Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Khalil, Muhammad , Saeed, Shaukat and Ahmad, Zahoor(2007) 'Properties of Binary Polyimide Blends Containing Hexafluoroisopropylidene Group', Journal of Macromolecular Science, Part A, 44: 1, 55 — 63
To link to this Article: DOI: 10.1080/10601320601044476
URL: http://dx.doi.org/10.1080/10601320601044476

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry (2006) **44**, 55–63
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ISSN: 1060-1325 print/1520-5738 online
DOI: 10.1080/10601320601044476

Properties of Binary Polyimide Blends Containing Hexafluoroisopropylidene Group

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Received April, 2005, Accepted July, 2006

Binary polyimide (PI) blends with hexafluoroisopropylidene (-C(CF_3)$_2$-) group were prepared using three poly(amic acid) solutions derived from 4,4′-hexafluoroisopropylidene diphthalic anhydride (6FDA), 4,4′-oxydianiline (ODA), p-phenylenediamine (PDA), and pyromellitic dianhydride (PMDA). Films of both blends: $PI_{6FDA\text{-}ODA}/PI_{6FDA\text{-}PDA}$ and $PI_{6FDA\text{-}ODA}/PI_{PMDA\text{-}ODA}$ were transparent, suggesting their homogeneity. Miscibility behavior of these polyimide pairs were characterized by DMA. The existence of single T_gs, intermediate to those of the component polyimides, indicated the blends miscibility. The introduction of the -C(CF_3)$_2$- group in the molecular structure of polyimides was found to significantly affect the optical and dielectric properties of respective polyimides and their blends. It was observed that the increase of fluorine content led to an increase in optical transparency and decrease in refractive index and dielectric constant. Thermal resistance of these polymers, based on decomposition profiles, was investigated by thermogravimetry (TG). These polyimide pairs showed good thermal stability with decomposition temperatures (10% wt loss) up to 554°C in air.

Keywords: poly(fluoro-imide) blends; optical and thermal mechanical properties

1 Introduction

The most popular of all high performance/high temperature polymers are polyimides (PIs) which are useful as adhesives, coatings, composite matrices, films, fibers, foams, and membranes in a variety of applications (1, 2). In recent years, interest in PIs having a favorable combination of properties such as high optical transparency, low refractive index, low dielectric constant, high glass transition temperature (T_g), and good mechanical properties has increased in the fields of optical and microelectronic devices (3, 4). However, PIs in many cases, due to their aromatic structures, exhibit significant color, which may arise from several sources such as conjugation, charge transfer complexes, chromophoric groups, and impurities in the monomers. These factors also increase the dielectric constant of PIs. Suggested principal ways to lower the coloration and dielectric constant of aromatic PIs are: (i) disruption of symmetry to reduce conjugation, charge transfer complexes, intermolecular interactions and, (ii) incorporation of perfluoro groups such as hexafluoroisopropylidene (-C(CF_3)$_2$-) within the PIs (5–11). However, these methods usually involve a compromise on other useful properties of the PIs such as T_g. In order to achieve a useful combination of desired properties, blending of different PIs is considered as a convenient route for the development of new PI materials. Among the advantages of blending polymer systems are: potential ease of processing or fabrication, improved properties, and reduced cost. In addition, synergistic interaction of different PIs can impart superior properties to the blend over that of either PI alone. Extensive literature (12–19) is available on PI-PI blends and blends of PIs with other polymers. Since favorable properties can be derived from miscible polymer blends, many attempts have been made to produce miscible PI pairs and their miscibility behavior has been discussed. Ree et al. (17) prepared binary blends of aromatic PIs by mixing different poly(amic acid) (PAA) precursors. They suggested that PI blends could exhibit complete immiscibility, as well as miscibility depending on the mixing time of the respective PAA solutions. The equilibrium between the PAA and its constituent anhydride and amine monomers provides a mechanism for the random distribution of a mixture of two PAAs via

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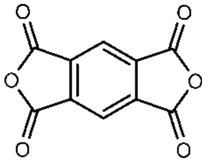
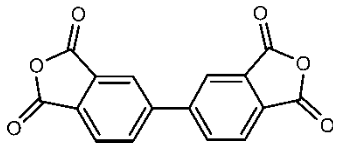
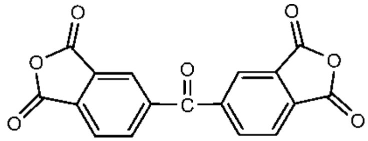
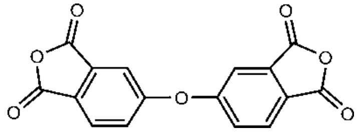
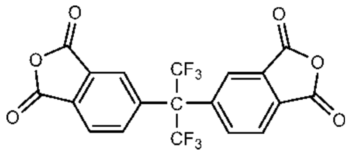
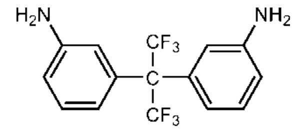
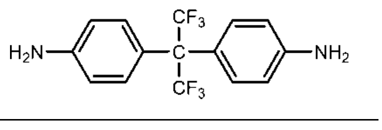
fragmentation and recombination of different fragments. The resulting segmented block copolymer aid in the compatibilization of remaining homopolymers to yield homogenous material. They further suggested that the chemical exchange occurs most readily in the ternary state (PAA-1/PAA-2/solvent) where the polymer-polymer interface is relatively broad. Chung et al. (18, 19) have discussed the miscibility behavior of a series of PI pairs containing hexafluoroisopropylidene (-$C(CF_3)_2$-) groups prepared from aromatic dianhydrides and diamines as shown in Table 1. They discovered that PIs with hexafluoroisopropylidene group were miscible with each other if (i) the dianhydride composition was the same in each pair and (ii) the diamine was changed from the 3,3′ (*meta*-substituted) 6F-diamine to the 4,4′ (*para*-substituted) 6F-diamine. In the present study, we have synthesized and investigated two binary PI blends containing hexafluoroisopropylidene group using three different PAA solutions derived from 4,4′-hexafluoroisopropylidene diphthalic anhydride (6FDA), 4,4′-oxydianiline (ODA), p-phenylenediamine (PDA), and pyromellitic dianhydride (PMDA). Miscibility of these blends ($\mathrm{PI}_{\mathrm{6FDA\text{-}ODA}}/\mathrm{PI}_{\mathrm{6FDA\text{-}PDA}}$ and $\mathrm{PI}_{\mathrm{6FDA\text{-}ODA}}/\mathrm{PI}_{\mathrm{PMDA\text{-}ODA}}$) was probed by studying their viscoelastic behavior as a function of temperature. Optical transparency, refractive index, dielectric constant at optical frequencies, and thermal stability of these PIs blends have also been studied.

