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Compatibilizing effect of polyarylate–polyamide-6 block copolymers on polyarylate/polyamide-6 blends: 2

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Ternary blends of polyarylate (PAr), polyamide-6 (PA-6) and PAr–PA-6 block copolymer were prepared by the dissolution/precipitation method or by melt blending. The compatibilizing effect of PAr–PA-6 block copolymer was observed with scanning electron microscopy and differential scanning calorimetry. The inward shift of the glass transition temperature (T_g) of PAr and PA-6 and the depression of the melting temperature (T_m) of PA-6 in ternary blends depended on the block length as well as on the amount of the block copolymer added. The shorter block length and the higher amount of block copolymer added caused greater shifts of T_g and T_m. The compatibilizing effect of the block copolymer was also confirmed from the enhanced mechanical properties. Copyright © 1996 Elsevier Science Ltd.

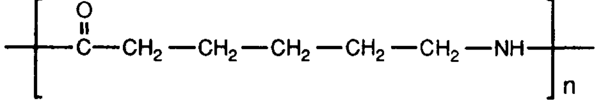
(Keywords: compatibilizing effect; polyarylate–polyamide-6 block copolymer; ternary blends)

INTRODUCTION

The physical properties of immiscible polymer blends can be improved by compatibilizers, which modify the interfacial conditions between the phases[1,2]. In a blend of A and B polymers, a block copolymer with segments A and B can be used as a compatibilizer.

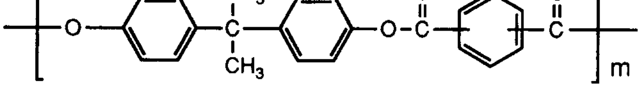
Polyamide-6 and bisphenol A polyarylate (PAr), an amorphous copolyester of isophthalic/terephthalic acid (1/1) mixture, are important engineering plastics with favourable properties and have the following chemical structures.

polyamide-6 :



$$\left[\overset{O}{\overset{\|}{C}} - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - NH \right]_n$$

PAr :



The good points of the PAr and PA-6 can be combined by the blend technology. However, PAr and PA-6 have been reported to be basically immiscible[3], although there is some evidence of partial mixing and adhesion between the segregated phases. According to our investigations[4], the dispersed particles of one polymer within the matrix of the other had diameters of 1–3 μm, which is in the range of heterogeneity enough to cause damage to the mechanical properties of blended materials. Blends of polycarbonate (similar to PAr in chemical structure) and PA-6 represented, throughout experiments measuring the various kinds of mechanical properties[5,6], a strong negative deviation from the values predicted by the linear additivity which is generally expected for miscible blend systems.

In our previous study[4], we synthesized and characterized the PAr–PA-6 block copolymer having various block lengths, and obtained fundamental data on the binary blends of PAr–PA-6 block copolymer with PAr and PA-6 homopolymer. It was suggested that the majority of block copolymers have PA-6–PAr–PA-6 triblock structure (*Table 1*). It is the goal of this research to examine the effect of the PAr–PA-6 block copolymer on the thermal, morphological and mechanical behaviour of immiscible PAr/PA-6 blends. These data may provide a useful guide to obtain PAr/PA-6 blends with improved properties from virgin or recycled resins.

Differential scanning calorimetry (d.s.c.) measurements were performed using a Perkin–Elmer DSC-4 instrument at heating and cooling rates of 20°C min^{-1} with a sensitivity of 42 mJ. Temperature calibration was

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Table 1 Characteristics of PA-6–PAr–PA-6 triblock copolymer

Designation	M_n of PAr block (Kg mol^{-1})	M_n of PA-6 block (Kg mol^{-1})	η_{inh} of block copolymer (dl g^{-1})	PAr content (wt%)
ARNY 1-1	1.5	3.0	0.627	24.3
ARNY 1-2	1.5	3.7	0.758	20.1
ARNY 1-3	1.5	4.2	0.815	18.0
ARNY 1-4	1.5	5.0	0.830	15.5
ARNY 2-2	2.9	3.8	0.734	29.5

η_{inh} = inherent viscosity

Table 2 Thermal properties of PAr/PA-6 blends (70/30) with various amounts of PAr–PA-6 block copolymer (ARNY 1-2)

