Effects of Polar Groups of Polymer Matrix on Reinforcement-Matrix Interaction in Kevlar Fiber-Reinforced Composites

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Synopsis

In order to investigate the interaction between the polar groups of reinforcement and matrix in polymer composite, mechanical properties were studied for the Kevlar fiber-reinforced composites (Kevlar is a registered trademark of E. I. duPont de Nemours Co. Inc.), in which the kind and fraction of polar components in matrix were varied using blended polymers. For the composites comprised of polymethyl methacrylate and poly(hydroxypropyl ether of bisphenol A) as the matrix, a subtransition, which can be ascribed to the interphase formed on the reinforcement surface by a strong interaction between reinforcement and matrix, appears at a temperature above the primary transition on the E'' versus temperature curves. Such a subtransition is obscured or diminished accompanying the decrease in fraction of the polar components in the matrix. The fiber efficiency factors for strength are also decreased with a decrease in the fraction of the polar components. These results imply that the reinforcement-matrix interaction is affected depending on the fraction of the polar components in matrix.

For the composite comprised of blending the two polar components as the matrix, each component can contribute to the interaction with the reinforcement.

The results obtained from the Fourier transform infrared spectroscopy on the matrix polymer-coated Kevlar cloth do not contradict those obtained by studying the mechanical properties.

INTRODUCTION

The interaction between the polar groups of reinforcement and matrix plays an important role in the performance of composite materials. Depending on the kind and concentration of polar groups in reinforcement and matrix, the nature and degree of the reinforcement-matrix interaction can be expected to change characteristically. It is therefore useful to elucidate the effects of polar groups on the interaction for the composite comprised of well-characterized reinforcement and matrix.

In this paper the reinforcement-matrix interaction was studied by measuring the mechanical properties and infrared spectra for the Kevlar fiber-reinforced composite, in which the kind and fraction of polar components in matrix were aimed to be varied and adjusted using blended polymers. Kevlar fiber was used as a well-characterized reinforcement with regard to the kind and concentration of the polar groups.

EXPERIMENTAL

Materials

Cut fiber (5 mm long) and plain cloth (0.12 mm thick) of Kevlar 49 (du Pont) were used as reinforcement. Polymethyl methacrylate (PMMA) (Acry pet VHF, Mitsubishi Rayon Co.), poly(hydroxypropyl ether of bisphenol A) (phenoxy) (PKHH, U.C.C.), and polystyrene (PST) (GPPS HF77, Mitsubishi Monsant Co.) were used as matrix. PMMA and phenoxy were used as polar components, and PST was used for adjustment of fraction of polar components by mixing with PMMA or phenoxy.

Preparation of Composites

The matrix component was dissolved in dichloromethane, and the cut fiber was added to this solution and dispersed uniformly by stirring. This reinforcement-matrix mixture was cast onto the glass plate. After the majority of the solvent was evaporated, the residual solvent was removed in a vacuum oven at elevated temperature. For measurement of mechanical properties, the specimen of composite was obtained by compressing at 240°C. 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 was 0.08. The composition of composite is tabulated in Table I. Three series of samples were obtained: (1) M/S-K samples, in which the fraction of PMMA was varied regularly, (2) P/S-K samples, in which the fraction of phenoxy was varied regularly, and (3) P/M-K samples, in which the mixing ratio of PMMA with phenoxy was varied at three levels.

TABLE I
Composition of Samples

Symbol of composite	Matrix		Reinforcement
	Component	Composition (wt%)	
M-K		100/0	
75M/S-K		75/25	
50M/S-K	M-S blend[a]	50/50	
25M/S-K		25/75	
10M/S-K		10/90	
S-K		0/100	8 vol% of Kevlar fiber (5 mm long)
P-K		100/0	
75P/S-K	P-S blend[b]	75/25	
50P/S-K		50/50	
25P/S-K		25/75	
75P/M-K		75/25	
50P/M-K	P-M blend	50/50	
25P/M-K		25/75	

[a] Polymethyl methacrylate-polystyrene.
[b] Poly(hydroxypropyl ether) of bisphenol A-polystyrene.

Measurement

The mechanical dispersion was measured by Rheovibron DDV-II (Toyo Boldwin Instruments Co.) at 11 Hz.

The tensile strength was measured using Tensilon (Toyo Boldwin Instruments Co.) at 40%/min strain rate at room temperature.

The Fourier transform infrared (FT-IR) spectra were obtained at 1 cm^{-1} resolution using JIR-100 (Nihon Denshi Co.) for matrix components and polymer matrix-coated Kevlar cloths. The spectra of matrix components were obtained by internal reflection spectroscopy (IRS) on a 45° germanium element. The spectra of polymer matrix-coated Kevlar cloth were obtained with the coated polymer pressed to the IRS element.[1] 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 polymer layer was approximately 200 Å thick on average on the Kevlar fiber.

