

Surface-Modified Kevlar Fiber-Reinforced Polyethylene and Ionomer

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Synopsis

The surface of poly(*p*-phenylene terephthalamide) (PPTA) fiber was modified by the polymer reaction via the metalation reaction in dimethyl sulfoxide to provide the fiber surface with several functional groups such as the *n*-octadecyl group, carboxymethyl group, and acrylonitrile. The discontinuous fibers thus modified could be isotropically dispersed in polyethylene and ionomer. The composite of ionomer and random-in-plane oriented discontinuous PPTA fibers with the surface modified by carboxymethyl groups was remarkably improved in its mechanical properties, and the fiber efficiency factors of about 0.4 for both strength and modulus are comparable to the values in the composite of unidirectionally oriented discontinuous PPTA fibers and ionomer. The heat resistance of ionomer was also greatly improved by the presence of this surface modified PPTA fibers, even with volume fractions as low as 2.2%.

INTRODUCTION

A most striking recent development in polymer technology was the invention by Kwolek, Morgan, and their co-workers at DuPont¹⁻⁷ of lower density, superhigh tensile modulus/high strength fibers from PPTA and the commercialization of Kevlar. This material is very interesting as a reinforcing fiber for composite materials. Namely, Kevlar 49 has a mean tensile strength of 2.7 GPa, which is somewhat higher than that of commercially available E-glass fibers, and a mean Young's modulus of 120 GPa, which is about 60% higher than that for E-glass fibers. When the lower density of Kevlar 49 is taken into account, i.e., 1.45 g/cm³ as compared to 2.52 g/cm³ for glass fibers and the values between 1.7 and 2.1 g/cm³ for carbon fibers, then one has a material with very useful specific properties.

Accordingly, a considerable amount of work has been reported on Kevlar fiber-reinforced polymeric materials.⁸⁻¹³ Composites in which PPTA fibers are discontinuous and controlled in orientation have good mechanical properties and can be fabricated into complex geometrics. In discontinuous fiber-reinforced composites, the performance and properties are generally a function of fiber type, fiber content, fiber aspect ratio, fiber orientation, fiber dispersion, fiber-matrix adhesion, processing methods, and properties of the matrix. In these factors, the fiber-matrix interface plays an essential role in determining the mechanical properties. At the interface, loads are transferred from the matrix to the fiber. This load transfer is dependent on the degree of fiber-to-matrix adhesion and on the fiber aspect ratio. If the aspect ratio is lower than the critical aspect ratio, insufficient stress will be transferred to the fibers to break

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TABLE I
Mechanical Properties of Reinforcements

Properties	Unit	Kevlar 29	Carbon fiber
Ultimate tensile strength	GPa	2.54	3.0
Tensile modulus	GPa	71.2	210
Elongation at break	%	3.5	1.3
Specific gravity	—	1.44	1.74
Fiber diameter	μm	12	8

them, and the reinforcement will be inefficient. Experimental work by Anderson and Lavengood¹⁴ indicated that aspect ratios in the range of 50–100 are necessary before fibers are used efficiently. On the other hand, the properties of Kevlar-to-matrix interface were measured by Eagles et al.¹¹ According to their results, sized Kevlar fibers had the greatest interfacial bond strength and frictional shear strength values for various matrix materials including polyethylene, ionomer, polycarbonate, and nylon, whereas the fiber with no finish exhibited adhesive values below those of the sized fiber. The tensile strength of discontinuous fiber-reinforced thermoplastic composites correlated well with the frictional shear strength measured in their study. However, it was not possible to disperse the cut fiber bundles so that the bulk composites of sized Kevlar fibers did not possess very good tensile properties.

Thus, this study presents the method to disperse the discontinuous Kevlar fibers with the aspect ratio of about 500 isotropically in the matrices such as low-density polyethylene and ionomer. For this purpose, the fiber-to-matrix adhesion strength is efficiently improved by adopting various surface reactions of the Kevlar fibers which are an application of the polymer reaction of PPTA developed in our laboratory.^{15,16}

