Miscibility, crystallization behaviour and mechanical properties of binary blends of aramids and poly(ether sulphone)s

Shoichi Nakata, Masa-aki Kakimoto and Yoshio Imai*
Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Meguro-ku, Tokyo 152, Japan

(Received 7 October 1991; revised 4 December 1991; accepted 16 December 1991)

The transparent solution blends of aramids and poly(ether sulphone)s in *N,N*-dimethylacetamide or *N*-methyl-2-pyrrolidone were obtained from three kinds of commercially available poly(ether sulphone)s and two kinds of aramids derived from isophthaloyl chloride and both 4,4′- and 3,4′-diaminodiphenyl ether. The as-prepared polymer blend films were transparent or somewhat translucent. Some of the blend films showed 'blend induced crystallization' behaviour, giving high temperature resistant films after annealing at 300°C. The tensile properties of the as-prepared and annealed blend films were investigated.

(Keywords: high temperature polymer blends; aramid/PES blends; miscibility; phase separation; crystallization behaviour; mechanical properties)

INTRODUCTION

Polymer blends are valuable means to improve the properties of the component polymers, and some blends have been marketed commercially. In addition, much attention is now being devoted to high temperature polymer blends for high performance applications. Binary polymer blends such as poly(ether sulphone) (PES)/poly(phenylene sulphide)[1], PESs/poly(ether ketone)s[2–6], poly(ether ketone)s/poly(ether imide)[7,8], poly(amide imide)/aramid[9], polyimides/polyimides[10,11], polybenzimidazole/polyimides[12–18] and polybenzimidazole/polyarylate[19] have been reported quite recently in the literature.

We recently found that a homogeneous mixture of aramid 44I, poly[*N,N*′-(oxydi-*p*-phenylene)isophthalamide], and PES E, poly(oxy-*p*-phenylenesulphonyl-*p*-phenylene), exhibited interesting crystallization behaviour; the crystallization of the aramid was induced and accelerated dramatically by blending with the PES, and the crystallized blend films exhibited high temperature resistance up to 400°C[20,21]. This was ascribed to the elevation of chain mobility of the aramid caused both by the decrease of the glass transition temperature (T_g) with blending a low T_g PES and by the partial dissociation of hydrogen bonding, and to the uphill diffusion associated with the liquid–liquid phase separation as well. Similar 'blend induced crystallization' behaviour has been reported quite recently by Nishimoto *et al.*[22].

This paper expands on the binary blends composed from combinations of two aramids and three PESs to elucidate the effect of the chemical structure of the component polymers for the blend systems on miscibility. In addition, the crystallization of behaviour and In addition, the crystallization behaviour and mechanical properties of the binary blend systems are described.

EXPERIMENTAL

Materials

Three kinds of commercially available PESs (PES E, PES U and PES R) were supplied by ICI Ltd and Amoco Performance Products Inc., and used as received (after drying). The structures, sources, inherent viscosities and T_gs of these PESs are summarized in *Table 1*.

Two aramids (44I and 34I) were synthesized by a conventional low temperature solution polycondensation method[23], starting from isophthaloyl chloride and both 4,4′- and 3,4′-diaminodiphenyl ether, respectively. A typical procedure for the synthesis of aramid 44I is as follows. In a 200 ml round-bottom flask equipped with a mechanical stirrer were placed 4,4′-diaminodiphenyl ether (10.0 g, 0.05 mol) and *N*-methyl-2-pyrrolidone (NMP, 100 ml). The solution was chilled with an ice–water bath. To the solution was added solid isophthaloyl chloride (10.2 g, 0.05 mol) and the solution was stirred at 0°C for 3 h under nitrogen. The viscous solution thus obtained was poured into methanol. The precipitated polymer was collected, washed with refluxing methanol and dried under vacuum. The polymer was further purified by reprecipitation from *N,N*-dimethylacetamide (DMAc) solution with water. *Table 2* lists the structures, inherent viscosities and T_gs of the aramids synthesized.

The solvents such as DMAc and NMP, employed for solution blending, were purified by vacuum distillation.