RESULTS AND DISCUSSION

Mechanical Dispersion

The loss modulus versus temperature curves of M/S-K samples are shown in Fig. 1. For M-K, two dispersions appear at about 130 and 150°C. The lower temperature dispersion corresponds to the primary transition of matrix (PMMA). The higher temperature dispersion, which does not appear in nonreinforced polymer, as shown by dotted curve in Fig. 1, can be attributed to the interphase formed on the reinforcing fiber surface by the strong interaction between reinforcement and matrix as reported previously by this author[2,3] and other investigators.[4,5] By mixing PST as a part of the matrix (75M/S-K), a dispersion corresponding to the primary transition of polystyrene (S-K) appears at about 120°C and the another dispersion also appears at about 150°C. By further increasing the PST content (50M/S-K and 25M/S-K), two dispersions can also be observed at nearly the same temperatures as those for 75M/S-K. However, the higher temperature dispersions are obscured in appearance with increase of PST content. For 10M/S-K, a dispersion corresponding to the primary transition of PST only can be observed.

The miscibility of PMMA with PST is poor, as shown by dotted curves in Fig. 1. It is likely that the domains of relatively pure PMMA and PST exist in matrix and the Kevlar fibers become preferentially surrounded by the PMMA domain, the domain of nonpolar polymer having difficulty in approaching the polar surface of Kevlar fibers. Nevertheless, the experimental results mentioned above could show the weakening tendencies of the reinforcement-matrix interaction with increase of the blending ratio of PST in matrix.

The loss modulus versus temperature curves of P/S-K samples are shown in Fig. 2. For P-K, two dispersions appear at about 110 and 140°C, similar to the case of M-K. Although the shape of the higher temperature dispersion differs characteristically from that of M-K, this dispersion can also be attributed to the interphase formed on the reinforcing fiber surface because of the lack of such dispersion in unreinforced polymer matrix, as shown by
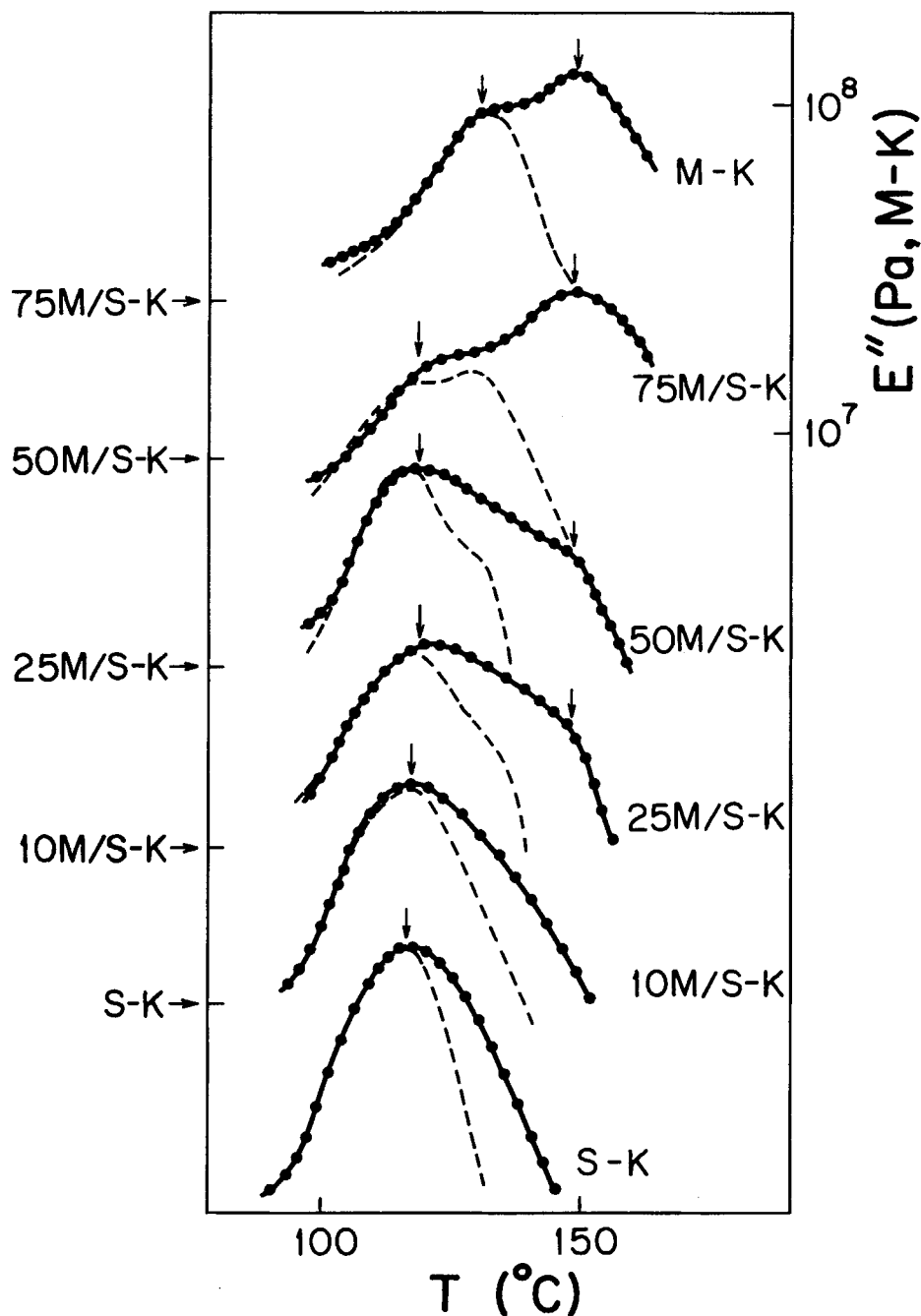
Fig. 1.   *E''* versus temperature curves for M/S-K samples. Left ordinate shows the positions of 10^8 Pa for each sample, and the scale is identical with that of the right side.

the dotted curve. For 75P/S-K and 50P/S-K, the dispersions based on the interphase also appear at about 140°C, but the dispersions are obscured in appearance with an increase in PST content in matrix. For 25P/S-K, the dispersion corresponding to the primary transition of PST only can be observed.