EXPERIMENTAL

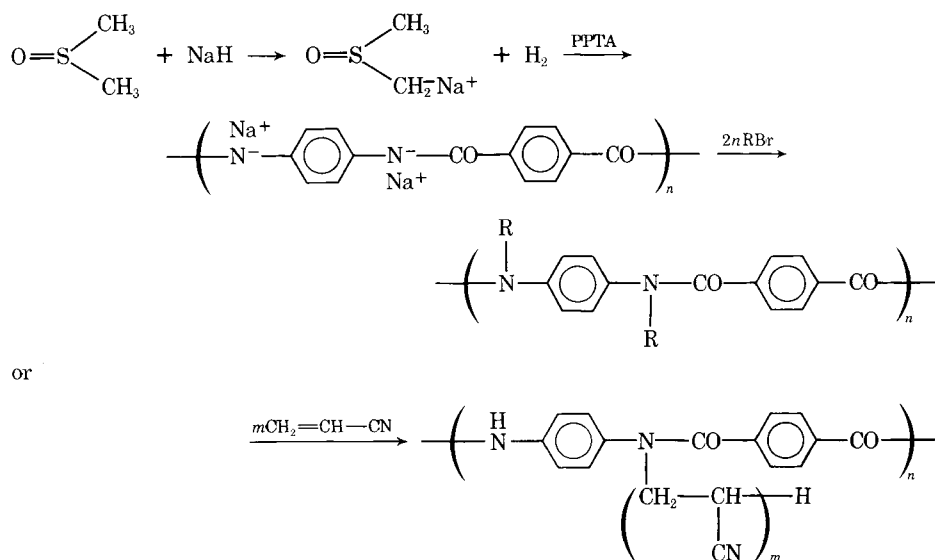
Materials

The polyethylene samples employed in this study were high-pressure low-density polyethylene (Asahi Dow Ltd.). The ethylene-type ionomer samples were Copolene resin containing methacrylic acid weight fractions of 16%, which was ionized 35 mol % by sodium ion (Asahi Dow Ltd.). The poly(*p*-phenylene terephthalamide) fibers were Kevlar 29 (DuPont). The carbon fibers were Torayca (Toray Co.). The properties of each fiber are given in Table I.

Preparation of PPTA Fiber with Modified-Surface Layer

The PPTA fiber samples with the surface modified by chemical reactions were obtained by the reaction of the metalated PPTA surface with *n*-octadecyl bromide, bromoacetic acid, or acrylonitrile. The polymer reaction via the metalation reaction in a solution of sodium methylsulfanylcarbanion in dimethyl sulfoxide

at low temperatures proceeds in the following scheme^{15,16}:



where R = $-\text{C}_{18}\text{H}_{37}$, $-\text{CH}_2\text{COOH}$.

Octadecylation Reaction

The PPTA fibers (1.0 g) were added to a solution (100 mL) of sodium methylsulfinylcarbanion in dimethyl sulfoxide at 303 K and the metalation reaction was continued for 1 h. The fibers maintained the original shape during the reaction. Then, *n*-octadecyl bromide (3.1 g) was added and the *N*-substitution reaction was continued at 303 K for 2 h, keeping the original shape of the fibers. The modified fibers were filtered and washed several times with water and acetone alternately. The surface modified PPTA fibers by *n*-octadecyl group were dispersed in xylene.

Carboxymethylation Reaction

A similar technique as used in the octadecylation reaction was used with the exception that the solution of bromoacetic acid in dimethyl sulfoxide was added to the reaction system at 323 K.

Grafting Reaction with Acrylonitrile

A similar technique as employed in the octadecylation reaction was used with the exception that acrylonitrile was added to the reaction system 323 K and that the reaction was continued for 5 h.

Composites of Polyethylene and the PPTA Fibers with the Surface Modified by Octadecyl Groups

A suspension of the surface-modified PPTA fibers (0.5 g) in xylene was added to a solution of polyethylene (9.5 g) in xylene at 393 K. The composites were precipitated by pouring into a large amount of methyl alcohol, filtered, and washed with methyl alcohol repeatedly. The composites were dried at 353 K for 10 h in a vacuum oven.

Composites of Ionomer and the PPTA Fibers with the Surface Modified by Various Substitutional Groups

A suspension of the surface-modified PPTA fibers (0.34 g) in xylene was added to a solution of ionomer (9.66 g) in a mixed solvent of xylene (160 mL) and *n*-butyl alcohol (40 mL) at 393 K. The composites were precipitated by the same procedure as described above. For measurements of mechanical properties, the specimens of polyethylene, ionomer, and each composite were prepared by compressing at 463 K. They were then quenched in ice water. Thus, the specimens prepared in this study were discontinuous fiber-reinforced composites made with random-in-plane fiber orientation. Measurements of physical properties were conducted by the conventional instruments, which are mentioned in the corresponding sections.

RESULTS AND DISCUSSION

Chemical Treatment on the Surface of PPTA Fiber

Figure 1 shows scanning electron micrographs of PPTA monofilament (a), PPTA filament with the surface by sodium ion (b), and the cross section of metalated fiber (filament assembly) (c). A comparison of the surface of PPTA monofilament [Fig. 1(a)] with that of PPTA fibers modified by sodium ion [Fig. 1(b)] shows that the modified fibers are much rougher, whereas the original PPTA fibers are very much smooth. Figure 1(c) shows that the metalation reaction proceeded into the inner part of the PPTA fiber under the experimental conditions described above, and the surface layer was about 1 μm thick. Figure 2 shows the scanning electron micrographs of PPTA filaments with the surface modified by carboxymethyl groups and with the surface modified by *n*-octadecyl

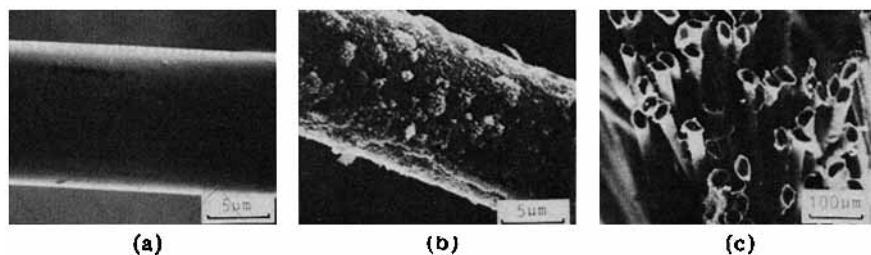


Fig. 1. Scanning electron micrographs of (a) PPTA filament, (b) PPTA filament modified by sodium hydride, and (c) the cross sections of metalated PPTA filament.

