Interaction between the Reinforcement and Matrix in Carbon-Fiber-Reinforced Composite: Effect of Forming the Thin Layer of Polyimide Resin on Carbon Fiber by *In Situ* Polymerization

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Synopsis

For the purpose of enhancing the reinforcement–matrix interaction in carbon-fiber-reinforced polymer composite, mechanical and spectroscopic studies were made on the epoxy resin composite reinforced with the carbon fiber coated with thin Layer of polyimide resin. On the loss modulus and loss tangent vs. temperature curves, a subtransition appears at a temperature above the primary transition. The T-peel strength of a laminated specimen and the fiber efficiency factors for modulus and strength are larger than those of the composite reinforced with nonpolyimide treated fiber. These results show the increased interaction between the epoxy resin and the carbon fiber coated with polyimide resin. The occurrence of specific interaction between an epoxy resin and the polyimide resin are recognized on Fourier transform infrared spectra.

INTRODUCTION

It was reported in the previous papers[1-3] that a characteristic subtransition, which can be ascribed to the interphase formed on the reinforcement surface by strong interaction between reinforcement and matrix, appears at a temperature above the primary transition for the composites comprised of polymer matrix and glass and polyaramid fibers. Such a subtransition is also observed for the composite reinforced with poly(ethylene terephthalate) fiber by other investigators.[4]

The subtransition, however, could not be observed by preliminary studies for the polymer composites reinforced with pitch-based[5] and polyacrylonitrile-based[6] carbon fibers. This can probably be attributed to the weaker interaction of carbon fiber with polymer matrix compared with the cases of glass and polyaramid fibers. To maximize the performance of the carbon-fiber-reinforced polymer composite (CFRP), it is necessary to increase further the interaction (or adhesion strength) between the fiber and matrix. For the purpose of increasing the reinforcement–matrix interaction for CFRP, oxidation, etching, resin coating, and so on were tried in the past[7] for carbon fiber, the effect of such treatment being not necessarily sufficient for the performance of CFRP.

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In this study, the coating of carbon fiber with polyimide resin was tried to improve the reinforcement–matrix interaction and the comparative studies for the mechanical and spectroscopic properties were made for the composites reinforced with thus treated fiber and non-polyimide-treated fiber. The coating of carbon fiber is tried already[7] with the polyimide and polyimide prepolymer prepared beforehand. The carbon fiber used in this study is, however, coated with the thin layer of polyimide resin in accordance with the method of *in situ* polymerization of monomer reactants.[8]

EXPERIMENTAL

Polyimide Coating on Carbon Fiber and Aluminum Foil

As-received reinforcements, which had the forms of plain cloth (0.15 mm thick) and cut fiber (10 mm long), were the high strength carbon fibers made from polyacrylonitrile (T-300, Toray), and were designated as CF–S. The sizing agent (surface treating agent) of CF–S was removed by washing in large amount of acetone. The desized fiber was designated as CF–N. The coating of polyimide on carbon fiber was made as follows. The mixture of 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BPTD) and 4,4′-diaminodiphenyl ether (DDE) was dissolved in methanol at a molar ratio of 5.9–6.0 to obtain a 1% solution. CF–N was immersed in this solution for 30 min. After taking out the CF–N from the solution, the solvent was evaporated at room temperature. Polymerization was carried out at 200°C for 2 h, followed by post-heating at 280°C for 3.5 h. The polyimide coated fiber thus obtained was designated as CF–P_1. The CF–N treated with the mixture of BPTD and *p*-phenylene diamine at a molar ratio of 6.5–6.9, for which the conditions of treatment were the same as the case of CF–P_1, was designated as CF–P_2. The CF–N treated with the mixture of pyromellitic dianhydride and DDE at a molar ratio of 6.0–6.1 was designated as CF–P_3. The amount of polyimide resins deposited on carbon fiber were 1.05, 1.04, and 1.04% by weight for CF–P_1, CF–P_2, and CF–P_3, respectively, the thickness of polyimide layer on carbon fiber being estimated at ca. 300 Å from the deposited resin. The solutions of resin components mentioned above were also coated on aluminum foil by the same conditions as for carbon fiber. The specimens thus obtained were designated as Al–P_1, Al–P_2, and Al–P_3 corresponding to CF–P_1, CF–P_2, and CF–P_3, respectively. The amount of polyimide resin deposited on aluminum foil was almost the same as the case for carbon fiber.

