

Blends of thermoplastic polyurethane and polyether–polyimide: preparation and properties

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Abstract

A series of blends of thermoplastic polyurethane (PU) and polyether–polyimide (PI) were prepared in two steps. The first step was the preparation of polyether–amic acid by the reaction of an oligomer based on polytetramethylene oxide glycol di-*p*-aminobenzoate (APTMO) of different molecular weight (650, 1000, and 2000) with benzenetetracarboxylic acid dianhydride (PMDA). The second step was mixing polyether–polyurethane and polyether–polyamic acid solution at room temperature in various weight ratios, and the blend films were obtained by casting and then heat imidization. Infrared spectroscopy (IR), dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), small-angle X-ray scattering (SACS) and wide-angle X-ray diffraction (WAXD) were used to study this family of blends. DSC analysis of the films showed that glass transition temperature (T_g) of PU–PI 650 and PU–PI 1000 series shifted depending on the ratio of PU and PI components. The shift of T_g , along with the transparency of the films, gave the evidence that soft segments of PU and PI were miscible to some extent in the PU–PI 650 and PU–PI 1000 series. DMA results indicated that the blends exhibited a well phase-separated structure and had a broad rubbery plateau from about -30 to 200°C , which varied with the PU content. Thermal stability of PU was found to increase by the incorporation of PI. The excellent tensile properties of the blends suggested that they could be potentially used as heat resistant thermoplastic elastomers. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polyether–polyimide; Polyether–polyurethane; Polymer blend

1. Introduction

Polyurethane elastomers (PU) have excellent abrasion resistance and the properties of both rubber and plastics. They are becoming more and more important as engineering materials [1–3]. Unfortunately, the conventional PU is known to exhibit small resistance to heat, which limits its applications. For example, the acceptable mechanical properties (strength, modulus, etc.) of PU disappear from about 80 – 90°C and thermal degradation takes place at processing temperature above 200°C [4].

Attempts to improve the thermal stability of PU have been made over a long period of time. One of the methods used to improve heat resistance of PU is the chemical modification of their structure by the introduction of thermally stable segments. Recently, more attention has been paid to the modification by heterocyclic groups. Polyimides (PI) are an important class of heterocyclic polymers with remarkable heat resistance and superior mechanical, electrical and

durable properties [5–7]. Various attempts to incorporate polyimide units into PU have been made. Reaction of isocyanate-terminated PU prepolymer with acid dianhydride is the method most often utilized to introduce the imide function into the PU backbone [8–11]. The linear poly(urethane–imide) elastomers were obtained, which showed considerably better mechanical properties and excellent thermal stability than the typical linear PU. Other approaches include the reaction of phenol-terminated PU prepolymer with poly(amic acid) to prepare poly(urethane–imide), which had a 3D network structure and showed excellent solvent resistance [12–14], and intermolecular Diels–Alder reaction of 4-methyl-1, 3-phenylenebis(2-furanylcarbamate) with various bismaleimides to give a series of copolymers, which were used as processable matrix resin for glass–fiber composites [15–17]. Among these methods given above, all of the poly(urethane–imide) were obtained by chemical reaction and relatively few papers have described the incorporation of polyimide into thermoplastic polyurethane to prepare PU/PI blends. Since normal PI is a thermosetting polymer prepared from polyamic acid at high imidization temperature, it makes the

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preparation of PU/PI blends difficult. In this paper, on the basis of our previous studies [18–19], we report the preparation of a novel type of polyurethane/polyimide blends. They were a mixture of two thermoplastic elastomers with the same polyether soft segment and were looked on as interpenetrated network because of heat imidization after mixing. The polymer synthesis and structure-property relationship of the blend films were studied by using infrared spectroscopy (IR), differential scanning calorimeter (DSC), dynamic mechanical analysis (DMA), wide-angle X-ray diffraction (WAXD), small-angle X-ray scattering (SAXS) and tensile testing.

2. Experimental

2.1. Materials

Three kinds of different molecular weight samples of polytetramethylene oxide glycol di-*p*-aminobenzoates (APTMO) were products of Polaroid Corporation (USA) under the trade name “POLAMINE”. The average molecular weights of the samples designated as POLAMINE 650, 1000 and 2000 were 808, 1204 and 1900, respectively. These oligomers were vacuum dried at 70°C for 24 h and kept in a desiccator for further use. Benzenetetracarboxylic acid dianhydride (PMDA) was purchased from Aldrich Chemical Company. The anhydride was dehydrated at 160°C for 6 h before use. Tetrahydrofuran (THF) (Aldrich HPLC grade) was kept dry over molecular sieves (Fisher 4Å). Polyurethane 510-x-55 (based on tetramethylene oxide) was purchased from Becton Dickinson Company (USA) with the weight percentage of hard segment estimated 46% (MDI + BD).

