ESCA and FT-IR Studies on Boundary-Phase Structure Between Blend Polymers and Polyamide Substrate

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Synopsis

Electron spectroscopy for chemical analysis (ESCA) and Fourier-transform infrared (FT-IR) attenuated total reflection (ATR) studies have been made on the film of blend polymers consisting of poly(hydroxypropyl ether) of bisphenol A (P) and poly(ethylene oxide) (E) or P and poly(ethylene adipate) (A) formed on nylon-6 (Ny) substrate to investigate the boundary-phase structure between the substrate and the polymer blends. For the case of P/A blend, A is enriched to the depths probed by both ESCA (below ca. 60 Å) and FT-IR-ATR (below ca. 0.7 μm) from the nylon-6 surface. For the P/E blend, though P is enriched to the depth probed by ESCA from the Ny surface, the enrichment of neither of the blend components can be found to the depth probed by FT-IR-ATR. These results indicate the different susceptibility between P/A and P/E blends to the influence from the Ny substrate.

INTRODUCTION

It was reported in a previous paper[1] that the reinforcement–matrix interaction in Kevlar-fiber-reinforced PHENOXY resin was increased by blending poly(ethylene oxide) or poly(ethylene adipate) with PHENOXY resin. The effect of increasing the interaction was more efficient for the case of blending poly(ethylene oxide) than for poly(ethylene adipate) from studies of the mechanical and infrared spectroscopic properties.

The purpose of this paper is to elucidate the origin of the difference of interactions between the Kevlar-fiber composites whose matrices are comprised of PHENOXY resin-poly(ethylene oxide) blend and PHENOXY resin-poly(ethylene adipate) blend. The difference in the interaction mentioned above would be related to the difference in the boundary-phase structures that are formed in the vicinity of substrate and are different from the bulk structure of matrix polymers. Electron spectroscopy for chemical analysis (ESCA) and Fourier-transform infrared spectroscopy (FT-IR) were applied to the film of the blend polymers formed on the substrate nylon-6, which was used as a model compound for Kevlar fibers.

It is generally known that ESCA and FT-IR can provide the information concerning the surface[2-5] and interface[6-9, 13] to depths of 50 to 100 Å and a few tenths to several μm, respectively.

EXPERIMENTAL

Materials

Poly(hydroxypropyl ether) of bisphenol A (PHENOXY, General Science Co., MW 32,000) (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 blend polymers. Nylon-6 (Novamide 1010, Mitsubishi Chemical Industries, Co.) (Ny) was used as the substrate on which the film of blend polymers was formed.

Specimens

The Ny plate was ca. 1 mm thick and was obtained by compression molding using 400 kg/cm^2 at 200°C between two flat metal plates.
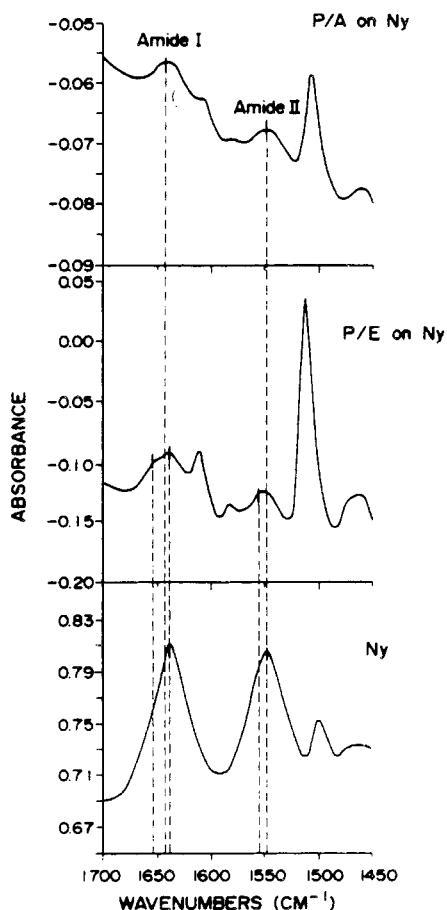

Fig. 1. FT-IR spectra for nylon-6 (Ny), Ny coated with PHENOXY/poly(ethylene oxide) blend (P/E on Ny), and Ny coated with PHENOXY/poly(ethylene adipate) blend (P/A on Ny).

