : 20) semi-IPN systems, and (f) cured PMDA–ODA (E) + MDAB (80 : 20) semi-IPN systems.

Table V   The FTIR Assignment of Functional Group of Polyimides and Crosslinkable Oligomers

Wavenumbers (cm^{-1})	Assignment
2215	—C≡C—
1780	C=O in-plane
1720	C=O out-of-plane
1706	C=O out-of-plane
1680	C=O stretching of complexed NMP
1652	Amide C=O stretching
1600	Aromatic ring
1550	Amic acid
1515	Aromatic ring
1408	CH_2 in NMP
1400	C—N—C
1370	C—N stretch
1182	C—N—C
1150	Maleimide
1120	Imide ring
1080	Imide ring
952	Aromatic ring
830	Aromatic ring
730	Imide ring

crosslinks (M_c). M_c for a polymer network can be determined using results from equilibrium swelling measurement according to the Flory–Huggins equation.[49] M_c can also be calculated by a mechanical test method. The equation is given as follows:

The phenylethynyl C≡C bond at 2215 cm^{-1} of BPDA–PDA + PEPA semi-IPN systems retained some residual intensity after curing, as shown in Figure 12.

This indicates that the phenylethynyl C≡C bond may not be fully reacted, possibly due to the steric hindrance of C≡C bonds and big phenyl rings. The crosslinking reaction mechanism for phenylethynyl group is very complex, and several possible reactions have been proposed as described in Figure 13.
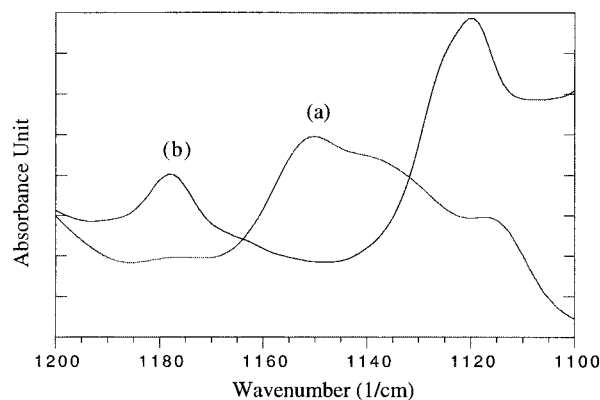
Crosslinking Network

Since there are crosslinks in these semi-IPN polyimide systems, the network can be characterized by the average molecular weight between
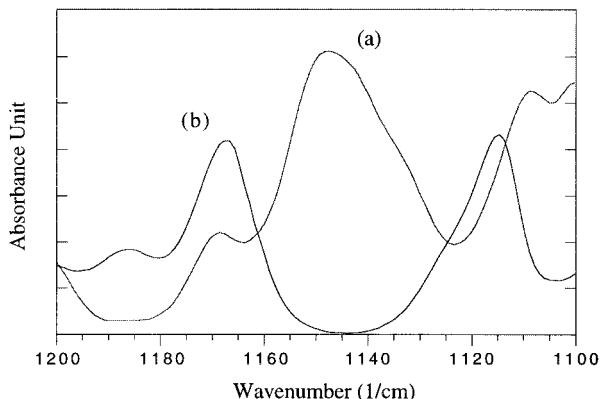

Figure 9 The FTIR spectra for BPDA–PDA + MDAB (80 : 20) semi-IPN systems between 1100 and 1200 cm^{-1}: (a) before cure; (b) after cure.

Figure 10 The FTIR spectra for PMDA–ODA (E) + MDAB (80 : 20) semi-IPN systems between 1100 and 1200 cm^{-1}: (a) before cure; (b) after cure.