ARNY 1-2 (phr)	$T_{g,PAr}$ (°C)	$T_{g,PA}$ (°C)	T_m (°C)	T_c (°C)	$T_m - T_c$ (°C)
0	189	49	221	173	48
2	185	51	215	172	43
5	180	54	211	170	41
10	170	58	211	167	44
20	167	63	208	159	49
50	161	62	205	144	61

performed with indium standard. All runs were carried out using samples of *ca.* 13 mg in N_2 atmosphere. Before scanning, samples were quenched to −20°C in a d.s.c. cell after maintaining for 5 min at 240°C to erase the previous thermal history. The glass transition temperature of the PA-6 phase ($T_{g,PA}$) and the PAr phase ($T_{g,PAr}$), and the melting temperature (T_m) of the PA-6 were measured on subsequent heating to 240°C. The crystallization temperature (T_c) was measured during the next cooling cycle from 240°C.

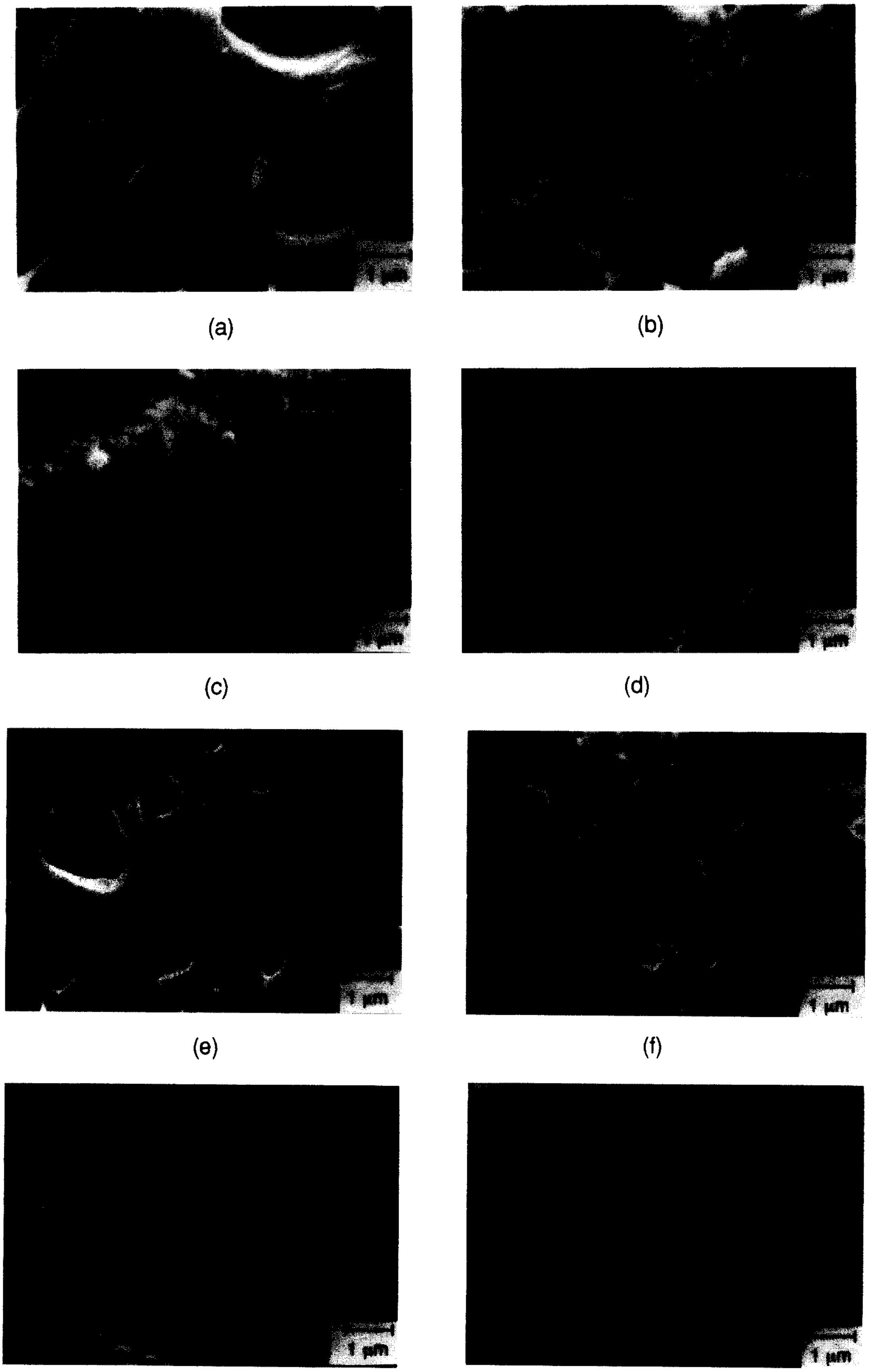
Scanning electron microscopy (SEM) of the blends was performed on a Jeol SEM (JSM-35CF) at an acceleration voltage of 25 kV. Samples were prepared by fracturing the mixture cryogenically in liquid nitrogen or by etching the PAr phase with chloroform in the case when PAr was the minor component, and the PA-6 phase with 5% LiCl–methanol in the case when PA-6 was the minor component by refluxing for 72 h.