Preparation of Composite

The matrix resins used in this experiment were the mixture of Epon 815 (Shell Chemical Co.) and isophoron diamine (abbreviated as IPD) at a weight ratio of 100 : 24 and that of Epon 815 and methyl hexahydrophthalic anhydride (abbreviated as CH_3–HHPA) at a weight ratio of 340 : 330. The plain cloth of carbon fiber and the web of cut fiber in random-in-plane orientation were impregnated with the matrix resin. By heating the reinforcement impregnated with the matrix resin, the composites were obtained in the form of a sheet. For the case of using the mixture of Epon 815 and IPD as matrix resin, the heating was carried out at 100°C for 1 h, followed by post-heating at 150°C

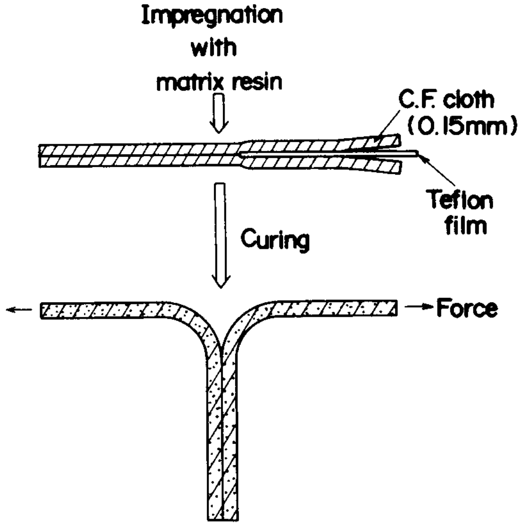

Fig. 1. Preparation of T-peel specimen.

for 3 h. For the case of using the mixture of Epon 815 and CH_3-HHPA as matrix resin, the heating was carried out at 120°C for 2 h, followed by post-heating at 140°C for 2 h.

Specimen and Measurement

The glass transition temperature was measured for the films of polyimide resins and neat matrix resin using the differential scanning calorimeter (TG-DSC, Rigaku Denki Co.).

The dynamic viscoelastic properties were measured using the Rheovibron (DDV-II, Toyo Baldwin Co.). The specimen of composite, which was reinforced with a sheet of the plain cloth at a volume fraction of 0.23, was loaded on the apparatus by making the woof of cloth to coincide with the direction of sample length.[1]

The T-peel test for the laminated specimen shown in Figure 1 schematically and the tensile test for the composite reinforced with the cut fiber of random-in-plane orientation were carried out using the Instron tensile tester. The volume fractions of reinforcement were 0.3 and 0.07 for the specimens of T-peel test and tensile test, respectively. The crosshead speeds for the tests were 40 and 10 mm/min for T-peel test and tensile test, respectively.

The Fourier transform infrared spectra were obtained by the reflection–absorption spectroscopy using a JIR-100 spectrometer (Nihon Denshi Co.) for the polyimide resin deposited on carbon fiber and aluminum foil. The spectral changes accompanied by overcoating the matrix resin on Al–P were also observed. For the case of Figure 9, the spectra were obtained by the transmission spectroscopy on KBr disk. The spectra were obtained by signal averaging of 500 scans at 4 cm^{-1} resolution except for the case of Figure 12, for which the resolution was set at 0.5 cm^{-1}.

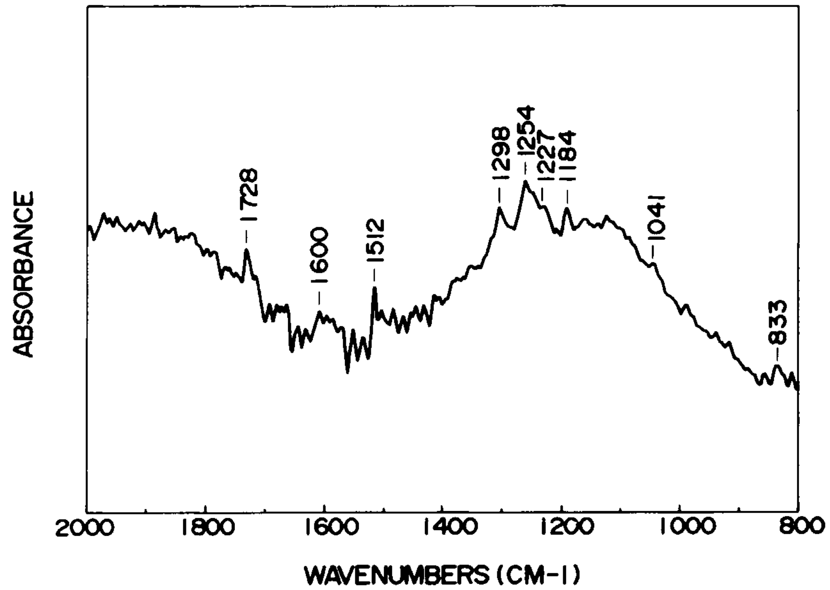

Fig. 2. FT-IR spectrum of CF–S (commercially available fiber).