2.2. Synthesis and characterization

The polycondensation reaction was carried out under a dry nitrogen atmosphere according to the general reaction scheme as shown in Fig. 1. A solution of 15 wt% dianhydride in THF was added to another THF solution containing a stoichiometric amount of polyetherdiamine (APTMO). The exothermic reaction raised the temperature to about 40°C after mixing. The solution was stirred at room temperature overnight, until FT-IR spectra showed that the amine absorption peak at 1680 cm⁻¹ had completely disappeared. A yellowish viscous solution was obtained and the polymer was precipitated with methanol, then filtered and dried under vacuum.

Polyamic acid obtained from the synthesis above was redissolved in THF and the solution was mixed with polyurethane solution in various weight ratios. The blend solutions were cast onto a polytetrafluoroethylene disc and then the solvent (THF) was evaporated at room temperature. Finally, the cast films were thermally treated at 140°C for 6 h in a vacuum oven and a series of blend films containing both polyurethane and polyimide were obtained.

All materials studied are described in Table 1. A sample made from polyurethane and polyimide containing “POLAMINE” 650 with weight ratio 3:1, is designated as PU-PI 650 3:1.

Infrared spectra were recorded with a Nicolet 5DX Fourier transform infrared spectrometer. Absorbance of 1778 and 725 cm⁻¹ bands was used to follow the formation of the imide groups.

Dynamic mechanical spectra were obtained using a Rheovibron DDV-II-EA dynamic viscoelastometer, which was controlled by a computer. The samples were measured

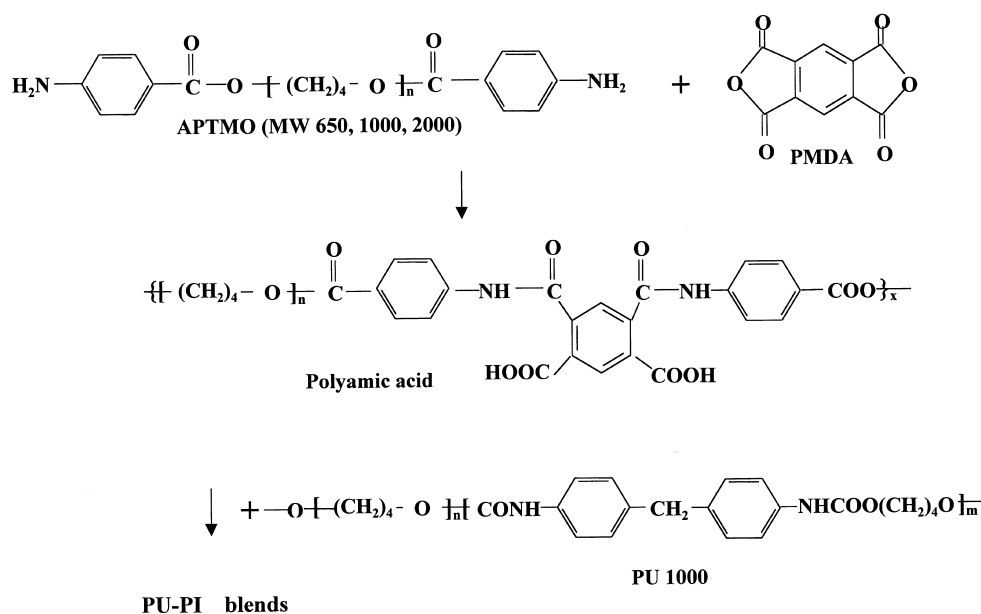


Fig. 1. Schematic representation for the preparation of PU-PI blends.

at a frequency of 110 Hz with a constant heating rate of 2°C/min under a nitrogen purge.

Thermal analysis was carried out using Perkin-Elmer DSC-2C apparatus. A heating rate of 20°C/min under an Ar purge was used. The data station software allowed automatic subtraction of the baseline and normalization of the thermogram for sample weight.

Room temperature uniaxial stress–strain data were taken on a WD-I tensile device (Shanghai, China) using a cross-head speed of 5 cm/min. Dumbbell-shaped samples with a gauge length of 1 cm and width of 0.4 cm were stamped out with a die. For each tensile strength reported, at least five sample measurements were averaged.

