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Polymerization blending for compatible poly(ether sulfone)/aramid blends based on polycondensation of *N*-silylated *m*-phenylenediamine with isophthaloyl chloride in poly(ether sulfone) solution

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Poly(oxy-1,4-phenylenesulfonyl-1,4-phenylene) (PES) and poly(*m*-phenyleneisophthalamide) (aramid PMIA) were blended readily by the polymerization blending method. That is, *N*,*N*′-bis(trimethylsilyl)-substituted *m*-phenylenediamine was reacted with isophthaloyl chloride in a PES solution in *N*,*N*-dimethylacetamide, and the resulting mixture was directly cast into films. The procedure afforded transparent films over the entire PES/PMIA composition range. Homogeneous mixing of the component polymers in the form of films was shown by a single glass transition temperature except for PES/PMIA 80/20, while a conventional solution blending method afforded less compatible blend films. This was also supported by the morphological studies. The tensile modulus and tensile strength of the blend films were improved over the entire PES/PMIA composition range by using the polymerization blending method. The polymerization-blended films had a high elongation at break over a relatively wide composition range from PES/PMIA 30/70 to PES/PMIA 60/40, leading to tough and ductile films. Annealing the blend films afforded high temperature resistant films with high tensile modulus and strength due to both crystallization and partial crosslinking of the aramid component.

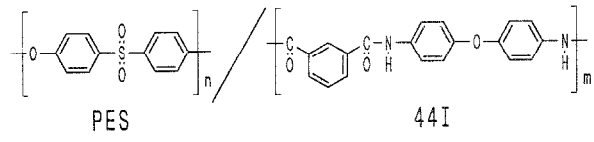
(Keywords: polymerization blending; solution blending; PES/PMIA blends)

INTRODUCTION

Polymer blends have been frequently meeting performance demands that cannot be satisfied by the currently available commodity polymers. For example, in the case of polymer blends based on aromatic poly(ether sulfone)s such as poly(oxy-1,4-phenyleneisopropylidene-1,4-phenyleneoxy-1,4-phenylenesulfonyl-1,4-phenylene) (PSF)[1] and poly(oxy-1,4-phenylenesulfonyl-1,4-phenylene) (PES)[2], PSF/poly(*p*-phenylene sulfide) (PPS)[3–7], PSF/poly(ether ketone) (PEK)[8,9], PES/PPS[10] and PES/PEK[11–13] have been reported.

Fundamentally, polymer blends are almost immiscible in general from a thermodynamic point of view. However, the miscibility or compatibility of a polymer blend can be increased by addition of a compatibilizer[14] or by copolymerization of the constituent polymers[15], both of which result in a better balance of properties for functional applications.

Recently, to improve the compatibility of the PES/poly[*N*,*N*′-(oxydi-*p*-phenylene)isophthalamide] (aramid 44I) blend in the form of solution-blended films[16], we developed the polymerization blending method; that is, *N*,*N*′-bis(trimethylsilyl)-substituted bis(4-aminophenyl) ether was reacted with isophthaloyl chloride in a PES solution in *N*,*N*-dimethylacetamide (DMAc), and the resulting mixture was directly cast into films[17]. The compatibility of the binary mixture of PES and 44I was greatly improved by the polymerization blending method, and hence the polymerization-blended films had better mechanical properties than the solution-blended films[17].



A similar *in situ* direct polycondensation in a polymer matrix was reported by Ogata *et al.*[18] who prepared opaque polyarylate films with finely dispersed rigid aramid or rigid polyarylate. In addition, the patent

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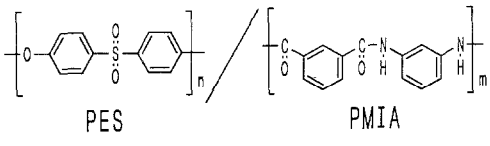
literature reports binary compositions prepared by the *in situ* melt polymerization of liquid crystalline polymers (LCPs) in the presence of thermoplastic polymers, which were, for example, PSF, PES, PPS and PEK[19,20]. These blend systems had better mechanical properties than the physical blends of the same compositions.

In addition to aramid 44I, we have also reported that poly(*m*-phenyleneisophthalamide) (PMIA), a common aramid having no ether linkages, as opposed to 44I, can be solution blended with PES to give phase-separated translucent or opaque films over the entire PES/PMIA composition range[21]. The results revealed that PMIA, with no ether linkages, has a lower compatibility with PES in comparison with 44I.



PES PMIA

Our purpose was to improve the compatibility of the PES/PMIA binary blend films by means of the polymerization blending method. In addition, this article reports the compatibility, mechanical properties and annealing of the polymerization-blended films of the PES/PMIA system, including those of the solution-blended films for comparison.