Figure 12 The FTIR spectra for BPDA–PDA + PEPA (80 : 20) semi-IPN systems around 2215 cm^{-1}: (a) before cure; (b) after cure.
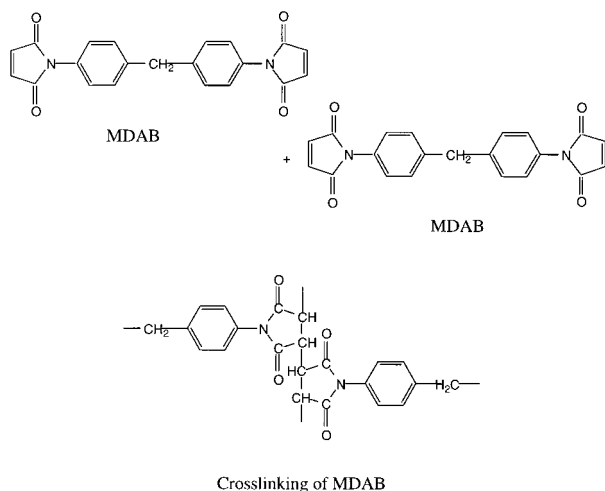
$$G = \frac{\rho RT}{M_c}$$

$$G = E/3 \tag{1}$$

where G is shear modulus, E is Young's modulus at rubbery state, ρ is density of the polymer, and T is absolute temperature.

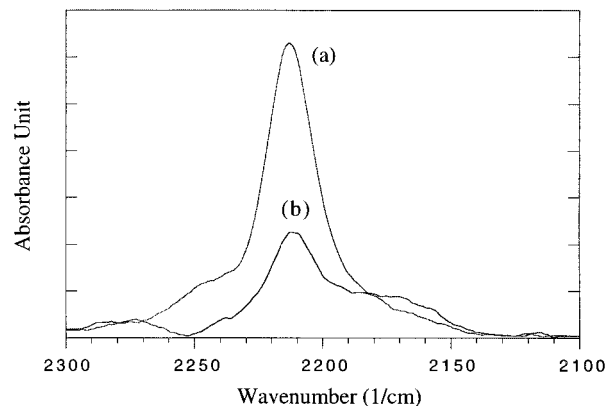The crosslinking density of the network (N) can be calculated using equation (2).[50,51]

$$N = \rho/M_c \tag{2}$$

The mechanical method to calculate the M_c of semi-IPN polyimide systems was selected. The Young's moduli of semi-IPN polyimide systems can be obtained from the modulus values at a

temperature higher than T_g (that is, at least 10 to 20°C higher than T_g, and the polymers would be in a rubbery state) in their DMTA data, as shown in Figures 14–16. The densities of semi-IPN polyimide systems measured by using a density column are shown in Figure 17. The density of these semi-IPN polyimide systems decreased with increasing content of oligomers. This indicates that molecular ordering and packing order are reduced by the addition of these oligomers. Although BPDA–PDA and PMDA–ODA (E) do not crosslink, similar calculations of M_c and N were made for comparison. The calculated values of M_c and N

