Polar–Polar Interaction between the Reinforcement and Matrix for Kevlar Fiber-Reinforced Composite: Effect of Using the Blend of Polar Polymers as Matrix

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Synopsis

For the purpose of investigating the polar–polar interaction between reinforcement and matrix in polymer composite, the mechanical dispersions were studied for the composite comprised of the Kevlar fiber and poly(hydroxy ether of bisphenol A) (I), with which poly(ethylene oxide) (II) or poly(ethylene adipate) (III) was blended as a part of matrix. It is shown by analyzing the storage modulus and loss modulus vs. temperature curves that the reinforcement–matrix interaction is increased relatively to the primary transition temperature of matrix by blending II or III with I, and II is more efficient for increase of the interaction than III. The results obtained from the mechanical dispersions do not contradict those from the Fourier transform infrared spectra on the matrix-polymer-coated Kevlar fiber and on the mixture of matrix polymers with benzanilide, which is used as a model compound for the Kevlar fiber.

INTRODUCTION

It is generally accepted that the nature of the matrix–reinforcement interaction plays an important role on the performance of composite material. In the previous paper[1] it was reported that the matrix–reinforcement interaction was increased with the fraction of the polar component in matrix for the composite comprised of Kevlar fiber and the blend of polystyrene with poly(methyl methacrylate) or with poly(hydroxy ether of bisphenol A) from the studies of the mechanical properties and infrared spectroscopic properties. It was also shown in the paper that a synergistic effect, which could not be expected from the additivity of components properties, could be observed in the matrix–reinforcement interaction for the composite comprised of Kevlar fiber and the blend of poly(methyl methacrylate) with poly(hydroxy ether of bisphenol A). The blends mentioned above show, however, the relatively poor miscibility. Therefore, the sample used in the work is not necessarily appropriate to study unambiguously the matrix–reinforcement interaction on a microscopic level.

The purpose of present work is to study further the polar–polar interaction in the composite comprised of Kevlar fiber and the blend of poly(hydroxy ether of bisphenol A) with a polyether or polyester. Poly(ethylene oxide) and poly(ehtylene adipate) were used as the components of polyether and polyester, respectively. The miscibility of the blend of poly(hydroxy ether of bisphenol A) with the polyether or polyester is known to be good as reported in

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the literature.[2,3] The matrix–reinforcement interaction was investigated from the mechanical dispersion and Fourier transform infrared spectroscopy.

EXPERIMENTAL

Materials

Cut fiber (5 mm long) and plain cloth (0.12 mm thick) of Kevlar 49 (DuPont) (K) were used as reinforcement. Poly(hydroxy propyl ether of bisphenol A) (U.C.C., MW 40,000) (P), poly(ethylene oxide) (Aldrich Chemical Co., MW 100,000) (E), and poly(ethylene adipate) (Scientific Polymer Products Inc., MW 7800) (A) were used as the components of matrix. Benznilide (Aldrich Chemical Co.) (B) was used as a model compound for Kevlar fiber.[4]

Preparation of Composites

The mixture of matrix components was dissolved in dichloromethane, and the cut fiber was added to this solution and dispersed uniformly by stirring. This matrix–reinforcement mixture was cast on to the glass plate. After the majority of solvent was evaporated, the residual solvent was removed in a vacuum oven at elevated temperature. For measurement of mechanical dispersions, the specimen of composite was obtained by compressing at 150–240°C depending on the composition of matrix.

TABLE I
Composition of Samples

Symbol of sample	Matrix		Reinforcement
	Component	Composition (wt %)	
P		100–0	
9P/E		90–10	
8P/E	Pᵃ–Eᵇ blend	80–20	
7P/E		70–30	
6P/E		60–40	None
9P/A		90–10	
8P/A	P–Aᶜ blend	80–20	
7P/A		70–30	
6P/A		60–40	
P–K		100–0	
9P/E–K		90–10	
8P/E–K	P–E blend	80–20	
7P/E–K		70–30	
6P/E–K		60–40	Kevlar fiber (5 mm long, 7% by vol)
9P/A–K		90–10	
8P/A–K	P–A blend	80–20	
7P/A–K		70–30	
6P/A–K		60–40	

ᵃ Poly(hydroxy propyl ether of bisphenol A).
ᵇ Poly(ethylene oxide).
ᶜ Poly(ethylene adipate).

