

Novel Miscible Blends Composed of Poly(Methyl Methacrylate) and 2,2-Bis(3,4-Carboxyphenyl)Hexafluoropropane Dianhydride-Based Polyimides with Optical Grade Clarity

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Several blends of polymers that varied concentrations of poly(methyl methacrylate) (PMMA) and polyimides based on 2,2'-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) were prepared in film form by solution casting and using various solvents. The miscibility of the blended films was correlated through a differential scanning calorimeter (DSC), Fourier transform infrared spectroscopy (FTIR), and an image analyzer. DSC thermograms revealed two glass-transition temperatures (T_g) for specimens using tetrahydrofuran (THF) as a casting solvent, indicating immiscibility; on the other hand, samples using methyl chloride (MC) and cyclohexanone showed a single T_g , indicating miscibility between the two polymers. The phase separation temperature for the miscible samples showed lower critical solution temperature type (LCST-type) behavior and reached its minimum when the content was about 70 mass% PMMA. Both the transmittance and haze of the miscible blended films were measured according to the American Standards Testing Method (ASTM) specification D1003. The transmittance for 6FDA-6FpDA/PMMA had a value of about 85% in the visual light range. However, 6FDA-6FpDA:DABA 2 : 1/PMMA showed a low transmittance below wavelengths of 550 nm. For haze, all of the films were clear with values of less than 1%. The mechanical scratch resistance was measured by pencil test (ASTM 3363). Increasing the 6FDA-6FpDA polyimide content was found to increase the scratch resistance of the films. [doi:10.2320/matertrans.MF200916]

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1. Introduction

Poly(methyl methacrylate) (PMMA) is one of the most widely used polymers in a variety of electronic applications where optical-grade materials are needed because of its excellent balanced properties paired with a reasonable price.¹⁾ PMMA has excellent clarity with high rigidity and toughness as a homopolymer, though deficient characteristics of PMMA such as low impact strength, poor radiation, thermal stability, and solvent resistance deter its application in some areas.¹⁻⁵⁾ There has been great interest in polymer blends for quite some time, as polymer blending is a fast and economical way of improving the properties of commercially available polymers without the laborious development of new polymers.⁶⁻¹⁰⁾ However, the physical properties of the newly developed polymer blends are strongly dependent upon the phase miscibility. Because of this, the study of the miscibility and phase behavior of polymers has attracted intense investigation in both the industrial and academic domains.⁶⁻¹²⁾

Aromatic polyimides are promising candidates for engineering plastics because of their excellent thermal and physical properties. However, in most of the cases, their poor optical property limits their application in optical usage. Recently, special types of optical grade polyimides, for example, a polyimide synthesized from 2,2'-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA), with excellent optical, thermal, and mechanical properties have been investigated.^{13,14)} Since practical products are made though a polymer-polymer blending process, many have attractive physical properties but their corresponding lack of solubility and miscibility has limited their usefulness for electronic applications needing optical-grade materials. The current focus of attention in this field has been directed to finding homogeneous mixtures and exploring

the beneficial properties that may be gained by blending.^{12,15-17)}

Early investigations related to blending PMMA with polyimides showed that PMMA did not form miscible blends with any of the polyimides it was paired with. Fluorine-containing polyimides, especially those based on 6FDA, have been of interest because of their excellent physical and optical properties and their solubility in common solvents, enabling their utilization in polymer-polymer blending solutions.¹⁸⁻²²⁾ However, the extremely high glass transition temperature of 6FDA-based polyimides has deterred their widespread application.²⁰⁻²²⁾ Blending PMMA with fluorine-containing polyimides offers an attractive opportunity for the development of novel materials exhibiting useful combinations of the two materials' respective properties. Compared to PMMA, the 6FDA-based polyimide provides enhanced chemical resistance and mechanical strength in blends. PMMA, on the other hand, permits lower processing temperatures than pure 6FDA-based polyimides.