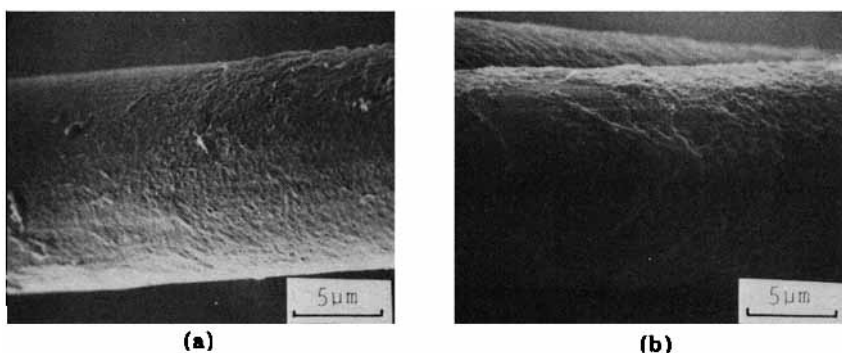


Fig. 2. Scanning electron micrographs of (a) PPTA filament modified by *n*-octadecyl group and (b) PPTA filament modified by carboxymethyl group.

groups. These surfaces are rough and are quite different from that of PPTA fibers. In the case of Figure 2(b), several little smooth portions are found, suggesting the presence of unreacted parts. In order to analyze the surface layers of the modified PPTA fibers, the fibers were dissolved in concentrated sulfuric acid for 30 s, and the solution was then poured into a large amount of water to recover the *N*-substituted PPTA including a portion of PPTA. Infrared spectra of these samples showed distinctive absorptions due to the alkyl groups and the carboxymethyl groups at 730 cm^{-1} and 1750 cm^{-1} , respectively. This fact shows that the surface layers of the PPTA fibers were reacted with the reactants such as *n*-octadecyl bromide and bromoacetic acid via the metalation reaction.

Mechanical Properties

The molded specimens were about 2 mm thick. Tensile tests were conducted using Tensilon (Toyo Baldwin Co.) at room temperature and 353 K. An apparent strain rate of 33%/min was used for all tests.

Figure 3 shows the stress-strain curves for polyethylene and its composites at room temperature. In the case of the composite with the surface-modified PPTA fibers by octadecyl groups, the fibers were dispersed into the matrix, whereas it was difficult to disperse unmodified PPTA fibers into the matrix.

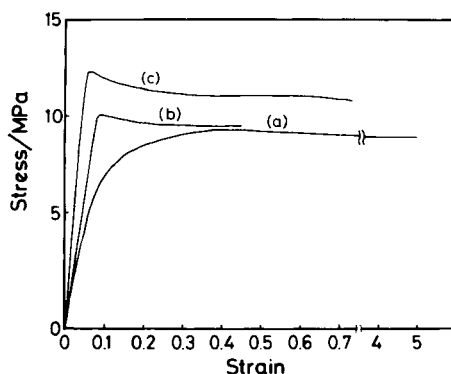


Fig. 3. Stress-strain curves for (a) polyethylene, (b) the composite of PPTA fibers and polyethylene, and (c) the composite of surface-modified PPTA fibers and polyethylene at room temperature. The weight ratio of reinforcement/polyethylene is 5/95 for both cases.

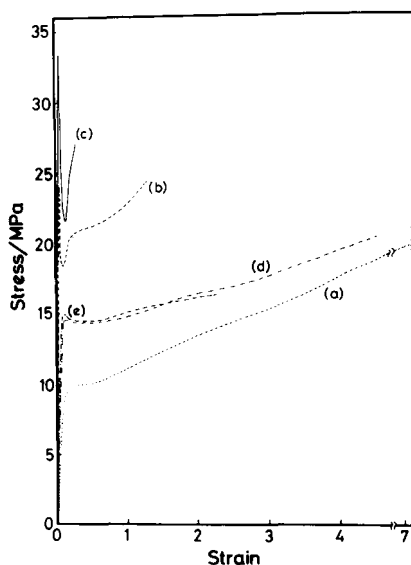


Fig. 4. Stress-strain curves for (a) ionomer, (b) the composite of PPTA fibers and ionomer, (c) the composite of PPTA fibers with the surface modified by carboxymethyl group and ionomer, (d) the composite of PPTA fibers with the surface modified by acrylonitrile and ionomer, and (e) the composite of carbon fibers and ionomer at room temperature. The volume ratio of reinforcement/ionomer is 2.2/97.8 for all cases.

The yield stress and the Young's modulus for the composite of polyethylene and the surface-modified PPTA fibers are improved, compared with those of the composite of polyethylene and PPTA fibers. It is thought that the adhesive strength of the surface-modified PPTA fibers to the matrix is stronger than that of untreated PPTA fibers to the matrix. With respect to this point, a further result is discussed in the section on the scanning electron microscopic observations. Figure 4 shows the stress-strain curves for ionomer and its composites. The reinforcements volume fractions are 0.022 for all cases and are statistically isotropic in the matrix. The effects of various functional groups of PPTA fiber surfaces on stress-strain behavior are remarkable. Table II lists the characteristic values of stress-strain curves of these composites. The composites of ionomer and unreacted PPTA fibers or the surface-modified PPTA fibers by carboxymethyl groups were remarkably improved in their yield stresses and Young's moduli, even by as small as an amount of 2.2 vol % of PPTA fibers, compared with ionomer only.