The mixture of P with E or A containing 80% P, for which composition the reinforcement-matrix interaction can be maximized,[1] was dissolved in tetrahydrofuran to obtain a 2% solution. The cleaned Ny plate was dip-coated with the solution at a thickness of ca. 0.5 mm by repeated coating. The solvent was removed in a vacuum oven at elevated temperature. The film formed on Ny was carefully separated after 4 days from the substrate so as not to damage the film surface. By leaving the coated specimen for 4 days in the air, the film became easily separated from the substrate. ESCA and FT-IR-ATR spectra were measured for the separated films on both surfaces that were faced to the air (air-facing side) and Ny (Ny-facing side). The films of P, E, and A were also prepared by a similar method.

Specimen of the Ny substrate coated with blend polymers was also prepared from a 0.05% solution.

Measurement of FT-IR-ATR Spectra

FT-IR spectra were obtained at 1 cm^{-1} resolution using a JIR-100 (Nihon Denshi Co.) for specimens of Ny substrate coated with blend polymers, the noncoated Ny substrate, and the polymer film separated from the substrate. The spectra were obtained by attenuated total reflection (ATR) spectroscopy on 45° and 60° germanium elements.

Measurement and Analysis of ESCA Spectra

ESCA spectra were obtained with a VG HB 50A scanning electron microscope equipped with a XPS option. An aluminum-anode X-ray source producing $AlK\alpha$ X-rays at 1486.6 eV operating at 12 kV and 20 mA was used. The hemispherical analyzer was operated in a constant electron-pass energy mode. An instrumental vacuum of at least 1×10^{-8} mbar was maintained for all analyses. The sample film was mounted on double-stick tape.
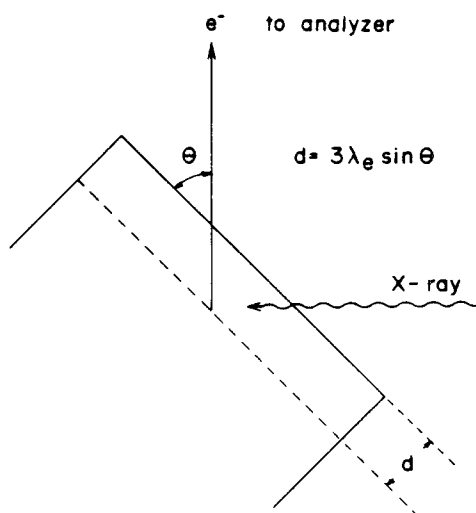

Fig. 2. Schematic of the effect of emission angle θ on effective sampling depth d.

The data were analyzed on the high resolution spectra of C_{1s} region. The overlapping peaks of the C_{1s} spectra were resolved into their individual components by assuming a Gaussian-type symmetric function[10,11] with respect to the photoelectron intensity I versus binding energy BE relation for each component:

$$I = I_0 \exp\left\{-a(BE - BE_0)^2\right\}$$
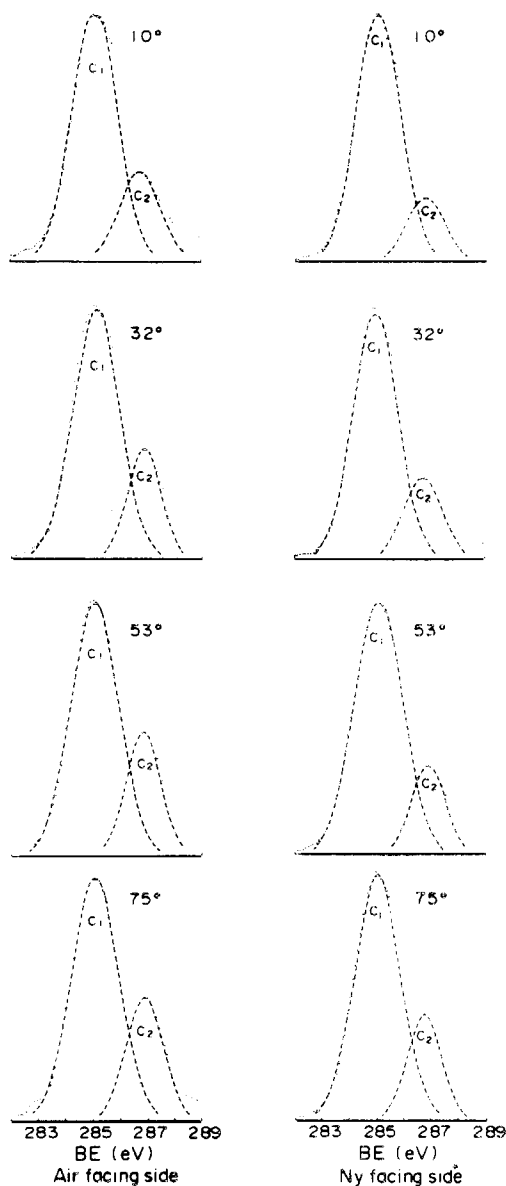
$$a = 4 \cdot \ln 2 / H_w^2$$