Stress–strain measurements of a dumbbell-shaped specimen prepared by injection moulding, of dimensions 160 × 19 mm with thickness 1.6 mm, were accomplished using an Instron 6022, employing a cross-head speed of 16.8 mm min^{-1} at room temperature. The Izod impact strength of the notched samples was measured using an Tinius Olsen model of the Izod impact tester. The density was measured with Toyoseiki's densitometer at 20°C.

RESULTS AND DISCUSSION

SEM was used to observe the morphology change of the blends by the compatibilizing effects of the block copolymer added. *Figure 1* represents the morphology of the etched surface of the ternary blends containing various amounts of block copolymer (ARNY 1-2) up to 10 phr. The morphology of PAr/PA-6 blends without block copolymer shows the phase separation and the size of dispersed domains is about 1–3 μm in both PAr and PA-6 rich compositions. The result of the microscopic observation is coincident with the previous report[3] informing some degrees of mixing between PAr and PA-6. With the addition of a small amount of block copolymer, the sizes of the etched out dispersed phases represented by the dark holes are reduced notably below 1 μm. The morphology of the blend containing 10 phr block copolymer appears homogeneous at this microscopic observation scale and no distinctive hole is observed. It can be clearly seen that the addition of the block copolymer reduces the domain size of the minor component within the matrix of the major component, and that the decrease of particle size is sensitive to the amount of copolymer added. The result suggests the reduction of interfacial tension between the segregated phases. The cryogenically fractured surfaces of the blends are displayed in *Figure 2*, showing morphology similar to the microscopic results observed with the etching technique. In the simple binary blends (*Figure 2a* and *c*), the voids at the interface of the separated phases can be observed.

The thermal properties of the blends containing various amounts of PAr–PA-6 block copolymer (ARNY1-2) up to 50 phr at a composition of PA/PA-6 of 70/30 are presented in *Table 2*. An inward migration in the glass transition temperatures of both PAr and PA-6 phases is observed with the addition of a small amount of copolymer, indicating the increase of the extent of mixing between PAr and PA-6. The glass transition temperatures do not vary much as the amount of block copolymer increases above 10 phr. T_m and T_c decrease steadily as the amount of copolymer increases. The depression of T_m is thought to be caused by the enhanced mutual dissolution between PAr and PA-6 molecules. When the miscibility of polymer blends increases, the increased interface may enhance nucleation for crystallization, whereas dilution by dissolving the other component may