The miscibility of phenoxy with PST is relatively good, as shown in Fig. 2 by dotted curves. However, as the nonpolar polymer is difficult to contact intimately with the polar surface of Kevlar fibers, the polar polymer comes in preferential contact with the Kevlar fibers. Nevertheless, the experimental results show that the reinforcement-matrix interaction is weakened
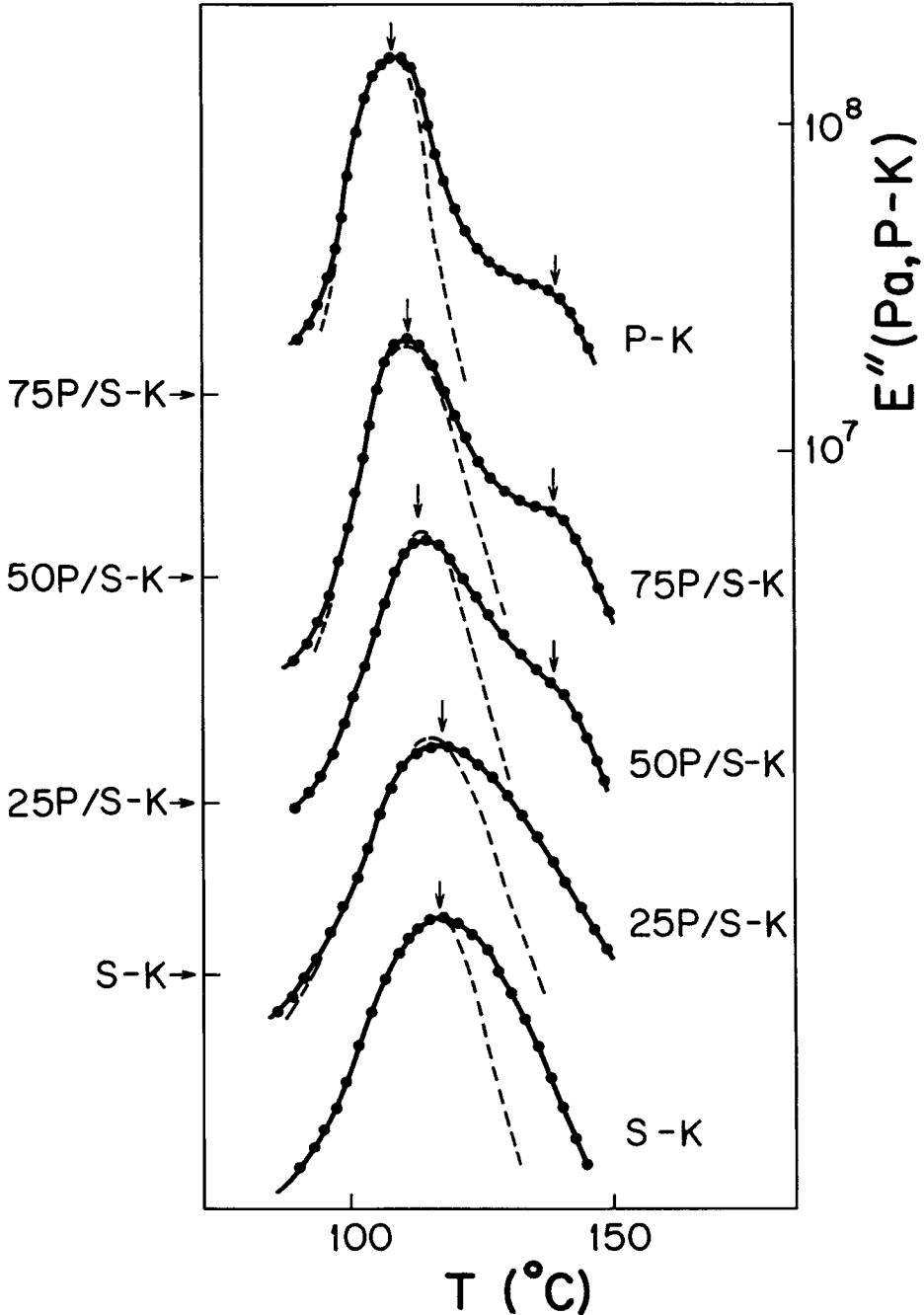

Fig. 2. E'' versus temperature curves for P/S-K samples. Left ordinate shows the positions of 10^8 Pa for each sample, and the scale is identical with that of the right side.

by incorporation of the nonpolar polymer in matrix, as is the case with the M/S-K samples.