Fig. 3.   ESCA spectra for PHENOXY/poly(ethylene oxide) blend (P/E) samples.

I_0, a, BE_0, and H_w are the I corresponding to the height of the peak, the parameter representing the sharpness of the function, the position of the peak, and the full width at half maximum, respectively. BE_0, I_0, and a for each function were adjusted so that the sum of the component Gaussian functions fits the observed spectrum as closely as possible. Where binding energy assignments for component Gaussian curves were made, the peak for the hydrocarbon component (the hydrogen carbon) was used as the reference and assigned the value of 285.0 eV to compensate for charging effects.
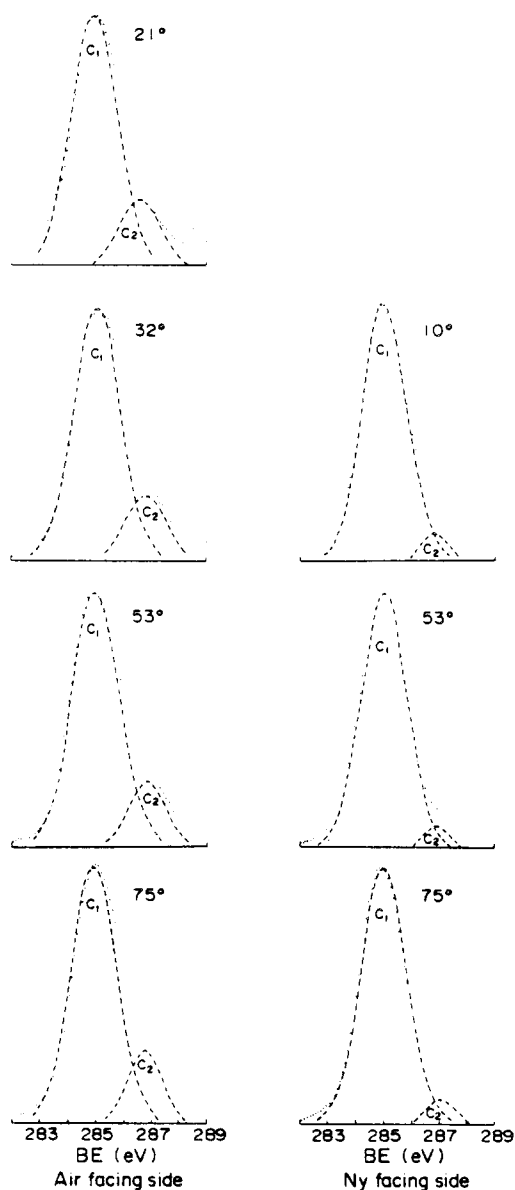

Fig. 4.   ESCA spectra for PHENOXY/poly(ethylene adipate) blend (P/A) samples.