RESULTS AND DISCUSSION

Surface Analyses of CF–S and CF–N

The Fourier transform infrared (FT-IR) spectrum of CF–S is shown in Figure 2. It can be said from the spectral feature that the sizing agent of CF–S is composed of mainly the bisphenol A based epoxy resin and the ester component. This result does not contradict the description of the patent specification.[9] The absorption band based on any resin component cannot be observed in the spectrum of CF–N. Thus, the sizing agent of CF–S can easily be removed by washing in acetone.

Identification of Polyimide on Carbon Fiber and Aluminum Foil

The FT-IR spectrum of CF–P_1 is shown in Figure 3. From the absorption bands in the spectrum, the formation of polyimide can be recognized. The spectrum of Al–P_1 is also shown in Figure 3. The wave number and intensity ratio of the absorption bands for CF–P_1 are almost the same as those for Al–P_1 at the corresponding bands. This shows that the same substance is formed on aluminum foil as on carbon fiber. Therefore, aluminum foil was used henceforth as the substrate for the measurement of FT-IR spectrum, because the better signal of S/N was obtained by using aluminum foil.

The resin component on CF–P_1 and Al–P_1 cannot be extracted at all in acetone at room temperature and dimethylformamide at 80°C.

The spectra of Al–P_2 and Al–P_3 are shown in Figure 4 compared with Al–P_1. The bands showing the formation of polyimide (ν_{C-N}, $\nu_{C=O}$) are observed in the spectra of Al–P_2 and Al–P_3, too.

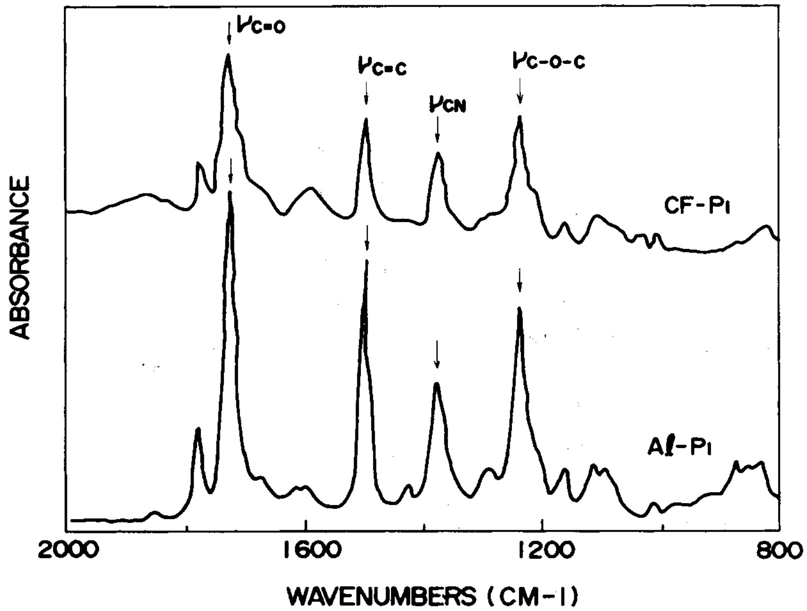

Fig. 3. FT-IR spectra of CF–P_1 and Al–P_1.

Glass Transition Temperature of Polyimide and Matrix Resin

The glass transition temperature of polyimide P_1 was 290°C, and those of P_2 and P_3 could not be observed unambiguously below 400°C. The glass transition temperatures of P_2 and P_3 are presumed to be considerably higher than that of P_1 by inspection of the data of Gillham and Gillham.[16] So the detection of the glass transition temperatures of P_2 and P_3 possibly becomes harder compared with the case of P_1. The glass transition temperature of the Epon 815 cured with IPD was 108°C and that of the Epon 815 cured with CH_3–HHPA was 111°C.

Mechanical Dispersion

The storage modulus E', loss modulus E'', and loss tangent $\tan\delta$ vs. temperature curves at 11 Hz are shown for the composites reinforced with CF–S and CF–N in Figure 5. Only the dispersion corresponding to the primary transition can be observed for both composites. This is the same tendency as the cases of previous studies,[5,6] and it can be said that the sizing agent of CF–S has no crucial influence on the mechanical dispersion except for the slight decrease in the E' at the higher temperature region, probably because of the lower reactivity of the sizing agent.