The loss modulus versus temperature curves of P/M-K samples are shown in Fig. 3. Although the curves become broader compared with those of P-K and M-K, two dispersions are observed likewise. As the PMMA content is
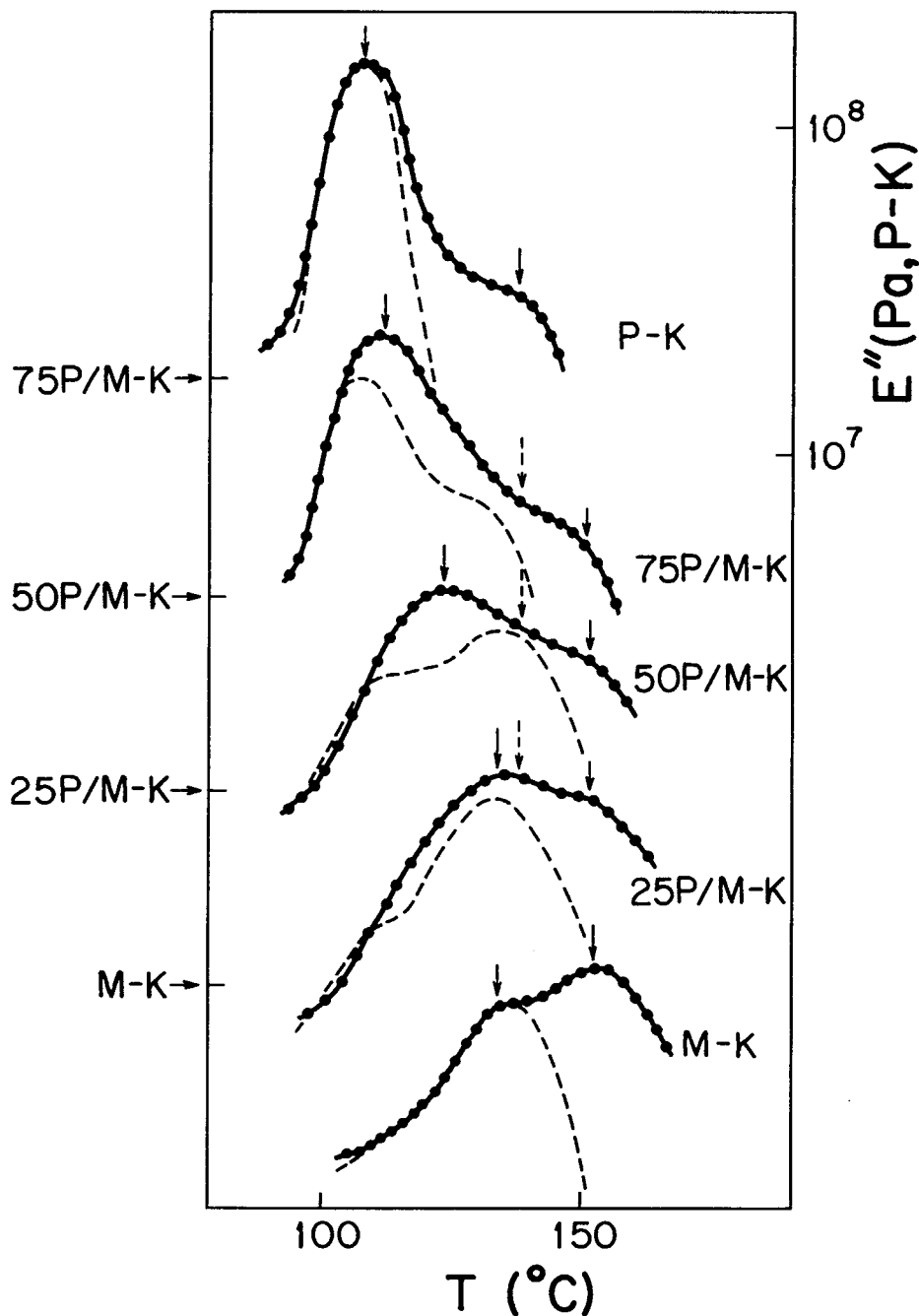

Fig. 3. E'' versus temperature curves for P/M-K samples. Left ordinate shows the position of 10^8 Pa for each sample, and the scale is identical with that of the right side.

increased in matrix, the lower temperature dispersion is shifted to the higher temperature side. The higher temperature dispersions of P/M-K appear at nearly the same temperature as that of M-K. The dispersion corresponding to the higher temperature dispersion of P-K is considered to be shielded from the higher temperature dispersion and the lower temperature dispersion as indicated by dotted arrows in Fig. 3. Thus, each polar component of matrix can be considered to contribute to the interphase formation.

Although the miscibility of PMMA with phenoxy is poor in unreinforced polymers, as shown by dotted curves in Fig. 3, the miscibility of both components in composite can be deduced to be increased from the appearance of a primary transition between those of P-K and M-K and the shift of this transition to the higher temperature side with increase of PMMA content.

The storage modulus versus temperature curves are shown in Fig. 4. For M/S-K and P/S-K, the storage modulus curves in the transition region run in parallel with each other and regularly depend on the composition of matrix. For P/M-K, the negative slopes of the curves are smaller than those of M-K and P-K. Especially for the case of 50P/M-K and 25P/M-K, the tendency is prominent and the curves cross with that of M-K at about 150°C. The unreinforced polymers have a nearly constant slope irrespective of the compositions. That is, the degree of decrease in storage modulus with temperature is smaller compared with others. This suggests that a specific reinforcing mechanism is operative in P/M-K samples.