TABLE II
Mechanical Properties of Ionomer and Its Composites with Various Fiber Reinforcement

Reinforcement ^a	Young's modulus (MPa)	Yield stress (MPa)	Ultimate strength (MPa)	Elongation at break (%)
None	152	10.0	19.7	705
Kevlar fiber	535	24.0	24.4	130
Kevlar fiber modified by carboxymethyl group	783	33.5	27.1	27
Kevlar fiber modified by acrylonitrile	305	14.5	20.3	450
Carbon fiber	420	15.0	16.3	225

^a The content of reinforcement is 2.2% by volume.

Especially, in the case of the latter, the yield stress increased from 10.0 to 33.5 MPa and the Young's modulus increased from 152 to 783 MPa. The ultimate strength increased a little from 19.7 to 27.1 MPa, while the ultimate elongation decreased from 705% to 27%. On the other hand, the yield stress and the Young's modulus for the composite of ionomer and PPTA fibers modified by grafting reaction with acrylonitrile decreased and the extensibility increased largely, compared with those of the composite of ionomer and PPTA fibers. This fact means that the interaction between the nitrile groups of PPTA fiber surfaces and ionomer is weaker than that between the amide groups of PPTA fibers and ionomer. Moreover, inspection of Table II suggests that anchoring of longer side branches of polyacrylonitrile into the ionomer matrix is very effective in extensibility. Microvoids located at the ends or the interfacial boundaries of PPTA fibers, which initiate the growth of cracks, might become ineffective by dissipative energy caused by the plastic deformation of anchored long acrylonitrile side chains in the ionomer matrix.

In spite of superior mechanical properties of carbon fiber itself, the composite of ionomer and carbon fibers was not so improved in the mechanical properties because of the weaker interaction at the interfacial boundaries between carbon fibers and ionomer. These data show that the surface properties of the fibers such as wettability and adhesive properties influence the mechanical properties of these composites more effectively than the mechanical properties of the reinforcing fibers.

Figure 5 shows the stress-strain curves for ionomer and its composites at 353 K. At 353 K, the moduli and the yield stresses for the composite with PPTA fibers or PPTA fibers having the surface modified by carboxymethyl groups were largely improved, especially in the case of the latter composite. Dimensional stability of ionomer at higher temperatures is also improved by the presence of the surface-modified PPTA fibers. On the other hand, the mechanical properties for the composite of carbon fibers and ionomer at 353 K was not improved, compared with those at room temperature. This fact indicates again that the interaction between carbon fibers and matrix is very weak at higher temperatures.

The rule of additivity of properties of components for the composites was applied to the data to evaluate the fiber efficiency factors for strength and

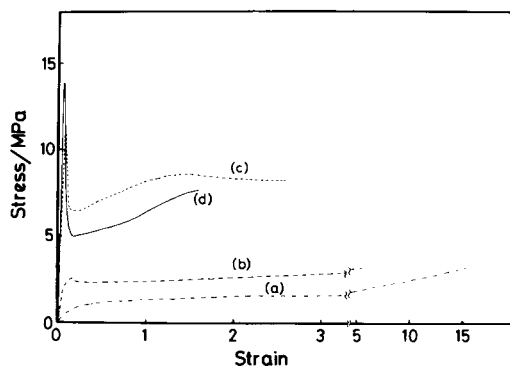


Fig. 5. Stress-strain curves for (a) ionomer, (b) the composite of carbon fibers and ionomer, (c) the composite of PPTA fibers and ionomer, and (d) the composite of PPTA fibers with the surface modified by carboxymethyl group and ionomer at 353 K.

modulus. The rule of additivity expressions for tensile strength and tensile modulus of discontinuous fiber-reinforced composites made with random-in-plane fiber orientation¹⁰ are

$$\sigma_c = K_\sigma \sigma_f V_f + \sigma_m (1 - V_f)$$

$$E_c = K_e E_f V_f + E_m (1 - V_f)$$

where σ_c is the ultimate strength of the composite; K_σ is the fiber efficiency factor for strength; σ_f is the ultimate strength of the reinforcing fiber; V_f is the fiber volume fraction; σ_m is the matrix stress at the fracture strain of the composite; E_c is the Young's modulus of the composite in the plane of the fibers; K_e is the fiber efficiency factor for modulus; E_f is the modulus of the reinforcing fiber; and E_m is the matrix modulus. K_e and K_σ values for the experimental composites are given in Table III. The efficiency factors of PPTA fiber for modulus at room temperature ranged from 0.10 to 0.40 and for strength from 0.08 to 0.42. The values of K_e and K_σ of the same system at 353 K for modulus ranged from 0.12 to 0.20 and for strength from 0.15 to 0.19, which are about half the value at room temperature. The K_e value of 0.25 obtained in the composite of ionomer and PPTA fibers accords with the value of 0.19 by Blumentritt et al.¹⁰ in the same composite, taking into consideration that the volume fraction in our study is lower than that in their study.