2 Experimental

2.1 Chemicals

High purity chemicals [4,4′-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) 99.9%, Aldrich; pyromellitic dianhydride (PMDA) 99%, Aldrich; dimethylacetamide

Table 1. Aromatic dianhydrides and diamines (18, 19)

1,2,4,5-benzenetetracarboxylic anhydride (PMDA)	
3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA)	
3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA)	
4,4′-oxydiphthalic anhydride (ODPA)	
4,4′-(hexafluoroisopropylidene) diphthalic anhydride (6FDA)	
3,3′-(hexafluoroisopropylidene) dianiline (3,3′-6F)	
4,4′-(hexafluoroisopropylidene) dianiline (4,4′-6F)	

(DMAc) 99.8% (water content < 0.005%), Aldrich; 4,4′-oxydianiline (ODA) 99.9%, Fluka; and p-phenylenediamine (PDA) 99.9%, Acros] were used as received.

2.2 Synthesis

The pure polyimides (Figure 1) and their blends were prepared using conventional two-stage thermal imidization process. In the first stage, three PAA solutions ($\mathrm{PAA_{6FDA\text{-}ODA}}$, $\mathrm{PAA_{6FDA\text{-}PDA}}$, and $\mathrm{PAA_{PMDA\text{-}ODA}}$) were prepared by the addition of stoichiometric amounts of solid dianhydrides to the stirring solutions of respective diamines, keeping 8 wt% solid content in dimethylacetamide (DMAc) solvent. The polymerization reactions were carried out at temperatures around 5°C for 12 h under complete anhydrous conditions. The anhydrous conditions were achieved in a sealed glove box by forced circulation of air in a closed-loop over dried calcium chloride and directed on a refrigeration plate fitted within the glove box. The refrigeration plate, maintained at −15°C, served to condense any moisture remaining in the air, as well as to lower the temperature of the reaction environment. Highly viscous PAA solutions thus obtained were mixed in the desired proportion to prepare the blends. Two types of blends were prepared; $\mathrm{PI_{6FDA\text{-}ODA}/PI_{6FDA\text{-}PDA}}$ blends, where proportion of each PI varied from 25, 50, and 75 wt% by combining $\mathrm{PAA_{6FDA\text{-}ODA}}$ with $\mathrm{PAA_{6FDA\text{-}PDA}}$ and $\mathrm{PI_{6FDA\text{-}ODA}/PI_{PMDA\text{-}ODA}}$ blend in 50/50 wt% by combining $\mathrm{PAA_{6FDA\text{-}ODA}}$ with $\mathrm{PAA_{PMDA\text{-}ODA}}$. Stirring of these mixtures in capped reagent bottles was then continued for another 6 h at room temperature. The PAA films were cast by solvent elution at 70°C. In the second stage, these films were thermally imidized by step-wise heating at 100°C (1 h), 200°C (1 h), 250°C (2 h), and 300°C (1 h).

2.3 Testing

The formation of polyimides was identified by IR spectroscopy using a Nicolet-6700 ATR-FTIR spectrometer (Thermo Electron Corporation). The UV-visible transmission spectra of polyimides and blends was obtained using a UV-1201 spectrophotometer (Shimadzu, Japan). Refractive index of the films was measured by a prism coupler, Model 2010 (Metricon, USA). Both in-plane and out-of-plane refractive indices were measured at 632.8 nm and used to compute the three-dimensional average refractive index (n). The dielectric constant (ε) at optical frequencies was calculated by the Maxwell relation ($\varepsilon = n^2$). Visco-elastic properties as a function of temperature were measured using a dynamic mechanical analyzer DMA Q800 (TA, USA). The DMA measurements were made under tension mode for a temperature range of 100–500°C under nitrogen gas, using a ramp of 5°C/min at fixed oscillation frequency of 5 Hz. All films were vacuum dried for 2 h at 120°C before testing. Peaks of tan δ (ratio of loss modulus to storage modulus) curves plotted against temperature gave a measure of the T_gs. Thermal stability based on decomposition profiles was measured by thermogravimetry (TG) using a thermal analyzer STA-409 (Netzsch, Germany). All samples were vacuum dried for 12 h at 120°C before testing. Thermogravimetric runs were conducted at a heating rate of 10°C/min in oxidative environment (air). The temperatures corresponding to maximum decomposition rate were measured from derivative plots of thermogravimetric data.