Tensile Strength

The tensile strength at room temperature is shown for the composite and its matrix in Table II. The rule of additivity of properties of components for the composite was applied to the data to evaluate the fiber efficiency factor for strength. The rule of additivity expression for tensile strength of discontinuous fiber-reinforced composite made with random-in-plane fiber orientation[6] are

$$\sigma c = K\sigma \sigma_f v_f + \sigma_m (1 - v_f)$$

where σc is the tensile strength of composite, $K\sigma$ is the fiber efficiency factor for strength; σ_f is the ultimate strength of reinforcing fiber; v_f is the fiber volume fraction; and σ_m is the ultimate strength of unreinforced polymer. $K\sigma$ is plotted as a function of matrix composition, as shown in Fig. 5. For M/S-K samples, $K\sigma$ increases linearly with PMMA content in matrix. For P/S-K samples, $K\sigma$ also increases almost linearly with phenoxy content. For P/M-K samples, $K\sigma$ becomes larger than that expected from the additivity of P and M components. These results would also imply that a specific reinforcing mechanism is operative in P/M-K samples.

Fourier Transform Infrared Spectroscopy

The Fourier transform infrared spectra of PMMA, Kevlar cloth and Kevlar cloth coated with PST (PST on Kevlar), Kevlar cloths coated with PMMA (PMMA on Kevlar) and PMMA-PST blend with 50 wt% PMMA (50M/S on Kevlar) are shown in Fig. 6. The NH stretching (ν_{NH}) of Kevlar cloth cannot be observed unambiguously by this experimental method. The amide I and
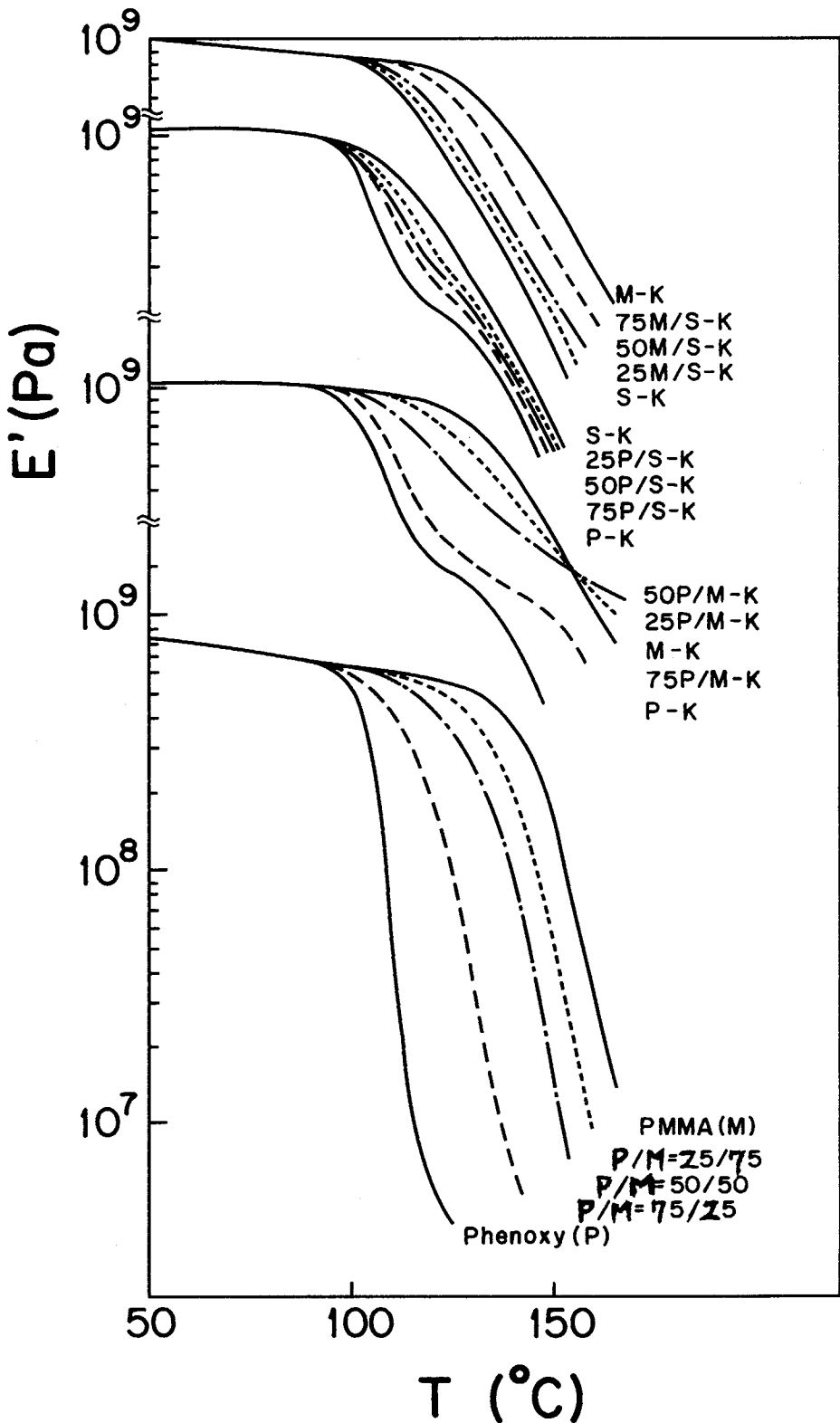
Fig. 4. *E'* versus temperature curves.