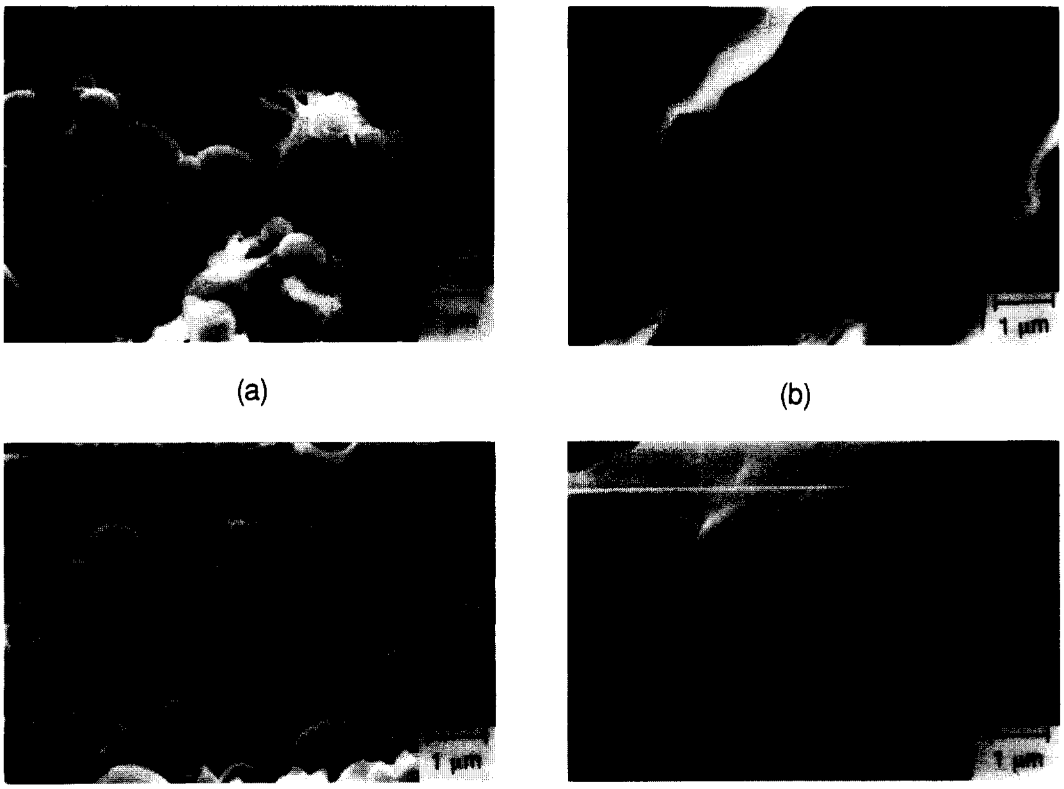
(a) (b)

(c) (d)

(e) (f)

(g) (h)

Figure 1 SEM photographs of etched surfaces of blends containing: (a) 0, (b) 2, (c) 5 and (d) 10 phr ARNY 1-2 (weight ratio of PAr/PA-6 is 30/70), and (e) 0, (f) 2, (g) 5 and (h) 10 phr ARNY 1-2 (weight ratio of PAr/PA-6 is 70/30)



(a) (b)

(c) (d)

Figure 2 SEM photographs of cryogenically fractured surfaces of blends containing: (a) 0 and (b) 5 phr ARNY 1-2 (weight ratio of PAr/PA-6 is 30/70), and (c) 0 and (d) 5 phr ARNY 1-2 (weight ratio of PAr/PA-6 is 70/30)

hinder crystallization procedures. The decreased supercooling for crystallization ($T_m - T_c$) in *Table 2*, when small amounts of PAr–PA-6 block copolymer were added, suggests that the enhanced nucleation is predominant over the dilution effect. The increased supercooling at high content of PAr–PA-6 block copolymer suggests a predominant dilution effect in blends with high mutual dissolution.

The thermal properties of blends at the whole range of compositions, with and without 10 phr block copolymer, are shown in *Table 3*. The PAr/PA-6 blends with no block copolymer represent the two separated T_gs corresponding to those of homopolymers, as in typical immiscible blends, and this result is entirely coincident with the previous results of Iruin *et al.*[3], except that the T_g of the PAr phase decreases more. The reduction of $T_{g,PAr}$ by some degree seems to be due to partial dissolution of PA-6 segments into the PAr domain. Little change of $T_{g,PA}$ from that of the PA-6 homopolymer (48°C) shows that the dissolution of PAr segment into PA-6 domain is limited. The enhanced shift of T_g by the addition of block copolymer suggests that the compatibilizing effect of block copolymer enhances the extent of dissolution of each homopolymer into the other domain quite effectively. The greater depression of T_m in compatibilized blends compared with that of simple blends indicates the increased miscibility due to the added block copolymer and the consequent premature melting of the PA-6 crystal. The compatibilized blends generally have decreased values of $T_m - T_c$ except at high PAr content, probably due to the enhanced rate of nucleation for crystallization of PA-6 caused by the increased area of interface in compatibilized blends.

