

Polymer Composite of Rigid and Flexible Molecules: Blend Systems of Poly (*p*-phenylene Terephthalamide) and ABS Resin

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Synopsis

Homogeneous coagulant of poly(*p*-phenylene terephthalamide) (PPTA) and ABS resin was obtained by pouring the dimethylsulfoxide solution of *N*-sodium PPTA and ABS into acidic water. Transmission electron microscopic observation proved that PPTA was dispersed in the matrix in a form of microfibril with a diameter of 10–30 nm. The T_g of the resin component in ABS shifted to higher temperatures with increasing fraction of PPTA. Stress-strain behavior of the polymer composite showed increased tensile modulus and strength with addition of PPTA. The transition temperature from brittle to ductile fracture, however, shifted to higher temperature resulting in lower extensibility. Incorporation of the block copolymer of PPTA and polybutadiene into ABS improved the ultimate extensibility, i.e., increased toughness was provided compared with the simple composite systems of ABS and PPTA microfibrils. Scanning electron microscopic observation showed that the polymer composite made with the block copolymer generated many crazes upon deformation, while the composite with PPTA homopolymer fractured without remarkable craze formation. Thus, a new type of thermoplastic with improved mechanical properties was obtained by use of PPTA block copolymer as a compatibilizer.

INTRODUCTION

Thermoplastics and thermosetting resins reinforced by fibers can provide high modulus, high strength, and heat resistance. Recently advanced composite reinforced by high performance fibers, such as carbon fiber and Kevlar [poly(*p*-phenylene terephthalamide)] (PPTA), have been developed, especially in the field of aerospace industry.

Takayanagi et al.¹ proposed that the rigid polymer molecules instead of macroscopic fibers dispersed in flexible polymer matrix in molecular level could provide a new type of composite named polymer composite. Rigid molecules can increase the function of tie molecules.

Kevlar aramid fiber commercialized by DuPont is known to have ultra-high modulus, high strength, and good thermal stability compared with other conventional organic fibers.² A blend of PPTA rigid molecules and flexible polymer in conventional organic solvent is usually difficult due to the poor solubility of PPTA, however.³ Takayanagi et al.¹ already reported that PPTA and nylon could be dissolved in isotropically in concentrated sulfuric acid as common solvent. The polymer composite prepared by rapid

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coagulation of the isotropic solution can provide high modulus and high yield strength even in the presence of small fraction of PPTA in nylon matrix. The system is one of the successful examples of the polymer blend of PPTA prepared by employing a common solvent.

Takayanagi and Katayose⁴ found the preparation method of *N*-substituted PPTAs via *N*-sodium PPTA. *N*-sodium PPTA could be blended with flexible polymer which is soluble in dimethylsulfoxide (DMSO), since *N*-sodium PPTA synthesized by sodium hydride in DMSO gives a homogeneous solution. *N*-sodium PPTA can be easily regenerated to PPTA by coagulation in poor solvent under acidic condition.

ABS resin, one of the most widely used thermoplastics, shows relatively low heat resistance. At 373°K the stress-strain behavior of ABS shows rubberlike consistency. Improvement of mechanical properties at elevated temperature of ABS, being soluble in DMSO, was attempted by homogeneous blend of PPTA according to the previous effort.¹

EXPERIMENTAL

Materials. ABS resin used in this study was JSR ABS 10 (Japan Synthetic Rubber Co., Ltd.), which contains 18.9 wt % acrylonitrile unit.

PPTA samples were prepared by low temperature polycondensation of *p*-phenylenediamine (PPDA) and terephthaloyl chloride (TPC) in a mixed solvent of hexamethylphosphoramide (HMPA) and *N*-methylpyrrolidone (NMP).⁵ Intrinsic viscosities of the PPTA samples in 97% sulfuric acid at 303°K were 0.20, 0.84, 4.31, and 6.96 dL/g. The molecular weights were evaluated from the viscosity equation of Arpin and Starazielle.⁶ The molecular weights of them were 1300, 4900, 25,100, and 34,000, respectively. Amino-group-terminated PPTA was prepared by polycondensation of the excess molar amount of PPDA with TPC.

Acid-chloride-terminated polybutadiene (PBD) was prepared from carboxylic acid terminated PBD (JSR CTPB, Japan Synthetic Rubber Co., Ltd.) by chlorination reaction with thionyl chloride according to the method of Jablonski et al.⁷ Number average molecular weight of CTPB determined by vapor pressure osmometry was 4600. Its microstructure was 18% *cis*-1,4, 30% *trans*-1,4, and 52% vinyl butadiene. The functionality of CTPB was 1.8.