Preparation of blend films

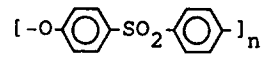
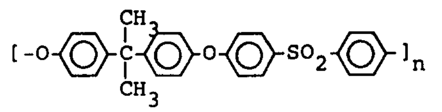
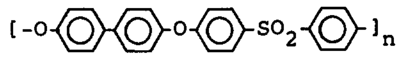
An aramid and a PES were dissolved individually in DMAc or NMP at a concentration of 15 wt%. These

---

* To whom correspondence should be addressed

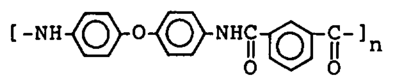
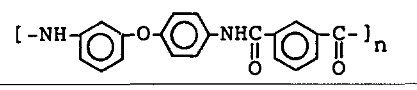
0032-3861/92/183873-05

Table 1 PESs used

PES	Structure	η_{inh}[a] (dl g^{-1})	T_g[b] (°C)	Remarks
E		0.41	220	Victrex PES 4800P (ICI)
U		0.51	187	Udel P-1800NT (Amoco)
R		0.42	218	Radel A-2000NT (Amoco)

[a] Measured at a concentration of 0.5 g dl^{-1} in DMAc at 30°C
[b] By d.s.c. at a heating rate of 20°C min^{-1} in nitrogen

Table 2 Aramids used

Aramid	Structure	η_{inh}[a] (dl g^{-1})	T_g[b] (°C)
44I		1.5	264
34I		1.1	240

[a] Measured at a concentration of 0.5 g dl^{-1} in DMAc at 30°C
[b] By d.s.c. at a heating rate of 20°C min^{-1} in nitrogen

Table 3 Miscibility of ternary aramid/PES/solvent systems[a]

		PES		
Aramid	Solvent	E	U	R
44I	NMP	M	M	M
	DMAc	M	M	M
34I	NMP	M	M	M
	DMAc	M	I	M/I[b]

[a] Miscibility was determined for compositions of aramid/PES = 70/30 and 40/60, and of polymer/solvent = 15/85 (wt%). M, solution was homogeneous; I, solution was heterogeneous
[b] Aramid/PES = 70/30 was M and 40/60 was I

two solutions were mixed and the mixed solution was stirred at room temperature for 24 h for stabilization. The solution was then cast on a glass plate. The cast film was dried under vacuum at room temperature for 24 h, then at 100°C for 24 h, and finally at 230°C for 24 h for complete removal of the solvent. The final film thickness was ~60 μm. The blend compositions studied were 70/30 and 40/60 aramid/PES (w/w).

Annealing of blend films

The as-prepared blend films were annealed at 300°C for 12 h in a vacuum oven.

Measurements

Inherent viscosity of the polymers was measured in DMAc at a concentration of 0.5 g dl^{-1} at 30°C with an Ostwald viscometer. I.r. spectra were recorded with a JASCO *FT*i.r.-5000 spectrophotometer. D.s.c. was performed with a Shimadzu thermal analyzer DSC-41M at a heating rate of 20°C min^{-1} in nitrogen. The reported T_g values are those measured as the onset and the values of the crystallization temperature (T_c) are the exothermic peak maximum. Dynamic thermomechanical analysis (d.m.a.) was performed with a Toyoseiki Rheolograph-Solid in tensile mode at a frequency of 10 Hz and at a heating rate of 2°C min^{-1}. Tensile properties of the films were determined from stress–strain curves obtained with an Orientech Tensilon UTM-II-20 at a strain rate of 20% min^{-1}. Measurements were performed at room temperature with film specimens 5 mm wide, 50 mm gauge length and 60 μm thick.

RESULTS AND DISCUSSION

Miscibility of ternary aramid/PES/solvent mixtures

An aramid and a PES were mixed in solution in DMAc or NMP with compositions of 70/30 and 40/60 for aramid/PES and 15/85 for polymer/solvent (wt%). *Table 3* gives the miscibility of the ternary mixtures of the aramid/PES/solvent system. All the systems containing NMP were miscible. In addition, the aramid 44I/PES/DMAc systems were also miscible, whereas aramid 34I showed lower miscibility with PESs in DMAc. NMP gave clear homogeneous solutions compared with DMAc, and this is probably because NMP was a better solvent for these aramids than DMAc. These results suggested the following miscibility trends: aramid 44I > aramid 34I and PES E > PES R > PES U. The second trend is ascribed to polar effects of the PESs. That is, the more polar PES is favoured for the blend systems, because the polarity of the PESs is lower than that of the aramids. The first trend seems to be more