It is noteworthy that the K_e value of 0.42 obtained in the composite of ionomer and 2.2 vol % PPTA fibers with the surface modified by carboxymethyl groups is comparable to the value for the composite of unidirectionally oriented discontinuous PPTA fibers (20–50 vol %) and ionomer reported by Blumentritt et al.⁹ This fact means that the surface modification of PPTA fiber by carboxymethyl groups plays an important role in the formation of a strong interface layer between PPTA fibers and the matrix, resulting in the great improvement of the mechanical properties of the composite of random-in-plane oriented discontinuous PPTA fibers and ionomer in comparison with those of the composite of unidirectionally oriented discontinuous PPTA fibers and ionomer. In the case of carbon fiber-reinforced composite, the fiber efficiency factor at room temperature for modulus was 0.06 and for strength 0.08, and the factors at 353 K for modulus was 0.008 and for strength 0.001, nearly equal to zero, indicating that these values are about one-eighth those at room temperature. Comparing with the values obtained in PPTA fiber-reinforced composites, the carbon fiber efficiency factors are very low, especially at 353 K. This suggests that the adhesion strength between carbon fibers and ionomer is very weak.

TABLE III
Fiber Efficiency Factors for Ionomer Composites

Reinforcement	K_e		K_σ	
	Room temp	353 K	Room temp	353 K
Kevlar fiber	0.25	0.12	0.25	0.15
Kevlar fiber modified by carboxymethyl group	0.40	0.20	0.42	0.19
Kevlar fiber modified by acrylonitrile	0.10	—	0.08	—
Carbon fiber	0.059	0.008	0.079	-0.001

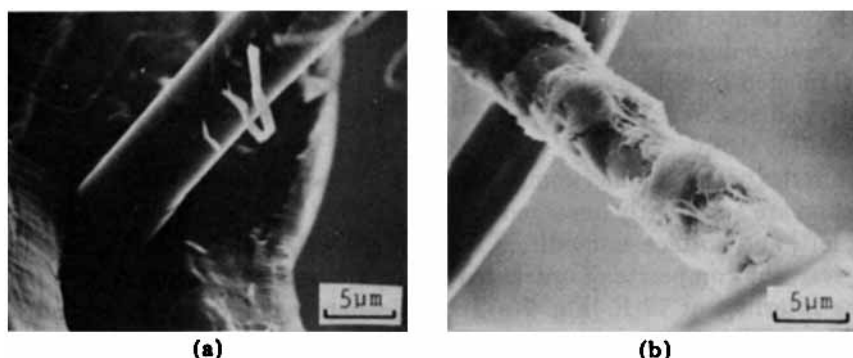


Fig. 6. Fracture surfaces of (a) PPTA fiber-reinforced polyethylene and (b) surface-modified PPTA fiber-reinforced polyethylene at room temperature.

Observation of Fractured Surfaces of Composites

A scanning electron microscope was used to study the fracture surfaces of the composites. Samples were prepared by fracturing at room temperature using a tensile tester and at 77 K in liquid nitrogen so that the extent of adhesion could be observed.

Figure 6 shows the fractured surface of the PPTA fiber-reinforced polyethylene (a) and the surface-modified PPTA fiber-reinforced polyethylene (b). Some indications of good fiber-matrix adhesion are observed in Figure 6(b), although the indications do not necessarily appear in all of PPTA fibers. A fracture during a tensile test can occur at the interface, in the fiber, or in the matrix. In our experiments, the observed failure mode was frequently complex. In the case of no surface treatment, the predominant mode was fracture at the interface. However, in some cases, cohesive failure of the fiber surface occurred during the test, resulting in a thin layer of material stripped from the fiber surface. This

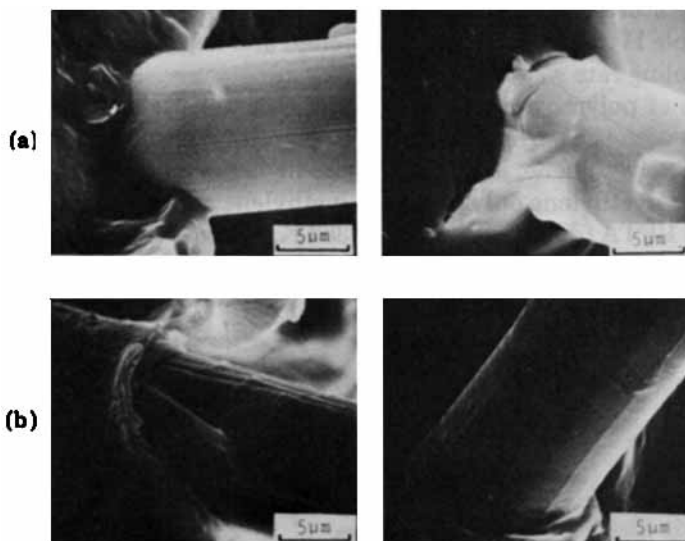


Fig. 7. Fracture surfaces of (a) PPTA fiber-reinforced ionomer at room temperature (left) and 77 K (right) and (b) surface-modified (carboxymethyl) PPTA fiber-reinforced ionomer at room temperature (left) and 77 K (right).

thin layer tended to form into a helix because of the release of stress associated with the high degree of orientation of the PPTA fiber. Figure 6(a) shows such strips formed by cohesive failure. A fibrillation of PPTA fibers reported by Greenwood and Rose⁸ and O'Conner¹² has not been observed in the composites used in this study.