All the solvents, HMPA, NMP, DMSO and benzene, were purified by fractional distillation at reduced or atmospheric pressure over calcium hydride and stored over molecular sieves.

A commercial sodium hydride (50% suspension in paraffin oil) as metalation agent was used as received.

Preparation of Polymer Composite. Polymer blends of PPTA and ABS resin were prepared by blending *N*-sodium PPTA with ABS resin in DMSO as a common solvent. The following procedure is a typical example for preparing polymer blend of PPTA and ABS resin.

1.5 g of PPTA ($M_w = 4900$, 12.6 meq amide unit) and 0.72 g of sodium hydride (15 mmol) were reacted in 50 mL of anhydrous DMSO at 333°K for 2 h under nitrogen atmosphere to give *N*-sodium PPTA. 58.5 g of ABS resin dissolved in 350 mL of DMSO was mixed with *N*-sodium PPTA solution

with stirring to give homogeneous solution. The solution was isotropic under a polarization optical microscope with crossed Nicols. The blend polymer in DMSO was recovered by coagulation in a large amount of acidic water with stirring and washed by hot water to remove inorganic salt which was produced at regeneration of PPTA. Then, the isolated product was dried at 373°K for 24 h *in vacuo*. Degradation of PPTA molecule was not observed during the metalation reaction. The intrinsic viscosity did not vary after regeneration of *N*-sodium PPTA.

PPTA-*b*-PBD was synthesized from amino-group-terminated PPTA and acid-chloride-terminated PBD by the Shotten-Baumann reaction.⁸ 2.3 g of amino-group-terminated PPTA ($M_w = 4900$) in 20 mL of NMP was reacted with 7.70 g of acid chloride terminated PBD in 100 mL of benzene at 303°K for 4 h. The yield of the block copolymer after extracting unreacted PBD with benzene was 4.18 g, which contained 55 wt % PPTA. 2.73 g of PPTA-*b*-PBD which corresponds to 1.5 g of PPTA (12.6 meq amide unit) was reacted with 0.72 g of sodium hydride (15 mmol) in 50 mL of DMSO at 333°K for 3 h under nitrogen atmosphere. Then 58.5 g of ABS resin and *N*-sodium PPTA were mixed in DMSO as a common solvent. The subsequent procedure were carried out in a similar manner to that of PPTA homopolymer blending.

Physical Properties. For measurements of mechanical properties, the specimens of the polymer composites were prepared by compression molding at 443°K, being followed by quenching in ice water.

Glass transition temperature was determined by differential scanning calorimetry (DSC) UNIX (Rigaku Denki Co.) at a heating rate 10°K/min under nitrogen atmosphere.

Dynamic mechanical properties, dynamic storage modulus E' , and $\tan \delta$ were measured by Rheovibron DDV-IIB (Toyo Baldwin Instruments Co.) under nitrogen atmosphere.

Stress-strain behavior was measured by Tensilon UTM III-500 (Toyo Baldwin Instruments Co.) at 40%/min strain rate.

Morphology. The dispersion state of PPTA in matrix was observed by using a polarized optical microscope under crossed Nicols (Nihon Kogaku Co.).

To inspect the morphology of PPTA in the composite, the residual PPTA after extracting matrix ABS resin with DMSO from the composite was observed by using a transmission electron microscope (TEM), Hitachi H-500 (Hitachi Co.).

The fractured surfaces were examined by a scanning electron microscope (SEM), Hitachi S-430 (Hitachi Co.).

RESULTS AND DISCUSSION

Morphology. Figures 1(a) and (b) show the polarized optical micrographs under crossed Nicols of thin films of the blends of PPTA/ABS and the blends of PPTA-*b*-PBD/ABS, respectively. ABS resin solely showed no birefringence because of its amorphous nature. When PPTA was blended with ABS resin, wholly birefringence appeared, which indicates a good dispersion state of PPTA in the matrix. Moreover, PPTA-*b*-PBD/ABS system also showed wholly birefringence.