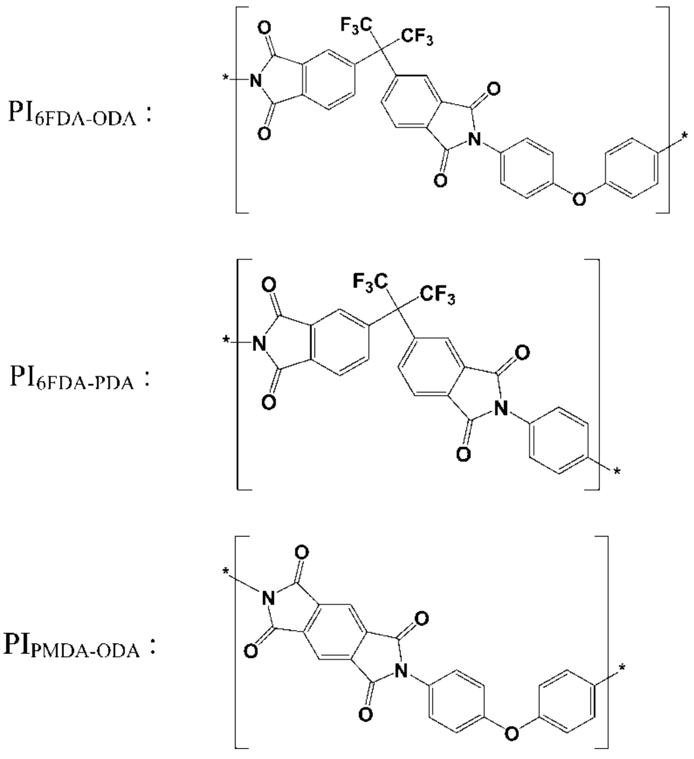


Fig. 1. Polyimides and structural formulae of their repeat units.

3 Results and Discussion

The conversion of the poly(amic acid)s to the fully cyclized PIs was determined by ATR-FTIR vibrational spectroscopy. The absorption bands most frequently utilized for determining the imide formation are 1780 cm^{-1} (C=O asymmetrical stretching), 1720 cm^{-1} (C=O symmetrical stretching), 1380 cm^{-1} (C-N stretching), and 725 cm^{-1} (C=O bending) (20, 21). Amide bands at ~1660 cm^{-1} (C=O) and ~1550 cm^{-1} (CNH), which may also appear as broad peaks, are useful for qualitative assessment of degree of imidization (22). The typical IR spectra of synthesized PIs and blends are shown in Figure 2. The characteristic absorption peaks of the imide ring were observed at 1776–1784 cm^{-1}, 1716–1720 cm^{-1}, 1354–1368 cm^{-1}, and 712–717 cm^{-1}. The absence of amide absorption bands in the spectra indicated complete imidization.

Both PI blends exhibited apparent homogeneity as evidenced by the formation of transparent films. The films

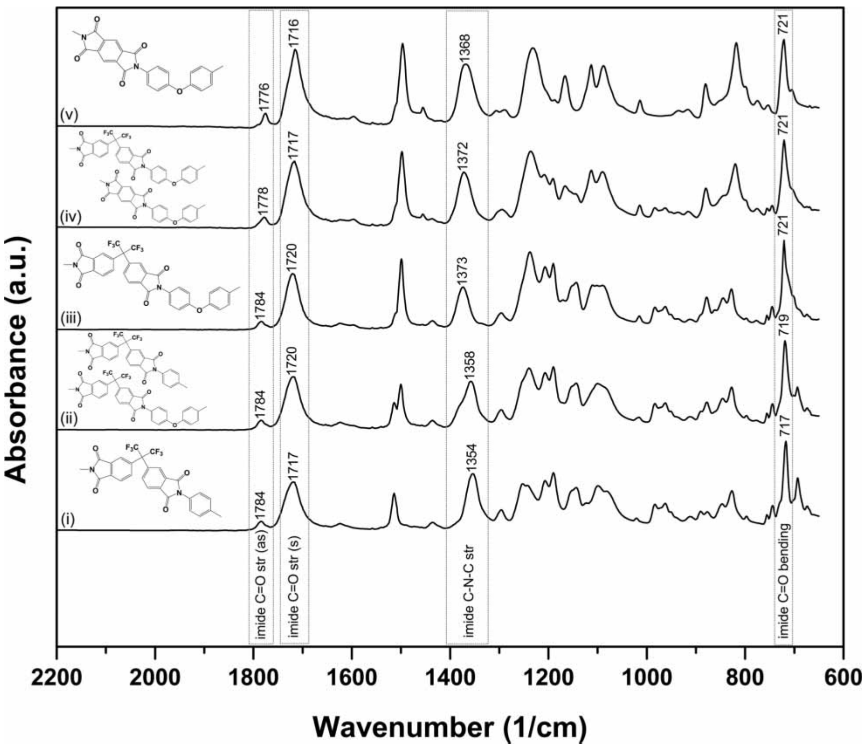


Fig. 2. ATR-FTIR spectra of polyimides and their blends: (i) $PI_{6FDA\text{-}ODA}$, (ii) 50/50 wt% $PI_{6FDA\text{-}ODA}/PI_{6FDA\text{-}PDA}$ blend, (iii) $PI_{6FDA\text{-}PDA}$, (iv) 50/50 wt% $PI_{6FDA\text{-}ODA}/PI_{PMDA\text{-}PDA}$ blend, and (v) $PI_{PMDA\text{-}ODA}$.