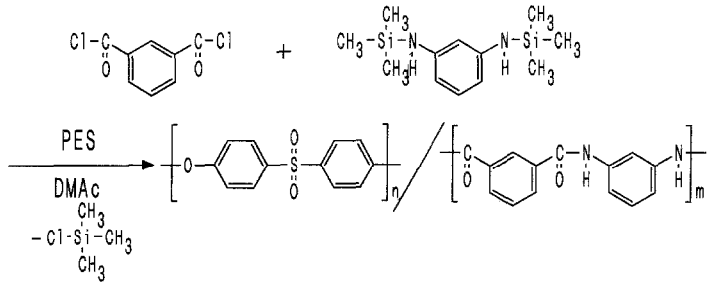
EXPERIMENTAL

Materials

The aromatic poly(ether sulfone) PES was supplied by ICI as Victrex PES 4800P and used as received. The aramid PMIA was prepared by a conventional low temperature solution polycondensation method[22], starting from isophthaloyl chloride and *m*-phenylenediamine. The inherent viscosities of PES and PMIA in *N*-methyl-2-pyrrolidone (NMP) at 30°C were 0.5 and 1.4 dl g^{-1}, respectively. Isophthaloyl chloride and *m*-phenylenediamine were obtained commercially and purified by vacuum distillation. *N*,*N*′-Bis(trimethylsilyl)-substituted *m*-phenylenediamine was synthesized according to the method reported previously[23]. All the solvents such as NMP and DMAc were purified by distillation under reduced pressure.

Preparation of polymerization-blended films

A typical example of the preparation of a polymerization-blended film (of 50/50 PES/PMIA composition on a weight basis) is as follows (see equation (1)). In a flask equipped with a mechanical stirrer, a nitrogen inlet and a condenser with a drying tube was placed 1.191 g of PES, and this was dissolved in 10 ml of DMAc with stirring under a slow stream of nitrogen. To the PES solution, 1.263 g (5 mmol) of *N*,*N*′-bis(trimethylsilyl)-substituted *m*-phenylenediamine was added and dissolved completely. This solution was cooled with an ice/water bath at 0°C. To the solution was added 1.015 g (5 mmol) of solid isophthaloyl chloride in one portion. The mixture was stirred at 0°C for 3 h under reduced pressure. As the polycondensation proceeded, the solution became viscous, forming PMIA. The resulting polymer solution was cast onto a glass plate, and the solvent was removed successively under vacuum at 0–5°C for 6 h, at room temperature for 24 h, at 100°C for 24 h and at 200°C for seven days; the resulting film was washed with methanol over 24 h. The film was further dried *in vacuo* at 200°C for two days. The inherent viscosity of PMIA formed in the blend was estimated to be 1.9 dl g^{-1}, measured at a concentration of 0.5 g dl^{-1} in NMP at 30°C, by extrapolation of the linear plot for the PES/PMIA composition *versus* the inherent viscosity of the blend to the intercept for PMIA. This relationship was based on the assumption that a plot of



(1)

the PES/PMIA composition *versus* the inherent viscosity of the blend gives a straight line, was already confirmed in the case of the PES/44I solution-blended system[17].

In the case of the PES/PMIA 60/40 and 80/20 compositions, the reaction mixture was stirred at room temperature for 3 h under reduced pressure, and the first drying stage was under vacuum at room temperature for 24 h.

The polymerization-blended films of about 30 μm thickness were transparent in appearance over the entire PES/PMIA composition range.

Preparation of solution-blended films

A typical example of the preparation of a solution-blended film (of 50/50 PES/PMIA composition on a weight basis) is as follows[21]. In a flask equipped with a mechanical stirrer, a nitrogen inlet and a condenser with a drying tube was placed 10 ml of DMAc. This was cooled with an ice/ethanol bath to −10°C. To the solvent was added 1.0 g of PMIA. The mixture was stirred at −10°C for 1 h and then the temperature was elevated slowly to room temperature under nitrogen. To the solution was added 1.0 g of PES in one portion. The mixture was stirred at room temperature for 24 h, giving the turbid ternary blend based on the two component polymers and the solvent. The blend solution was then cast onto a glass plate, and the solvent was removed successively *in vacuo* at 0–5°C for 6 h, at room temperature for 24 h, at 100°C for 24 h and at 200°C for seven days; the resulting film was washed with

methanol over 24 h. The film was further dried *in vacuo* at 200°C for two days. The solution-blended films of about 30 μm thickness were translucent or opaque in appearance, depending on the PES/PMIA composition.

Annealing of samples

Annealing of the blend films was carried out under vacuum at 330°C for 12 h.