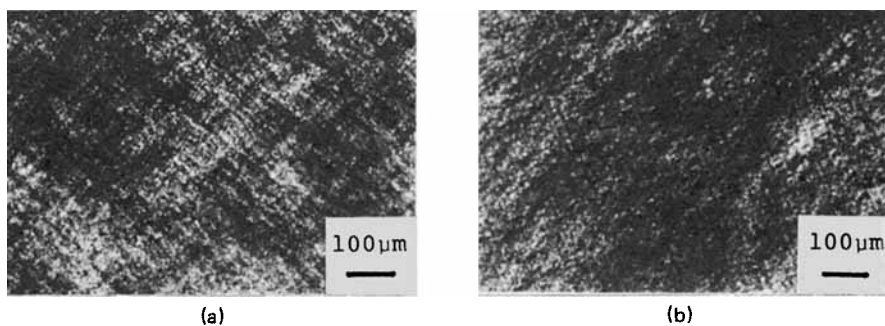


Fig. 1. Polarized micrographs under crossed nicols of thin films of (a) the blends of PPTA/ABS = 2.5/97.5 and (b) the blends of PPTA-*b*-PBD/ABS = 4.4/95.6 (net 2.5 wt % PPTA).

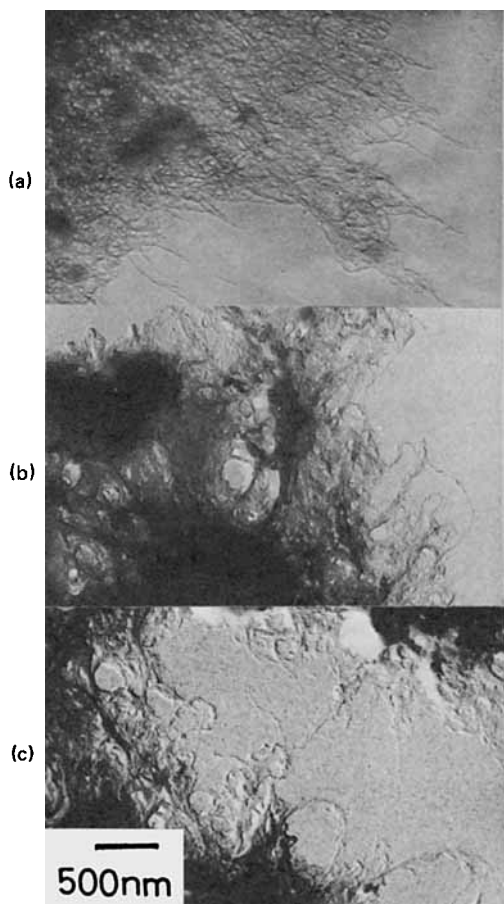
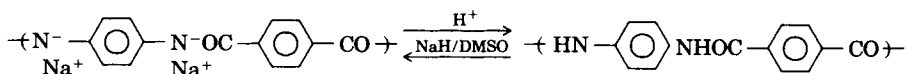


Fig. 2. Transmission electron micrographs of PPTA microfibrils extracted from the polymer composites with DMSO: (a) 2.5 wt % PPTA; (b) 25 wt % PPTA; (c) 50 wt % PPTA in ABS resin. The molecular weight of PPTA is 4900 for all cases.

To investigate the higher-order structure of PPTA dispersed in the composite, the remained insoluble parts after extracting from the blends with DMSO was inspected by TEM. Figures 2(a), (b), and (c) show the images of remained PPTA at different content in the matrix. It clearly indicated that PPTA was finely dispersed as microfibrils with a diameter of 10–30 nm at 2.5 wt % PPTA in the matrix. The size of PPTA essentially corresponded to that of the system of PPTA/nylon.^{1,9} The more detailed inspection of TEM morphology of PPTA in Figures 2(a), (b), and (c) revealed that in the samples with decreased fraction of PPTA, the more homogeneous dispersion was realized in a microfibrillar form. It is suspected that PPTA molecules tend to form microfibrillar crystals by the regeneration of metalated PPTA with acidic water. Microfibrils in Figure 2 are PPTA itself, because they are insoluble in DMSO. Metalated ones are soluble in DMSO.

Based on the aspects of PPTA microfibrils, the polymer composites are composed of ABS resin as a matrix and PPTA microfibrils as a reinforcement with diameter of 10–30 nm, which are considered to be dispersed in 3-dimensional space more uniformly at the lower concentration of PPTA than the more concentrated system such as 25% or 50%. In the latter systems, the PPTA microfibrils have a strong tendency to aggregate to result in somewhat more heterogeneous dispersion of PPTA in the matrix.