Wide-angle and small-angle X-ray studies were performed with a Rigaku D/MAX-RA X-ray diffractometer (40 KV, 150 mA). Nickel-filtered Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) was used as an incident X-ray beam. The scattering angle, 2θ , was within the range of $0.1 \sim 3.5^\circ$ while small-angle X-ray studies were carried out.

3. Results and discussion

3.1. Preparation of PU/PI blend films

Polyurethane solution and polyamic acid solution were mixed in various weight ratios. All the blend solutions were clear and transparent at any component weight ratio. After the heat treatment at 140°C for 6 h in a vacuum oven, all the films based on PI 650 and PI 1000 were still transparent. However, the films based on PI 2000 were opaque after heat imidization. This suggests that a difference of phase separation exists between PU–PI 650, 1000 blend series and PU–PI 2000 series. The domain of phase separation should have become small in the case of PU–PI 650 and PU–PI 1000, but relatively large in the case of PU–PI 2000.

The reaction schemes and polymer structures are

illustrated in Fig. 1. The progress of blend films heat treatment was monitored by using FT-IR spectra as shown in Fig. 2. The spectra confirm the formation of PU/PI blends. After 140°C for 6 h heat treatment, the absorption of amide acid at 1680 cm^{-1} decreased, while characteristic absorption due to the imide function appeared at 1778 and 725 cm^{-1} . The urethane function appeared at 3330 and 1710 cm^{-1} . With further increase in temperature or reaction time, no change was observed in the spectra, which gave the evidence that imidization reaction completed in this reaction condition. These results indicate that the preparation of PU/PI blends can be carried at lower temperature than conventional imidization methods, which is consistent with the previous work of Yu et al. [18]. All synthesized materials are summarized in Table 1.

3.2. Dynamic mechanical analysis

Fig. 3 displays the temperature dependence of the storage modulus and loss factor, $\tan \delta$, of PU–PI 650 series materials. The $\tan \delta$ – T curves show a mechanical relaxation region due to micro-Brownian motions of the PTMO polyether soft segments in each blend material. The loss tangent peak of PU 1000 is around 10°C. It is shifted to low temperature and becomes narrow in width with increasing the mass of polyether–polyimide in blends. This indicates that the micro-phase separation between soft and hard segments in PU–PI 650 blends becomes more complete with an increase in polyether–polyimide component of blends. Anyway, all materials exhibit a well-developed rubbery plateau region, which is characteristic of micro-phase-separated block polymers. It can be seen that the polyimide-containing PU–PI 650 3:1 polymer, with a slightly higher (0.5%) weight fraction of hard segment than PU 1000 polymer, has a obvious higher plateau modulus, a higher level of phase separation and a wider plateau temperature range than PU 1000 polymer. This suggests that

Table 1
Materials studied

Sample code	PU content (wt%)	MW of APTMO	Hard segment (wt%) ^a	Film quality
PU 1000	100	–	46.0	Flexible, transparent
PU–PI 650 3:1	75	808	46.5	Flexible, transparent
PU–PI 650 1:1	50	808	46.9	
PU–PI 650 1:3	25	808	47.4	
PI 650	0	808	47.8	
PU–PI 1000 3:1	75	1204	43.1	Flexible, transparent
PU–PI 1000 1:1	50	1204	40.3	
PU–PI 1000 1:3	25	1204	37.4	
PI 1000	0	1204	34.5	
PU–PI 2000 3:1	75	1900	40.3	Flexible, opaque
PU–PI 2000 1:1	50	1900	34.6	
PU–PI 2000 1:3	25	1900	28.8	
PI 2000	0	1900	23.1	

^a Calculated by addition of the hard segment content of PU and PI.

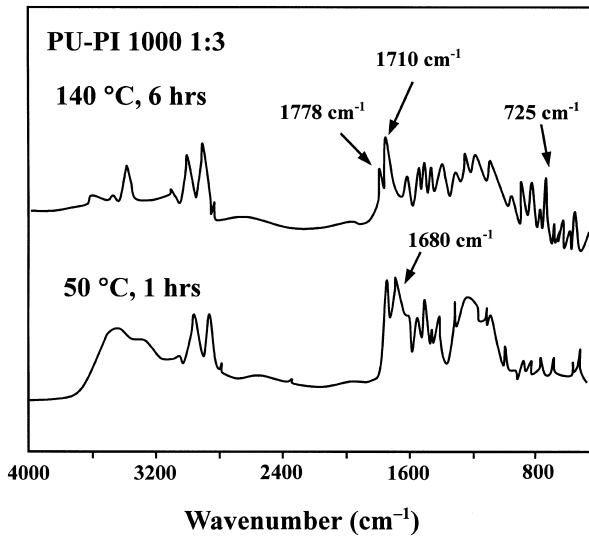


Fig. 2. FT-IR spectra of PU–PI 1000 1:3 after curing at various conditions.

the molecular rigidity of the hard segment of PI 650 is stronger than that of PU 1000, which plays a significant role in determining the physical properties of this system. The incorporation of polyimide into polyurethane increases the heat-resistance of polyurethane.