In a series of the ionomer composites (Fig. 7), indications of good fiber-matrix adhesion are apparently observed in both cases of surface-modified fibers [Fig. 7(b), left] and surface-unmodified fibers [Fig. 7(a), left] at room temperature. However, the composite of untreated PPTA fibers and ionomer was fractured at the interface at 77 K [Fig. 7(a), right], whereas the composite of surface-modified PPTA fibers and ionomer was not fractured at the interface, even with fracture temperatures as low as 77 K [Fig. 7(b), right].

Figure 8 shows the fractured surfaces of the carbon fiber-reinforced ionomer at room temperature and 77 K. Some evidences of good fiber-matrix adhesion are observed on the surface of carbon fibers fractured at room temperature [Fig. 8(b)]. It is thought that they are due to the roughness of the carbon fiber surface, which causes a physical adhesional force, or the carbon fiber surface-induced crystallization because of its high-surface energy in the matrix. With respect to the latter point, a further result is discussed in the section of crystallization. On the other hand, no evidence was observed on the surface when the composite was fractured at 77 K [Fig. 8(c)]. Moreover, the fracture mode was the interfacial type. These observations suggest that, in spite of some adhesive strength between carbon fiber and ionomer at room temperature, it is very weak at 77 K. The great difference in the linear thermal expansion coefficient between carbon fiber and ionomer might induce the residual stress at 77 K, which acts to decrease the adhesive strength at the interface.

Crystallization

The temperature of crystallization and the crystallinity obtained by DSC are shown in Table IV. The samples were melted and kept molten at 453 K for 20 min: the cooling rate was 10 K/min.

In a series of polyethylene composites, the composite of polyethylene and PPTA fibers with the surface modified by octadecyl groups induced the crystallization of polyethylene, judging from the higher crystallization temperature than that of polyethylene only. Pure polyethylene and the composite of polyethylene and PPTA fibers crystallized at 363 K, whereas the composite with the surface-modified PPTA fibers crystallized at 367 K. On the other hand, its crystallinity (29%) was lower than those of the formers (about 35%). It is con-

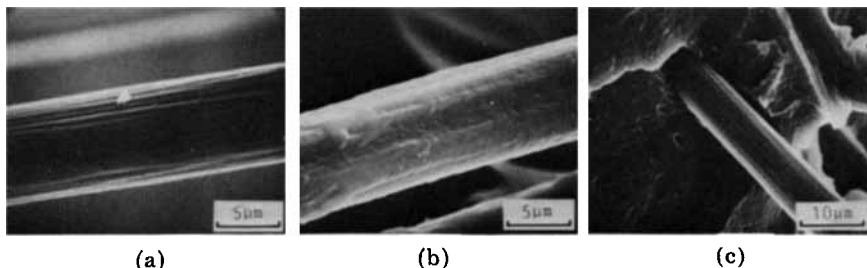


Fig. 8. Scanning electron micrographs of (a) carbon fiber and (b) fracture surfaces of the carbon fiber-reinforced ionomer at room temperature and (c) at 77 K.

TABLE IV
Temperature of Crystallization and Crystallinity

Sample	Temperature of crystallization (K)	Crystallinity (%)
PE ^a	363	35
Kevlar fiber/PE	363	36
Oc—Kevlar fiber ^b /PE	367	29
Ionomer	335	17
Kevlar fiber/ionomer	334	18
Cm—Kevlar fiber ^c /ionomer	334	17
Carbon fiber/ionomer	334	25

^a Polyethylene.

^b Kevlar fiber with the surface modified by octadecyl group.

^c Kevlar fiber with the surface modified by carboxymethyl group.

ceivable that the surface-modified fibers induced the crystallization of polyethylene.

In a series of ionomer composites, both composites of ionomer with PPTA fibers and with surface-modified PPTA fibers by carboxymethyl groups did not exhibit any changes in the crystallization process. The composite of ionomer and carbon fibers crystallized at the same temperature as those of ionomer only and the composites with PPTA fibers, but its crystallinity of 25% was higher than those of other composites of about 17%. The carbon fibers might act as a nucleating agent, which has relatively high-surface energy in polyethylene matrix,¹⁷ and the crystallinity was therefore developed in ionomer matrix, which shows the same crystal structure as that of polyethylene. This presents the possibility of producing a crystallite-rich inner layer whose modulus is intermediate between that of carbon fiber and the bulk resin. Another evidence for a crystallite-rich innerlayer is that the surface of carbon fibers fractured at room temperature (Fig. 8) is quite different from that of the original surface of carbon fibers.

Thermomechanical Analyses

Rheovibron measurements at 11 Hz on polyethylene, ionomer, and their composites are shown in Figures 9–12. In a series of polyethylene and its composites, the height of the primary $\tan \delta$ peak in polyethylene located around 270

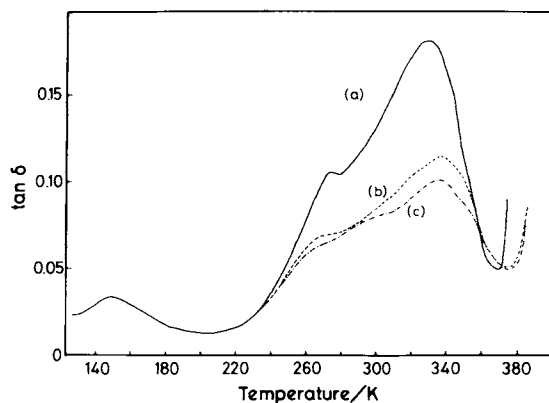


Fig. 9. Plots of $\tan \delta$ vs. temperature for (a) polyethylene, (b) the composite with PPTA fibers, and (c) the composite with surface-modified PPTA fibers.