TABLE II
Tensile Strengths of Composite (σ_c) and
Its Matrix $(\sigma_m)^a$

	σ_c (MPa)	σ_m (MPa)
S-K	36	16
25M/S-K	55	26
50M/S-K	71	32
75M/S-K	89	40
M-K	108	48
25P/S-K	42	20
50P/S-K	49	23
75P/S-K	57	27
P-K	65	30
25P/M-K	102	44
50P/M-K	96	39
75P/M-K	91	35

^{a} The values are averages of five tests.
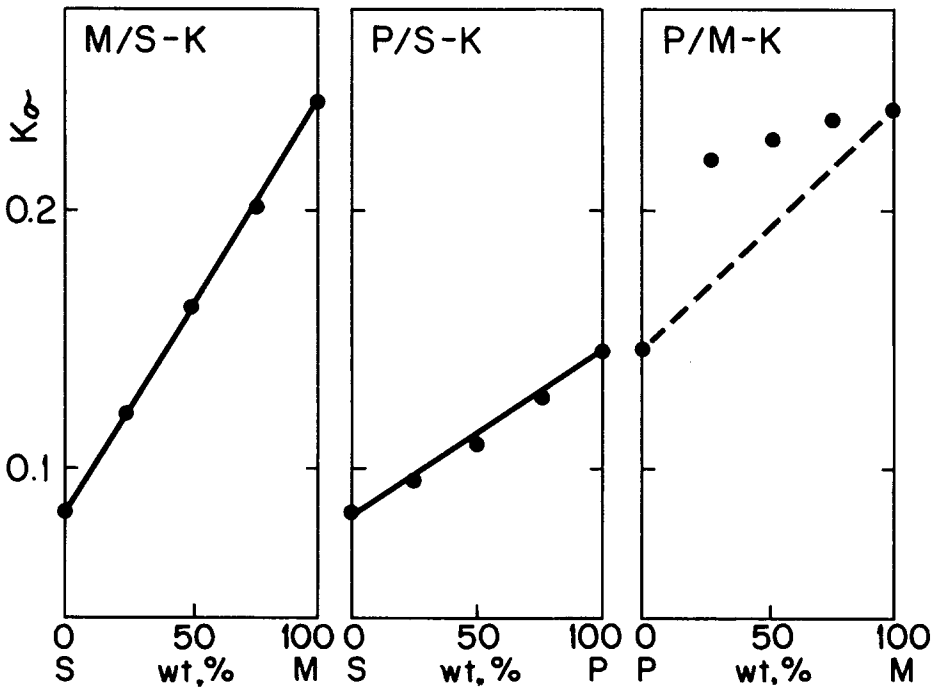
Fig. 5.   Fiber efficiency factor for strength $K\sigma$ versus composition of matrix; S, M, and P represent PST, PMMA, and phenoxy, respectively.

II bands of Kevlar cloth and PST on Kevlar appear at the same frequency, respectively. For PMMA on Kevlar, the amide I and II bands of Kevlar cloth shift to the higher frequencies and the carbonyl stretching (ν_{CO}) of PMMA shifts to the lower frequency. These changes imply[7] the strengthening of interaction between the carbonyl group of PMMA and NH group of Kevlar fiber, probably by the formation of hydrogen bonding. This strengthening
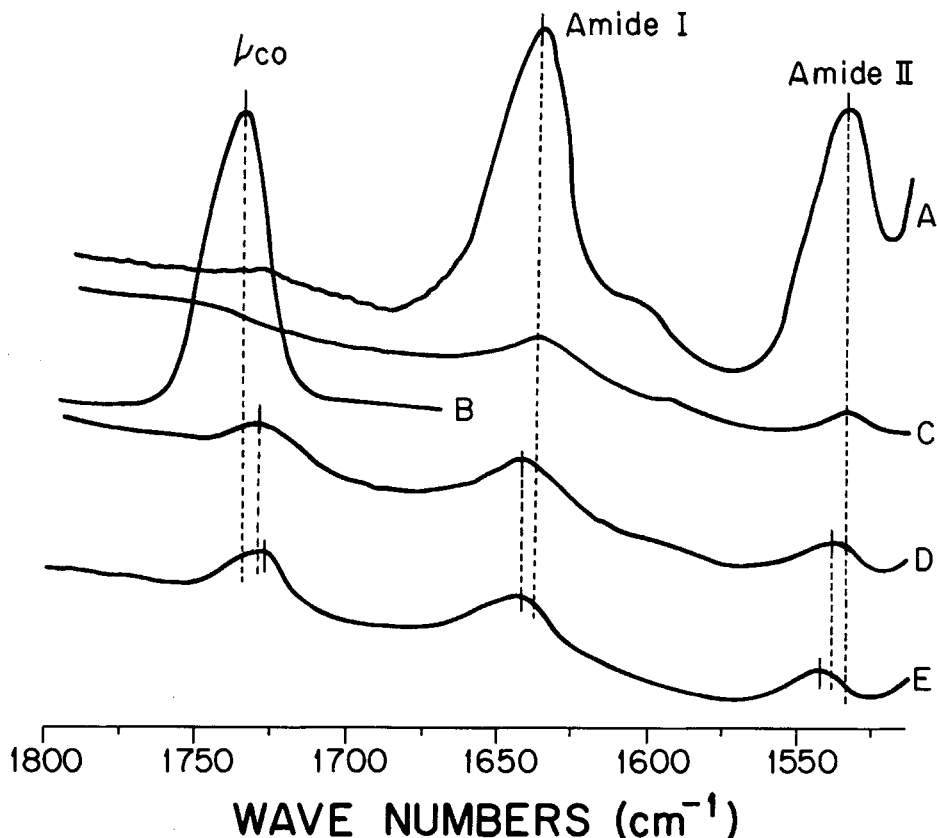
Fig. 6. FT-IR spectra recorded at room temperature: (A) Kevlar cloth, (B) PMMA, (C) PST on Kevlar cloth, (D) 50M/S on Kevlar cloth, (E) PMMA on Kevlar cloth.