It was also of interest to investigate how the thermal properties of blends could be influenced by the different

Table 3 Thermal properties (°C) of PAr/PA-6 blends with and without 10 phr of PAr–PA-6 block copolymer (ARNY 1-2)

	Without block copolymer					With 10 phr block copolymer				
PAr/PA-6 (by weight)	$T_{g,PAr}$	$T_{g,PA}$	T_m	T_c	$T_m - T_c$	$T_{g,PAr}$	$T_{g,PA}$	T_m	T_c	$T_m - T_c$
0/100	–	48	223	177	46	–	–	–	–	–
10/90	–	49	222	176	46	–	56	220	174	46
30/70	–	49	222	174	48	–	57	215	172	43
50/50	184	49	221	174	47	171	58	212	170	42
70/30	189	49	221	173	48	170	58	211	167	44
90/10	198	49	220	170	50	183	58	209	155	54
100/0	205	–	–	–	–	–	–	–	–	–

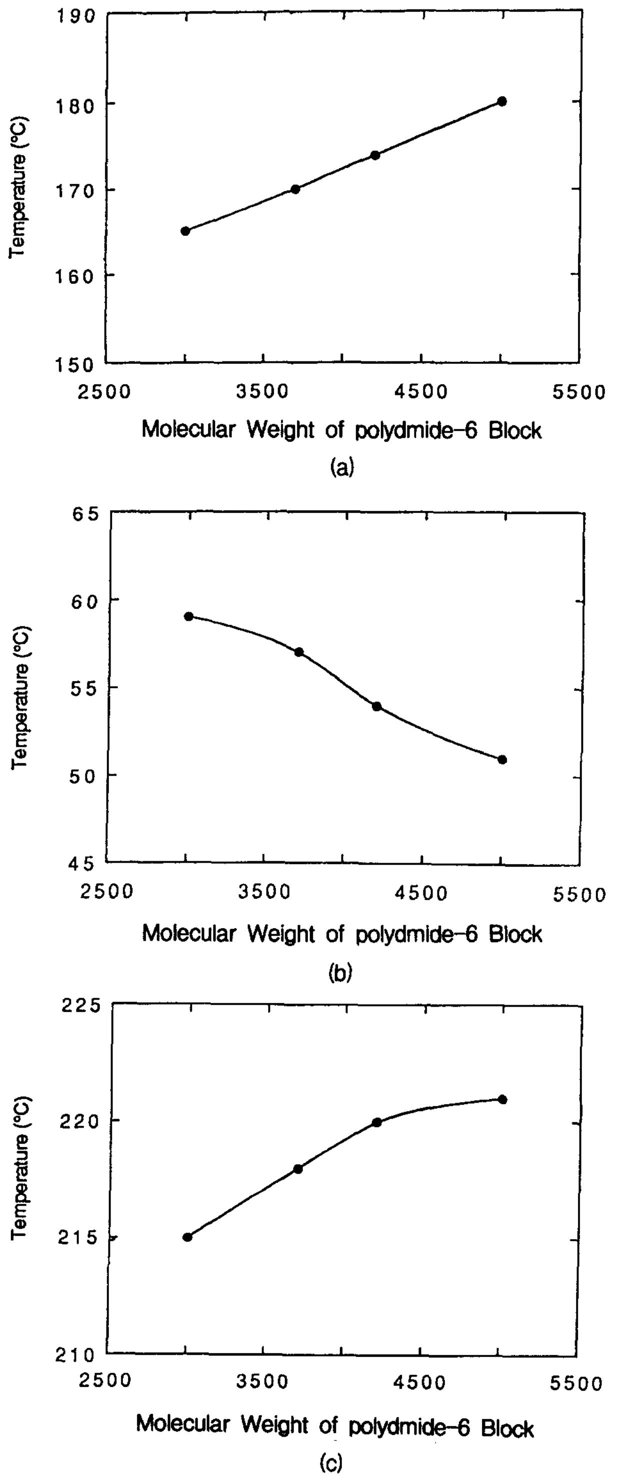


Figure 3 (a) $T_{g,PAr}$, (b) $T_{g,PA}$ and (c) T_m of PAr/PA-6/PAr-PA-6 block copolymer (50/50/10) ternary blends at various molecular weights of PA-6 block