RESULTS AND DISCUSSION

Interaction of Substrate and Blend Polymers

The FT-IR-ATR spectra for Ny, Ny coated with P/E blend containing 20% E(P/E on Ny), and Ny coated with P/A blend containing 20% A(P/A on Ny) are shown in Figure 1, recorded on a 45° germanium element. The spectra for P/E and P/A on Ny are obtained with the coated polymer pressed to the germanium element. For P/E on Ny, a shoulder appears at the higher frequency of the main band corresponding to the amide I band of Ny. The amide I band of P/A on Ny shifts to the higher frequency as compared with that of Ny. Although the amide II bands of P/A on Ny and Ny appear at almost the same positions, that of P/E on Ny shifts to the higher frequency as compared with the others. These spectral changes imply the presence of an interaction[12] between the amide group in Ny and P/E or P/A blend, and are almost the same as for the Kevlar-fiber substrate.[1] Ny can be used as a model compound for Kevlar fiber at least in the amide I and II regions.
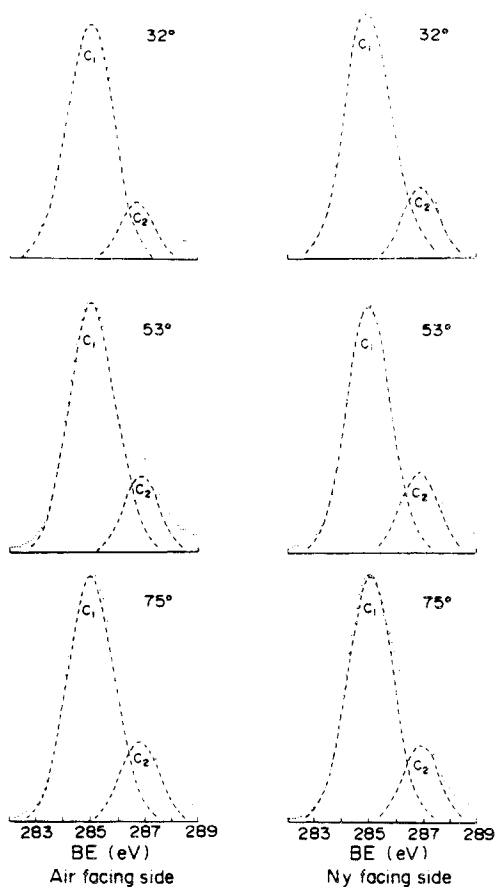

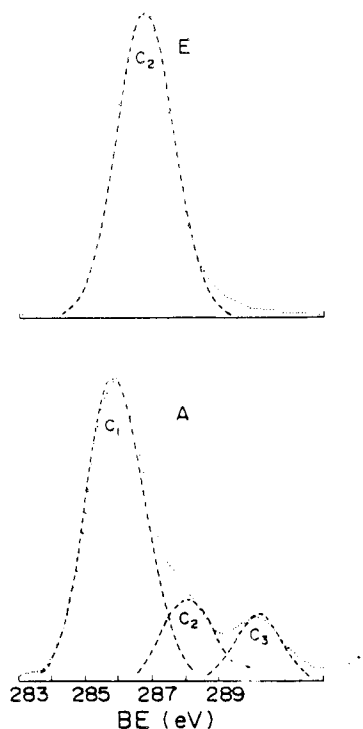Fig. 5.   ESCA spectra for PHENOXY (P) samples.

Fig. 6. ESCA spectra for poly(ethylene oxide) (E) and poly(ethylene adipate) (A).

ESCA Spectra

Angular-dependent ESCA measurements were carried out by tilting the surface of sample so that the emission angle of photoelectrons would decrease with respect to the direction of the analyzer. The method for varying the effective sampling depth is illustrated in Figure 2,[16] where θ is the emission angle and d is the sampling depth. From the consideration of the electron mean free path length, λ_c = 10–20 Å, the sampling depth d at the emission angle θ is $3\lambda_c \sin \theta$, corresponding to ca. 5–60 Å at θ = 10 to 90°. Figures 3 and 4 show C_{1s} spectra for the air-facing side and the Ny-facing side of P/E and P/A blends at various emission angles. The spectra for P, the main component in the blends, are also observed by the same procedure as blend polymers as shown in Figure 5. The spectra for E and A, the minor component in the blends, are observed for the air-facing side at the emission angle at 75° as shown in Figure 6. The broken curves in Figures 3–6 show the resolved components from the observed spectra. For P/E, P/A, and P samples the observed spectra could be fitted with two Gaussian functions (C_1 and C_2).

The peak position, full width at half maximum and relative peak area are shown for each Gaussian function in Table I. The C_2 components for P samples centered at the range of 286.8–286.9 eV can be assigned to the carbon atom bound to the oxygen.[2,15] Thus, the spectrum of E ought to overlap with the C_2 component of P in P/E sample since the C_{1s} spectrum of E is composed of only the carbon atom bound to the oxygen (the shoulder

TABLE I

The Values Characterizing the Gaussian Curves Resolved from the Observed ESCA Spectra.