Polycarbonate (PC) and PC-based blends such as PC/PMMA are widely used in the field of optical grade application because of their excellent thermal and physical properties and transparency. However, the color of PC changes when exposed to ultraviolet radiations and PC/PMMA blends have a relatively low phase separation temperature (approximately 120°C); these features limit their widespread application.^{23,24)}

This work examines blends of PMMA with 6FDA-based polyimides to develop miscible blends that overcome the drawbacks of PMMA and have optical-grade clarity.⁴⁻⁷⁾ The miscibility of polymer blends is often judged from specimens prepared by melt blending or solution casting methods. However, an inappropriate choice in temperature or solvent may lead to an erroneous judgment about miscibility due to phase separation resulting from LCST type phase behavior,

or the so-called solvent effect.^{25,26} In this study, blend samples were prepared by solvent casting. Because the miscibility of the blends examined here was sensitive to preparation methods, various solvent casting methods were used for the preparation of the blend samples. When the prepared samples were transparent, phase separation temperatures were examined through annealing so that the closest true equilibrium temperature could be found. The optical properties involved in the miscible blends were quantified according to the total light transmittance and haze, measured in accordance with the American Standards Testing Method (ASTM) specification D1003.^{27,28} In addition to the anti-scratch property, studies on scratch resistance of blends film are also presented in this paper.²⁹

2. Experimental

The chemical structure and physical properties of the polymers used in this study are shown in Table 1 and Fig. 1, respectively. Commercially available PMMA (HR grade) from LG Chemicals and four different glassy 6FDA-based polyimides were used in this work.^{30,31} All were based on 2,2-bis(3,4-carboxyphenyl) hexafluoropropane dianhydride (6FDA), which was reacted with either 4,4'-hexafluoroisopropylidene diamine (6FpDA) to form 6FDA-6FpDA, or with diaminomesitylene (DAM) to form 6FDA-DAM polyimides with and without 3,5-diaminobenzoic acid (DABA); there was a 2 : 1 ratio in favor of the polymer blends with DABA. The 6FDA monomer was obtained from Lancaster while all of the diamine monomers were from Aldrich. The detailed procedure of synthesis and several physical properties have been described previously.³⁰ PMMA and synthesized 6FDA-based polyimides were dried in a vacuum oven for a day prior to processing at 80°C and 150°C respectively. Molecular weight information for the polymers was obtained

with gel permeation chromatography calibrated to Polystyrene standards, and the density of synthesized 6FDA-based polyimide was determined by density gradient column.

Three different methods, coded S1, S2 and S3 respectively, were used to prepare the blends. Different solvents with different casting temperatures were used in each method in order to prevent erroneous judgment about miscibility stemming from the so-called solvent effect.^{25,26} In S1, the blend was prepared in film form by casting solutions containing 5 mass% tetrahydrofuran (THF) onto petri dishes at 60°C. After slow drying at 80°C for a day, the blends were dried in a vacuum oven at 150°C for a week. S2 followed the same procedure as S1, except that the solvent was methylene chloride (MC) and was evaporated at room temperature. For S3 the same procedure as S1 was used, except that the solvent was cyclohexanone and was evaporated at 120°C.

Fourier transform infrared (FT-IR) measurements were carried out with FTIR-GX Perkin-Elmer spectrophotometer with a horizontal attenuated total reflection (ATR) accessory in the 4000–450 cm⁻¹ region using zinc selenate crystals. Thermal analysis was conducted at a heating rate of 20°C/min with the TA instrument, TA-2010. The glass-transition temperature (*T_g*) was defined as the onset of change in the heat capacity during the second heating from room temperature to 250°C. The temperature at which phase separation was caused by LCST-type phase behavior was measured by an annealing technique so that the closest true equilibrium temperature could be found. Changes in the morphology of the blends with the temperature were observed by an image analyzer (LEICA Q550 IWB) equipped with a hot stage (Linkam THMS 600). The total light transmittance and haze of PMMA, 6FDA-based polyimides, and the blends were measured in accordance with ASTM D1003.²⁸ Each experiment was performed at least five times, and data was reported as the means of these values. The scratch resistance of the blends was measured according to the pencil test ASTM D3363.²⁹ The coated panel was placed on a firm horizontal surface, and the pencil was held firmly against the film at a 45° angle and pushed away in a smooth stroke with uniform pressure. The process was started with the hardest pencil and continued down the scale of hardness until the pencil used did not gouge or scratch the film. The range of pencils used in order of increasing hardness was as follows:

6B–5B–4B–3B–2B–B–HB–F–H–2H–3H–4H–5H–6H
Softer ← → Harder

Table 1 Physical properties of polymers used in this study.