The results of dynamic mechanical testing of PU–PI 1000 and PU–PI 2000 series blends are shown in Figs. 4 and 5, respectively, and the observed trends in both loss peak and modulus are consistent with those observed in Fig. 3. It is observed that PU–PI 1000 3:1 and PU–PI 2000 3:1 blends, with lower weight fraction of hard segment than

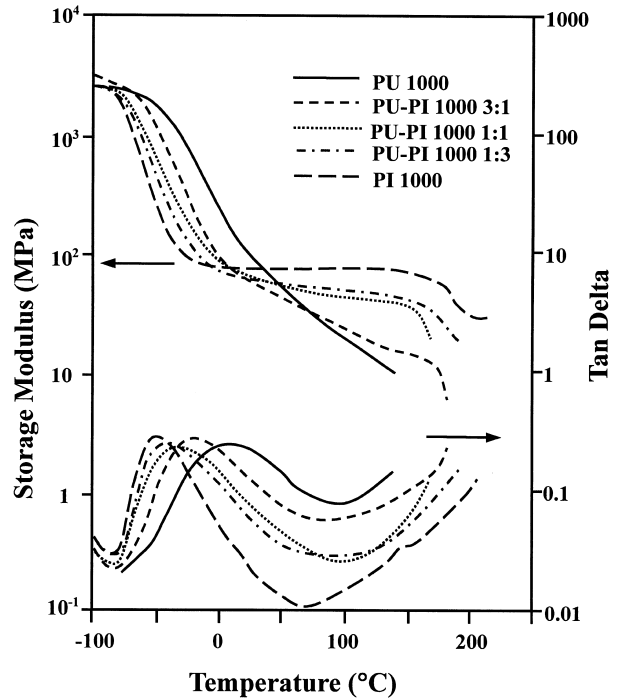


Fig. 4. Dynamic mechanical testing results for PU–PI 1000 series.

PU 1000 polymer, however, possess a higher modulus and a wider plateau temperature ranger. A possible explanation is that polyimide incorporation increases the rigidity of hard segment of material and results in the enhancement of the heat-resistance of blends. It is clear that

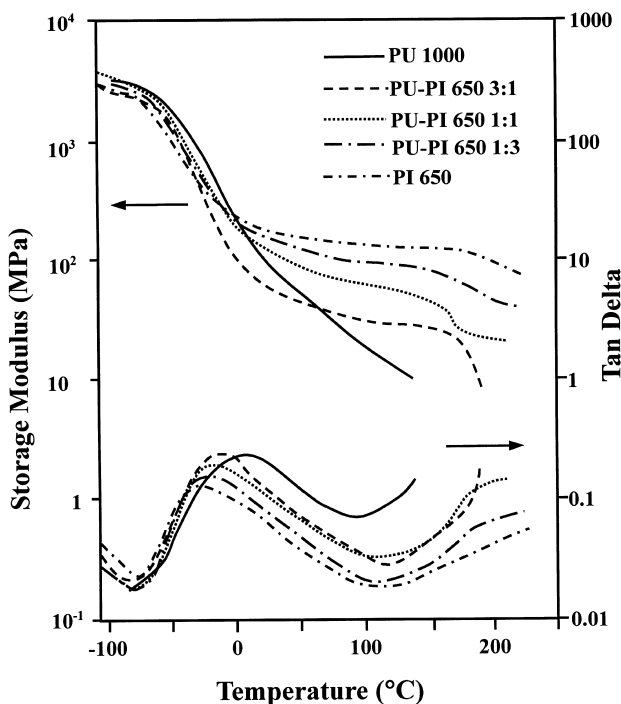


Fig. 3. Dynamic mechanical testing results for PU–PI 650 series.