As for the coagulation–regeneration process, there are two possibilities: one is the regeneration of metalated PPTA followed by coagulation of PPTA, and the other process is the coagulation of metalated PPTA followed by its regeneration of PPTA with acidic water. The experimental observation seems to support the latter case. The DMSO solution of metalated PPTA showed red color, which turns to slightly yellow color after regeneration to PPTA. The precipitates from the DMSO solution with acidic water showed first red color, and then it changed to yellow color with lapse of time. This means that metalated PPTA first coprecipitated with ABS resin, which gradually changed to the blend of PPTA and ABS. The reaction scheme is as follows:



The process of microfibril formation is conceived to be *in situ* crystallization of regenerated PPTA molecules in the matrix of coagulated ABS. In such a matrix, rigid molecules such as PPTA cannot easily migrate and crystallize. Crystallization takes place in restricted region of molecular environments, which results in very thin microfibrils with diameter from 10 to 30 nm. Such a process is preferable to form a homogeneous distribution of microfibril in the ABS matrix. Mechanical properties of such a system might be profitable owing to uniform distribution of the applied external stress.

Glass Transition Temperature. Figure 3 proves a linear relationship between glass transition temperature (T_g) and volume fraction of PPTA ($M_w = 4900$) in polymer composites, which can be represented by the following equation:

$$T_g (\text{K}) = 370 + 215 V_f$$

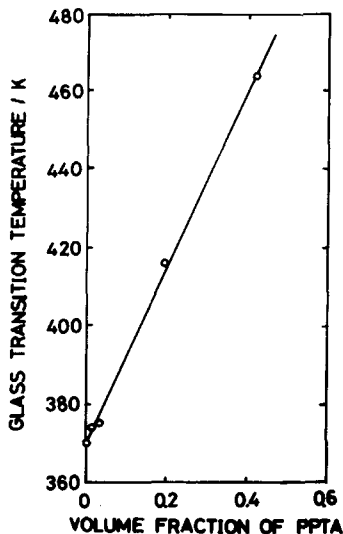


Fig. 3. Glass transition temperature of polymer composites systems as a function of volume fraction of PPTA. The molecular weight of PPTA is 4900.

where V_f is the volume fraction of PPTA in the composites. It indicates that the corresponding T_g of poly(acrylonitrile-co-styrene) (SAN) component, 370 K, in ABS resin shifted to the higher temperature side with increasing PPTA ratio in the composites. This fact suggests that PPTA is apparently compatible with the SAN component in ABS resin. Perhaps interaction at the interface between microfibrillar surface of PPTA and SAN is very strong so that this system resembles the wholly compatible system.

Dynamic Mechanical Properties. Rheovibron measurements at 11 Hz on ABS resin and its blends with varying the blend amount of PPTA ($M_w = 4900$) are shown in Figure 4 (E') and Figure 5 ($\tan \delta$). In ABS resin

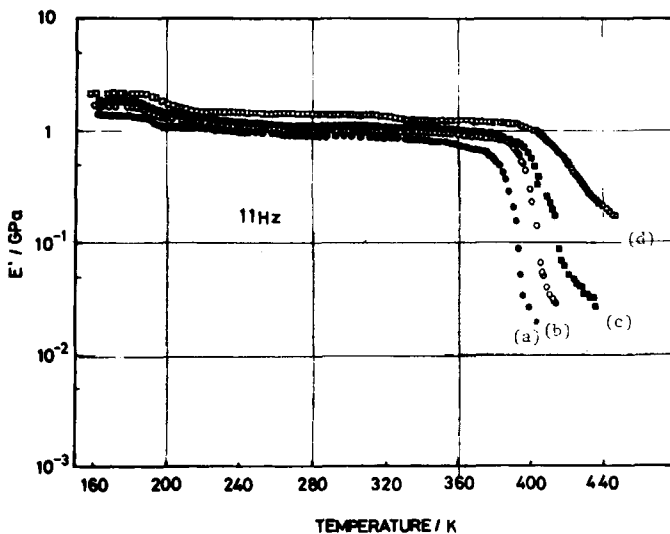


Fig. 4. Plots of E' vs. temperature for ABS and the polymer composites: (a) ABS; (b) PPTA/ABS = 2.5/97.5; (c) PPTA/ABS = 5/95; (d) PPTA/ABS = 10/90 (by weight).