Thus, the specimen prepared in this study was discontinuous fiber-reinforced composite made with random in-plane fiber orientation. The volume fraction of Kevlar fiber in composite was 0.07. The specimen of nonreinforced polymers was also prepared. The composition of samples is tabulated in Table I. Two series of composite samples were obtained: (1) P/E–K samples, in which the ratio of P to E was varied, and (2) P/A–K samples, in which the ratio of P to A was varied.

Measurements

The mechanical dispersions were measured by Rheovibron DDV-II (Toyo Boldwin Instrument Co.) at 11 Hz.

The Fourier transform infrared (FT–IR) spectra were obtained at 1 cm^{-1} resolution using JIR-100 (Nihon Denshi Co.). The spectra of the polymer matrix-coated Kevlar cloth were obtained by the internal reflection spectroscopy (IRS) on 45° germanium element.[5] The coating of Kevlar cloth was made with 0.05% polymer solution in dichloromethane and the solvent was completely removed in a vacuum oven. The spectra of the mixture of polymer matrix with B were obtained by the transmission method on a sample film coated onto potassium bromide window. The coating of sample film was made from a 1% solution of mixture of the matrix polymer and B in dichloromethane, and the solvent was completely removed in a vacuum oven.

RESULTS AND DISCUSSION

Mechanical Dispersions

The storage modulus E' and loss modules E'' vs. temperature curves of P/E–K and P/E samples are shown in Figures 1 and 2, respectively. For P–K, two dispersions appear at about 110 and 140°C. The lower temperature dispersion (α) corresponds to the primary transition of matrix (P). The higher temperature dispersion (α'), which does not appear in nonreinforced polymer as shown in Figure 2 (P), can be attributed to the interphase formed on reinforcing fiber surface by the strong interaction between the reinforcement and matrix as reported in the previous paper.[1] By blending E with P as a part of matrix (9P/E–K), the E' vs. temperature curve broadens and shifts to lower temperature side, and the temperature interval between the higher and lower temperature dispersions on the E'' vs. temperature curve increases compared with the case of P–K. By further increasing the blending ratio of E (8P/E–K, 7P/E–K), the broadening and shift to lower temperature side of the E' vs. temperature curves and the increases of the temperature interval between the two dispersions on the E'' vs. temperature curves can also be observed as the case of 9P/E–K. For 6P/E–K, the E' vs. temperature curve becomes sharp and shifts to higher temperature side compared with 7P/E–K, and the temperature interval between the two dispersions decreases compared with the cases of 7P/E–K, 8P/E–K, and 9P/E–K. This is probably attributed to the incipience of crystallization of E component in the vicinity of this blend ratio.[2] For nonreinforced polymers, the E' vs. temperature curves run almost in parallel with each other and the primary transition can only be observed on the E'' vs. temperature curves, irrespective of the blend ratio of P to E as shown in Figure 2.
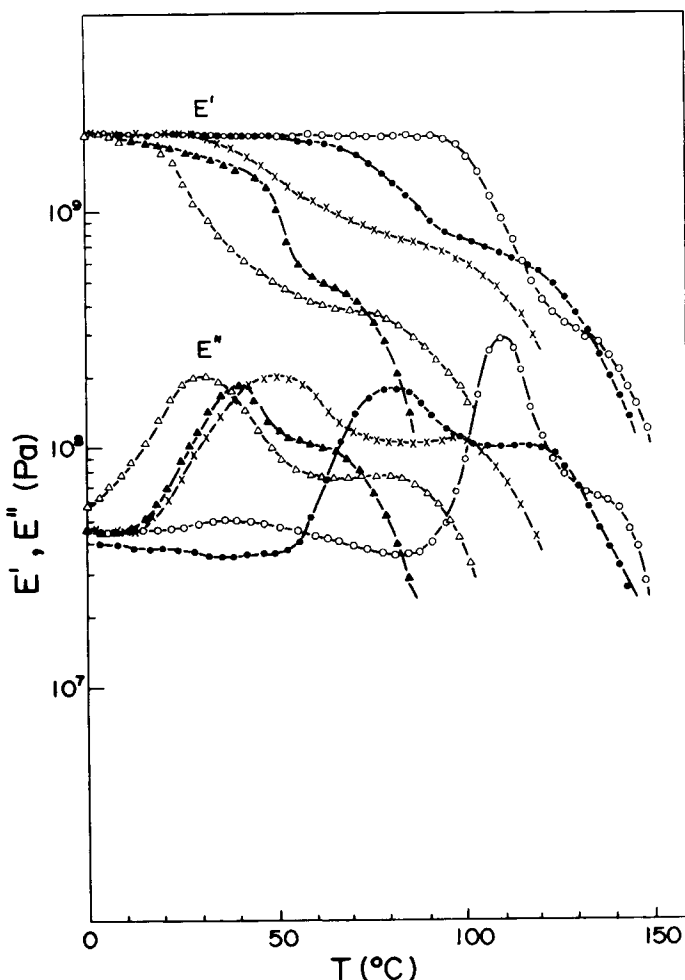
Fig. 1. E' and E'' vs. temperature curves for P/E-K samples: (○) P-K; (●) 9P/E-K; (×) 8P/E-K; (△) 7P/E-K; (▲) 6P/E-K.