The mechanical dispersions of the composite reinforced with CF–P_1 are shown in Figures 6 (a) and (b) being the composites composed of the matrix curable with IPD and CH_3–HHPA, respectively. A subtransition appears at a higher temperature above the primary transition for both composites irrespective of the kind of curing agent of matrix resin, though the shape of the

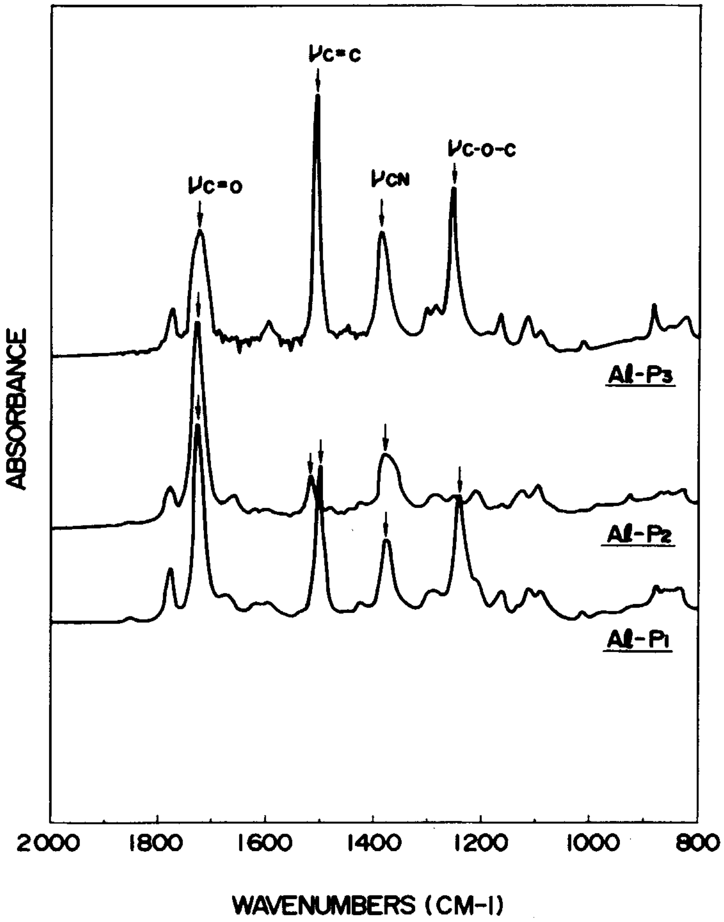

Fig. 4. FT-IR spectra of Al–P_1, Al–P_2, and Al–P_3.

dispersion curves shows subtle difference between the both composites. Such a subtransition is the same kind as that observed for the composites reinforced with glass and polyaramid fiber,[1,2,5] and it can be said that the coating of polyimide P_1 on carbon fiber has the effect of increasing the reinforcement–matrix interaction, contrary to the cases of composites reinforced with CF–S and CF–N.

The mechanical dispersions of the composites reinforced with CF–P_2 and CF–P_3 are shown in Figure 7. The subtransitions also appear for both composites. This shows that the polyimides having the molecular structures such as P_2 and P_3 can also contribute to the enhancement of the interaction with the matrix resin as the case of polyimide P_1.

The thickness of the polyimide layer on carbon fiber is ca. 300 Å as stated above section. Though the optimum thickness of the polyimide layer for the composite cannot be determined from this experiment alone, the polyimide layer can evidently contribute to the formation of immobilized interfacial layer of the thickness in the vicinity of 1 μm as discussed previously[1] by the polar–polar interaction between the polyimide and matrix components.