Crosslinking of MDAB

Figure 11 The crosslinking mechanism of MDAB.
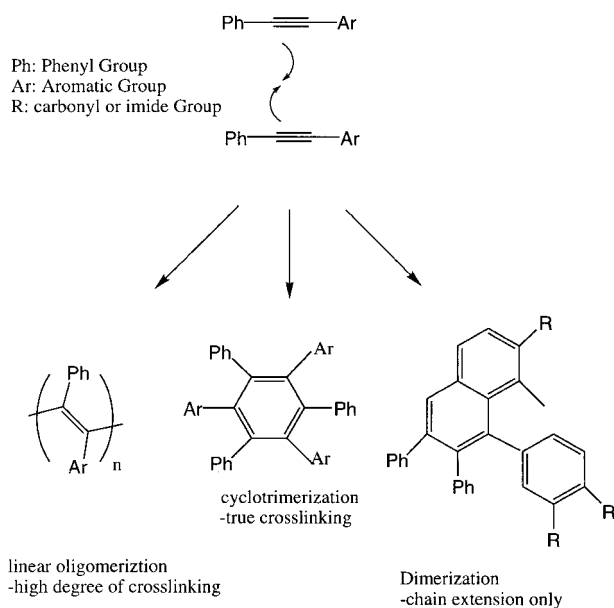
Figure 13 Possible reactions for phenylethynyl end-capped imide oligomer (PEPA).
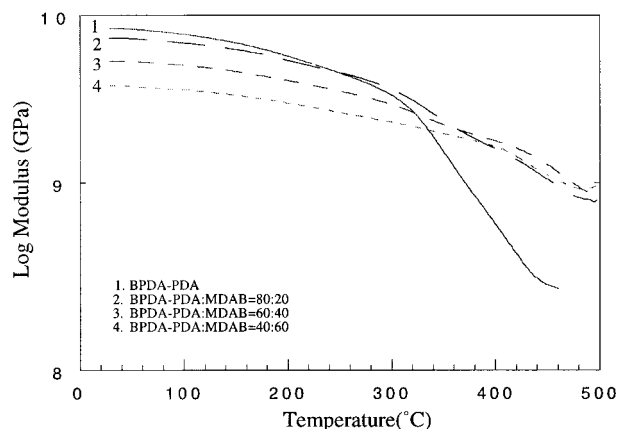
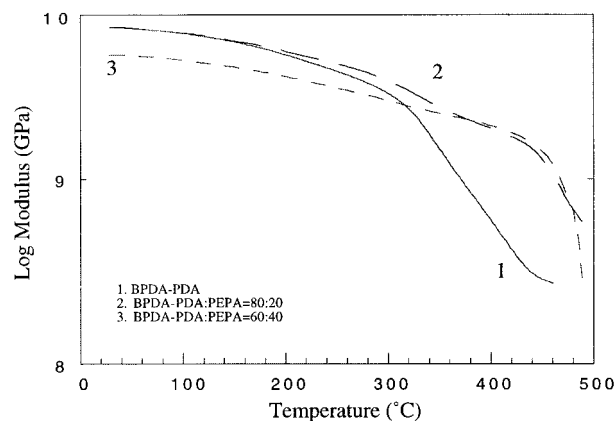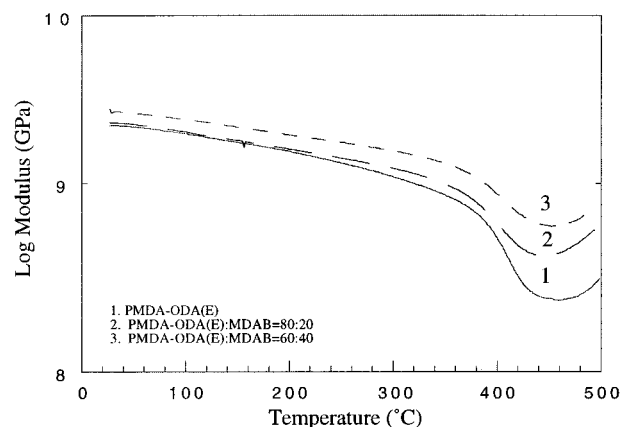**Figure 14** DMTA data for BPDA–PDA + MDAB semi-IPN systems.

Figure 16 DMTA data for PMDA–ODA (E) + MDAB semi-IPN systems.

data using equations (3)–(4) are shown in Figure 18. It can be seen that a network forms within the semi-IPN polyimide systems and that the crosslinking density of these semi-IPN polyimide systems increases with increasing crosslinker weight percentage.

Another evidence of crosslinking in the polymer is the enhancement the mechanical properties of the polymers at high temperature.[52] It was observed that the mechanical properties of semi-IPN polyimide systems were enhanced at high temperature, as shown in Figures 14–16. Since less relaxation can occur in a crosslinked polymer, the height of the relaxation peak at high temperature should be reduced when the crosslinking density is increased. The DMTA data of semi-IPN polyimide systems show reduced relaxation peaks when the crosslinker concentration increases, as shown in Figures 2–4.

Wide Angle X-ray Diffraction

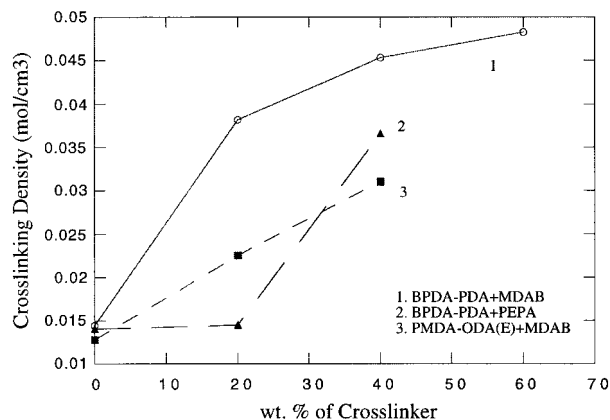BPDA–PDA is a semicrystalline-like polyimide with high in-plane ordering developed during curing at temperatures above 350°C.[18] BPDA–PDA polyimide molecules are in a frozen smectic-E type of crystalline-like state based on orthorhombic crystal-like unit cell[18] with parameters $a = 13$ Å, $b = 7.0$ Å, and $c = 31.6$ Å.[53] There are 3 peaks at 18°, 21.1° and 25.4° in 2θ angle, assigned to be the reflections of the (204), (300), and (020) planes, respectively.[4,54] These planes indicate chain misalignment, planar unit edge-on separation, and interplanar separation, respectively. The WAXD data for BPDA–PDA + MDAB semi-IPN systems are shown in Figure 19.