Measurements

Inherent viscosities of the polymers were measured at a concentration of 0.5 g dl^{-1} in NMP at 30°C with an Ostwald viscometer. Infra-red spectra were recorded at room temperature on a JASCO FT/IR-5000 spectrophotometer. Differential scanning calorimetry (d.s.c.) was performed with a Shimadzu DSC-41M thermal analyser at a heating rate of 20°C min^{-1} in a nitrogen atmosphere. The midpoint of the slope change in the heat capacity plot of the first d.s.c. scan was taken as the glass transition temperature (T_g). Dynamic mechanical analysis was performed with a Toyoseiki Reolograph-Solid at a frequency of 10 Hz and a heating rate of 2°C min^{-1} in air. Tensile properties were measured at room temperature using a Toyo Baldwin Tension UTM-II-20 with film specimens of 5 mm width, 40 mm gauge length and 30 μm thickness. Five specimens for each sample were measured at a strain rate of 20% min^{-1}. The results for the sample having the maximum elongation at break were taken as the data for elongation at break and tensile strength. Scanning electron micrographs were obtained with a JEOL JSM-25SIII scanning electron microscope at an accelerating voltage of 15–30 kV. The sampling method for the observation of morphology with scanning electron microscopy (SEM) was carried out as follows. The blend film was fractured at liquid nitrogen temperature, and the fracture surface was treated with chloroform at room temperature for 24 h to remove the PES domain. After that, the surface was coated with gold by vacuum deposition. Wide angle X-ray diffraction patterns were recorded using a Rigakudenki XG X-ray diffractometer with nickel-filtered CuKα radiation detected by scintillation counters (35 kV, 20 mA).

RESULTS AND DISCUSSION

Preparation of polymerization-blended films

The polycondensation of *N*,*N*′-bis(trimethylsilyl)-substituted *m*-phenylenediamine with isophthaloyl chloride proceeded homogeneously in the PES solution in DMAc at 0°C except for the PES/PMIA 60/40 and 80/20 compositions. In the case of the PES/PMIA 60/40 and 80/20 compositions, the polycondensation proceeded homogeneously at room temperature. The inherent viscosities of the PMIA formed were controlled in the range 1.0–1.9 dl g^{-1} as shown in *Table 1*, since the molecular weight can affect the compatibility of the binary polymer blend. *Figure 1* shows the infra-red spectra of the component polymers and the PES/PMIA 50/50 blend film obtained by polymerization blending. The appearance of an absorption band at 1650 cm^{-1} (C=O stretching) confirms the formation of PMIA in the PES solution.

Table 1 Inherent viscosities of PMIA prepared by polymerization blending

PES/PMIA (w/w)	30/70	40/60	50/50	60/40	80/20
η_{inh}[a] (dl g^{-1})	1.6	1.6	1.9	1.5	1.0

[a] Measured at a concentration of 0.5 g dl^{-1} in NMP at 30°C

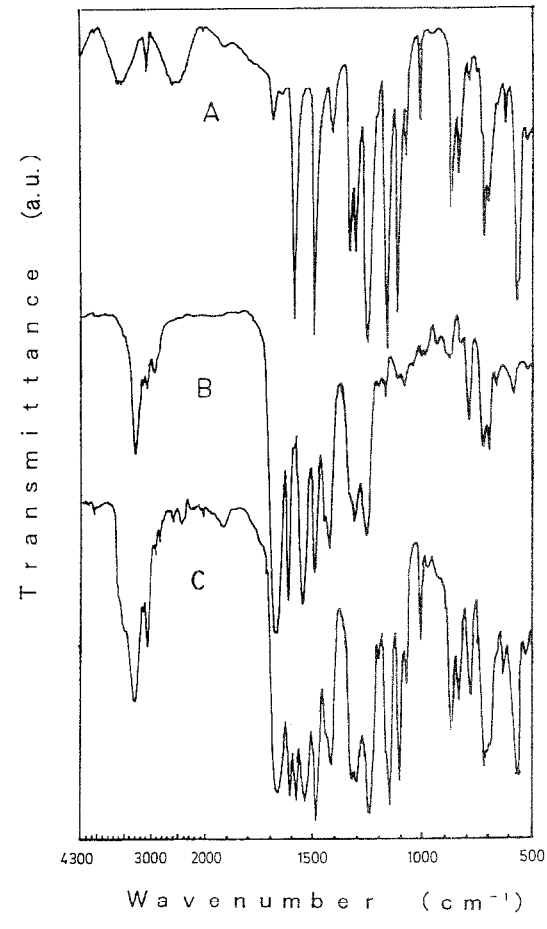


Figure 1 Infra-red spectra of the polymer films: (a) PES; (b) PMIA; (c) PES/PMIA 50/50 blend obtained by polymerization blending

Compatibility of polymerization blends

The compatibility between PMIA and PES was first studied for the ternary mixtures composed of PES, PMIA and DMAc obtained by both polymerization and solution blending with the compositions 30/70, 40/60, 50/50, 60/40 and 80/20 for PES/PMIA and 15–20/80–85 for polymer/solvent on a weight basis. All the PES/PMIA/DMAc polymerization blends gave clear solutions and hence were compatible at room temperature, whereas all the solution blends were turbid and incompatible. However, the polymerization blends with the PES/PMIA 60/40 composition gradually showed phase separation during the polycondensation at 0°C. In the case of the PES/44I/DMAc system, all of the polymerization blends and solution blends were compatible at room temperature[17]. These results show that the PES/PMIA/DMAc system has low compatibility compared with the PES/44I/DMAc system.