obtained from $PI_{6FDA\text{-}PDA}$, $PI_{6FDA\text{-}ODA}$ and their blends were pale-yellow in color. Yellow colored films were obtained from $PI_{PMDA\text{-}ODA}$, however, its 50 wt% blend with $PI_{6FDA\text{-}ODA}$ produced bright-yellow films. In general, coloration of aromatic polymer is due to their conjugated aromatic structures and/or the intermolecular and intramolecular charge-transfer complex (CTC) formation (7, 8). However, the presence of an electron-withdrawing group -$C(CF_3)_2$- in the polymer backbone decreased (5, 7–9) the extent of conjugation and CTC.

Optical transparency of the films was experimentally measured by UV-visible spectroscopy and the results are shown in Table 2. From the transmission spectra (Figure 3), it is evident that as the $PI_{6FDA\text{-}ODA}$ content in films of blend $PI_{6FDA\text{-}ODA}/PI_{6FDA\text{-}PDA}$ increased from 0 to 100 wt%, the transmittance at 500 nm wavelength decreased from 84 to 76% and exhibited a shift in the cutoff wavelength (λ_{cutoff}) from 365 to 388 nm. This showed that $PI_{6FDA\text{-}PDA}$ is optically more transparent than $PI_{6FDA\text{-}ODA}$. However, all the films in this system showed transparency higher than 80% above 543 nm. Compared to pure $PI_{PMDA\text{-}ODA}$, its 50 wt% blend with $PI_{6FDA\text{-}ODA}$ showed an increase in transmittance from 5 to 30% at 500 nm and a shift in the wavelength for 80% transmittance ($\lambda_{80\%}$) from 716 to 616 nm. This reveals that

Table 2. Optical transparency of films derived from pure polyimides and their blends

Blend	$PI_{6FDA\text{-}ODA}$ content (wt%)	Fluorine content (wt%)	Film thickness (μm)	T_{500}[a] (%)	$\lambda_{80\%}$[b] (nm)	λ_{cutoff}[c] (nm)
$PI_{6FDA\text{-}ODA}/PI_{6FDA\text{-}PDA}$	0	20.86	120	84	470	365
	25	20.11	140	83	479	365
	50	19.36	140	80	498	373
	75	18.60	110	77	536	375
	100	17.85	130	76	543	388
$PI_{6FDA\text{-}ODA}/PI_{PMDA\text{-}ODA}$	0	0	140	5	716	416
	50	8.92	140	30	616	416
	100	17.85	130	76	543	388

[a] Transmittance at 500 nm.
[b] Wavelength of 80% transmittance.
[c] Wavelength of UV cutoff.

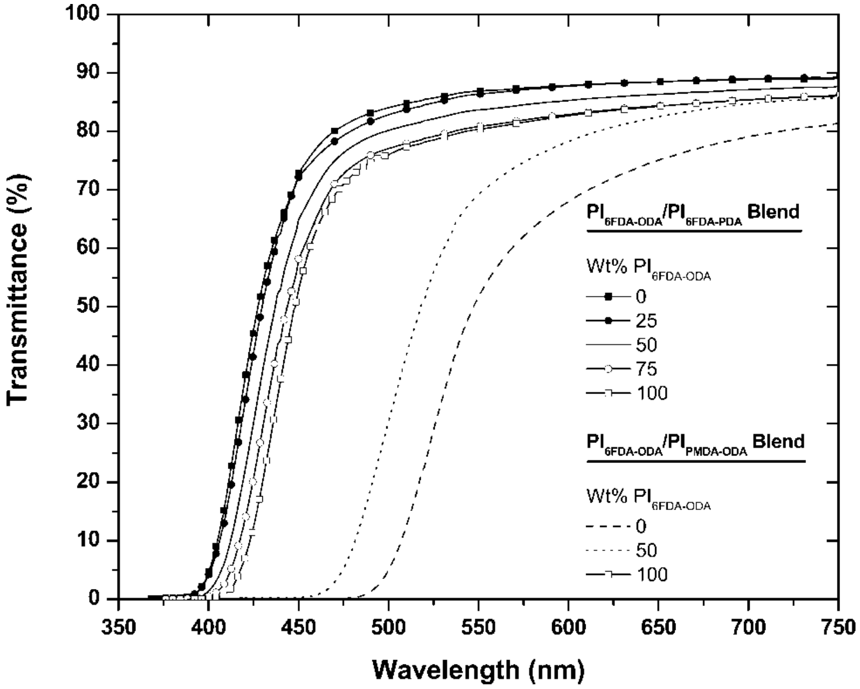


Fig. 3. UV-visible transmission spectra of polyimides and blends.

the presence of a hexafluoroisopropylidene group enhances the transparency of polyimide films and widens the transparency band in visible region. St. Clair et al. (9) reported that the incorporation of bulky electron-withdrawing groups such as $-CF_3$ or SO_2 and separator groups such as -O- linkages is a necessary condition for obtaining maximum transparency. In our study, we found that $PI_{6FDA\text{-}PDA}$ (having no spacer group) was optically more transparent than $PI_{6FDA\text{-}ODA}$ (having -O- linkage), showing that the overall content of substituted fluorine has a more significant role in controlling the optical transparency. The transmittance at 500 nm (T_{500}) increased with increasing the overall fluorine content (Table 2).