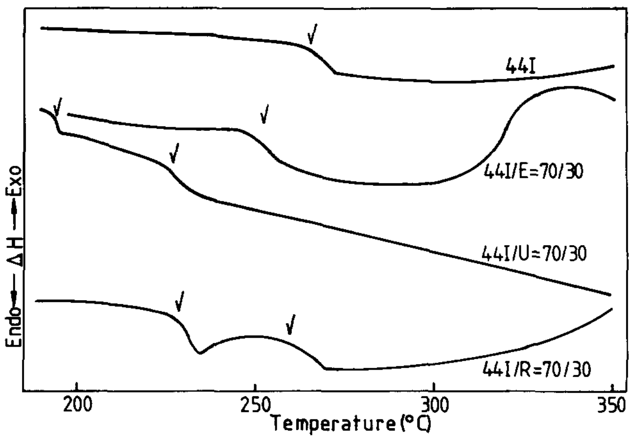


Figure 1 D.s.c. thermograms of the blend films

Table 4 Thermal behaviour of the blend films[a]

	D.s.c.				
	First scan			Second scan	
Composition	T_g (°C)		T_c (°C)	T_g (°C)	
441/E					
70/30	245		333	222	257
40/60	225	254	—	226	264
441/U					
70/30	193	240	—	182	260
40/60	190	259	—	186	263
441/R					
70/30	228	260	—	215	260
40/60	225	258	343	218	260
341/E					
70/30	216	228	—	220	240
40/60	218	236	—	217	236
341/R					
70/30	223	235	—	216	236

[a] Cast from the DMAc solution

complicated, and a delicate difference of the interaction between the aramids and PESs may be responsible.

Compatibility of binary aramid/PES blends

The ternary solutions were cast onto glass plates giving blend films. All the as-prepared films were transparent or somewhat translucent. These films were subjected to thermal characterization using d.s.c. and d.m.a. *Figure 1* shows the d.s.c. curves for representative aramid/PES blends, and the thermal behaviour is summarized in *Table 4*. The d.s.c. data indicated that homogeneous mixing at molecular level, evidenced by a single T_g, was only achieved in the 70/30 aramid 441/PES E system. The rest of the blend systems gave double T_gs corresponding to two phases.

The i.r. spectra of the blend films showed an apparent blue shift, indicating dissociation of hydrogen bonding between amide groups (*Table 5*). Since the dissociation is caused by dilution of aramid molecules, the larger value of the blue shift implies higher compatibility. In addition, the blue shift implies enthalpy loss relating to the dissociation of hydrogen bonding, and hence to the thermodynamic immiscibility of the binary systems.

Consequently, the following trends of compatibility are apparent: aramid 441 > aramid 341 and PES E > PES R > PES U. We believe that the miscibility of the ternary blend systems reflects the compatibility of the binary polymer blends.

All the blend systems showed two T_gs which are very close to those of the pure component polymers from the second scan (*Table 4*). This clearly indicated that the phase separation was facilitated during the first scan up to 350°C, and that the binary systems are thermodynamically immiscible. The freezing of metastable homogeneous states is often observed in polymer blend experiments using the solution casting method[22,24], particularly when the evaporation speed is relatively high[24]. In the present case, the low molecular mobility nature of such stiff chains may hinder the phase separation of the ternary systems.

Crystallization behaviour of binary aramid/PES blends

As can be seen from *Figure 1*, the 70/30 aramid 441/PES E blend exhibited a remarkable exothermic peak at 333°C due to crystallization of the aramid, and a gradual exothermic shift was observed near 350°C for both the aramid 441/PES R blend and neat aramid 441. The results indicated that the aramid 441/PES E blend had the highest rate of crystallization. The aramid 441/PES R blend crystallized more slowly, but was still faster than neat aramid 441. The aramid 441/PES U blend did not crystallize during the d.s.c. scan. This strongly suggested that homogeneous mixing of polymer molecules is essential for the acceleration of crystallization accompanied by phase separation.

The aramid 441 based blend films were subjected to annealing at 300°C (above the T_g of the aramid) for 12 h in order to crystallize the aramid completely. The aramid 441/PES E and aramid 441/PES R blend films became translucent by annealing, but remained tough and gained high temperature resistance up to 400°C (*Figure 2*). On the other hand, the aramid 441/PES U blend film became very brittle. The trend of high temperature resistance shown in *Figure 2* is the same as that of the crystallizability of the blend systems discussed above. Therefore, the acceleration of crystallization of the polymer blends probably causes high crystallinity and its fine dispersion of crystals of the aramid, resulting in the toughness and high temperature resistance of the blend films.