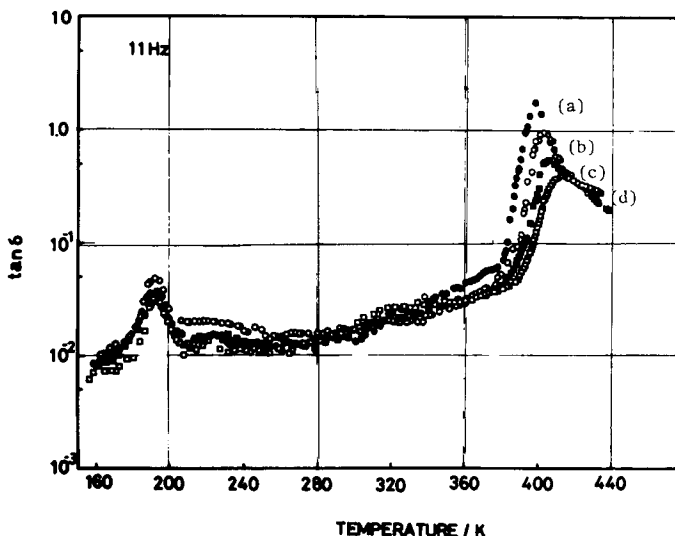


Fig. 5. Plots of $\tan \delta$ curves vs. temperature for ABS and the polymer composites: (a) ABS; (b) PPTA/ABS = 2.5/97.5; (c) PPTA/ABS = 5/95; (d) PPTA/ABS = 10/90 (by weight). The molecular weight of PPTA is 4900 for all cases.

there are two $\tan \delta$ peaks located around 190°K and 400°K, which are associated with the dispersion of rubber component and resin component, respectively. This fact indicates that the ABS resin is a multiphase system.¹⁰ The primary $\tan \delta$ peak of rubber component around 190°K did not shift with the fraction of PPTA, whereas the primary $\tan \delta$ peak of resin component shifted to the higher temperature side in proportion to the blend amount of PPTA. These facts accorded with the variation of the T_g of the polymer composite measured by DSC curves and indicate that PPTA microfibrils are dispersed mainly in SAN resin matrix because of their strong interaction at the interface. Micro-Brownian motion of SAN molecules suffers the restraining force from the surroundings.

The effect of the molecular weight of PPTA on the intensity of $\tan \delta$ in the polymer composite is shown in Figure 6. The intensity of $\tan \delta$ tends

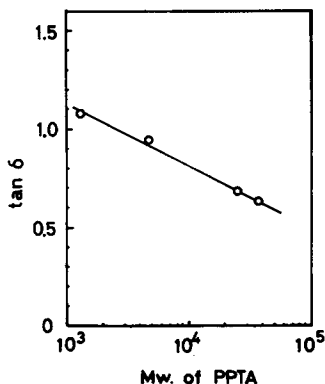


Fig. 6. Relationship between the intensity of $\tan \delta$ at the dispersion temperature of the resin component and molecular weight of PPTA in composite system. (PPTA/ABS = 2.5/97.5 by weight)

to decrease with increasing molecular weight of PPTA, supporting that the higher molecular weight of PPTA can provide well-developed microfibrillar surface, which in turn increases the interfacial interaction between the ABS matrix and the microfibril.

The reason for strong interaction between PPTA surface and the matrix may come from the intermolecular hydrogen bond between —NH bond in PPTA and —CN bond of acrylonitrile (AN) in ABS matrix. The —CN group chemically resembles the halogen atom. Actually IR band shift in the hydrogen bond between benzanilide as a model compound of PPTA and poly(vinyl chloride)¹¹ was ascertained.

Another evidence for strong interaction between AN unit in the matrix polymer and PPTA microfibrillar surface was observed in the system of nitrile butadiene rubber (NBR) and PPTA polymer composite. In this system, it was found that the increasing content of AN in NBR induced the increased reinforcing effect of the PPTA microfibrils.¹²

Stress-Strain Behavior. Table I shows the temperature dependence of the characteristic values of stress-strain behavior of ABS resin and the polymer composites with varying the molecular weight of PPTA. The weight fraction of PPTA was kept constant, 2.5 wt %, throughout these cases. Young's modulus E , yield stress σ_y , and tensile strength at break σ_b increased with increasing molecular weight of PPTA. The reinforcing effects of PPTA are remarkable. By blending PPTA of the highest molecular weight ($M_w = 34,000$), Young's modulus increased by 1.50 times and tensile strength at break 1.31 times compared with the original ABS. The toughness of the composites decreased by blending PPTA, i.e., the elongation at break ϵ_b decreased and the specimens broke before yielding. The transition temperature from brittle to ductile fracture of the polymer composites shifted above room temperature. The transition temperature depended on the molecular weight of PPTA. For oligomer of PPTA ($M_w = 1300$) the transition temperature was located below room temperature. For the highest molecular weight of PPTA the transition existed between 353°K and 373°K, while that of the original ABS resin existed below room temperature.