The ternary solutions were cast onto glass plates, giving binary polymer blend films. The polymerization blending gave transparent PES/PMIA films over the entire composition range. In contrast, all the solution-

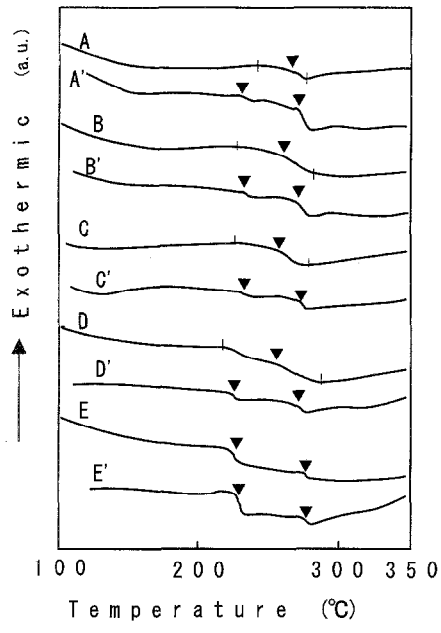


Figure 2 D.s.c. thermograms of the first runs for the blend films: (A) 30/70 PES/PMIA polymerization blend; (A′) 30/70 solution blend; (B) 40/60 polymerization blend; (B′) 40/60 solution blend; (C) 50/50 polymerization blend; (C′) 50/50 solution blend; (D) 60/40 polymerization blend; (D′) 60/40 solution blend; (E) 80/20 polymerization blend; (E′) 80/20 solution blend

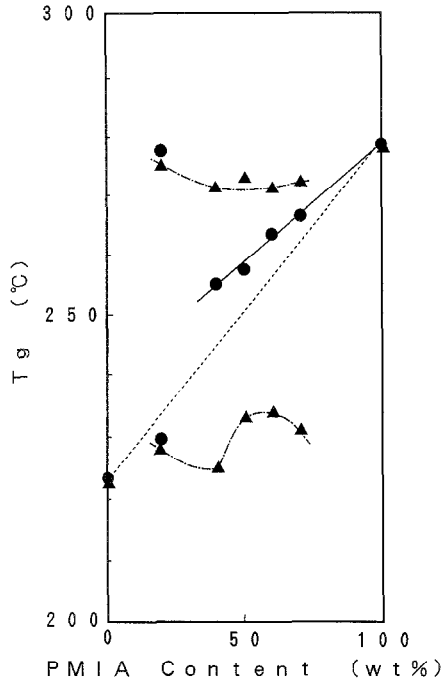


Figure 3 Composition dependence of T_g for the blend films: (●) polymerization blend; (▲) solution blend. The dashed line is for the calculated T_g values based on the linear mixture rule

blended films were opaque or translucent. These films were subjected to thermal characterization by d.s.c. *Figure 2* shows the d.s.c. thermograms of the first runs for the polymerization-blended films and the solution-blended films over the entire composition range. As shown in this figure, the polymerization blends each exhibit a single T_g except for the PES/PMIA 80/20 composition, while all the solution blends exhibit two T_g values. This indicates that the compatibility of the PES/PMIA 80/20 composition is different from that of the other compositions. One reason for this is that the molecular weight of PMIA in the PES/PMIA 80/20 polymerization blend is appreciably lower than that in the other polymerization blends. The T_g width of the polymerization blends increased with increasing PES content, and the PES/PMIA 60/40 composition especially showed a very broad transition. From these results, this polymerization blend system can be regarded as semicompatible for PES-rich compositions. In the case of the PES/44I binary system, the polymerization-blended films each exhibited a single T_g over the entire composition range and the T_g width did not increase with increasing PES content, whereas the solution-blended films exhibited two T_g values for PES-rich compositions[17]. Thus the compatibility of the PES/PMIA blend system is lower than that of the PES/44I system.

Figure 3 shows the composition dependence of T_g for the polymerization blends and the solution blends. The T_g of the polymerization blends exhibits a positive deviation from a linear mixture rule with increasing PES content. We can write the linear mixture rule as

$$T_g = W_1 T_{g1} + W_2 T_{g2}$$

where T_{gi} and W_i are the T_g and the weight fraction of the ith component, respectively. This may be ascribed to the ready formation of some interactions like hydrogen bonding between PES and PMIA during the polymerization blending. In the case of the solution blends, these films displayed two T_g values corresponding to the composition of each phase.

Figure 4 shows the SEM micrographs of the polymerization-blended films and the solution-blended films. The polymerization-blended films with 30/70, 40/60 and 50/50 PES/PMIA compositions were homogeneous, but the 60/40 composition was somewhat heterogeneous. This corresponds well to the fact that these films were all transparent. In the case of the solution-blended films, all the films were heterogeneous and had a two-phase structure with the PES domain dispersed in the PMIA matrix. In fact, the phase separation led to opaque or translucent films for these blends.

From these results, it is clear that the compatibility of the binary mixture of PES and PMIA was greatly improved by polymerization blending. This is probably because the growing PMIA molecules are interpenetrated with the PES molecules in solution, resulting in the formation of a highly entangled mixture of PES and PMIA, and hence the mixture is very difficult to phase separate into the component polymers during the casting of films. However, in the case of the solution blends, the degree of entanglement of PMIA and PES is lower than that in the polymerization blends.