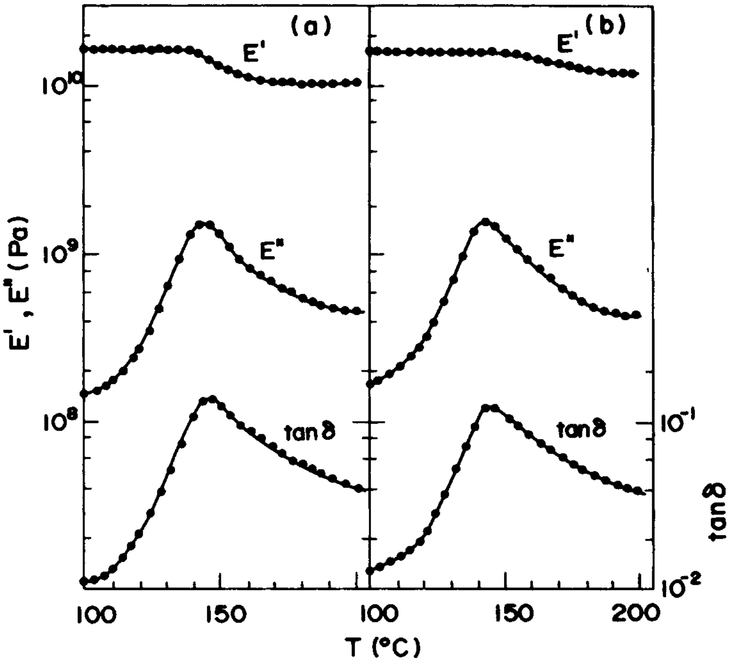

Fig. 5. *E'*, *E''*, and tan δ vs. temperature curves for composite reinforced with CF–S (a) and CF–N (b). Epon 815 and isophoron diamine are used as matrix resin and curing agent, respectively, for both composites.

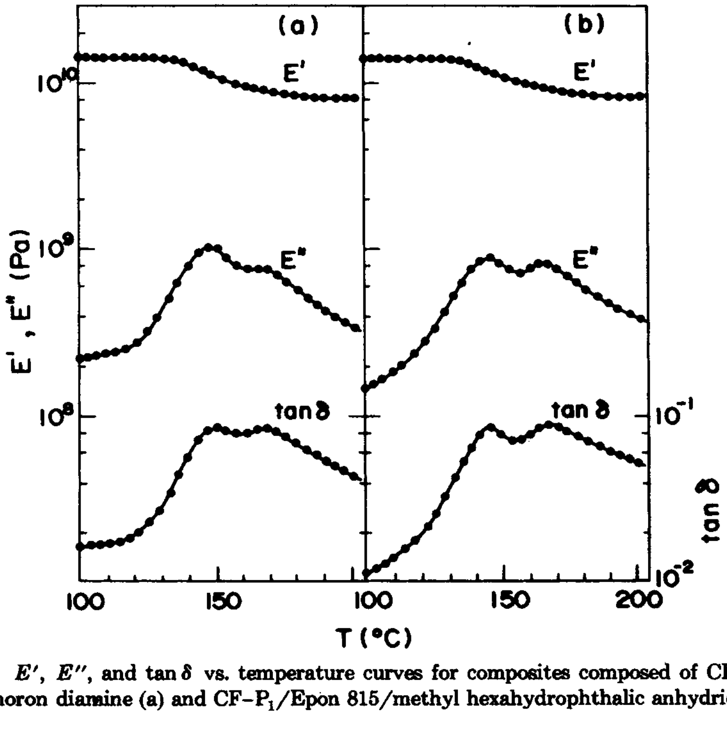

Fig. 6. *E'*, *E''*, and tan δ vs. temperature curves for composites composed of CF–P_1/Epon 815/isophoron diamine (a) and CF–P_1/Epon 815/methyl hexahydrophthalic anhydride (b).

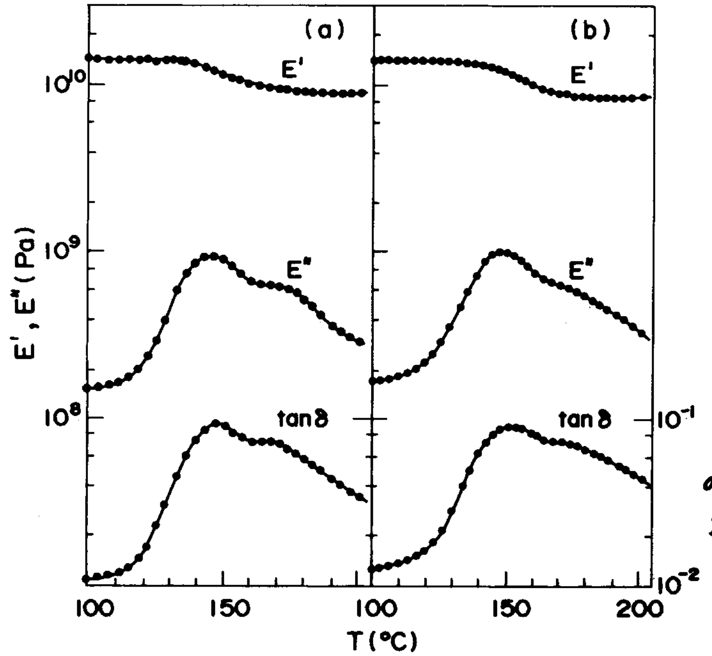

Fig. 7. E', E'', and tan δ vs. temperature curves for composites reinforced with CF–P_2 (a) and CF–P_3 (b). Epon 815 and isophoron diamine are used as matrix resin and curing agent, respectively, for both composites.