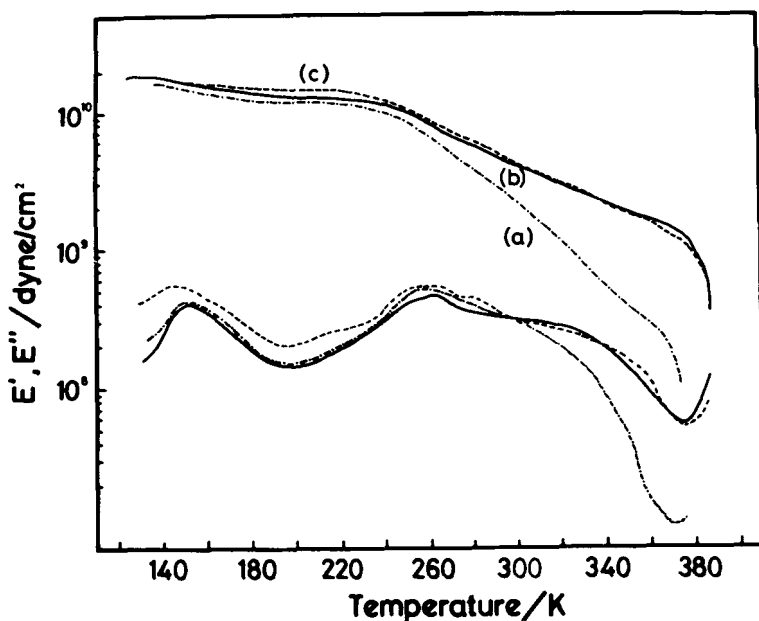


Fig. 10. Plots of E' and E'' vs. temperature for (a) polyethylene, (b) the composite with PPTA fibers, and (c) the composite with surface-modified (octadecyl group) PPTA fibers.

K decreased considerably in its composites. The crystalline relaxation located around 340 K shows a similar tendency. The great difference in $\tan \delta$ between the composite with PPTA fibers and surface-modified PPTA fibers was not observed (Fig. 9). Another feature of the composites is that the steep increase of $\tan \delta$ curves associated with crystal melting shifts to the higher temperature side for the composites. The same tendency can be seen in the E'' curves in Figure 10. The decrease in the height of the crystalline $\tan \delta$ peak or the absorption magnitude in the composites means that the vibrational or reorientational motion of molecules within the crystals of polyethylene suffers the restraint from the surroundings. A similar situation holds for the primary relaxation

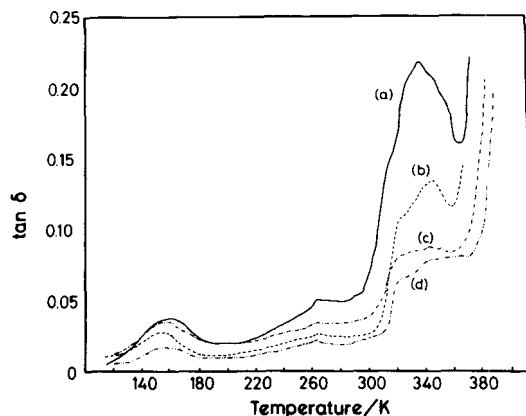


Fig. 11. Plots of $\tan \delta$ vs. temperature for ionomer and its composites with various PPTA fibers or carbon fibers: (a) ionomer; (b) carbon fiber; (c) PPTA fiber; (d) PPTA fiber with the surface modified by carboxymethyl group.

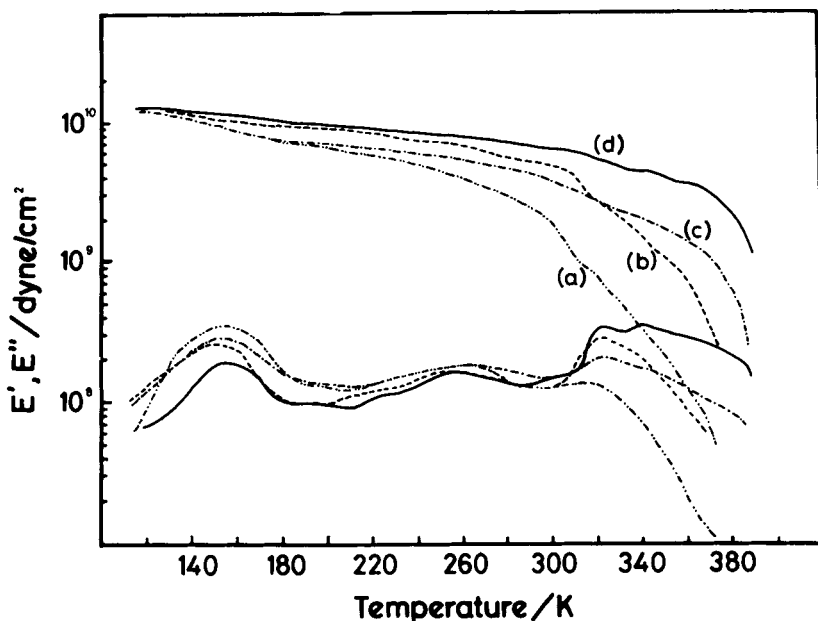


Fig. 12. Plots of E' and E'' vs. temperature for ionomer and its composites with various PPTA fibers or carbon fibers: (a) ionomer; (b) carbon fiber; (c) PPTA fiber; (d) PPTA fiber with the surface modified by carboxymethyl group.