Polymers	<i>T_g</i> , °C	<i>M_w</i>	<i>M_n</i>	Density, (ρ/g·cm ⁻³)
PMMA	100	76,000*	48,300*	1.1650
6FDA-6FpDA	298	47,000	21,000	1.4781
6FDA-6FpDA:DABA	319	24,400	13,310	1.4823
6FDA-DAM	372	56,200	28,340	1.3342
6FDA-DAM:DABA	376	73,030	38,210	1.3936

*Molecular weight information was provided by the supplier.

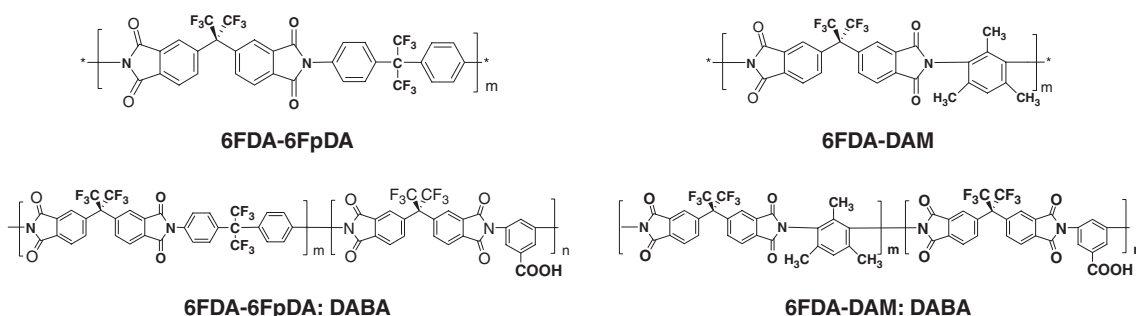


Fig. 1 Structure of the polyimide materials used in this study.

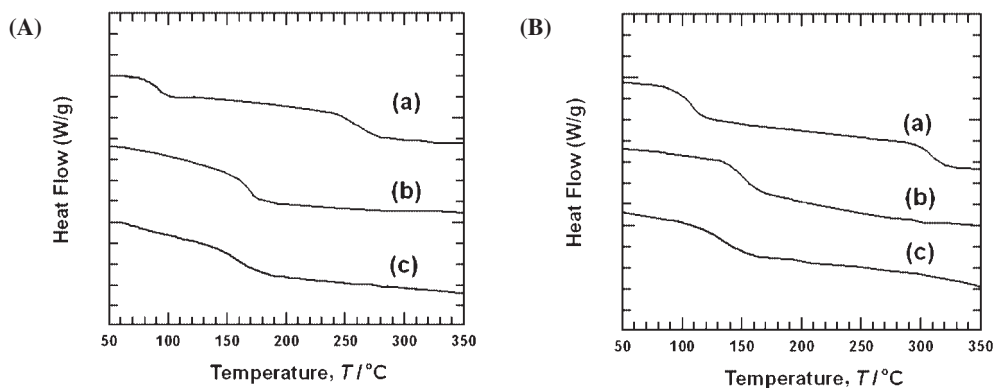


Fig. 2 DSC diagrams for (A) 6/4 PMMA/6FDA-6FpDA blends and (B) 6/4 PMMA/6FDA-6FpDA blends: (a) cast from tetrahydrofuran at 60°C, (b) cast from methylene chloride at room temperature, and (c) cast from cyclohexanone at 120°C.