The (204) peak increased with increasing MDAB content, but the (300) and (020) peaks decrease with increasing MDAB content. This indicates that adding MDAB to BPDA–PDA increased the chain misalignment and decreased
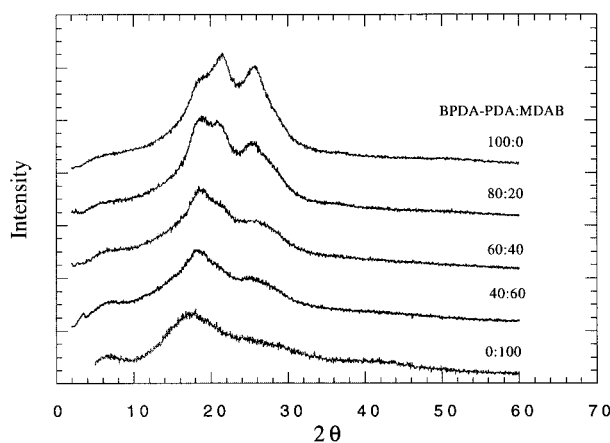
Figure 15 DMTA data for BPDA–PDA + PEPA semi-IPN systems.
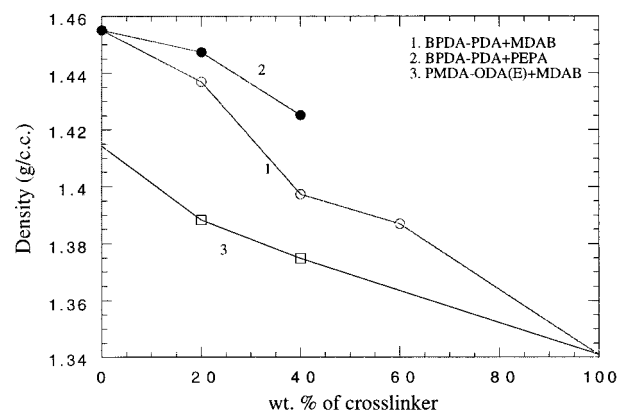
Figure 17 Densities for semi-IPN polyimide systems.

Figure 18 Crosslinking densities for semi-IPN polyimide systems.

Figure 20 WAXD data for BPDA–PDA + PEPA semi-IPN systems.

the interplanar packing in BPDA–PDA. Therefore, the in-plane molecular ordering of BPDA–PDA is decreased by the addition of MDAB. In addition, the crystalline-like phase of BPDA–PDA decreased with increasing MDAB content. Since MDAB itself is amorphous, adding MDAB to the semicrystalline-like BPDA–PDA disrupts the BPDA–PDA packing and led to the decrease in the percentage of the crystalline-like phase in BPDA–PDA + MDAB semi-IPN systems.

PEPA has a main chain similar to BPDA–PDA but is end-capped with biphenylethynyl groups. The WAXD data obtained for BPDA–PDA + PEPA semi-IPN systems are shown in Figure 20. The percentage of crystalline-like phase in BPDA–PDA and PEPA semi-IPN systems increased with increasing PEPA content because PEPA has a rigid rod-like structure. Due to the

rigid-rod-like structure, the system appeared to form a polymer with larger crystalline-like phase more easily. It can therefore be inferred that the planar unit edge-on separation and the interplanar separation in BPDA–PDA + PEPA semi-IPN systems decreased with increasing PEPA content. However, the chain misalignment increased as PEPA concentration was increased. Inserting PEPA can therefore disrupt the in-plane orientation of BPDA–PDA.