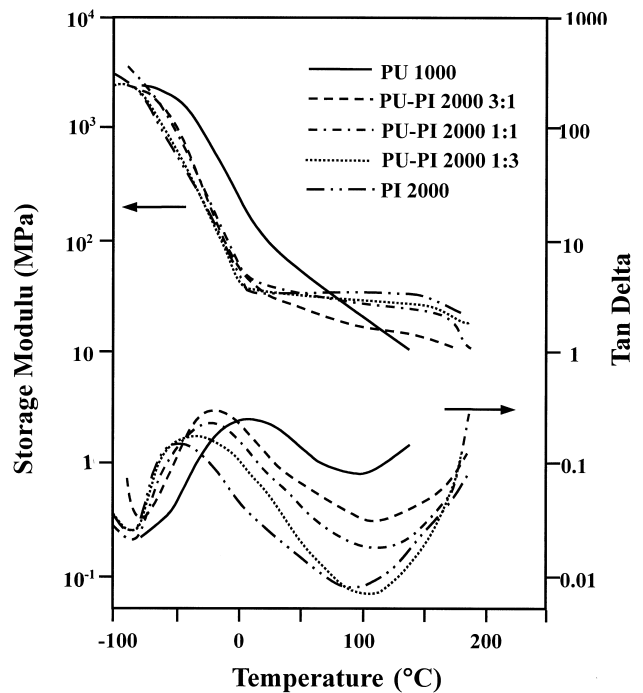


Fig. 5. Dynamic mechanical testing results for PU–PI 2000 series.

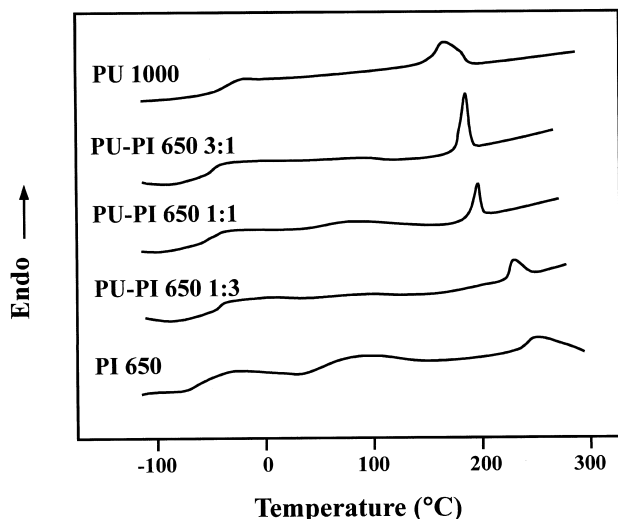


Fig. 6. DSC curves for the PU–PI 650 series.

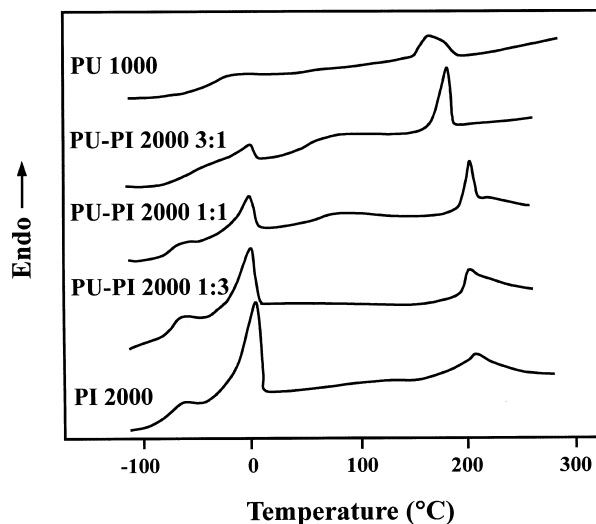


Fig. 8. DSC curves for the PU–PI 2000 series.

polyimide incorporation results in a significant PU modification.

3.3. Thermal analysis

Differential scanning calorimetry (DSC) curves are shown in Figs. 6–8, for the materials studied, and all data are summarized in Table 2. In the DSC curves for PU–PI 650 and PU–PI 1000 samples, there exist both a glass transition of soft segment in the region of $-75 \sim -40^\circ\text{C}$ and a crystalline peak of hard segment, respectively, as shown in Figs. 6 and 7. The correlation between soft segment T_g values and polyimide content is shown in Fig. 9. The trends are consistent with the DMA results, showing the decrease in soft segment T_g as the relative proportion of polyimide in the blend increases. It can be found that two soft segments of