Mechanical properties of polymerization-blended films

Figure 5 shows the stress–strain curves for the films of PES, PMIA, the PES/PMIA 50/50 polymerization blend and the 50/50 solution blend. A comparison of the curves shows a significant increase in the elongation at break of both polymerization-blended and solution-blended films, regardless of the blending method. The composi-

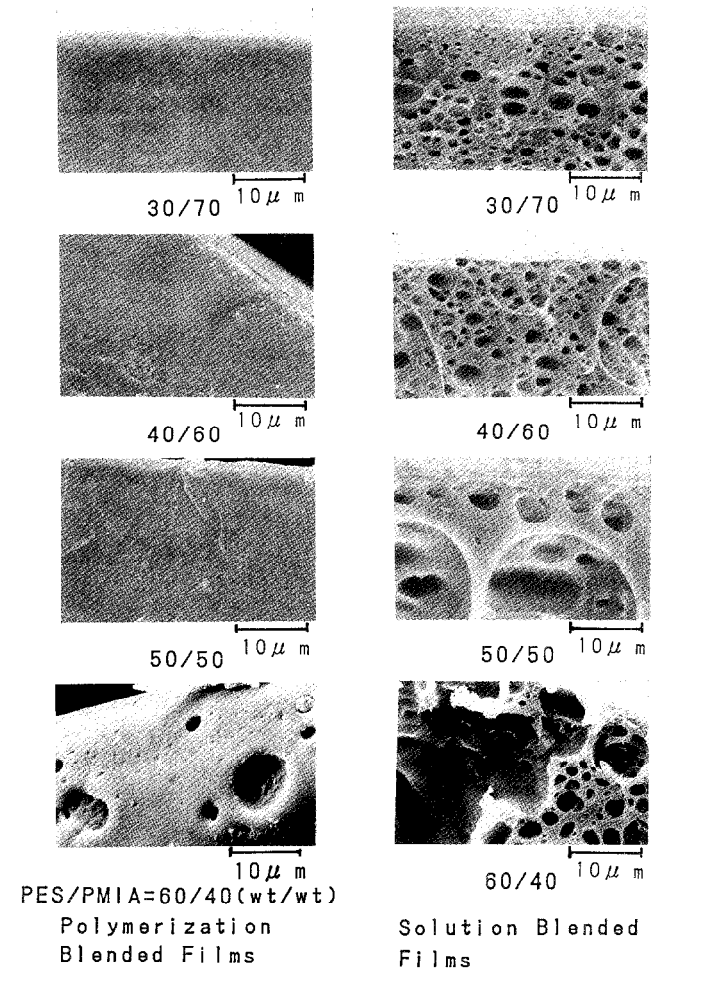


Figure 4 SEM micrographs of the fractured surfaces of the blend films

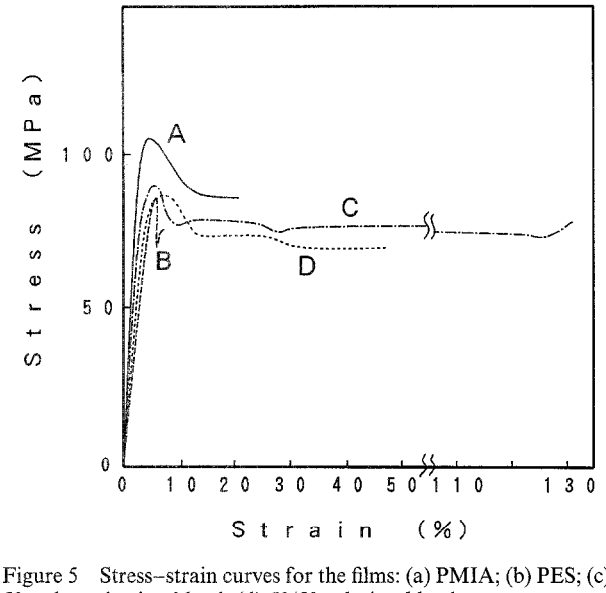


Figure 5 Stress–strain curves for the films: (a) PMIA; (b) PES; (c) 50/50 polymerization blend; (d) 50/50 solution blend