The results of in-plane (n_{TE}), out-of-plane (n_{TM}), and three-dimensional average (n) refractive indices of films are given in Table 3. At optical frequencies (10^{14} Hz), where only electronic polarization occurs, the value of dielectric constant can be calculated from Maxwell's identity ($\varepsilon = n^2$) (10, 23–25). The estimated values of 'ε' are given in Table 3. The value for 'n' is in the following order: $PI_{6FDA\text{-}PDA}$ (20.86 wt% F) < $PI_{6FDA\text{-}ODA}$ (17.85 wt% F) < $PI_{PMDA\text{-}ODA}$ (0 wt% F).

Table 3. Refractive index and optical dielectric constant as a function of fluorine content

Blend	$PI_{6FDA\text{-}ODA}$ content (wt%)	Fluorine content (wt%)	n_{TE}[a]	n_{TM}[b]	$\Delta n_{\perp}$[c]	n[d]	ε[e]
$PI_{6FDA\text{-}ODA}/PI_{6FDA\text{-}PDA}$	0	20.86	1.5841	1.5826	0.0014	1.5836	2.508
	25	20.11	1.5855	1.5849	0.0006	1.5853	2.513
	50	19.36	1.5883	1.5875	0.0008	1.5880	2.522
	75	18.60	1.5906	1.5903	0.0002	1.5905	2.530
	100	17.85	1.5925	1.5921	0.0003	1.5923	2.536
$PI_{6FDA\text{-}ODA}/PI_{PMDA\text{-}ODA}$	0	0	1.6919	1.6895	0.0024	1.6911	2.860
	50	8.92	1.6403	1.6408	0.0005	1.6405	2.691
	100	17.85	1.5925	1.5921	0.0003	1.5923	2.536

[a] Refractive index parallel to the film plane.

[b] Refractive index perpendicular to the film plane.

[c] Anisotropy in refractive indices between parallel (n_{TE}) and perpendicular (n_{TM}) to the film plane: $\Delta n_{\perp} = |n_{TE} - n_{TM}|$.

[d] Three-dimensional average refractive index of the bulk of the polymer: $n = (2 \times n_{TE} + n_{TM})/3$.

[e] Dielectric constant at optical frequencies: $\epsilon = n^2$ (Maxwell relation).

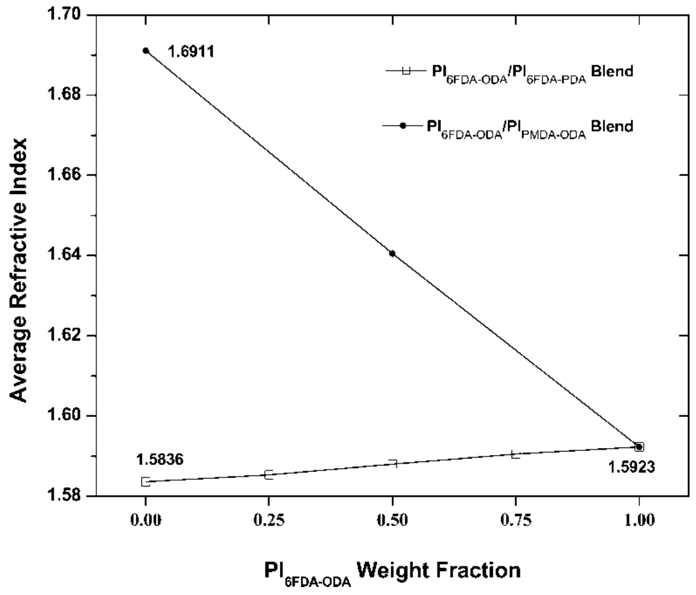


Fig. 4. Refractive indices of blends as a function of $PI_{6FDA\text{-}ODA}$ weight fraction.

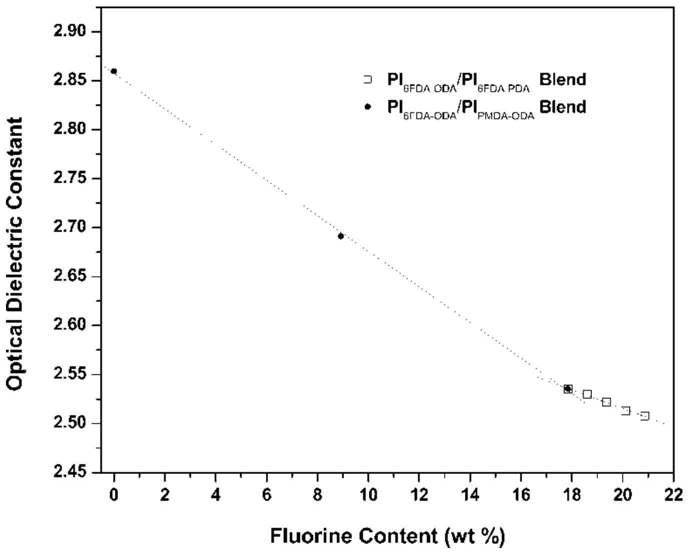


Fig. 5. Optical dielectric constant as a function of fluorine content.