A modulus plateau, which appears above the primary transition temperature and drops off at the higher temperature, can be found in the E' vs. temperature curves for the composites. The plateau is extended by incorporation of E in matrix as shown in Figure 1. Generally, the modulus plateau is observed at rubbery region on the storage modulus vs. temperature curve as a strong function of molecular weight for linear polymers. In this experiment, however, the plateau cannot be found for the nonreinforced polymers as shown in Figure 2. This fact shows that the appearance of the modulus plateau is not a molecular weight effect. The origin of the plateau should be ascribed to the specific interaction among the matrix polymers and reinforcement. Consequently, the α' dispersion can also be ascribed to the strong interaction between the matrix and reinforcement as mentioned above.

The E' and E'' vs. temperature curves of P/A-K and P/A samples are shown in Figures 3 and 4, respectively. The E' vs. temperature curves of P/A
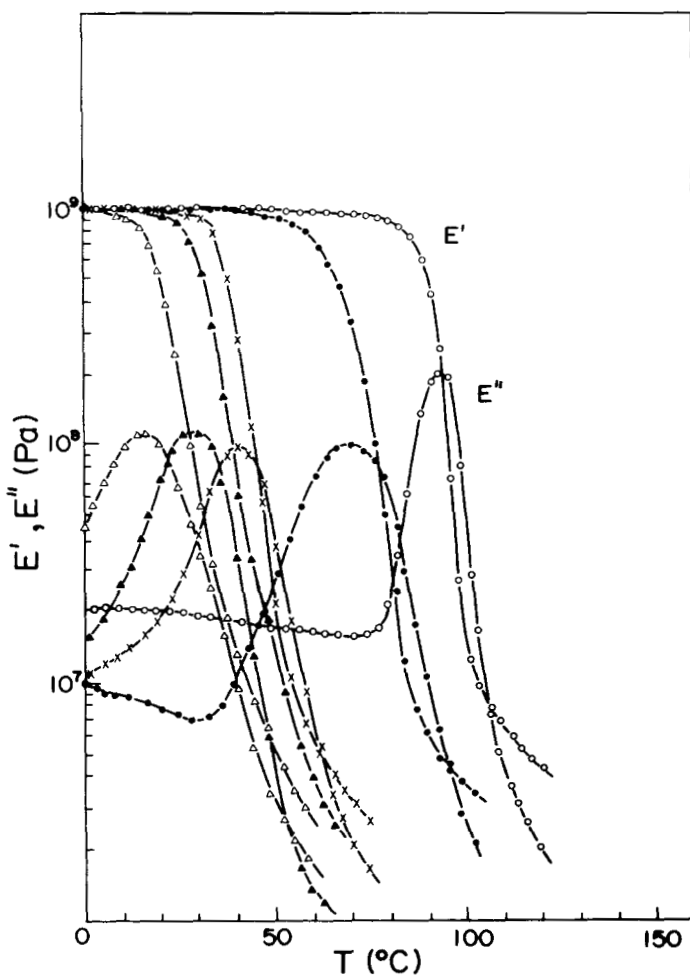
Fig. 2. E' and E'' vs. temperature curves for P/E samples: (○) P; (●) 9P/E; (×) 8P/E; (△) 7P/E; (▲) 6P/E.

samples run almost in parallel with each other and the slopes at transition region are nearly constant and equal to those of P/E samples. For P/A–K samples, the broadening of the E' vs. temperature curves by blending A with P as a part of matrix is less than the cases of P/E–K samples except for 6P/E–K. The degree of the increase of the temperature interval between the two dispersions on the E'' vs. temperature curves by blending A with P is also smaller than the cases of P/E–K samples.