of the interaction is considered responsible for the formation of the inter-phase in M-K, as mentioned above. For 50M/S on Kevlar, the degrees of shifts to the higher frequencies of the amide II and to the lower frequency of ν_{CO} become somewhat smaller compared with PMMA on Kevlar. This would imply that the interaction between Kevlar fiber and polymer matrix is affected by incorporation of PST.

The FT-IR spectrum of phenoxy-coated Kevlar cloth (phenoxy on Kevlar) is shown in Fig. 7. The OH stretching (ν_{OH}) of phenoxy cannot be observed unambiguously by this experimental method. By coating with phenoxy (phenoxy on Kevlar), although the amide I band does not change its position, the amide II band shifts to the higher frequency. The spectrum of Kevlar cloth coated with phenoxy-PST blend with 50 wt% phenoxy (50P/S on Kevlar) hardly change from that of phenoxy on Kevlar with regard to the amide I and II bands.

By taking into account that the CO and NH groups are strongly hydrogen bonded originally in Kevlar fiber,[8] it can be deduced from the result of Fig. 7 (for phenoxy-coated Kevlar, although the amide I does not change its position, the amide II shifts to the higher frequency) that the hydroxyl groups of phenoxy on Kevlar fiber are hydrogen bonded with the CO groups of Kevlar fiber.
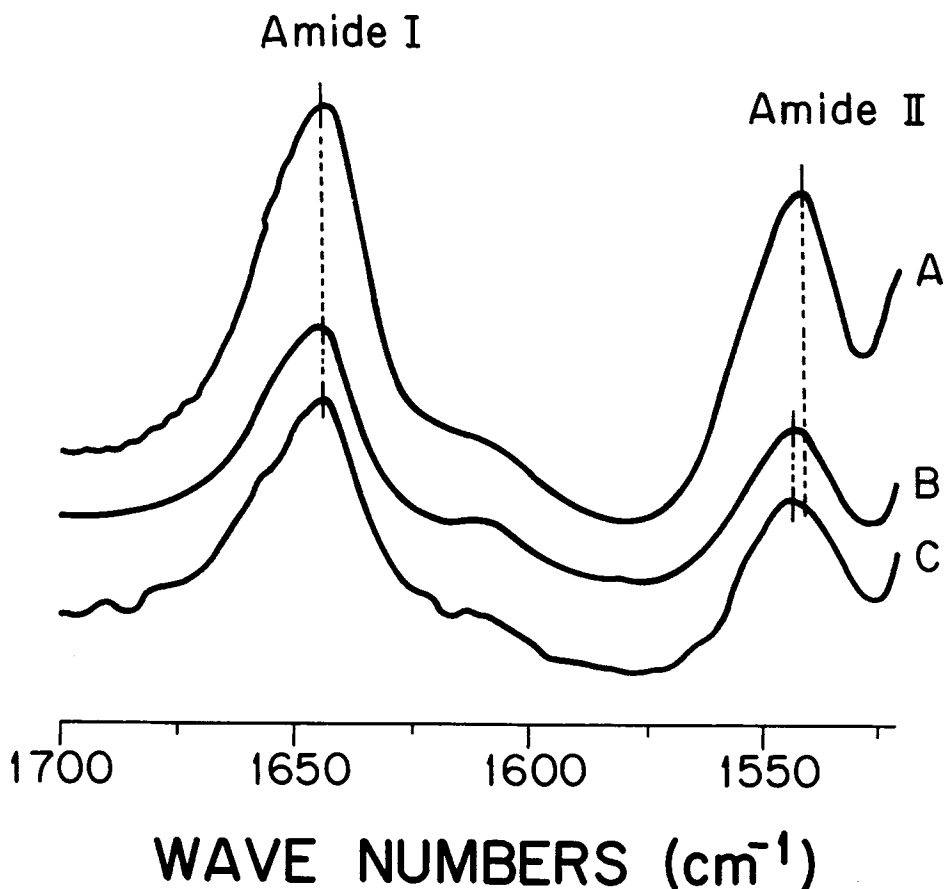
Fig. 7.   FT-IR spectra of the region from 1525 to 1700 cm^{-1} recorded at room temperature: (A) Kevlar cloth, (B) phenoxy on Kevlar cloth, (C) 50P/S on Kevlar cloth.