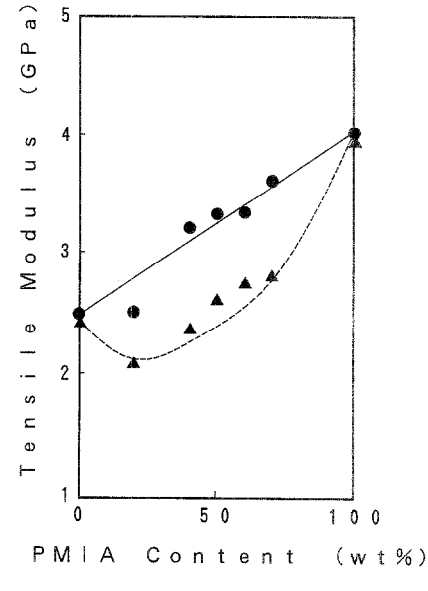


Figure 6 Composition dependence of the tensile modulus for the blend films: (●) polymerization blend; (▲) solution blend

tion dependences of the tensile modulus, tensile strength and elongation at break for both polymerization-blended and solution-blended films are shown in *Figures 6*, *7* and *8*, respectively. *Figure 9* shows the morphology of the deformed tensile specimens for the polymerization-blended and solution-blended films, observed from the fractured surfaces of the specimens without treating with chloroform. The tensile modulus and tensile strength of the polymerization-blended films

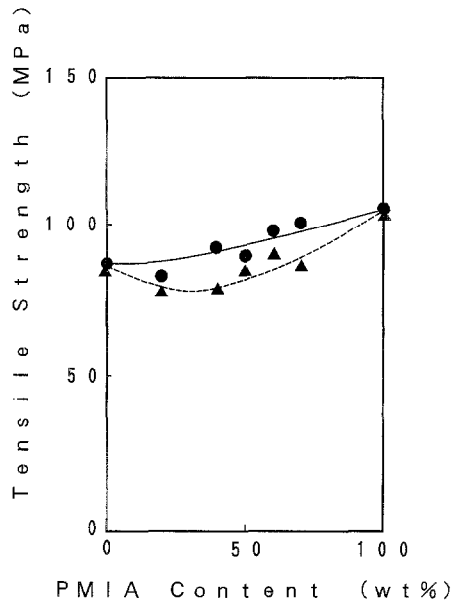


Figure 7 Composition dependence of the tensile strength for the blend films: (●) polymerization blend; (▲) solution blend

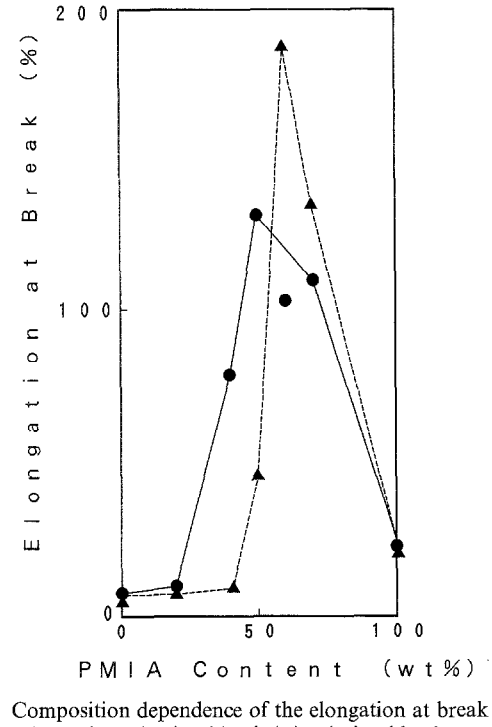


Figure 8 Composition dependence of the elongation at break for the blend films: (●) polymerization blend; (▲) solution blend

increase linearly with increasing PMIA content except for the PES/PMIA 80/20 composition, whereas those of the solution-blended films exhibit a negative deviation from a simple addition rule of mixtures. In particular, the tensile modulus of the solution-blended films is much lower than that of the polymerization-blended films. This is because, as shown in *Figure 9*, the morphology of the deformed tensile specimens for the polymerization-blended films is homogeneous in comparison with that of the solution-blended films. In the case of the PES/44I blend system, the tensile moduli for the polymerization-blended films were slightly higher than those of the solution-blended films[17]. The reason why the differences in the tensile modulus and tensile strength between the polymerization blends and solution blends are small, compared with the PES/PMIA blend system, is that the differences in compatibility between the polymerization blends and the solution blends are so small as not to affect the tensile modulus and tensile strength.

The polymerization-blended films had the characteristic of a high elongation at break, and the blends especially yielded films with an elongation of over 50% over a relatively wide composition range from PES/PMIA 60/40 to PES/PMIA 30/70 compared with the solution-blended films. The PES/44I polymerization-blended films also had similar elongation behaviour[17]. This may be explained as follows. The elongation at break of neat PES film cast from DMAc solution was only 6%, whereas that of the commercial extrusion-moulded film is 226% (Sumitomo Chemical Co.). The former is because DMAc is a poor solvent for PES and because the macromolecular chain of PES in the solvent has a collapsed structure, which is retained owing to the relatively high evaporation speed of DMAc during casting of the film, and hence the degree of entanglement of the PES chain is relatively low. The polymerization-blended films in the composition range 60/40 to 30/70 PES/PMIA probably have a mutually entangled structure of PMIA and PES due to good compatibility, and therefore high elongation results from the entanglement. In the case of solution blending, as shown in *Figure 9*, the low elongation at break for the solution-blended films with 60/40 and 50/50 PES/PMIA compositions is attributed to the absence of interphase adhesion between the PES particles and the PMIA matrix. On the other hand, the PES/PMIA 40/60 and 30/70 blends showed interphase adhesion due to the highly entangled structure, which resulted in ductile films.