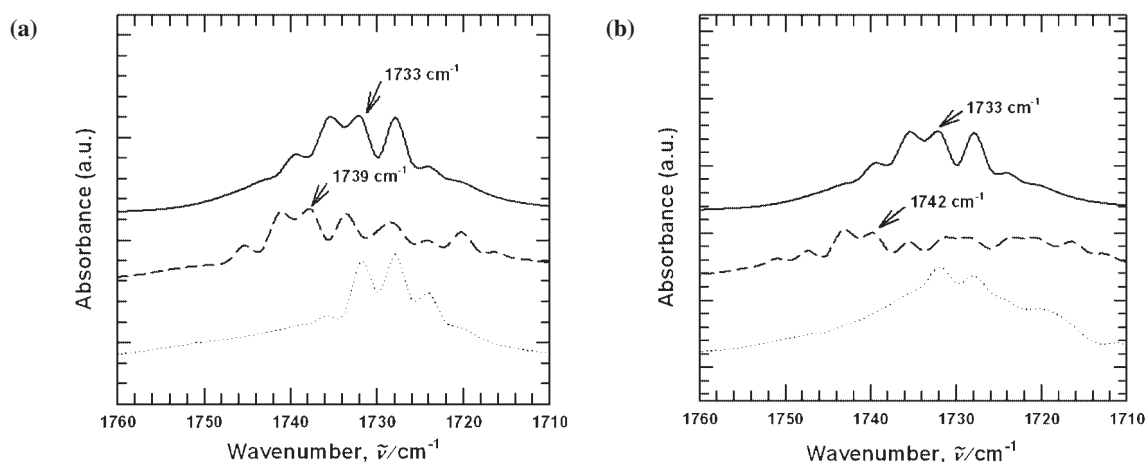


Fig. 3 FT-IR spectra of (a) 5/5 PMMA/6FDA-6FpDA blend and (b) 5/5 PMMA/6FDA-6FpDA:DABA 2:1 blend in the 1800–1700 cm^{-1} spectral region.

3. Results and Discussion

3.1 Miscibility of blends

The blends containing DAM, such as 6FDA-DAM and 6FDA-DAM:DABA 2:1, were immiscible regardless of the kind of solvent and preparation method. These blends were translucent, and their thermograms revealed two T_g , indicating immiscibility. Because of the immiscibility of the blends containing DAM, only the 6FDA-6FpDA and 6FDA-6FpDA:DABA blends were used for further study.

Figure 2(A) and 2(B) show the differential scanning calorimetry (DSC) thermograms of the PMMA/6FDA-6FpDA and PMMA/6FDA-6FpDA:DABA 2:1 blends prepared at a ratio of 6:4 by the three different preparation methods. The blends cast with THF (S1) were opaque and visually heterogeneous regardless of the casting temperature. DSC thermograms revealed two T_g for both specimens (Fig. 2(A)-(a) and 2(B)-(a)). However, the blend cast using MC at room temperature (S2) was transparent, and its thermogram revealed a single T_g (Fig. 2(A)-(b) and 2(B)-(b)). A blend was also prepared by dissolution in cyclohexanone and subsequently casting the solution into a film at 120°C (S3). The T_g behavior of the blends prepared by S3 was similar to those prepared by S2 (Fig. 2(A)-(c) and 2(B)-

(c)). PMMA blends containing varying amounts of 6FDA-6FpDA polyimides also showed a similar T_g behavior that depended on the preparation methods. The miscibility of a binary pair does not ensure that the ternary composition will be as well. The immiscibility of ternary solvent/polymer/polymer mixtures is induced by the asymmetry of binary interactions or the so-called $\Delta\chi$ effects.^{25,32,33} This implies that a miscible polymer-polymer mixture can be made immiscible by using a solvent during the preparation of the polymer samples. Therefore, in this study, the samples prepared by three different methods show different miscibilities. Figure 3 shows the FT-IR spectra of the PMMA/6FDA-6FpDA and PMMA/6FDA-6FpDA:DABA 2:1 blends. The spectra of immiscible polymers are simply the sum of the spectra of the pure polymer components. In the case of miscible blends, frequency shifts usually indicate specific interactions between the characteristic groups of the pure polymers.^{34–37} For pure PMMA, the infrared spectrum generally shows absorption bands at 1150, 1380 and 1730 cm^{-1} due to the stretching of the C–O, $-\text{CH}_3$, and C=O groups respectively. Figure 3 represents the absorption peaks of blend membranes in the range of 1720 to 1760 cm^{-1} ; this is to investigate the absorption shift caused by interactions between the functional groups of each

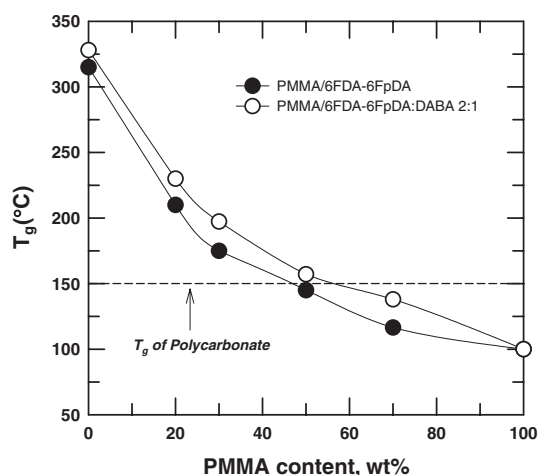


Fig. 4 Glass transition behavior for PMMA/6FDA-6FpDA and 6FDA-6FpDA:DABA 2 : 1 blends.