| Samples	θ [a] (°)	Peak position (eV)		H_w [b]		Relative peak Area (%)	
		C_1	C_2	C_1	C_2	C_1	C_2
Air-facing	75	285.0	286.9	2.1	1.6	84	16
side for	53	285.0	286.8	2.1	1.6	85	15
P	32	285.0	286.8	2.0	1.5	88	12
Ny-facing	75	285.0	286.9	2.1	1.5	82	18
side for	53	285.0	286.9	2.0	1.6	83	17
P	32	285.0	286.9	2.1	1.5	85	15
Air-facing	75	285.0	286.9	2.1	1.7	74	26
side for	53	285.0	286.8	2.1	1.5	75	25
P/E	32	285.0	286.8	2.1	1.5	78	22
	10	285.0	286.7	2.0	1.7	80	20
Ny-facing	75	285.0	286.8	2.1	1.6	78	22
side for	53	285.0	286.9	2.1	1.6	83	17
P/E	32	285.0	286.8	2.0	1.7	82	18
	10	285.0	286.8	1.9	1.7	86	14
Air-facing	75	285.0	286.9	2.0	1.5	87	13
side for	53	285.0	286.9	2.1	1.6	87	13
P/A	32	285.0	286.8	2.1	1.7	87	13
	21	285.0	286.7	2.0	1.7	86	14
Ny-facing	75	285.0	286.9	2.0	1.0	98	2
side for	53	285.0	286.9	2.0	1.0	98	2
P/A	10	285.0	286.8	1.9	1.1	97	3

[a] Emission angle of photoelectron.
[b] Full width at half maximum.
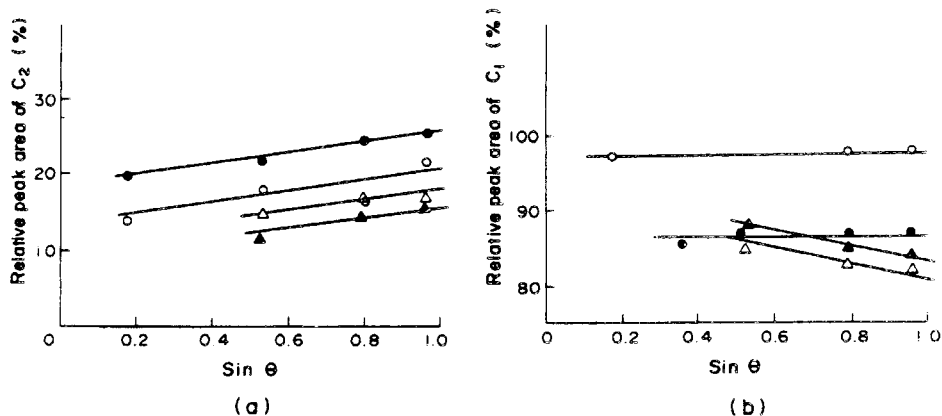
Fig. 7. Relative peak area of (a) C_2 (●, air-facing side for P/E samples. ○, Ny-facing side for P/E samples; ▲, air-facing side for P samples; △, Ny-facing side for P samples) and (b) C_1 (●, air-facing side for P/A samples; ○, Ny-facing side for P/A samples; ▲, air-facing side for P samples; △, Ny-facing side for P samples) components versus emission angle θ.

observable at the lower binding energy side in Figure 6 can be attributable to the hydrocarbon contamination mentioned below). The C_{1s} spectrum of A can be resolved into three components as shown in Figure 6. The main component at 285.0 eV overlaps with the main component of P, and the other components of A hardly contribute to the spectra of P/A samples because A is the minor component in the P/A blend.

The relative peak area of the C_2 component (C_2 ratio) is plotted as a function of emission angle θ for P/E samples in Figure 7(a) relative to P samples. The C_2 ratios are somewhat smaller compared with the values anticipated from the chemical structure and composition (27.8 and 42.2% for P and P/E, respectively). This is probably due to the increase in the relative peak area of C_1 on account of the hydrocarbon contamination layer deposited on sample during the experiments.[5] The apparent decrease of the C_2 ratio with θ would also be attributed mainly to the contamination. Therefore, detailed discussion cannot be done concerning the dependence of the C_2 ratio on θ by this experiment alone. The C_2 ratio of the P/E samples is very close to that of P samples for the Ny-facing side. However, the difference of the C_2 ratios between P/E and P samples is relatively large for the air-facing side. The difference of the C_2 ratio between P/E and P samples represents the degree of contribution of E to the C_2 component in the P/E sample. It is apparent from Figure 7(a) that this difference is larger for the air-facing side than for the Ny-facing side. This means that E is apt to concentrate on the air-facing side. That is, a larger proportion of P is present at the Ny-facing side as compared with the air-facing side. Furthermore, the polar group in P can be considered to come close to the Ny-facing side as compared with the non polar group. This is so because the C_2 ratio for P samples is larger for the Ny-facing side than for the air-facing side. These situations would be favorable in strengthening substrate–blend polymer interactions.