The annealed aramid 441/PES E and aramid 441/PES R blend films as well as annealed neat aramid 441 films showed a strong absorption near 3285 cm^{-1} for the N–H stretching band in the i.r. spectra. We believe this

Table 5 Wavenumbers at the N–H stretching absorption maximum of the blend films[a]

	Wavenumber (cm^{-1})	
Composition	As-prepared film	Annealed film[b]
441	3304	3284
441/E		
70/30	3324	3280
441/U		
70/30	3316	—
441/R		
70/30	3321	3285
341	3306	—
341/E		
70/30	3308	—

[a] Cast from the DMAc solution
[b] Annealed at 330°C for 12 h

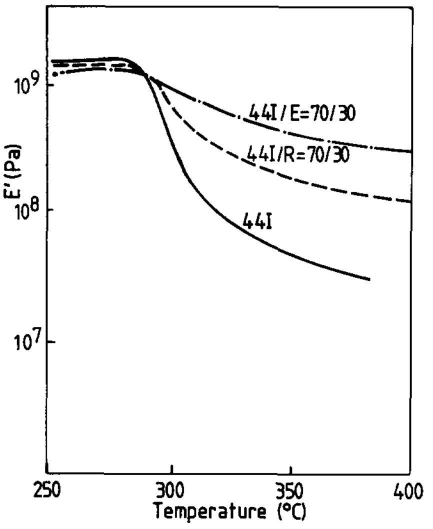


Figure 2 Storage modulus curves of the blend films

Table 6 Mechanical properties of the blend films (441 series)[a]

Composition	Film[a]	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (GPa)
441	A.p.	115	9.7	3.0
	Ann.	99	7.8	3.1
441/E				
70/30	A.p.	72	13.0	2.1
	Ann.	85	8.6	2.1
40/60	A.p.	72	33.0	2.0
	Ann.	72	5.8	1.9
441/U				
70/30	A.p.	70	23.0	2.5
40/60	A.p.	72	25.0	2.2
441/R				
70/30	A.p.	76	33.0	2.6
	Ann.	82	16.0	2.8
40/60	A.p.	84	45.0	2.0
	Ann.	87	8.6	2.4
E	A.p.	88	7.8	2.6
U	A.p.	67	6.1	2.0
R	A.p.	74	5.0	1.9

[a] A.p., as-prepared film; Ann., film annealed at 300°C for 12 h

Table 7 Mechanical properties of the blend films (341 series, as-prepared)

Composition	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (GPa)
341	99	9.0	3.0
341/E			
70/30	96	7.9	2.8
40/60	77	31.0	2.6
341/R			
70/30	68	6.2	2.2
E	88	7.8	2.6
R	74	5.0	1.9

absorption is assigned to N–H groups in aramid 441 crystals.

The neat aramid 341 and the aramid based blend films did not crystallize in any of the conditions used, and hence aramid 341 is believed to be essentially amorphous.

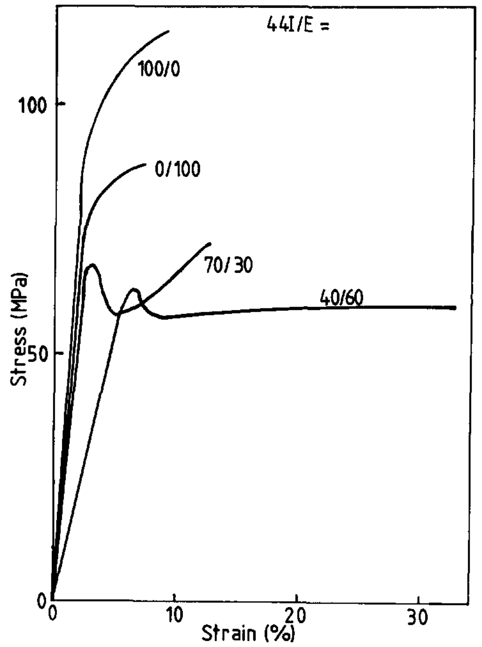


Figure 3 Stress–strain curves of the as-prepared aramid 441/PES E blend films

Mechanical properties of binary aramid/PES blend films

The tensile properties of the aramid/PES blend films are shown in *Tables 6* and *7* and in *Figure 3*. It is noteworthy that the elongation at break of the PESs could be improved greatly by blending with aramids, while both tensile strength and modulus were lowered. The increase in the elongation is attributed to necking behaviour of the blend films. The neat aramid films showed low elongation after yielding, and neat PES cast films broke without yielding.