polymer, fluorinated carbon in polyimides and the carbonyl group in PMMA. Figure 3(a) indicates that the strong frequency shift (6 cm^{-1}) for the PMMA carbonyl group (from 1733 to 1739 cm^{-1}) is because of its interaction with the fluorinated carbons of 6FDA-6FpDA. The 6FDA-6FpDA:DABA/PMMA blend also shows a frequency shift for the carbonyl group from 1733 to 1742 cm^{-1} , as shown in Fig. 3(b). These spectra shifts suggest the interaction between PMMA and 6FDA-6FpDA polyimides and the mixing of those two components takes place at the molecular level. Therefore, these structural analysis results further support the suggestion indicated by macroscopic and microscopic observations of the compatible nature between PMMA and 6FDA-6FpDA-based polyimide in a blend. The results from microscopic observation are further discussed in the next section.

Figure 4 shows representative results of the glass-transition behavior for PMMA/6FDA-6FpDA and PMMA/6FDA-6FpDA:DABA 2 : 1 blends. Hot-cast blends of PMMA with 6FDA-6FpDA polyimides were transparent and showed a single T_g that varied regularly with the overall blend composition. For the evaluation of thermal property of both blend films, we compare T_g of both films with that of PC (dotted line). As shown in Fig. 4, T_g of both blend films increases with a decrease in the PMMA content. T_g of PMMA-rich blends is lower than that of PC, whereas the T_g of blends with a PMMA content of less than 50 mass% is higher than that of PC. Additionally, note that T_g of the 6FDA-6FpDA-base polyimide/PMMA films is significantly higher than that of PC/PMMA blends reported in literatures. All of these results indicate that the thermal property of the 6FDA-6FpDA-based polyimide/PMMA blend is similar or better than that of PC. For the evolution of thermal property of both blends film, we compare T_g of both blend film to that of PC (dotted line). As shown in Fig. 4, the T_g of both blend film increased by decreasing of PMMA contents. In the PMMA-rich blend, T_g of blends are lower than that of PC, whereas the T_g of blend is over that of PC when the PMMA composition in the blend is less than 50 mass%. Additionally, note that all of T_g s for 6FDA-6FpDA-base polyimide/PMMA films are significantly higher than the T_g reported in

the literature for the PC/PMMA blends.³⁸⁾ All of these results indicated that 6FDA-6FpDA-based polyimide/PMMA blend has equal or more excellent thermal property than PC. The miscibility of two candidate polymer materials to form miscible blend mixtures can be evidenced by their optical properties and morphology. A preliminary indication that two polymers are miscible is the single glass transition temperature of the resulting mixture. In addition, optical microscopy can reveal the possible existence of phase separation in the polymer mixture. In immiscible blends, when clear phase distinction is observed it is the result of incompatibility between the pure polymers.

Phase separation temperatures due to LCST-type phase behavior were measured by an annealing technique.^{10,35)} To observe the phase separation temperature caused by LCST-type phase behavior, the specimen was mounted on a hot stage and covered with a glass cover. Changes in the image with the change in temperature were observed as the specimens were heated at a scanning rate of $10^\circ\text{C}/\text{min}$. The temperature at which the image first started to change was taken as the approximate value of the phase separation temperature. To determine the true equilibrium temperature, the blend specimens were annealed in the hot stage at fixed temperatures in the vicinity of the expected phase boundary, after which they were quenched to room temperature. The images were observed to determine whether a change had occurred as a result of annealing. The temperature at which the image first started to change was taken as the phase separation temperature. Note that the annealed sample became turbid at the temperature at which the image first started to change.