polyurethane and polyimide for PU–PI 650 and PU–PI 1000 series materials are miscible and result in transparent films, as their T_g of the soft segment is directly proportional to the PI content. However, it is not linear correlation for PU–PI 2000 series blends. The possible explanation is that the formation of soft segment crystallite in PI 2000 polymer, which can be confirmed from the endothermic melting peak near 0°C shown in Fig. 8, results in micro-phase separation with polyether soft segment of PU 1000. Therefore, there are two soft domains for PU–PI 2000 series and their blend films are opaque. On comparing Fig. 8 with DMA results, as shown in Fig. 5, DMA spectra are insensitive to the formation of soft segment crystallite in PI 2000. The reasonable explanation is that DSC is sensitive to the relaxation accompanying a thermal variation, but DMA is only sensitive to damping procedure. Therefore, it is difficult to observe changes on the $\tan \delta - T$ curves for the crystallite molten in rubber phase.

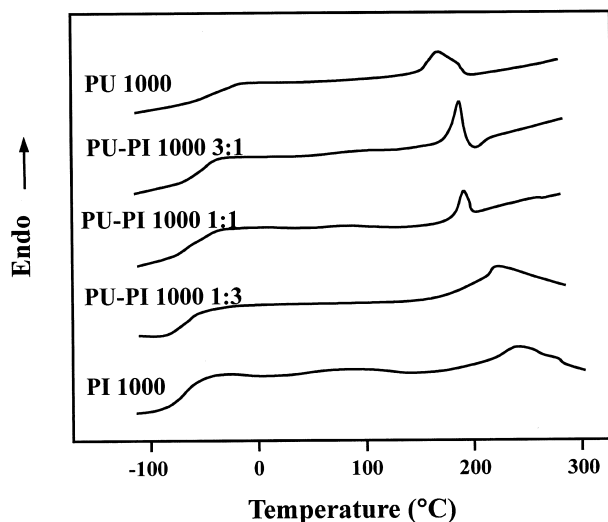


Fig. 7. DSC curves for the PU–PI 1000 series.

Table 2
DSC data for the materials studied

Sample code	T_g ($^\circ\text{C}$)	Breadth ($^\circ\text{C}$)	T_m ($^\circ\text{C}$)
PU 1000	-40.6	42.2	164.4
PU–PI 650 3:1	-44.6	56.2	185.5
PU–PI 650 1:1	-46.2	61.6	194.4
PU–PI 650 1:3	-50.0	57.0	209.0
PI 650	-52.6	43.0	246.2
PU–PI 1000 3:1	-53.7	62.8	180.7
PU–PI 1000 1:1	-56.5	69.8	187.4
PU–PI 1000 1:3	-62.8	66.8	211.0
PI 1000	-69.4	35.7	236.6
PU–PI 2000 3:1	-67.0	42.5	178.5
PU–PI 2000 1:1	-74.1	24.5	200.1
PU–PI 2000 1:3	-74.5	27.6	200.3
PI 2000	-75.4	29.4	204.5

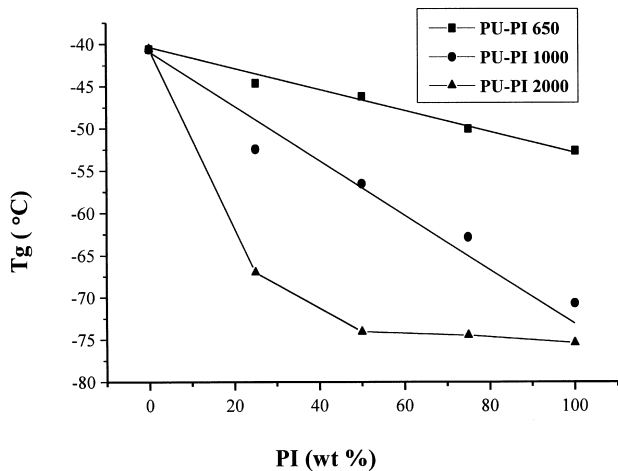


Fig. 9. Correlation between the glass transition temperature (T_g) of polyether soft segment and polyimide content in blend materials.

For each blend sample studied, the DSC curves show the existence of one endotherm peak at temperature over 160°C . The position of the peak shifts to high temperature as the proportion of polyimide in the blend increases. The endotherm peak of each material is postulated to result from the disordering or melting of hard segment sequences. Since all materials were prepared from heat treatment at 140°C for 6 h, it is likely that dissociation and recombination of the hard domain of PU occurred during this process, which aided the formation of high melting-temperature structure [20]. With incorporation of hard segment of PI, it is possible that two hard segments cohere and form crystallites during annealing, which melt at higher temperature due to the stiffness and regularity of the PI structure. The crystalline state of hard segment for blends can be followed by WAXD as shown in Fig. 12.