Annealing of polymerization-blended films

We recently reported that the crystallization of 44I in a PES/44I solution-blended film with the 30/70 composition was accelerated dramatically by the presence of PES during annealing of the film, and the annealed film exhibited a high modulus (350 MPa) at high temperature (400°C)[16,24]. The accelerated crystallization was ascribed to the increase in chain mobility of 44I effected by blending with PES, probably caused by a decrease in T_g by blending with the low T_g component (PES). In addition, the other contributions are from the partial dissociation of 44I/44I interactions (hydrogen-bonded NH) and the uphill diffusion[25] associated with the liquid/liquid phase separation.

The effect as described above may be expected also for the present PES/PMIA polymerization blend system. That is, the crystallization of PMIA in the blend films would be accelerated remarkably during annealing, resulting in high temperature resistant films. The polymerization-blended films were subjected to annealing at 330°C (above the T_g of PMIA) for 12 h in order to crystallize PMIA. *Figure 10* shows the temperature dependences of the dynamic storage modulus and loss modulus for the non-annealed films of neat PMIA, the polymerization blend and the solution blend with the 50/50 PES/PMIA composition, and *Figure 11* shows the temperature dependences of the dynamic storage modulus and loss modulus for the annealed films. The compatible blend system obtained by polymerization

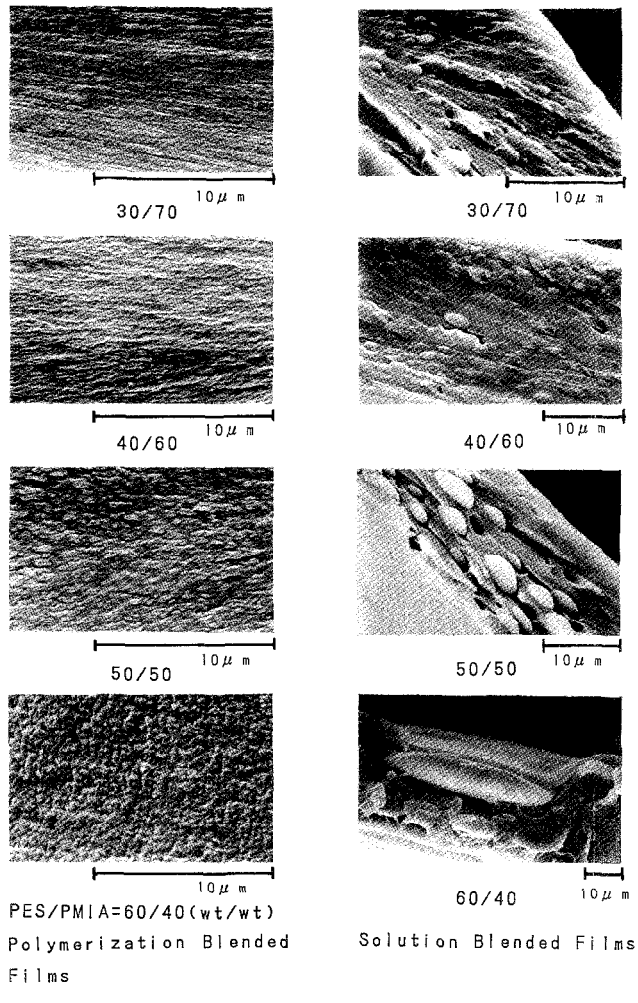


Figure 9 SEM micrographs of the deformed morphology in PES/PMIA blends (fractured surfaces of the tensile specimens) without removal of PES by chloroform

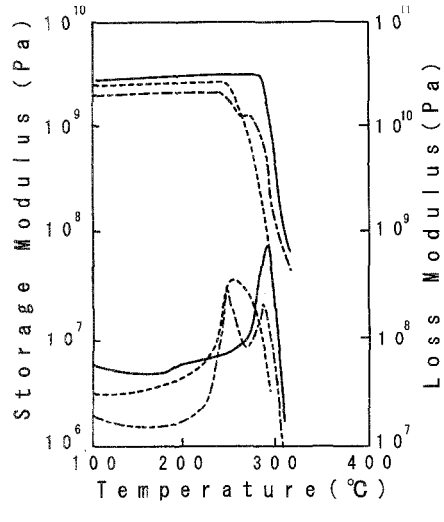


Figure 10 Temperature dependences of the dynamic storage modulus and loss modulus for the non-annealed films: (——) neat PMIA film; (– – –) PES/PMIA 50/50 polymerization-blended film; (– – – – –) 50/50 solution-blended film