Figure 5(a) displays the morphology of the PMMA/6FDA-6FpDA 50/50 blend after annealing at 260°C for 20 min. The blend film was still transparent and changes in its morphology were not observed. However, after annealing at 270°C the transparent film became opaque and changes in the image were observed, as shown in Fig. 5(b). Therefore, the phase boundary appears to lie between 260 and 270°C for this blend. By successively repeating annealing process within the determined temperature range, the location of the phase boundary was determined. Figure 6 shows the phase separation temperatures for both miscible PMMA/6FDA-6FpDA and PMMA/6FDA-6FpDA:DABA 2 : 1 blends. The phase separation temperature of the 6FDA-6FpDA/PMMA blend is always higher than that of the 6FDA-6FpDA:DABA/PMMA blend for a given blend composition. The presence of DABA groups in polyimides enables the intermolecular bonding of hydrogen with adjacent chains. This implies that polyimides containing DABA groups may behave as supramolecules because of the intermolecular association. The self-association of polyimide molecules may also decrease the specific interactions between the functional groups of polyimides and PMMA. Further, an increase in molecular weight due to self-association and a decrease in the interaction between polyimides and PMMA are always unfavorable for blend miscibility. Therefore, the 6FDA-6FpDA:DABA/PMMA blend may exhibit a lower phase separation temperature than the 6FDA-6FpDA/PMMA blend. The phase separation temperature of the miscible blends first decreases gradually with increasing PMMA content, plateaus at a minimum

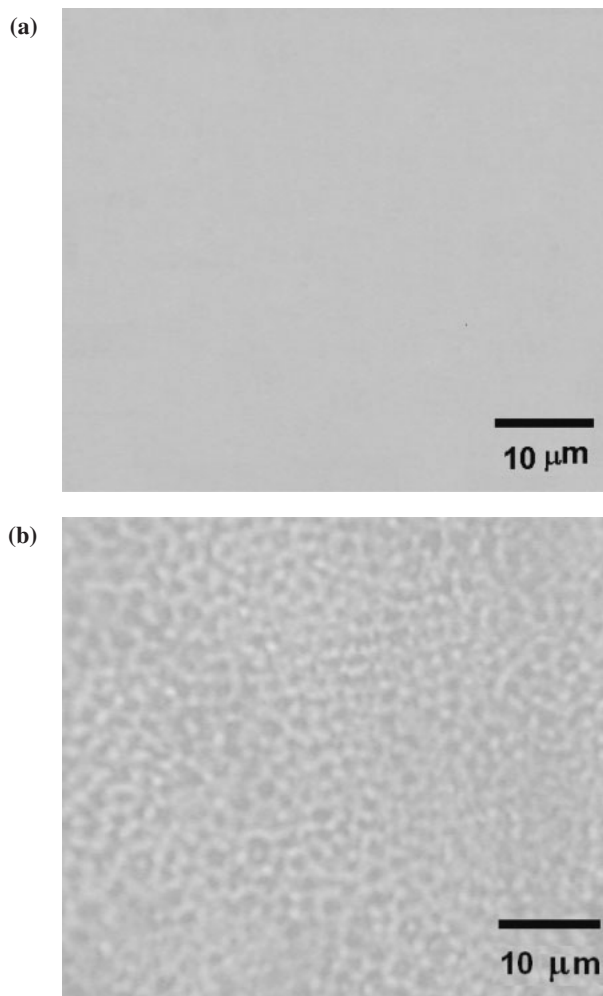


Fig. 5 Microphotographs of PMMA/6FDA-6FpDA 5/5 blend observed with an optical microscope at 260 and 270°C respectively: (a) morphology observed at 260°C; (b) morphology observed at 270°C.

centered at about 70 mass% PMMA, and then increases just prior to the limiting content of PMMA for miscibility with both 6FDA-6FpDA and 6FDA-6FpDA:DABA 2 : 1. Since blends having less favorable energetic interaction exhibit lower LCST, these results indicate that a 7/3 proportion might have the least favorable interaction for the blends of PMMA with 6FDA-6FpDA polyimides.^{10,24,35} The phase separation temperature of the 6FDA-6FpDA/PMMA blend was always higher than that of the 6FDA-6FpDA:DABA/PMMA blend when blend composition was fixed. It was known that the presence of the DABA groups in polyimide facilitated intermolecular hydrogen bonding with adjacent chains.^{39,40} It means that polyimide containing DABA groups may behave as a supramolecule because of intermolecular association. Self-association between polyimide molecules also may lower the specific interactions between functional groups in polyimide and PMMA. Since an increase in the molecular weight caused by self-association and a lowered interaction between the polyimide and PMMA are always unfavorable for the blend miscibility, 6FDA-6FpDA:DABA/PMMA blend may exhibit a lower phase separation temperature than the 6FDA-6FpDA/PMMA blend.