In Fig. 8 the difference spectrum obtained by subtracting the spectrum of Kevlar cloth from that of phenoxy-coated Kevlar cloth is shown by comparison with the spectrum of phenoxy from 1160 to 1280 cm^{-1}. The absorption around 1240 cm^{-1} is the ether linkage stretching (vc-o-c) of phenoxy. The absorption peak of the difference spectrum appears at the higher frequency compared with that of phenoxy. Phenoxy polymer is said[9] to self-associate through strong intermolecular hydrogen bonding of the hydroxyl groups. The ether linkages of phenoxy polymer may contribute to the self-association. If so, it is reasonable to consider that the self-associated hydroxyl and ether linkage are destroyed on Kevlar fiber (v_c-o-c shifts to the higher frequency), and the deassociated ether linkage interacts with the polar group in Kevlar, probably with the NH group. The shift of the amide II band to the higher frequency in phenoxy on Kevlar (Fig. 7) supports the above consideration. Thus, both the hydroxyl group and the ether linkage of phenoxy polymer possibly interact with the polar groups in Kevlar fiber.

The FT-IR spectrum of Kevlar cloth coated with phenoxy-PMMA blend with 50 wt% phenoxy (50P/M on Kevlar) is shown in Fig. 9. The absorption peak of v_c = o for 50P/M on Kevlar appears at the same frequency as that
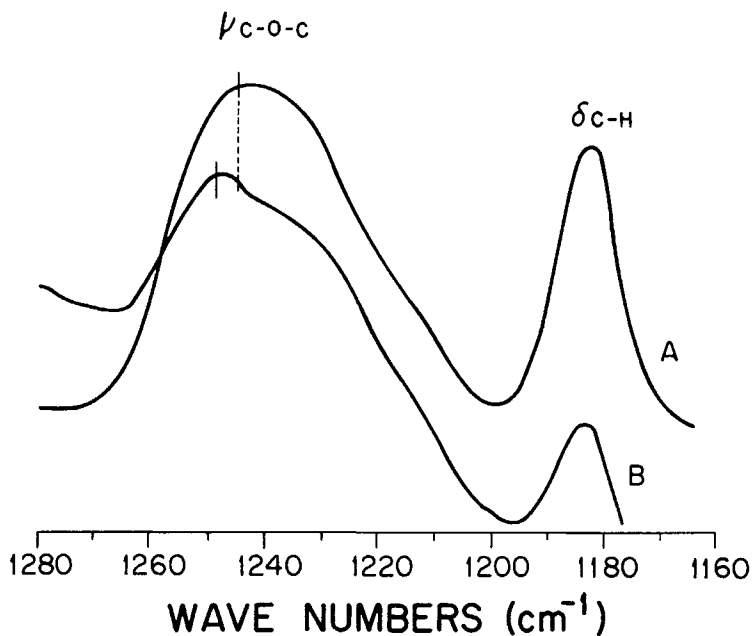
Fig. 8. FT-IR spectra of the region from 1160 to 1280 cm^{-1} recorded at room temperature: (A) phenoxy, (B) difference spectrum obtained by subtracting the spectrum of Kevlar cloth from that of phenoxy on Kevlar.
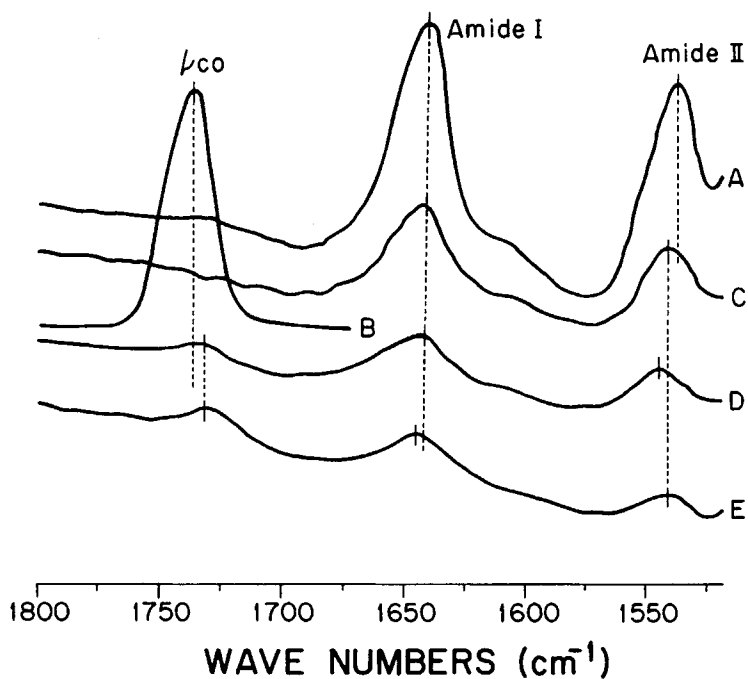

Fig. 9. FT-IR spectra recorded at room temperature: (A) Kevlar cloth, (B) PMMA, (C) 50P/S on Kevlar cloth, (D) 50P/M on Kevlar cloth, (E) 50M/S on Kevlar cloth.

for 50M/S on Kevlar. The amide I band for 50P/M on Kevlar appears at the same frequency as that for 50P/S on Kevlar. The amide II band for 50P/M on Kevlar appears at a higher frequency than those for 50M/S on Kevlar and 50P/S on Kevlar. Thus, for 50P/M on Kevlar, both the components of matrix can be regarded to contribute to the interaction with Kevlar.

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