T-Peel Strength

The average values of T-peel strength of five specimens were 675 g/2.5 cm width and 785 g/2.5 cm width for the composites reinforced with CF–S and CF–P_1, respectively. A feature of the fractured test piece is shown in Figure 8 schematically. The fracture occurs mainly close by the fiber surface as shown in Figure 8 for both composites, and so this method is considered to be a good one[11] for the evaluation of the adhesion strength between the reinforcement and matrix. The FT-IR spectra were measured for the samples obtained from the surfaces of portions A and B in Figure 8. As shown in Figure 9, the bands based on the polyimide (ν_{C-N}, $\nu_{C=O}$) can be observed for the spectrum of portion A, though such bands cannot be observed for the spectrum of portion B. This implies that most polyimide resin remains on the carbon fiber and that the adhesion strength between the carbon fiber and polyimide resin is sufficient for the composite.

Fiber Efficiency Factors for Modulus and Strength for Composite

The initial modulus E, ultimate strength σ, and elongation at break ϵ, which are obtained from the tensile test for the composite reinforced with the cut fiber of random-in-place orientation are tabulated in Table I. The data for the non-reinforced matrix resin are also shown in Table I. From the results of Table I, the fiber efficiency factors for modulus (K_E) and strength (K_σ) were obtained using the relations (1) and (2) by assuming the additivity of the properties of the fiber (f) and matrix (m) for the modulus (E_c) and strength

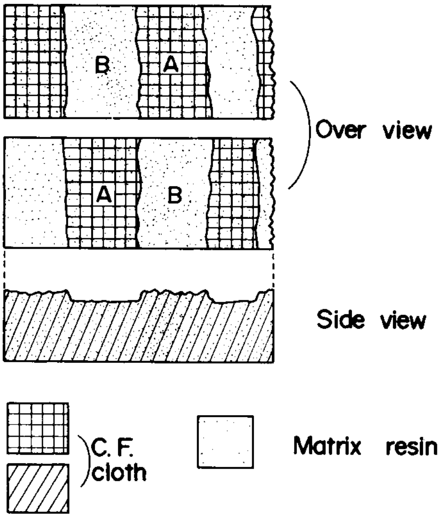

Fig. 8. Schematics of fractured pieces of T-peel specimen.

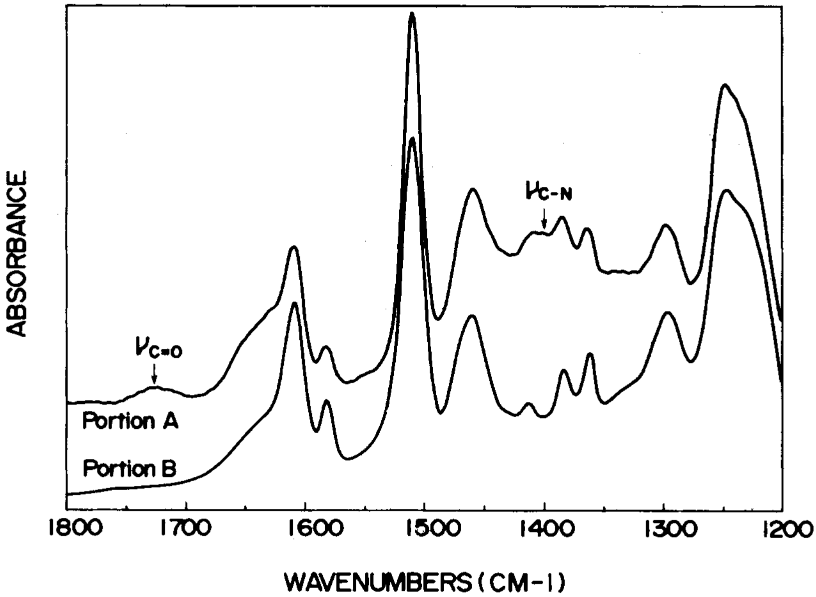

Fig. 9. FT-IR spectra of surface materials at portions A and B in Figure 8.