A modulus plateau can also be found in the E' vs. temperature curves of Figure 3 at relatively ambiguous appearance as compared with the case of Figure 1. The arise of the plateau should also be ascribed to the same origin as that described at above section.

The rule of additivity of properties of components for the composite was applied to the E' data to evaluate the fiber efficiency factor for modulus. The rule of additivity expression for modulus of discontinuous fiber-reinforced
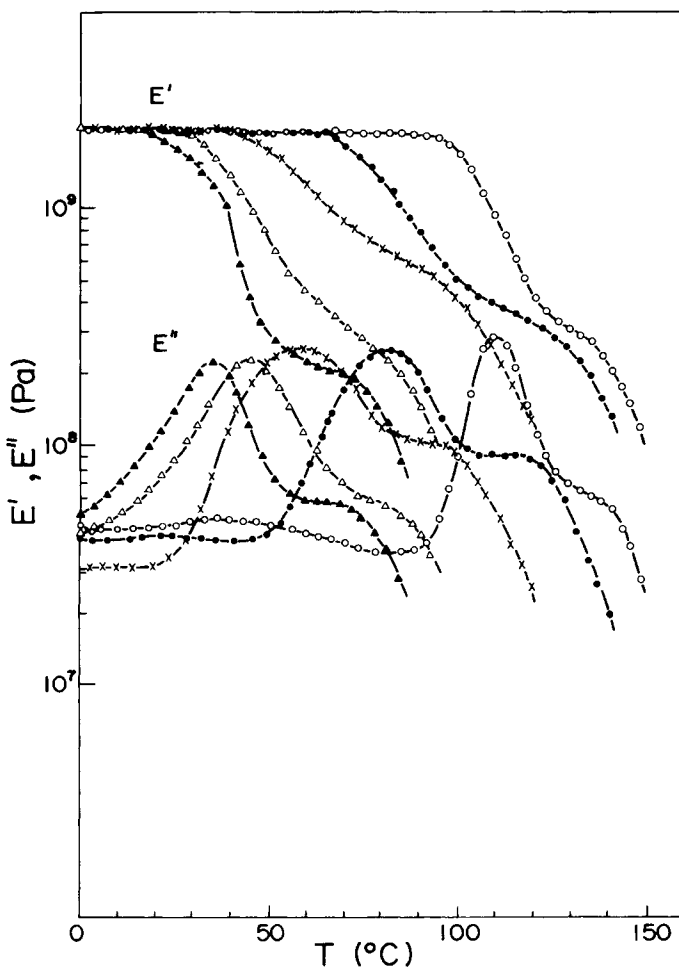
Fig. 3. E' and E'' vs. temperature curves for P/A–K samples: (○) P–K; (●) 9P/A–K; (×) 8P/A–K; (△) 7P/A–K; (▲) 6P/A–K.

composite made with random-in-plane fiber orientation[6] is

$$E_c = K_E E_f v_f + E_m(1 - v_f)$$

where E_c is the modulus of composite, K_E is the fiber efficiency factor for modulus, E_f is the modulus of reinforcement [1.2×10^{11} Pa for Kevlar 49 [7]], v_f is the fiber volume fraction, and E_m is the modulus of the nonreinforced polymer. In Figure 5, K_E is plotted as a function of $T - T_\alpha$, where the primary transition temperature T_α is used for the purpose of comparing the data at a corresponding state. K_E decreases with increase of temperature,[8] and the decrease is prominent above T_α. K_E of P/E–K and P/A–K is larger than that of P–K above T_α. This implies that the blending of E or A with P increases the fiber efficiency factor for modulus above T_α.