A similar order was found for 'ε' values. The refractive index of blends $PI_{6FDA\text{-}ODA}/PI_{6FDA\text{-}PDA}$ increases linearly with the $PI_{6FDA\text{-}ODA}$ content, while that of the blend $PI_{6FDA\text{-}ODA}/PI_{PMDA\text{-}ODA}$ decreases linearly with increasing the $PI_{6FDA\text{-}ODA}$ content (Figure 4). The dielectric constant decreases almost linearly with increasing fluorine content (Figure 5). The results suggest that 'n' and 'ε' can be precisely controlled within the extreme values for pure polyimides, by varying the composition of the blends. Regarding resolution of the refractive index measurements, most of the films showed fairly sharp critical angles (not shown), which gave good measurement accuracy and resolution (roughly ± 0.0003). This resolution suggested that index differences of 0.0005–6 or less might not be real (i.e., within the error bars of the measurement). Hence, only $PI_{6FDA\text{-}PDA}$ and $PI_{PMDA\text{-}ODA}$ showed significant anisotropy in refractive index ($\Delta n_{\perp} = n_{TE} - n_{TM}|$) and it is in the order of $PI_{6FDA\text{-}PDA} < PI_{PMDA\text{-}ODA}$. This means the chains of $PI_{6FDA\text{-}PDA}$ and $PI_{PMDA\text{-}ODA}$ have some tendency to align in the film plane due to their less flexible backbone structures (Figure 1) than $PI_{6FDA\text{-}ODA}$.

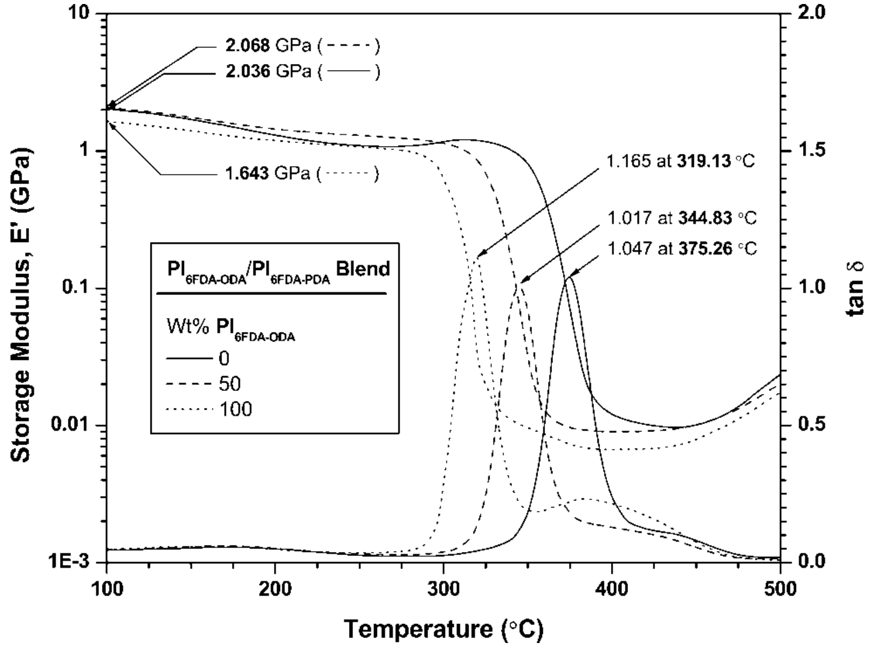


Fig. 6. Temperature variation of storage modulus and tan δ of $PI_{6FDA\text{-}ODA}/PI_{6FDA\text{-}PDA}$ blend.

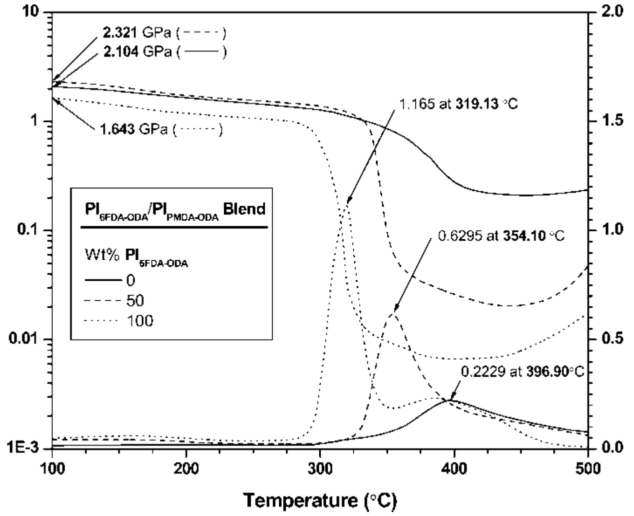


Fig. 7. Temperature variation of storage modulus and tan δ of PI$_{\text{6FDA-ODA}}$/PI$_{\text{PMDA-ODA}}$ blend.

Table 4. Glass transition temperature (T_g) of pure polyimides and their blends

Blend	PI$_{\text{6FDA-ODA}}$ content (wt%)	T_g experimentally measured (°C)^a	T_g calculated using Fox equation (°C)^b
PI$_{\text{6FDA-ODA}}$/ PI$_{\text{6FDA-PDA}}$	0	375.26	–
	50	344.83	344.93
	100	319.13	–
PI$_{\text{6FDA-ODA}}$/ PI$_{\text{PMDA-ODA}}$	0	396.90	–
	50	354.10	353.79
	100	319.13	–

[a] From tan δ maxima in DMA analysis.
[b] Fox's equation: $1/T_g = w_1/T_{g1} + w_2/T_{g2}$.