located around 270 K. The reinforcements do not restrain the local mode motions of linear methylene sequences, which is reflected in the γ peak at around 150 K. Figure 10 shows an increase in the storage modulus of the composites over the whole temperature range above 160 K, compared with that of polyethylene. The very important fact is that the moduli for the composites are maintained at the temperature close to the melting point of polyethylene and the heat endurance of polyethylene was therefore improved by the presence of the reinforcement of 5% by weight.

In a series of ionomer and its composites, the primary $\tan \delta$ peak in ionomer located at around 340 K, designated the α relaxation, which has been assigned to the motions associated with the ionic phase and can be considered as a softening temperature of the ionic domains,¹⁸ decreased in its magnitude in order of the composite with carbon fibers, PPTA fibers, and PPTA fibers having the surface modified by carboxymethyl groups (Fig. 11). In the case of the composite with carbon fibers, the steep increase of $\tan \delta$ curve associated crystal melting is the same as that of ionomer, whereas the steep increase of $\tan \delta$ curves shifts to higher temperature sides for the composite with PPTA fibers and surface-modified PPTA fibers. Especially, the composite with surface-modified PPTA fibers shows the biggest shift in these composites and also the same splitting of the α peak as that of the highly ionized ionomers, which may be due to the overlapping by the peak of the onset of melting.¹⁹ The same tendency can be seen in the E'' curves in Figure 12 with exception that the E'' curve for the composite with carbon fibers becomes smaller than that of the composite with PPTA fibers above 340 K. The fact that the α peak shifts to higher temperatures suggests that the motions including the ionic phase suffer the greater restraint from the surroundings associated with the PPTA fibers having the surface modified by carboxymethyl groups.

The secondary $\tan \delta$ peak in ionomer, designated the β' relaxation, which is due to the motions of branched-chain segments and involves the breaking and reforming of interchain hydrogen bonds at around 290 K, cannot be seen in these samples employed in this study because of high sodium content.

The β peak around 260 K, assigned to a relaxation occurring in the amorphous branched polyethylene phaser, from which most of the ionic material has been excluded, remains at the same position in all of the composites. The $\tan \delta$ peak decreases in its magnitude in order of the composite with PPTA fibers, carbon fibers, and surface-modified PPTA fibers. The degree of the peak represents the increase of immobilization of amorphous chains.

The γ relaxation peak, being mainly due to a crankshaft motion of short hydrocarbon segments in the amorphous phase, decreases in its magnitude for the composite with surface-modified PPTA fibers, whereas those for other composites exhibit no change. These facts indicate that surface-modified PPTA fibers are effective in imposing a greater restraint to the molecular motions of the amorphous phase including ionic domains in the matrix and, therefore, improve the Young's modulus for ionomer most efficiently in these composites. Figure 12 shows a marked increase of the storage moduli for the composites compared with that of ionomer. Especially for the composite with surface-modified PPTA fibers, the highest modulus values were held over the whole range of temperature. It is noteworthy that the retention of the modulus is retained even at the temperatures above the melting temperature of ionomer. The heat resistance of ionomer is remarkably improved by the presence of surface-modified PPTA fibers by an amount of 60°C at the E' level of 0.3 MPa, even with weight fractions as low as 3.4%.

CONCLUSIONS

The surface of PPTA fiber was modified by the polymer reaction via the metalation reaction in a solution of sodium methylsulfinylcarbanion in dimethyl sulfoxide and was combined with several functional groups such as octadecyl, carboxymethyl, and acrylonitrile. The modified surface was much rougher than that of the original fibers, and the surface layer was about 1 μm thick according to the scanning electron microscopic observation. These discontinuous fibers could be isotropically dispersed in polyethylene and ionomer.

In the case of polyethylene composites, the mechanical properties were improved for the composite with the surface-modified PPTA fibers by octadecyl groups, compared with the composite of polyethylene and PPTA fibers, and the crystallization was induced by the surface-modified PPTA fibers.

In the case of ionomer composites, the mechanical properties of the composite of ionomer and PPTA fibers with the surface modified by carboxymethyl groups were remarkably improved, compared with those of other ionomer composites such as PPTA fiber/ionomer and carbon fiber/ionomer. The fiber efficiency factors of about 0.4 for both strength and modulus for the composite with random-in-plane oriented discontinuous PPTA fibers modified by carboxymethyl groups are comparable to the values for the composite with unidirectionally oriented discontinuous PPTA fibers. The surface-modified PPTA fibers did not affect the crystallization process, whereas they strikingly influenced molecular motions of amorphous phases including an ionic domain, with the result

that the magnitudes of the α , β , and γ relaxations decreased greatly, especially the α relaxation. The heat resistance of ionomer was remarkably improved by the presence of surface-modified PPTA fibers, even with volume fractions as low as 2.2%.

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