The definite tendency of the changes in K_E with temperature becomes unclear below T_α, probably because of the smaller temperature dependence of
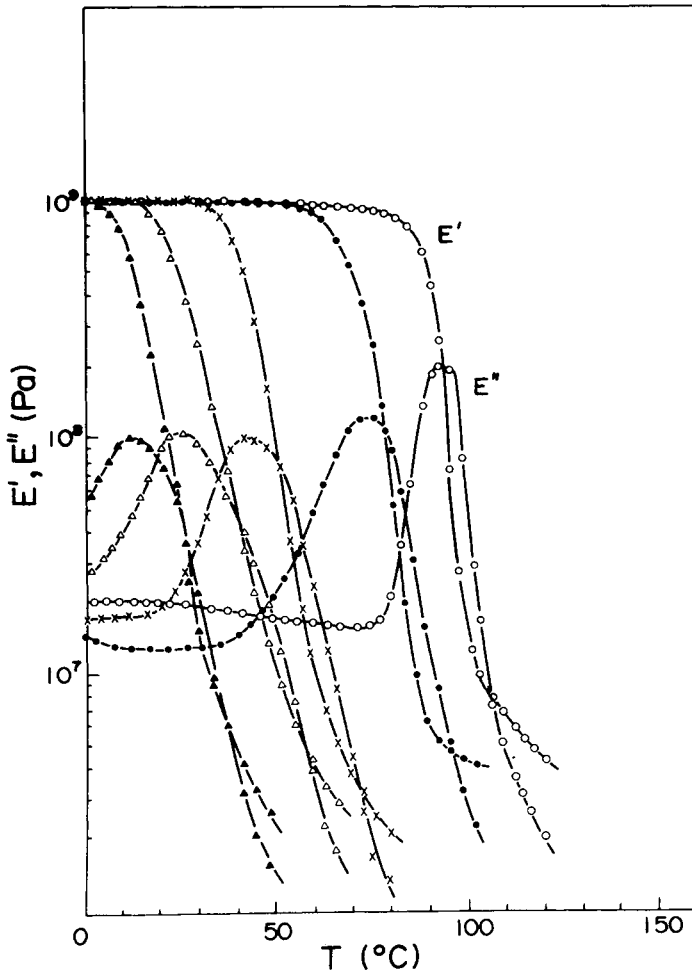
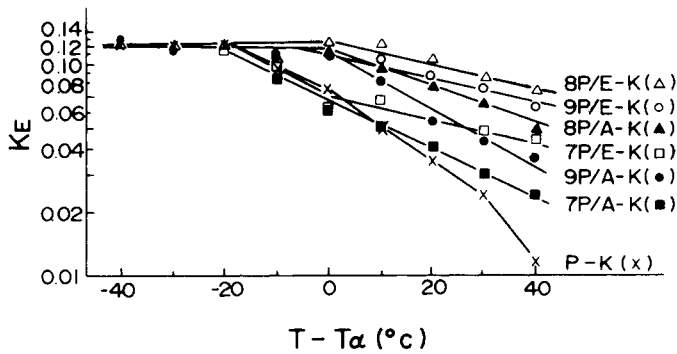Fig. 4. E' and E'' vs. temperature curves for P/A samples: (○) P; (●) 9P/E; (×) 8P/E; (△) 7P/E; (▲) 6P/E.

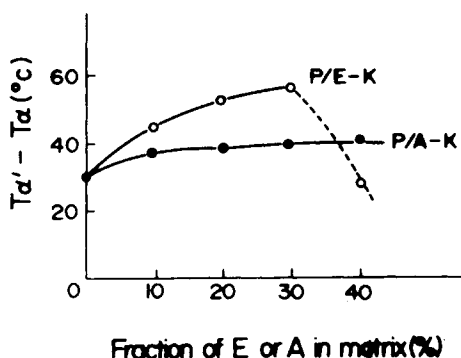Fig. 5. Fiber efficiency factor K_E vs. temperature relations for composites.

Fig. 6. Dependence of the temperature interval between the α' and α dispersions on the fraction of E or A in matrix.

E' in contrast to the temperature region above T_α. The tendencies mentioned above concerning the behavior of K_E, however, ought to be retained below T_α. K_E of P/E–K is larger than that of P/A–K and the negative slope of K_E vs. $T - T_\alpha$ relation above T_α is always smaller for P/E–K than for P/A–K at the same content of P. These facts would imply that E is more efficient to enhance the fiber–matrix interaction than A when the polymers are used as a part of matrix by blending with P.

K_E vs. $T - T_\alpha$ relations shown in Figure 5 are relative representations for the samples having the wide range of T_α. Therefore, the representation should be thought to have no practical utility as it is.

The temperature interval between the two dispersions on the E'' vs. temperature curve ($T_\alpha' - T_\alpha$) is plotted in Figure 6 as a function of E or A fraction in matrix. $T_\alpha' - T_\alpha$ is larger for P/E–K than for P/A–K except for the point of P/E–K of the highest fraction of E. That is, the interphase formed in the vicinity of the fiber surface has higher transition temperature for P/E–K than for P/A–K. This would also imply that the interaction between the fiber and matrix is stronger for the composite containing E than for the composite containing A.