Temperature variation of the storage modulus (E′) and the ratio of loss modulus to storage modulus (tan δ) for the two blend pairs are shown in Figures 6 and 7. The values of E′ at 100°C for pure polyimides PI$_{\text{PMDA-ODA}}$, PI$_{\text{6FDA-PDA}}$, and PI$_{\text{6FDA-ODA}}$ are 2.104, 2.036, and 1.643 GPa, respectively. However, 50 wt% blends in both systems show improvement in storage modulus. At 100°C, the value of E′ is raised to 2.068 GPa in the case of PI$_{\text{6FDA-ODA}}$/PI$_{\text{6FDA-PDA}}$ and 2.321 GPa in the case of PI$_{\text{6FDA-ODA}}$/PI$_{\text{PMDA-ODA}}$ blend. This synergistic effect on E′ is noticeable up to ~300°C in the first case, and up to 330°C in the second case. The increase in E′ is indicative of favorable inter-chain interactions inhancing the chains packing. Such compatibility may originate from the formation of segmented block copolymers via fragmentation and recombination of different fragments because of chemical exchange reactions taking place during solution blending of binary poly(amic acid) mixtures. Both systems also revealed significant changes in E′ as a function of temperature above their T_gs. The region above the T_g is known as the rubbery plateau and the magnitude of E′ in this region depends on the crosslink density of the material. As the rubbery plateau showed an increase in E′, it is indicative of crosslinking of the chains due to free radical formation by degradation of polymers at elevated temperature.

The magnitude of tan δ indicates the relative amount of mechanical energy dissipated by the material during cyclic stress in DMA testing. A material is perfectly elastic if tan δ is zero; perfectly viscous if tan δ is infinite; and equally elastic and viscous if tan δ is one. The favorable interactions between the chains decrease the free volume in blend and it behaves more elastically, thus showing a decrease in the intensity of the tan δ peak. For the 50/50 wt% PI$_{\text{6FDA-ODA}}$/PI$_{\text{6FDA-PDA}}$ blend, decreased intensity in tan δ curve was observed (peak value 1.017) compared to those for component polyimides PI$_{\text{6FDA-ODA}}$ and PI$_{\text{6FDA-PDA}}$ (peak values 1.165 and 1.047, respectively). This indicates that blending has enhanced the interaction between molecular chains compared to that in pure polyimides. Similar behavior was also observed for 50/50 wt% PI$_{\text{6FDA-ODA}}$/PI$_{\text{PMDA-ODA}}$ blend relative to the component PI$_{\text{6FDA-ODA}}$. Squeezed breadth of the tan δ relaxation in this blend compared to that of pure PI$_{\text{PMDA-ODA}}$ is indicative of the cooperative nature of the relaxation process of polymer chains.

One of the most important ways of characterizing miscible polymer blends is the determination of the composition dependencies of their T_g values. The T_g values given in Table 4 were measured from the maxima of tan δ curves. The 50/50 wt% of PI$_{\text{6FDA-ODA}}$/PI$_{\text{6FDA-PDA}}$ and PI$_{\text{6FDA-ODA}}$/PI$_{\text{PMDA-ODA}}$ blends have shown single T_g values and also exactly obeyed the Fox equation (26), displaying an intimate and uniform mixing (i.e., complete miscibility). This high degree of miscibility is indicative of strong inter-chain/intra-chain interactions for these polyimide blends.

Table 5. Temperatures corresponding to 10% wt loss and maximum decomposition rate for polyimides and blends at heating rate of 10°C/min in air

Blend	PI$_{\text{6FDA-ODA}}$ content (wt%)	T_{10} (°C)^a	T_{max} (°C)^b
PI$_{\text{6FDA-ODA}}$/ PI$_{\text{6FDA-PDA}}$	0	535	586
	25	536	587
	50	539	587
	75	539	588
	100	538	592
PI$_{\text{6FDA-ODA}}$/ PI$_{\text{PMDA-ODA}}$	0	578	617
	50	554	626
	100	538	592

[a] Temperature corresponding to 10% weight loss.
[b] Temperature corresponding to maximum decomposition rate.

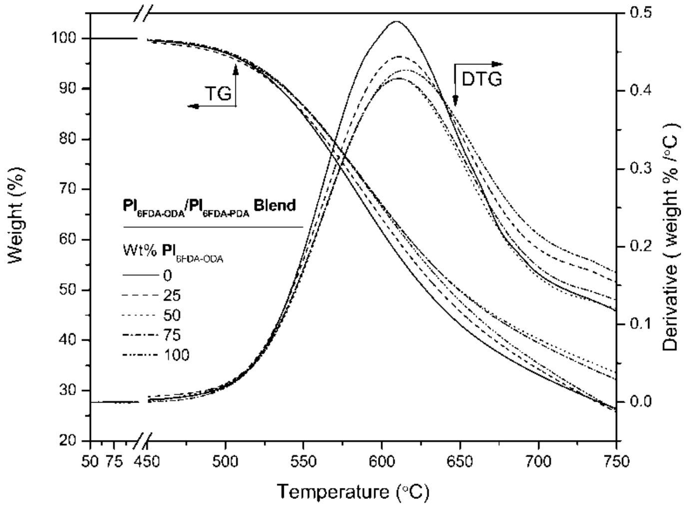


Fig. 8. TG and DTG curves for $PI_{6FDA\text{-}ODA}/PI_{6FDA\text{-}PDA}$ blends at heating rate of 10°C/min in oxidating atmosphere (air).