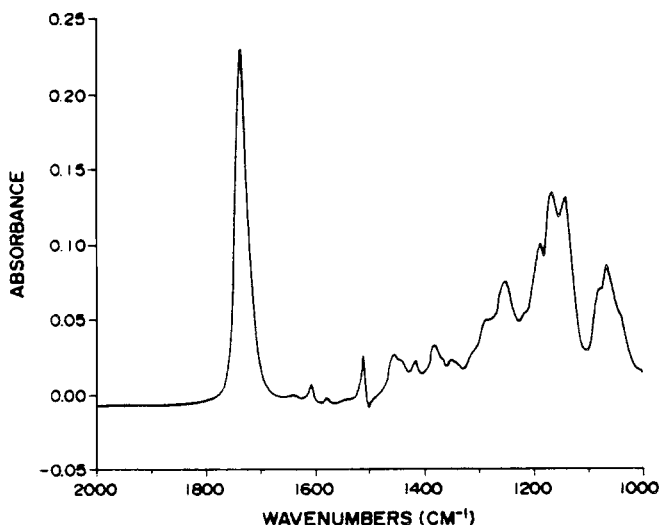

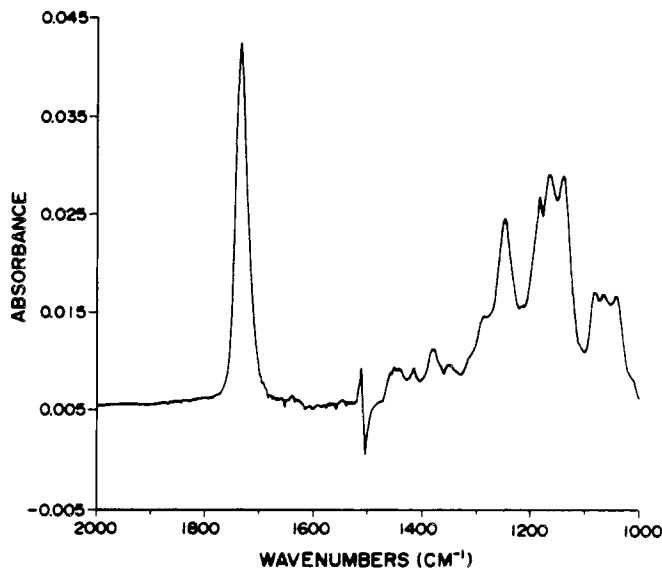Fig. 8. FT-IR difference spectrum of PHENOXY/poly(ethylene adipate) blend (P/A) recorded at incident angle 45°.

Fig. 9. FT-IR difference spectrum of PHENOXY/poly(ethylene adipate) blend (P/A) recorded at incident angle 60°.

The relative peak area of C_1 component (C_1 ratio) is plotted as a function of emission angle θ for P/A samples compared with P samples in Figure 7(b). The C_1 ratio for P/A samples is very close to that for P samples at the air-facing side. However, the difference of the C_1 ratios between P/A and P samples is substantially larger at the Ny-facing side. This means that A is apt to concentrate on the Ny-facing side compared with the air-facing side. Consequently, the main component in the blend P is possibly restrained from coming close to the Ny surface and the substrate-blend polymer interaction would be weakened contrary to the case of P/E blend. The C_1 ratio of P/A and P samples are somewhat larger compared with the values anticipated from the chemical structure and composition (67.8 and 72.2% for P and P/A, respectively). This can also be attributed to the hydrocarbon contamination. Therefore, the discussion of the dependence of the C_1 ratio on θ can not also be done by this experiment alone as the case of P/E samples.