(σ_c) of composite[12]:

$$E_c = K_E E_f v_f + E_m(1 - v_f) \tag{1}$$

$$\sigma_c = K_\sigma v_f \sigma_f + \sigma_m(1 - v_f) \tag{2}$$

K_E and K_σ are tabulated in Table II. Though the values of K_E and K_σ are smaller compared with the other cases[12-14] probably because of the somewhat poor dispersion of the cut fibers in composite, the value for CF–P_1 are

TABLE I
Results of Tensile Test

Sample	E (GPa)	σ (GPa)	ϵ (%)
CF–S composite	2.0	0.053	3.9
CF–P_1 composite	2.3	0.058	2.9
Matrix resin	1.8	0.042	6.6

TABLE II
Fiber Efficiency Factors for Modulus (K_E) and Strength (K_σ)[a]

Fiber	K_E	K_σ
CF–S	0.020	0.064
CF–P_1	0.038	0.087

[a] E_f = 235 GPa; σ_f = 3.1 GPa.[12]

significantly larger than those for CF–S. This implies that the transmission of stress can be made more efficiently for the case of CF–P_1 than the case of CF–S on account of the stronger interaction of CF–P_1 with the matrix than the case of CF–S.

Study of Molecular Interaction by Fourier Transform Infrared Spectroscopy

The interaction between the polyimide and matrix resin was studied from the change in FT-IR spectrum by overcoating the varying thickness of Epon 828 layer on Al–P_2. The overcoated specimen was abbreviated as Al–P_2–828. It can be expected that the polyimide–Epon 828 interaction becomes observable clearly with decrease in the thickness of Epon 828 layer on Al–P_2. Epon 828 was used as a model compound for Epon 815, and the overcoating was carried out from the solutions at varying concentration of Epon 828 in acetone, followed by removing the solvent at reduced pressure and heating at 80°C for 30 min. Though the spectral changes accompanied with the coating of Epon 828 on Al–P_1 are the same in tendency as the case of Epon 828 on Al–P_2, the changes can be observed more definitely for the latter cases than the former. Therefore, the results for the latter cases were shown in this paper.

The spectral changes are observable for the bands at 916 cm^{-1}, 1386 cm^{-1} and in the vicinity of 1730 cm^{-1}.

The spectral changes at 916 cm^{-1} (stretching vibration of oxirane group) are shown in Figure 10 using the difference spectra obtained by subtracting the spectrum of Al–P_2 from that of Al–P_2–828 at varying concentration of Epon 828. It is apparent from the comparison of the ratios of absorption intensity at 916 cm^{-1} to that at 1148 cm^{-1} (in-plane bending vibration of CH in benzene ring) among the spectra that the absorption at 916 cm^{-1} is decreased with decrease in the concentration of Epon 828 on Al–P_2. This implies that the opening of oxirane ring occurs at the interface of the polyimide and Epon 828.

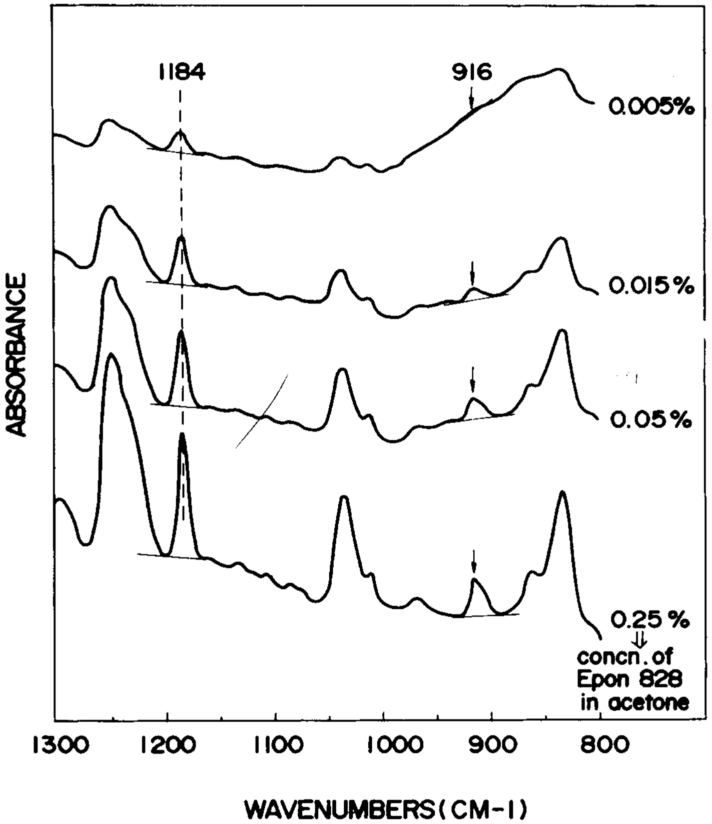

Fig. 10. FT-IR difference spectra obtained by subtracting spectrum of Al–P_2 from that of Al–P_2–828 at varying concentration of Epon 828 in the range of 800–1300 cm^{-1}.