Figure 7 shows the stress-strain curves of ABS resin and the polymer composites with 2.5 wt % of various molecular weights of PPTA at 373°K. At this temperature ABS became rubbery and fractured with flow. The reinforcing effects at 373°K, near the T_g of the matrix ABS, are more remarkable. The highest molecular weight of PPTA could increase the Young's modulus by 88.8 times and the yield stress by 17.1 times compared with those of ABS resin. Even in the blend of PPTA oligomer, Young's modulus increased by 12.8 times and the tensile strength at break 6 times. This outstanding effect at elevated temperature apparently originates from the rise of the T_g of the composites because of strong interaction between the reinforcement and the matrix and the stress-supporting microfibrillar network in ABS matrix.

Table I also shows the characteristic values of stress-strain behavior of the polymer composites with varying the amount of blending PPTA. The Young's modulus and the tensile strength increased, while the extensibility decreased. The reinforcing effects of PPTA of the highest molecular weight ($M_w = 34,000$) with 2.5 wt % was superior to that of the low molecular

weight PPTA ($M_w = 4900$) with 5.0 wt %. The transition temperature from brittle to ductile fracture also shifted to the higher temperature side by increasing the fraction of PPTA. These results mean that higher molecular weight of PPTA can form stronger microfibrils which act more effectively as reinforcement. Moreover, PPTA microfibrils are miscible in supermolecular level into SAN matrix of ABS.

In order to improve extensibility of the composites, while keeping the strength, incorporation of soft segment to rigid molecules was attempted. PPTA-*b*-PBD was prepared as described previously⁸ and metalated as similarly as in the case of PPTA homopolymer. Figures 8 and 9 show the stress-strain curves of ABS, the blend of the block copolymer (PPTA-*b*-PBD/ABS = 4.4/95.6) and that of PPTA homopolymer with ABS at 298°K and 373°K,

TABLE I
Temperature Dependence of the Mechanical Properties of ABS Resin and the Polymer Composites of PPTA/ABS

Polymer composite	M_w of PPTA	Temp (K)	E (MPa)	σ_y (MPa)	σ_b (MPa)	ϵ_b (%)
ABS resin		298	1030	27.1	24.9	15
		353	706	19.6	17.3	53
		373	8	—	0.7	380
		393	2	—	0.4	> 1200
		413	1	—	0.2	200
PPTA/ABS 2.5/97.5	1300	298	1098	27.9	26.5	12
		353	970	18.3	14.7	88
		373	100	2.8	4.1	256
		393	3	—	0.6	350
		413	2	—	0.3	125
PPTA/ABS 2.5/97.5	4900	298	1226	—	32.4	5
		353	970	19.2	15.5	41
		373	530	10.8	10.5	140
		393	11	—	1.6	560
		413	7	—	0.8	194
PPTA/ABS 5/95	4900	298	1491	—	33.4	4
		353	1020	—	19.8	6
		373	618	12.3	12.3	20
		393	39	—	3.9	85
		413	9	—	1.2	50
PPTA/ABS 10/90	4900	298	1870	—	36.6	2
		353	1150	—	22.2	4
		373	723	14.6	14.4	18
		393	75	—	5.2	14
		413	12	—	1.4	10
PPTA/ABS 2.5/97.5	25100	298	1495	—	33.8	4
		353	1000	—	19.2	12
		373	644	11.1	10.8	130
		393	14	—	2.3	167
		413	11	—	0.9	88
PPTA/ABS 2.5/97.5	34000	298	1549	—	35.4	4
		353	1079	—	21.2	10
		373	696	11.8	11.2	131
		393	17	—	2.5	85
		413	13	—	1.2	69

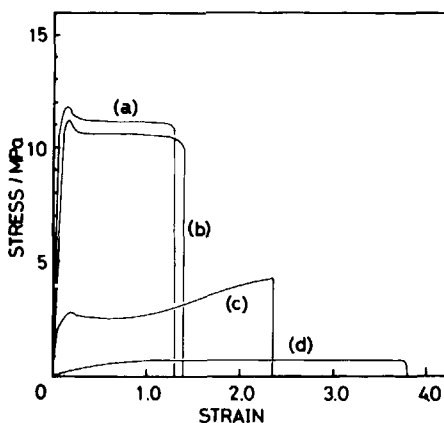


Fig. 7. Stress-strain curves of ABS and polymer composite (PPTA/ABS = 2.5/97.5) with various molecular weights of PPTA in composite at 373°K: (a) 34,000; (b) 4900; (c) 1300 (d) ABS.