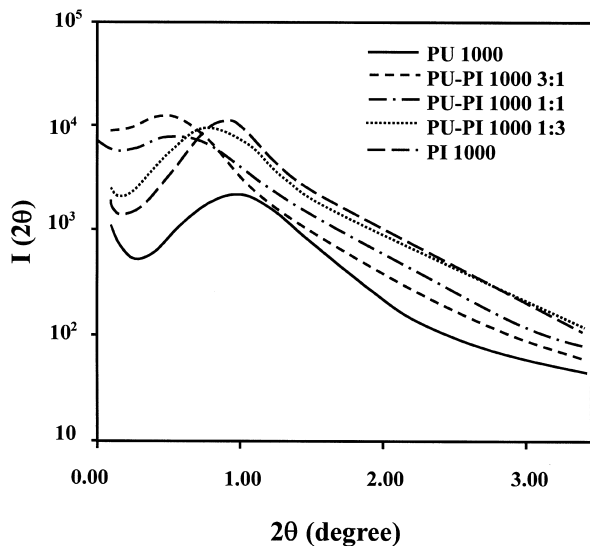


Fig. 10. SAXS curves for PU-PI 1000 series.

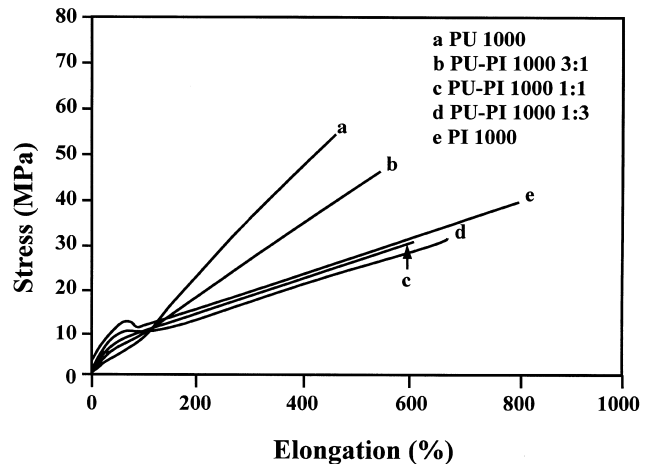


Fig. 11. Stress-strain curves for PU-PI series.

3.4. Small-angle X-ray scattering analysis

PU-PI 1000 series were chosen for SAXS testing to survey the phase-separation of the blend system. The curves of SAXS testing are shown in Fig. 10. It's obvious that there exist microphase separation structures for PU-PI blend materials according to the scattering curves. The SAXS peak of PI is narrower and higher than that of PU, suggesting that the size of the hard domain of PI-1000 is more regular, and phase separation between soft and hard segments is more complete than that of PU 1000. The shape of the SAXS peak is broadened with the increase of PU-1000 content, indicating that the hard domain of blends is more irregular and the compatibility between soft and hard domain of the blend increase. The trend of SAXS

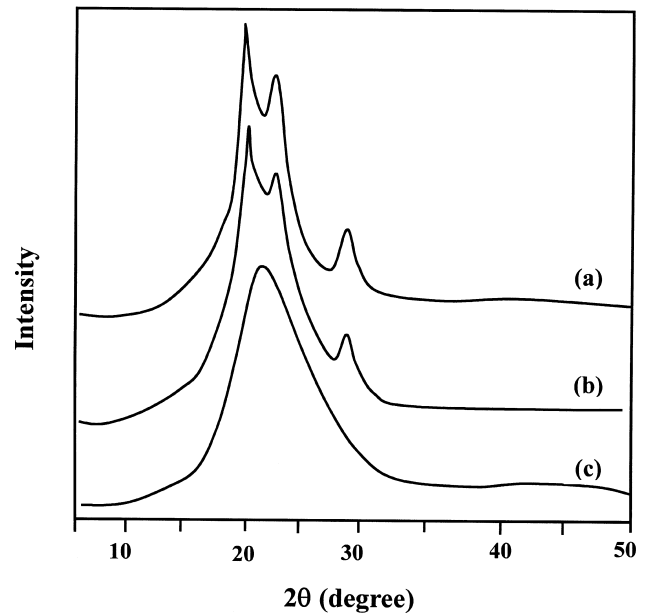


Fig. 12. WAXD curves for PU-PI 1000 series. (a) PI 1000, (b) PU-PI 1000 1:1, and (c) PU 1000.