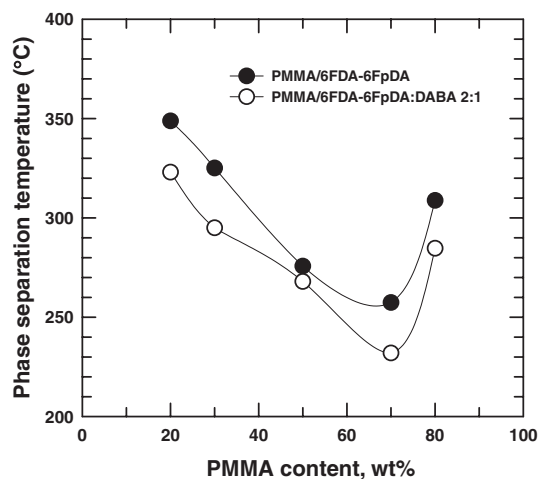


Fig. 6 Phase separation temperatures for PMMA/6FDA-6FpDA and 6FDA-6FpDA:DABA 2 : 1 blends.

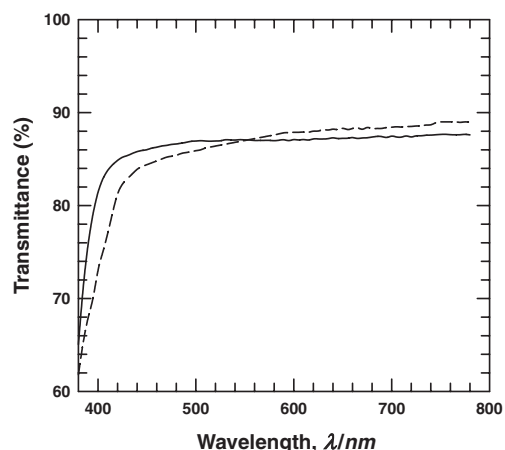


Fig. 7 Wavelength-dependent transmittance of PMMA/6FDA-6FpDA polyimide blend films.

3.2 Optical properties of blend films

To examine the potential usefulness of these blend films in optical applications, their various optical properties were investigated. The transmittance over the visual spectrum of a PMMA/6FDA-6FpDA based polyimide at a 5/5 proportion was plotted and shown in Fig. 7. Note that the samples were measured in accordance with ASTM D1003.²⁴ The path length for the test samples was 2 mm thick and that the samples were polished to reduce any surface imperfections resulting from molding that would otherwise increase the light scattering behavior. Figure 7 clearly shows that the transmittances of the PMMA/6FDA-6FpDA blend films were above 85% over the visual spectrum, indicating that the optical transparency of the films is not reduced when the blend system is miscible. Meanwhile, the PMMA/6FDA-6FpDA:DABA 2 : 1 blend film showed low transmittance below wavelengths of 550 nm due to the present of carboxyl acid group on 6FDA-6FpDA:DABA 2 : 1 polyimide, which absorbed low frequency spectrum. Even though small decrease of transmittance at low wavelength region was observed, in the visual light region, transmittance greatly increased to higher than 90%. For further exploration, the