The contributing factors towards such strong interactions may be: (i) almost similar backbone structure of homopolymers sharing a common monomer (dianhydride in one case and diamine in other) and (ii) formation of segmented block copolymers as a result of chemical exchange reactions taking place in binary poly (amic acid) mixtures.

Thermal resistance of these polyimides was determined by TG. In order to simulate behavior under operating conditions, analyses were conducted in oxidative environment. The temperatures needed to exhibit a 10% mass loss (T_{10}), in controlled heating at the rate of 10°C/min, were determined from TG curves. The temperatures corresponding to maximum decomposition rate (T_{max}) were highlighted from derivative plots of thermogravimetric data (derivative thermogravimetry, DTG). The T_{10} and T_{max} values (Table 5) obtained from TG/DTG plots (Figures 8 and 9) indicate that all compositions of $PI_{6FDA\text{-}ODA}/PI_{6FDA\text{-}PDA}$ blend have almost similar thermal stability ($T_{10} = 535–538°C$, $T_{max} = 586–592°C$). However, a remarkable variation in T_{10} and T_{max} values with composition was observed for $PI_{6FDA\text{-}ODA}/PI_{PMDA\text{-}ODA}$ system. A positive shift in T_{max}, shown by 50/50 wt% $PI_{6FDA\text{-}ODA}/PI_{PMDA\text{-}ODA}$ blend, indicates that blending has a stabilizing effect on degradation of component PIs. This stability may arise from the favourable interactions that might occur between component polymers during degradation and among the products of degradation.

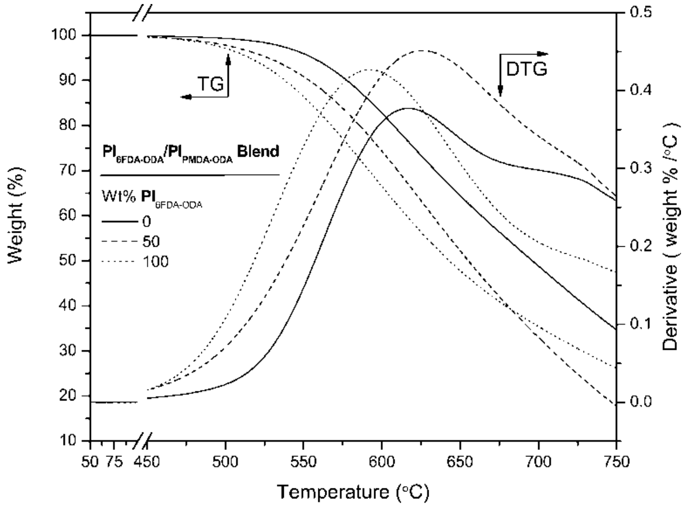


Fig. 9. TG and DTG curves for $PI_{6FDA\text{-}ODA}/PI_{PMDA\text{-}ODA}$ blends at heating rate of 10°C/min in oxidating atmosphere (air).

4 Conclusions

It has been demonstrated that the hexafluoroisopropylidene (-$C(CF_3)_2$-) group containing polyimide blends: $PI_{6FDA\text{-}ODA}/PI_{6FDA\text{-}PDA}$ and $PI_{6FDA\text{-}ODA}/PI_{PMDA\text{-}ODA}$ are miscible on the basis of optical clarity and DMA data. The DMA results show single composition-dependent T_gs and well-defined single tan δ relaxations for these blends. The 50/50 wt% of $PI_{6FDA\text{-}ODA}/PI_{6FDA\text{-}PDA}$ and $PI_{6FDA\text{-}ODA}/PI_{PMDA\text{-}ODA}$ blend pairs showed T_g values intermediate between those of the pure components and exactly obeyed the Fox equation, displaying high degree of miscibility. From the miscibility behavior, it is suggested that the strong inter-chain/intra-chain interactions present in both types of polyimide pairs are contributed by: (i) almost similar backbone structure of homopolymers sharing a common monomer and (ii) formation of segmented block copolymers resulting from re-equilibration occurrences in binary poly(amic acid) mixtures.

The introduction of -$C(CF_3)_2$- group in the molecular structure of polyimides was found to significantly affect the optical and dielectric properties of polyimides and blends studied. The optical transparency was found in the order of $PI_{6FDA\text{-}PDA} > PI_{6FDA\text{-}ODA} > PI_{PMDA\text{-}ODA}$ while the refractive index (n) and dielectric constant (ε) in the reverse order. In general, these properties were found depending linearly on overall fluorine content. The results suggest that 'n' and 'ε' can be precisely controlled, within the extreme values of the pure polyimides, by varying the composition of the blends.

Thermal resistance of these polymers, as investigated by thermogravimetry, is very high with decomposition temperatures (10% wt loss) up to 554°C in air. An increase in T_{max}, shown by $PI_{6FDA\text{-}ODA}/PI_{PMDA\text{-}ODA}$ blend, indicated a stabilizing effect of blending on the degradation of component polyimides. The stability may be the result of better cohesion between the polymer chains thus reducing the effect of thermo-oxidative degradation with-in the polymeric blends.

5 Acknowledgements

The authors express their appreciation to the Higher Education Commission (HEC) of Pakistan for providing financial support. Special thanks are extended to Mr. John H. Jackson (Metricon Corporation, USA) for his help in refractive index and index anisotropy measurements.

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