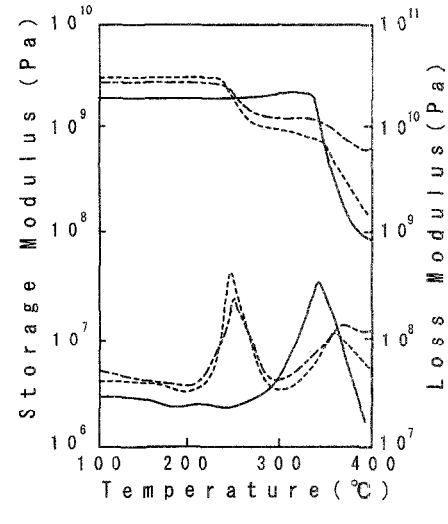


Figure 11 Temperature dependences of the dynamic storage modulus and loss modulus for the annealed films: (——) neat PMIA film; (– – –) PES/PMIA 50/50 polymerization-blended film; (– – – – –) 50/50 solution-blended film

blending showed phase separation upon annealing, and this means that the PES/PMIA polymerization blend system is thermodynamically immiscible. It is apparent that the T_g of PMIA shifts to higher temperature by about 50–80°C in the polymerization-blended film, the solution-blended film and the neat PMIA film upon annealing, and these annealed films exhibit a high modulus (> 1 GPa) at high temperature (300°C) because of their high T_g values. The shift of the T_g towards higher temperature is probably due to the crystallization or

Table 2 Mechanical properties of annealed blend films

PES/PMIA (w/w)	Blending of film	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (GPa)
0/100		161 (105)[a]	9.2 (22)	4.7 (4.0)
30/70	Polymerization	122 (100)	9.2 (108)	3.5 (3.6)
	Solution	123 (86)	4.0 (134)	4.1 (2.8)
50/50	Polymerization	120 (89)	7.4 (130)	3.3 (3.3)
	Solution	120 (86)	6.2 (46)	3.5 (2.6)

[a] The values in parentheses are those of the non-annealed blended films

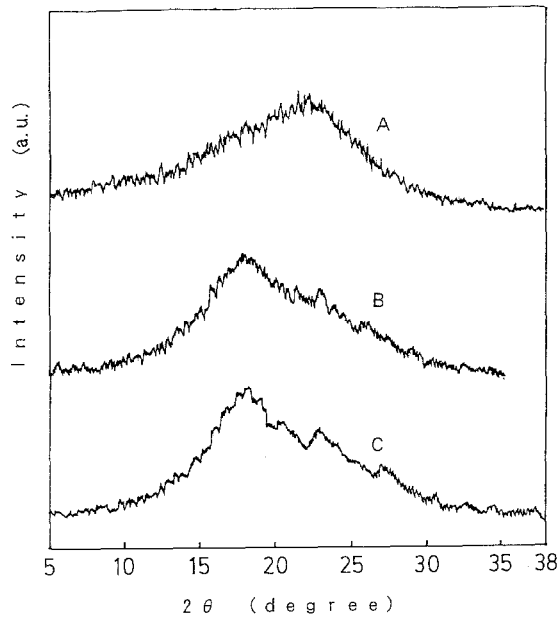


Figure 12 X-Ray diffraction patterns for annealed films: (a) annealed PMIA film; (b) annealed PES/PMIA 50/50 polymerization-blended film; (c) annealed 50/50 solution-blended film

partial crosslinking of PMIA. *Figure 12* shows the X-ray diffraction patterns for the annealed neat PMIA film, the annealed polymerization-blended film and the annealed solution-blended film with the 50/50 PES/PMIA composition. It is evident that the annealed blend film is slightly crystalline, while the annealed neat PMIA film is amorphous. According to the X-ray diffraction patterns, the degree of crystallinity of PMIA for the annealed polymerization-blended film is slightly lower than that for the annealed solution-blended film. The annealed neat PMIA film, the annealed polymerization-blended film and the annealed solution-blended film were quite insoluble in concentrated sulfuric acid. From these results, it can be concluded that the shift in T_g towards higher temperature occurs because of both crystallization and partial crosslinking through annealing for the blend films, whereas the similar shift in T_g for the neat PMIA film occurred only because of crosslinking[26].

Mechanical properties of the annealed polymerization-blended films

The tensile properties of the annealed blend films are summarized in *Table 2*. It is noteworthy that the tensile strength of both the neat PMIA and the blend films could be improved greatly by annealing, while the elongation at break was drastically lowered. The tensile modulus of both the neat PMIA and the solution-blended films increased upon annealing, but that of the polymerization-blended films did not increase. The increases in the tensile strength and modulus are attributed to the partially crystalline and/or crosslinked structures of the aramid component.

CONCLUSIONS

It was found that the compatibility of the binary mixture of PES and PMIA was greatly improved by the polymerization blending method. The polymerization blending gave films having better tensile properties than films from solution blending, especially a high elongation at break over a relatively wide PES/PMIA composition range. Therefore, this method is advantageous over solution blending and widely applicable to improve the compatibility of many immiscible blend systems and the tensile properties of blend films as well.

Both the annealed polymerization-blended films and the annealed solution-blended films afforded high temperature resistant films with high tensile modulus and high tensile strength owing to partially crystalline and crosslinked structures. Therefore, the PES/PMIA blended films are considered to be promising high temperature plastic films.

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