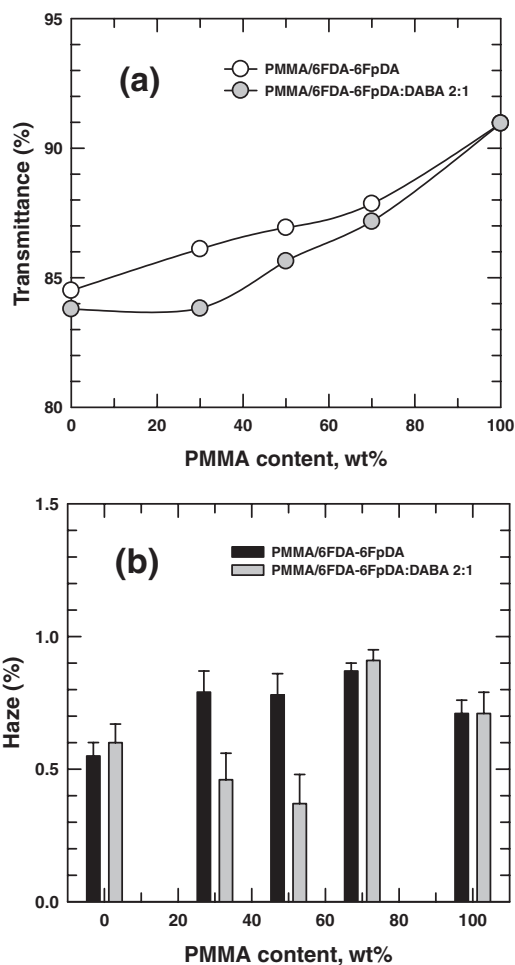


Fig. 8 Total light transmittance (a) and haze (b) of PMMA, PMMA/6FDA-6FpDA polyimides, and 6FDA-6FpDA polyimides measured in accordance with ASTM D1003.

change in the total light transmittance and the haze of the PMMA/6FDA-6FpDA and PMMA/6FDA-6FpDA:DABA 2 : 1 polyimide blend films were monitored as a function of PMMA content. As shown in Fig. 8(a) and 8(b), the total light transmittances and the haze were similar to those of PMMA and the 6FDA-6FpDA polyimides. Of particular note is the haze, as all of the blend films were extremely clear with very low percentages (<1%) of haze. This result has direct consequences on the possibility that films based on PMMA/6FDA-6FpDA polyimides may be used in optical applications.

3.3 Scratch resistance by pencil test

For actual commercial application of blend films, reasonable physical properties in terms of mechanical strength, chemical resistance and scratch resistance are needed. Among these, scratch resistance is essential for various optical applications such as glass substitutes, coating films, and protection films, due to the tough circumstances of usage. In this study, the scratch resistance was measured using the traditional pencil test.²⁵⁾ Please note that other mechanical properties were not measured in this study because it is beyond the scope of this paper to explore the specific measurements of the mechanical properties. More detailed

		Pencil Scratch Hardness					
		HB	F	H	2H	3H	4H
PMMA/ 6FDA-6FpDA	PMMA, wt%						
	0						
	30						
	50						
	70						
PMMA/6FDA-6FpDA:DABA 2:1	0						
	30						
	50						
	70						
	100						

Fig. 9 Pencil scratch hardness of PMMA, PMMA/6FDA-6FpDA polyimide and 6FDA-6FpDA polyimide films.

studies will report on these in the future. The scratch resistance of a blend film refers to the hardest pencil that will not gouge the film. The pencil test was performed on each of the formulations to compare their relative scratch resistance values. The data compiled in Fig. 9 revealed that increasing the content of 6FDA-6FpDA-based polyimide enhances the scratch resistance of the blend films. It is evident from these results that as the 6FDA-6FpDA polyimides have relatively large fluorine-containing polyimide molecules that harden the blend film, these same molecules strengthen the scratch resistance. These results correlate well with the density of these materials presented in Table 1.

4. Conclusions

PMMA can be incorporated into a miscible blend film with 6FDA-based polyimides except those containing DAM, such as 6FDA-DAM and 6FDA-DAM:DABA. The miscibility of blend films composed of PMMA/6FDA-6FpDA and PMMA/6FDA-6FpDA:DABA was affected by the type of casting solvent. DSC thermograms revealed two T_g in specimens using THF as a casting solvent, showing immiscibility; samples using methyl chloride (MC) and cyclohexanone showed a single T_g , representing the miscibility between the two polymers. The frequency shift of carbonyl peaks in the blend films indicated that the functional groups on both polymers, fluorinated carbon of 6FDA-based materials and the carbonyl group of PMMA, have high levels of interaction with each other. The transmittance and haze for blend films were measured according to ASTM specifications. Each blend film was transparent in the visual light range and the optical transparency of the blend films was not reduced when the blend system was miscible. However, the total fraction of transmittance light for PMMA/6FDA-6FpDA:DABA 2 : 1 had a low value due to light absorption by the film. The total light transmittance of blend films as a function of PMMA content varied monotonically between the values of the two pure component polymers. Both films showed high clarity with very low percentages of haze (<1%). The scratch resistance of the blend films was investigated using a standard pencil test (ASTM D3363). As the content of 6FDA-6FpDA polyimide increased, the hardness of the blend film also increased.

These results indicate that the fluorinated polyimide molecule, having a relatively large and stiff aromatic chain, leads to an increase in hardness for blend films.

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