Table 3

SAXS data for the materials studied (φ_h , volume fraction of hard segment; φ_s , volume fraction of soft segment; D , average interdomain spacing value; σ , parameter for thickness of interface; L_h , average length of hard domain; L_s , average length of soft domain)

Sample code	PU 1000	PU–PI 1000 3:1	PU–PI 1000 1:1	PU–PI 1000 1:3	PI 1000
φ_h (%)	0.368	0.321	0.302	0.273	0.232
φ_s (%)	0.632	0.679	0.698	0.727	0.768
D (Å)	85	192	155	103	98
σ (Å)	5.4	4.9	4.3	3.8	3.5
L_h (Å)	24	21	20	18	16
L_s (Å)	41	43	47	50	53

curves is consistent with the DMA results. The data of SAXS testing are summarized in Table 3. The values of parameter for thickness of interface, σ and average length of hard domain, L_h for PU-1000 are higher and the average interdomain spacing value is lower than that of PI-1000. It can be inferred that with the increase of the volume fraction of hard segment from PI 1000 to PU 1000, the interdomain spacing become smaller, the size of hard domain become bigger, and compatibility between two phases increases.

3.5. Tensile properties

Table 4 shows the mechanical property data for all materials studied, and the stress–strain curves of PU–PI 1000 blend series are shown in Fig. 11. It can be seen that an increase in the PI content leads to low ultimate stress and high elongation at break for PU–PI blend series. This observation can be attributed to the better phase separation and weaker cohesion of hard segment with the increase of PI content in blend materials. The low Young's modulus may be associated with the low hard segment content when PI content increases. In addition, the blend films with high PI contents show a yield phenomenon in their stress–strain curves. The curves of stress–strain for PU–PI 650 and PU–PI 1000 series are not shown, whose trends are consistent with that in Fig. 11. The yield can be attributed to the

disruption of the hard segment domain interconnection. As a result, all blend materials are typical elastomers, whose elongation is more than 300% and possess high tensile strength.

3.6. Wide-angle X-ray diffraction analysis

In order to verify the crystalline state in these polymers, X-ray diffraction patterns were obtained as shown in Fig. 12. The bottom curve shows the PU-1000 sample to be semicrystalline in nature because there is a wide peak at 21.5°. The top curve definitely shows PI-1000 sample to be crystalline since there are three sharp peaks at 20, 22.5, and 28.5°. The same result as PI 1000 can be observed for PU–PI 1000 1:1 at the middle curve. From these results, it is inferred that the existence of polyether soft segment can facilitate polyimide chain of PI 1000 toward crystalline order. While mixing the precursor of crystalline PI 1000 and semicrystalline PU 1000 to prepare PU–PI 1000 1:1 blend there still exist three crystalline peaks, indicating that the heating process for the preparation of PU–PI 1000 1:1 blend promoted the crystallization of PU 1000, which is originally semicrystalline. It is also possible that hard segments of PU 1000 and PI 1000 interact in this process to form co-crystallite. The deficient crystallite in PU 1000 is owed to the fact that imidization temperature did not reach its completely crystalline temperature.

Table 4

Summary of the tensile properties

Sample code	Ultimate stress (MPa)	Elongation at break (%)	Young's modulus (MPa) 100%
PU 1000	54.0	460	10.6
PU–PI 650 3:1	48.1	467	11.5
PU–PI 650 1:1	44.4	487	13.7
PU–PI 650 1:3	41.7	547	15.1
PI 650	35.3	767	16.6
PU–PI 1000 3:1	46.0	540	11.1
PU–PI 1000 1:1	31.8	600	11.3
PU–PI 1000 1:3	31.7	667	11.7
PI 1000	39.9	800	12.5
PU–PI 2000 3:1	53.0	500	9.1
PU–PI 2000 1:1	51.0	533	8.8
PU–PI 2000 1:3	41.5	653	8.1
PI 2000	37.5	900	7.7

4. Conclusions

PU–PI blend materials, which were prepared by mixing polyurethane and polyamic acid solution followed by low thermal treatment, are a novel type of thermoplastic elastomers which exhibit a well phase-separated morphology, possess a wide range of service temperature and have good tensile properties. Transparent blend films were obtained when PI 650 and PI 1000 were used, due to the miscibility of soft segments between polyurethane and polyimide. Incorporation of a small amount of PI component improved the heat-resistance of polyurethane.

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