The annealing resulted in a marked decrease of the elongation with recovery of some of the losses of the strength and modulus, and hence the annealed blend films still retained a sufficiently high level of tensile properties.

CONCLUSIONS

The solution blending of three kinds of commercially available PESs and two aramids (441 and 341) in DMAc or NMP afforded transparent blend solutions, which in turn gave transparent or somewhat translucent polymer blend films. Some of the blends, especially the 70/30 aramid 441/PES E system, showed 'blend induced crystallization' behaviour, giving high temperature resistant films after annealing at 300°C. The as-prepared blend films obtained from aramid 441 and the PESs were transparent and tough. Annealing afforded good quality translucent blend films. Therefore, these aramid/PES blend films can be used as high temperature plastic films.

REFERENCES

1 Zeng, H. and Mai, K. *Makromol. Chem.* 1986, **187**, 1787
2 Sham, C. K., Lae, C. H., Williams, D. J., Karasz, F. E. and MacKnight, W. J. *Br. Polym. J.* 1988, **20**, 149
3 Guo, Q., Huang, J. and Chen, T. *Polym. Bull.* 1988, **20**, 517
4 Guo, Q., Huang, J., Chen, T., Zhang, H., Yang, Y., Hou, C. and Feng, Z. *Polym. Eng. Sci.* 1990, **30**, 44
5 Wu, Z., Zheng, Y., Yu, X., Nakamura, T. and Yosomiya, R. *Angew. Makromol. Chem.* 1989, **171**, 119
6 Wu, Z., Zheng, Y., Yan, H., Nakamura, T., Nozawa, T. and Yosomiya, R. *Angew. Makromol. Chem.* 1989, **173**, 163

7 Harris, J. E. and Robeson, L. M. *J. Appl. Polym. Sci.* 1988, **35**, 1877

8 Crevecoeur, G. and Groeninckx, G. *Macromolecules* 1991, **24**, 1190

9 Yamada, K., Mitsutake, T., Takayanagi, M. and Kajiyama, T. *J. Macromol. Sci. Chem.* 1989, **A26**, 891

10 Yokota, R., Horiuchi, R., Kochi, M., Soma, H. and Mita, I. *J. Polym. Sci., Polym. Lett. Edn* 1988, **26**, 215

11 Mita, I., Kochi, M., Hasegawa, M., Iizuka, T., Soma, H., Yokota, R. and Horiuchi, R. 'Polyimides: Materials, Chemistry and Characterization' (Eds C. Feger, M. M. Khojasteh and J. E. McGrath), Elsevier, Amsterdam, 1989, pp. 1–24

12 Leung, L., Williams, D. J., Karasz, F. E. and MacKnight, W. J. *Polym. Bull.* 1986, **16**, 457

13 Guerra, G., Williams, D. J., Karasz, F. E. and MacKnight, W. J. *J. Polym. Sci., Polym. Phys Edn* 1988, **26**, 301

14 Stankovic, S., Guerra, G., Williams, D. J., Karasz, F. E. and MacKnight, W. J. *Polym. Commun.* 1988, **29**, 14

15 Guerra, G., Choe, S., Williams, D. J., Karasz, F. E. and MacKnight, W. J. *Macromolecules* 1988, **21**, 231

16 Musto, P., Karasz, F. E. and MacKnight, W. J. *Polymer* 1989, **30**, 1012

17 Grobelny, J., Rice, D. M., Karasz, F. E. and MacKnight, W. J. *Macromolecules* 1990, **23**, 2139

18 Lee, D. S. and Quin, G. *Polym. J.* 1989, **21**, 751

19 Chung, T. and Chen, P. N. *Polym. Eng. Sci.* 1990, **30**, 1

20 Nakata, S., Kakimoto, M., Imai, Y. and Inoue, T. *Polym. J.* 1990, **22**, 80

21 Matsuura, M., Saito, H., Nakata, S., Imai, Y. and Inoue, T. *Polymer* 1992, **33**, 3210

22 Nishimoto, M., Keskkula, H. and Paul, D. R. *Polymer* 1991, **32**, 272

23 Morgan, P. W. *Macromolecules* 1977, **10**, 1381

24 Imoue, T., Ougisawa, T., Yasuda, O. and Miyasaka, K. *Macromolecules* 1985, **18**, 57