Fourier Transform Infrared Spectroscopy

The FT–IR spectra recorded at room temperature for Kevlar cloth (KC), Kevlar cloth coated with P/A blend containing 30% A (P/A on KC), and Kevlar cloth coated with P/E blend containing 30% E (P/E on KC) are shown in Figure 7. Above 1800 cm^{-1} and vicinity, the spectrum cannot be observed unambiguously by this experimental method as reported in the previous paper,[1] probably because of anomalous dispersion of refractive index. The amide I band of P/A on KC and P/E on KC appear at the same frequency, but the frequency is higher than that of KC. The amide II band of P/A on KC appears at the same frequency as that of KC, and that of P/E on KC shifts to higher frequency as compared with KC. These spectral features imply that the interaction arises[1] between the amide group in Kevlar fiber and P/E or P/A blend, but the interaction at room temperature is stronger[9] for P/E on KC than for P/A on KC. Thus, the results obtained from the
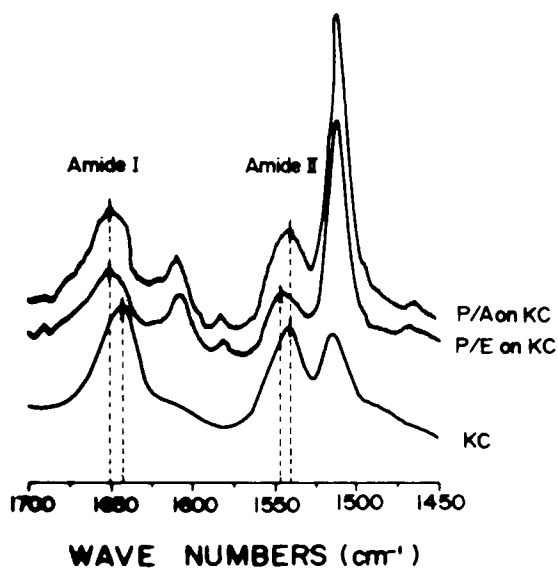
Amide I Amide II

P/A on KC

P/E on KC

KC

1700 1650 1600 1550 1500 1450

WAVE NUMBERS (cm⁻¹)

Fig. 7. FT–IR spectra of the region from 1700 to 1450 cm⁻¹ recorded at room temperature by the IRS method.

FT–IR spectroscopy does not contradict that from the mechanical dispersions.

The FT–IR spectra of B, the mixture of P/A containing 30% A with B in weight ratio of 10 to 8 (P/A/B), and the mixture of P/E containing 30% E with B in weight ratio of 10 to 8 (P/E/B) are shown in Figure 8 in the amide I and II regions. The mixing ratio of B to P/E or P/A is selected as the most desirable one for the observation of spectral features accompanied with the
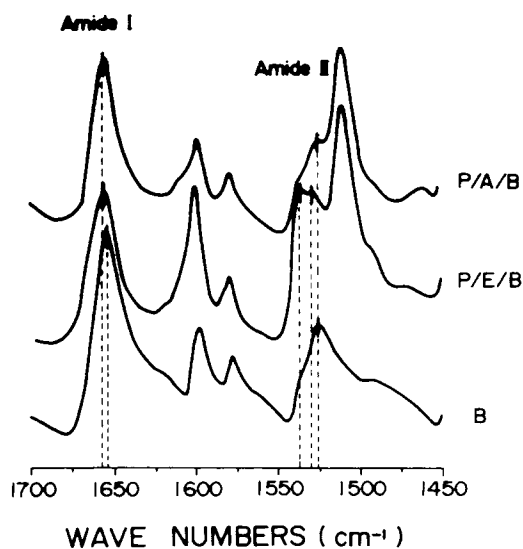
Amide I

Amide II

P/A/B

P/E/B

B

1700 1650 1600 1550 1500 1450

WAVE NUMBERS (cm⁻¹)

Fig. 8. FT–IR spectra of the region from 1700 to 1450 cm⁻¹ recorded at room temperature by the transmission method.