respectively. The net weight of PPTA was kept constant at 2.5 wt %. The drastic increase in toughness can be seen for the composite of ABS reinforced by PPTA-*b*-PBD. The fracture energy, estimated from the stress-strain curves, of the block copolymer composite was more than that of the original ABS both at 298°K and 373°K. Incorporation of PBD blocks to PPTA is effective in shifting the transition temperature from brittle to ductile fracture of the polymer composite at temperatures below 298°K and thus, improving toughness. In the polymer composite containing the block copolymer, elongation at yield decreased and elongation from yield to break increased compared to the original ABS. These facts suggest that the craze of the composite easily generates and the number of crazes increases until break compared to the ABS resin. The structure of these PPTA-*b*-PBD was conceived to be multiblock copolymer terminated with PBD blocks. In PPTA

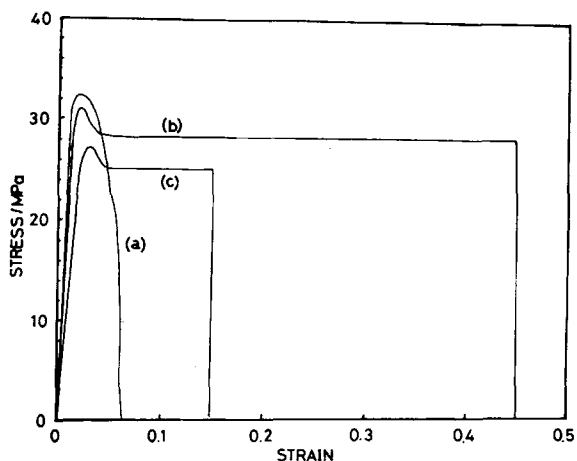


Fig. 8. Stress-strain curves for: (a) the polymer composite of PPTA/ABS (2.5 wt % PPTA); (b) PPTA-*b*-PBD/ABS (net 2.5 wt % PPTA); (c) ABS at 298°K. The molecular weight of PPTA is 4900 for both cases.

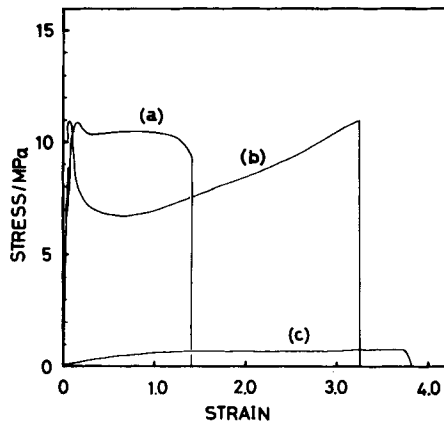


Fig. 9. Stress-strain curves for: (a) the polymer composite of PPTA/ABS (2.5 wt % PPTA); (b) PPTA-*b*-PBD/ABS (net 2.5 wt % PPTA); (c) ABS at 373°K.

homopolymer blend, microvoids located at the end of PPTA microfibrils might initiate the growth of crack. PBD blocks bound to PPTA microfibril will act to decrease the defects at the end of microfibril and thus to result in improving toughness. Improved state of dispersion of PPTA in presence of PBD blocks is also helpful to this tendency.

Observation of Fractured Surface of Composite. SEM was used to study the fractured surfaces of ABS resin and the PPTA composites. Specimens were prepared by fracture in liquid nitrogen. Figure 10 shows the fractured surface of the original ABS resin. Many round particles with diameter of 0.2–0.5 μm of PBD or PBD-*g*-SAN were observed, indicating a microheterogeneous texture of ABS. Some voids were also observed, suggesting that some rubber particles were segregated from the matrix because of poor adhesion at interface. In the polymer composite containing 5 wt % PPTA, aggregates of particles with diameter of 0.2–0.5 μm were found as shown in Figure 11. This fact shows that the PPTA promotes a separate

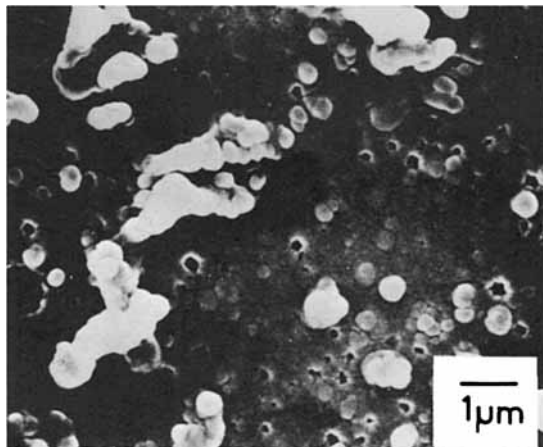


Fig. 10. Fractured surface of ABS resin at 77°K.