block lengths of block copolymer. The thermal properties of blends containing block copolymers with various PA-6 block lengths (ARNY 1-1, 1-2, 1-3, and 1-4) are illustrated in *Figure 3*. The T_m depression and the inward shifts of the $T_{g,PAr}$ and $T_{g,PA}$ are more evident with the block copolymer with shorter PA-6 block. According to the studies on compatibilizing capacities of block copolymers with different block lengths in incompatible blend systems[7,8], the block copolymers can exist both at the interface of segregated phases and within the bulk of the dispersed or matrix phase. The block copolymers located at the interface, with constituent blocks being diffused into the corresponding phase of the same chemical structure or molecular level miscibility, promote the miscibility by reducing the interfacial tension. The distribution of the block copolymers' location is governed by the block length and the amount of block copolymer, as well as the degree of miscibility between the component polymers. The more prominent shifts of T_m and T_g in the blend, including the block copolymer with shorter block length (as shown in *Figure 3*) gives clues for the deduction that the block copolymer with shorter block length is easily migrated to the interfaces of the segregated phases. In the blend of polystyrene and polycarbonate compatibilized with polystyrene-*b*-polycaprolactone block copolymer, the block copolymer composed of shorter blocks had been reported to be more effective in making the segregated phases homogeneous on microscopic observation[9].

The density of the blend modified by the block copolymer (ARNY2-2) and the uncompatibilized one is shown in *Figure 4*. The sample for the density measurement was obtained from the injection moulded specimen. The density of the immiscible blends is lower than the weight average values of the constituent polymers. The negative deviation of the density is thought to mainly stem from the voids existing at the interface of the segregated phases (see *Figures 2a* and *c*). Similar negative deviation of density by the void at the interface in the immiscible blend was observed in amorphous polymer blend[2]. With a small addition of the block copolymer, the density approaches the weight average value, which suggests effective compatibilization of the block copolymer, promoting adhesivity between the segregated phases.

To investigate the effect of the block copolymer on the mechanical performance, stress–strain experiment was undertaken, since the mechanical properties of the blends are primarily affected by the miscibility of the blend system. The results on the tensile modulus and elongation at break are shown in *Figures 5a* and *b*. The tensile moduli of the uncompatibilized blends show a considerably unfavourable negative deviation. According to the studies on the elastic modulus of the immiscible

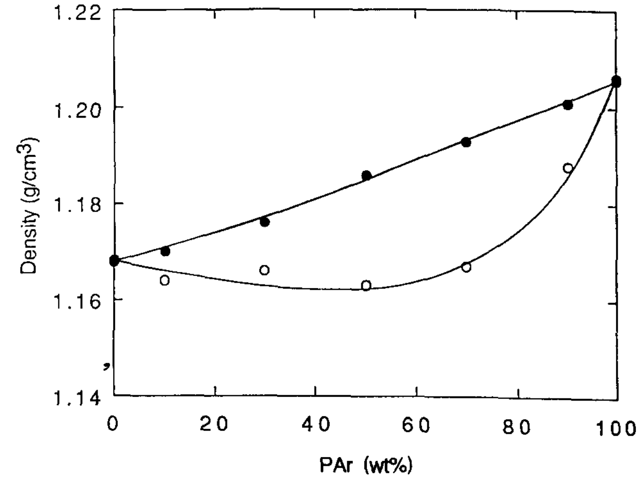


Figure 4 Density of PAr-PA-6 blends with (●) and without (○) 5 phr of ARNY 2-2

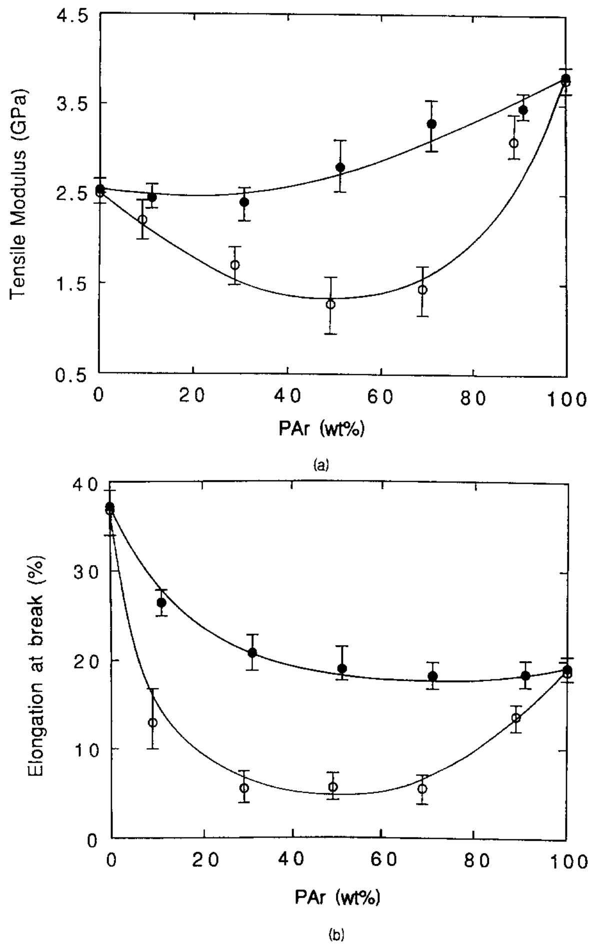


Figure 5 (a) Tensile moduli and (b) elongation at break of PAr/PA-6 blends with (●) and without (○) 5 phr of ARNY 2-2