FT-IR-ATR Spectra

The difference spectra of P/A samples obtained by subtracting the spectra for the air-facing side from the spectra for Ny-facing side are shown in Figures 8 and 9, recorded at the incident angles of 45° and 60°, respectively. The spectral subtraction was made to compensate for the absorptions of P in the blend as fully as possible. In Figures 10 and 11 the spectra of P and A are recorded for the air-facing side at the incident angle of 45°. It is apparent from the comparisons of Figures 8 and 9 with Figure 10 or 11 that the difference spectra are almost composed of the characteristic absorption of A. That is, the difference spectra show the tendency of the concentration of A on the Ny-facing side. For the frequencies of 1000 to 2000 cm^{-1} in Figures 8 and 9, the penetration depth of the light can be estimated to be 0.33–0.66 μm and
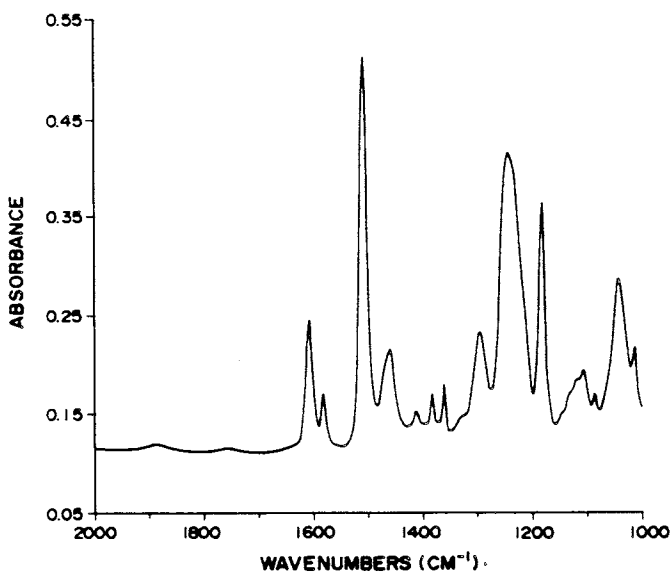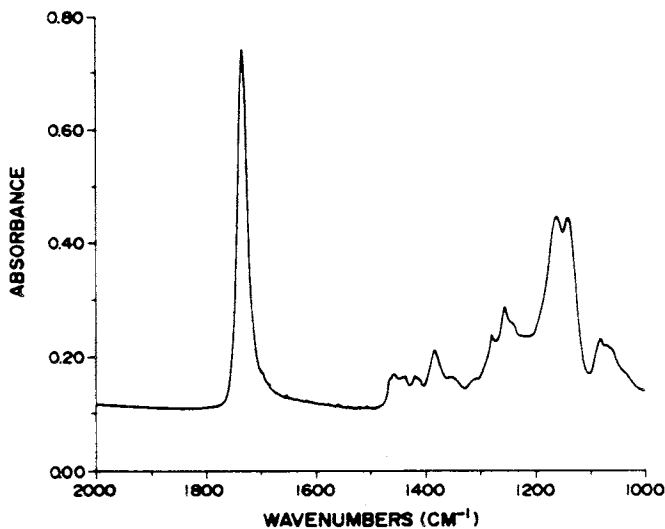
Fig. 10.   FT-IR spectrum of PHENOXY (P).

Fig. 11.   FT-IR spectrum of poly(ethylene adipate) (A).

0.25–0.51 μm for the incident angles of 45° and 60°, respectively.[13,14] A is considered to extend to such a depth as estimated above.

The difference spectra of the Ny-facing side and the air-facing side were also measured for P/E samples using the same procedure as for the P/A samples, but the difference spectra did not show distinctly the dominant residual component. This means that the blend compositions at this depth do not vary appreciably between the Ny-facing and the air-facing sides.

SUMMARY AND CONCLUSION

For P/E samples, though P is enriched at the Ny-facing side compared with the air-facing side to the depth probed by ESCA, the difference in blend compositions between the Ny- and the air-facing sides cannot be found to the depth probed by FT-IR-ATR. On the contrary, for P/A samples, A is also enriched for the Ny-facing side compared with the air-facing side to the depth probed by FT-IR-ATR as well as to the depth probed by ESCA. These results imply that the susceptibility to the influence from Ny substrate varies between P/E and P/A blends, and the difference of reinforcement–matrix interaction for the Kevlar fiber-reinforced P/E and P/A blends previously reported[1] can possibly be attributed to the difference of the spectroscopic features mentioned above.

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