PMDA–ODA (E) is a polyimide with a small portion of crystalline-like phase. This polyimide has an orthorhombic crystal-like unit cell with lattice parameters $a = 12.8$ Å, $b = 8$ Å, and $c = 32$ Å.[51] Three peaks have been identified at 14.7, 22.2, and 26.2°, which correspond to the (101), (010), and (111) peaks, respectively.[4,54] PMDA–ODA (E) + MDAB semi-IPN systems became more amorphous with increasing MDAB concentration, as shown in Figure 21. The decrease in (111) peak indicates that the PMDA–ODA (E) + MDAB semi-IPN systems became more disordered with increasing MDAB content.

From the WAXD data, it was found that the change in the percentage of crystalline-like phase in semi-IPN polyimide systems is dependent on the crystalline-like phase of the individual polyimides. In addition, the molecular ordering of semi-IPN polyimide systems became more disordered when the crosslinkable oligomers was added. A similar conclusion was made in a recent report that observed that the crystalline-like phase of a crystalline oligomer decreases when a amorphous polyimide is used.[32]

Figure 19 WAXD data of BPDA–PDA + MDAB semi-IPN systems.
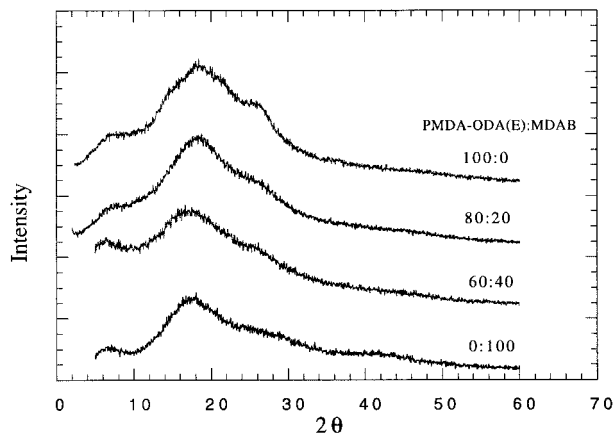
Figure 21 WAXD data for PMDA–ODA (E) + MDAB semi-IPN systems.

CONCLUSIONS

Three semi-IPN polyimide systems, BPDA–PDA + MDAB, BPDA–PDA + PEPA, and PMDA–ODA (E) + MDAB, have been investigated. No phase separation could be detected in these semi-IPN polyimide systems neither before nor after cure under a cross-polarized optical microscope. However, with the T_g method, both MDAB and PEPA were found to be miscible with BPDA–PDA, but MDAB was immiscible with PMDA–ODA (E). It implies that PMDA–ODA (E) and MDAB blends have small domains less than 0.25 μm, which is beyond the resolution limit of optical polarized microscope.

The FTIR results show that the maleimide C=C bond at 1150 cm^{-1} and the phenylethynyl group (C≡C bond) at 2215 cm^{-1} were reacted after curing. However, the PEPA may not totally react in the BPDA–PDA + PEPA semi-IPN systems. This may be caused by the steric hindrance of C≡C bonds and phenyl rings. The calculated crosslinking density of semi-IPN polyimide systems increased with an increasing weight percentage of oligomers. In addition, the DMTA data of semi-IPN polyimide systems show reduced relaxation peaks when oligomer content increases and enhanced mechanical property at high temperature. Therefore, there are crosslinking network in these semi-IPN polyimide systems.

The WAXD data also shows that the crystalline-like phase decreased with increasing MDAB content for BPDA–PDA and PMDA–ODA (E). However, the crystalline-like phase of BPDA–PDA + PEPA semi-IPN systems increased as PEPA concentration increased because PEPA has

a rigid rod-like structure. The density of semi-IPN polyimide systems decreased with increasing content of oligomers. This result suggests that the molecular ordering and packing order of BPDA–PDA and PMDA–ODA (E) may be reduced by the addition of these oligomers, which was confirmed by the WAXD data. The addition of MDAB and PEPA to BPDA–PDA increased the chain misalignment and decreased the interplanar packing in BPDA–PDA. Similar results were observed for PMDA–ODA (E) + MDAB semi-IPN system. As a result, the molecular ordering and packing order were reduced by the addition of these oligomers for these semi-IPN polyimide systems.

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