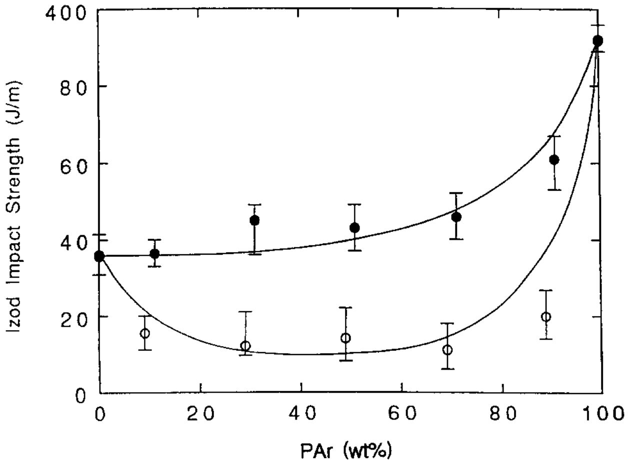


Figure 6 Izod impact strength of PAr/PA-6 blends with (●) and without (○) 5 phr of ARNY 2-2

blend [6,10], the adhesivity at the interface of the matrix and dispersed particles controls the extent of the deviation below the straight line connecting the values of the homopolymers' moduli, indicating those obtainable for miscible blends. In *Figure 5a*, the increment of modulus toward the average value by the addition of block copolymer suggests enhanced adhesivity between the phases, which is a trend analogous with the density behaviour. Elongation at break has been perceived to vary susceptibly according to the extent of micro separation of segregated phases. The uncompatibilized blends show brittle fracture in which elongation is below 10%. This is presumed to be due to the crack desperately occurring under stress at defects such as voids existing at the interface. The compatibilized blends exhibit elongation at break reaching up to the level of the PAr homopolymer, and the augmented ductility is thought to be enabled by the enhanced miscibility by the added block copolymer.

It has been reported that the addition of block copolymer in the immiscible blends led the controversy results about ductility behaviour of compatibilized blend. In the blend of polypropylene and polystyrene, reported by Paul *et al.*[11], the blend modified with Kraton showed a much increased elongation at break. According to Teyssie *et al.*[12], the addition of poly(hydrogenated butadiene)-*b*-polystyrene block copolymer into the polyethylene/polystyrene blend increased the elongation at break up to the level of values predicted by additivity from the level corresponding to that of brittle polystyrene. The polystyrene/polycarbonate blend modified by polystyrene-*b*-polycaprolactone block copolymer[9], in which polycaprolactone had been reported to be miscible with polycarbonate, exhibited brittle fracture, while the unmodified one showed ductile fracture.

Figure 6 represents the result of notched Izod impact strength measured using 6.4 mm thick specimens. With the small addition of PA-6 into PAr without block copolymer, the impact strengths of blends decreased sharply below one tenth of the PAr homopolymer's. The impact strength increases with the addition of block copolymer but still shows the negative deviation. The impact strength of blend is greatly dependent upon the capacity of dissipating impact energy through the matrix and the delivery of the internal stress of the continuous phase to the dispersed phase, so the interfacial condition between the phases is important. It seems that the enhanced adhesion of interface resulting from the compatibilization of block copolymer reduced the extent of diminution of impact strength.

CONCLUSIONS

The compatibilizing effect of PA-6–PAr–PA-6 triblock copolymers in immiscible PAr/PA-6 blends was ascertained from the following observations in compatibilized blends

(1) Homogenized morphology observed by SEM and increased density.

(2) Inward shift of T_gs of PAr and PA-6 and the depression of T_m of PA-6.

(3) Improved tensile properties and impact strength.

The change in thermal properties was more evident by the block copolymer with shorter PA-6 block.

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