TABLE II
Wavenumbers for $\nu_{co\phi}$, ν_{coc}, and ν_{co} (cm^{-1})

	$\nu_{co\phi}$	ν_{coc}	ν_{co}
P	1246	—	—
E	—	1110	—
A	—	—	1740
P/E	1248	1107	—
P/E/B	1249	1109	—
P/A	1250	—	1739
P/A/B	1248	—	1738

interaction among the components. The amide I bands of P/A/B and P/E/B appear at the same frequency, but the frequency is slightly higher than that of B. The bands of amide II for P/A/B and B appear at the same frequency, and that for P/E/B splits into the doublet and shifts to higher frequency as compared with B. These spectral features are the same in tendency as those of Figure 7. That is, it can be said that B can be used as a good model compound for Kevlar fiber at least in the amide I and II regions.

The frequencies of stretching vibration of the ether linkages in P ($\nu_{co\phi}$) and E (ν_{coc}) and the carbonyl group in A (ν_{co}) are tabulated in Table II for P/E, P/E/B, P/A, and P/A/B. $\nu_{co\phi}$ and ν_{coc} of P/E/B are slightly higher than those of P/E. $\nu_{co\phi}$ and ν_{co} of P/A/B are, however, slightly lower than those of P/A. These results represent the changes in the interaction acting among the functional groups of matrix polymers by mixing B with P/E or P/A.

The spectrum above 1800 cm^{-1} and vicinity can be observed by the transmission method. The spectra of the hydroxyl stretching region are shown for P, P/E, P/E/B, P/A, and P/A/B in Figure 9. For P, the absorption at 3565 and 3450 cm^{-1} can be attributed to the free hydroxyl group and the hydrogen-bonded hydroxyl group, respectively.[10] For P/E, though the band of the free hydroxyl group appears at the same frequency as that of P, the band of hydrogen-bonded hydroxyl group shifts to lower frequency.[10] For P/A, though the band of the free hydroxyl group disappears, the band of the hydrogen-bonded hydroxyl group splits into two modes, the higher frequency mode representing comparatively weak hydrogen bonding. By mixing P/E with B (P/E/B), the band corresponding to the hydrogen-bonded hydroxyl group of P/E appears at higher frequency as compared with P/E.

By taking into account of the results of Table II, this change represents the weakening of the interaction acting among the functional groups of matrix by incorporation of B. Consequently, the interaction would be apt to arise between the matrix and B. By mixing P/A with B (P/A/B), the band corresponding to the hydrogen-bonded hydroxyl group centered at 3463 cm^{-1} for P/A appears at lower frequency as compared with P/A. By taking into account the results of Table II, this change represents the strengthening of the interaction acting among the functional groups of matrix by incorporation of B, contrary to the case of the former. Consequently, the interaction between the matrix and B would be hard to arise as compared with the case of P/E/B. For the case of P/E, the band of free hydroxyl group shifts to lower
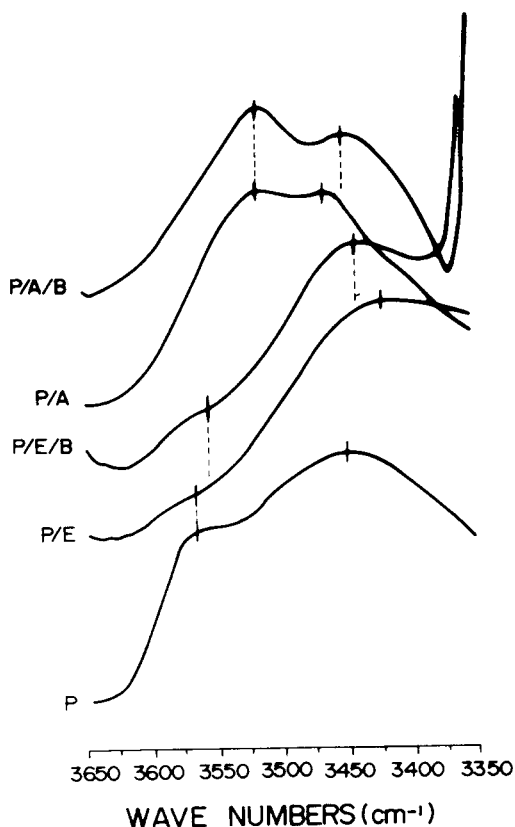
Fig. 9. FT–IR spectra of the region from 3650 to 3350 cm^{-1} recorded at room temperature by the transmission method.

frequency by incorporation of B. This change implies that the free hydroxyl group in P/E is apt to arise the interaction with B.

Thus, on account of above consideration, the interaction between P/E with B or K would possibly become stronger than that between P/A with B or K as shown in Figures 7 and 8.

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