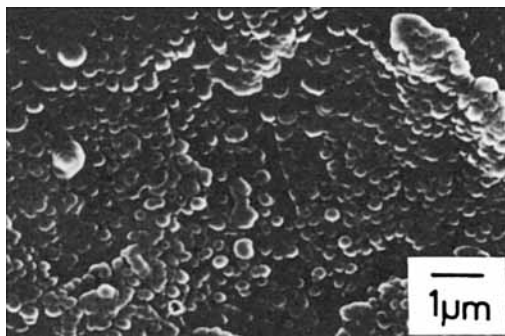


Fig. 11. Fractured surface of the polymer composite composed of PPTA/ABS = 5/95 at 77°K. M_w of PPTA is 4900.

rubber phase to form rubber spheres and to decrease adhesion between rubber and matrix. It is thought that the aggregation of rubber particles occurred at the coagulation and the regeneration of PPTA owing to incompatibility between PBD and PPTA. In this multiphase system, rubber particles with poor adhesion at the interface could not prevent the propagation of cracks, which resulted in decreasing toughness as seen in the stress-strain curves in Figure 8. Figure 12 shows the SEM of the polymer composite containing 4.4 wt % PPTA-*b*-PBD (net 2.5 wt % PPTA). Rubber particles were adhered tightly with the matrix through PBD blocks and voids were scarcely observed in it. The block copolymer would be effective in dispersing rubber particles and SAN phase uniformly in the matrix, acting as a compatibilizer. ABS usually exhibits the stress-whitening phenomenon upon deformation. The strain energy is dissipated during the course of the stress whitening, with the crazes being generated and propagated. The stress whitening was observed in the block copolymer composite, while not observed in the case of the PPTA homopolymer composite. Figure 13 shows the SEM of the stress whitening in the polymer composite of the block

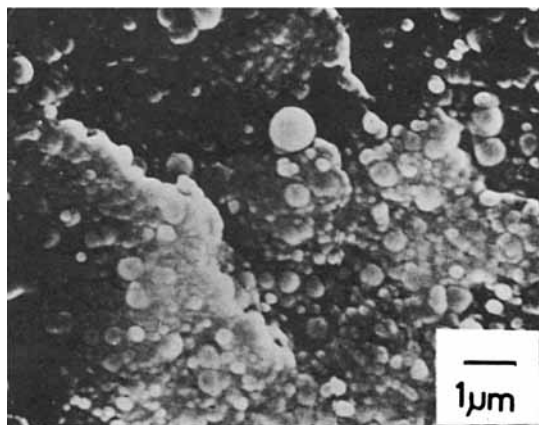


Fig. 12. Fractured surface of the polymer composite composed of PPTA-*b*-PBD/ABS = 4.4/95.6 at 77°K.

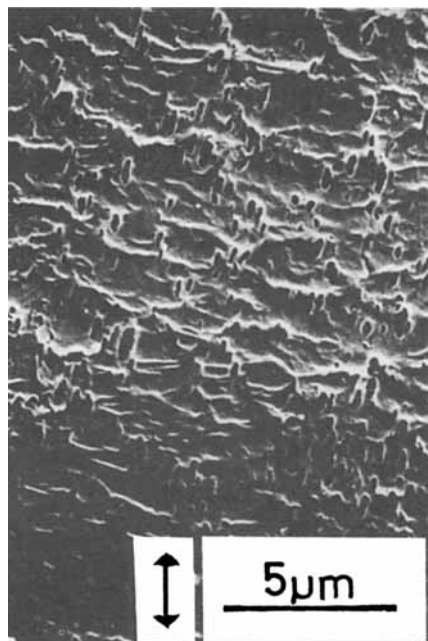


Fig. 13. Scanning electron micrograph of crazing generated upon stretching in PPTA-*b*-PBD/ABS composite system. The arrow shows the direction of stretching.

copolymer. Many crazes which dissipate the strain energy by plastic deformation were observed. These electron micrographs of the polymer composite composed of the PPTA block copolymer and ABS support the stress-strain behavior, indicating increase of extensibility and toughness.

A new type of thermoplastics with improved mechanical properties was obtained according to the polymer composite concept.

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Received May 9, 1983

Accepted December 23, 1983