The spectral changes at 1386 cm^{-1} are shown in Figure 11, using the difference spectra obtained by the same procedure as the case of Figure 10. It is apparent from the comparison of the ratio of absorption intensity at 1386 cm^{-1} to that at 1184 cm^{-1} among the spectra that the absorption at 1386 cm^{-1} is increased with decrease in the concentration of Epon 828 on Al–P_2. The absorptions attributable to the C—N and CH_3 vibration (ν_{C-N}, δ_{CH_3}) ought to arise in the vicinity of 1386 cm^{-1}. As the increase in the concentration of CH_3 cannot be considered in this experiment the above spectral change can be attributable to the increase in C—N bond. Though the formation of imide ring and the reaction of oxirane ring with terminal NH_2 group of polyimide can be supposed for the increase of C—N bond, the latter mechanism has a larger possibility by taking into account the decrease in the absorption at 916 cm^{-1} as mentioned above.

The spectra in the vicinity of 1730 cm^{-1} (stretching vibration of the carbonyl group in polyimide) are shown in Figure 12 for Al–P_2 and Al–P_2–828. The absorption, which appears at 1731 cm^{-1} for Al–P_2 shifts to 1727 cm^{-1} for Al–P_2–828. This implies the occurrence of any interaction between the carbonyl group in polyimide and Epon 828. Though the mechanisms of such an interaction can generally be attributable to hydrogen bonding, dipole–dipole

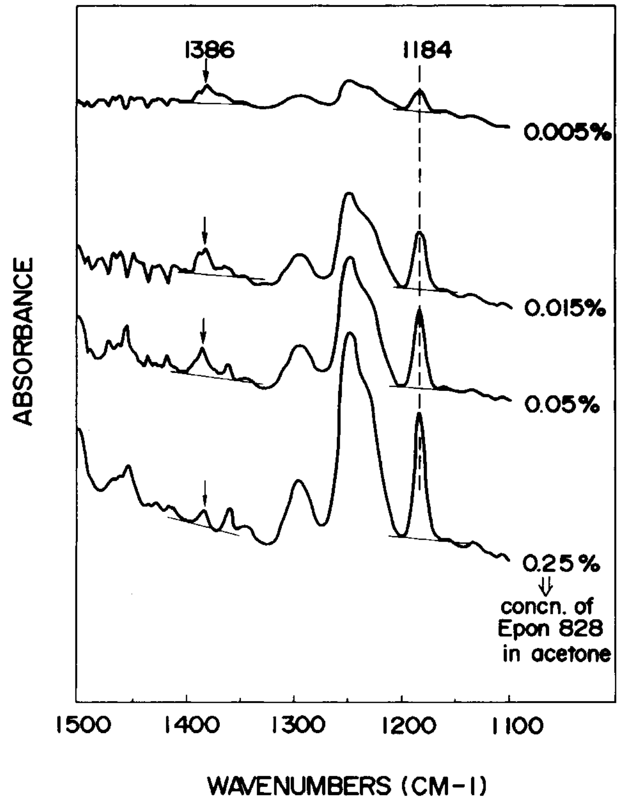

Fig. 11. FT-IR difference spectra obtained by subtracting spectrum of Al–P_2 from that of Al–P_2–828 at varying concentration of Epon 828 in the range of 1100–1500 cm^{-1}.

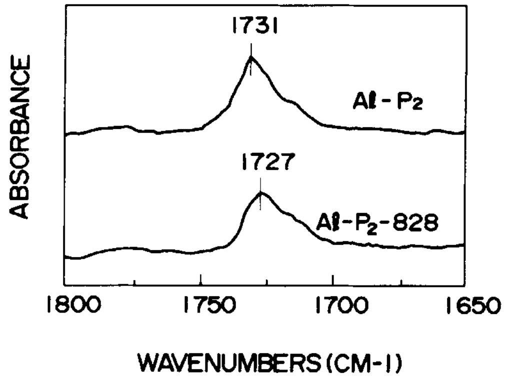

Fig. 12. Comparison of FT-IR spectra of Al–P_2 with Al–P_2–929 (coated with 0.005% solution of Epon 828) in the vicinity of 1730 cm^{-1}.

interaction, complex formation, and so on,[15,16] it can possibly be considered that the hydrogen bonding is formed between the active hydrogen atom in Epon 828 and the carboxyl group of polyimide in this experiment.

The spectral changes observed at 916 and 1386 cm^{-1}, as mentioned above, are attributable to the chemical changes occurring at the interface between the polyimide and Epon 828, and that observed in the vicinity of 1730 cm^{-1} is the physical change based on the large amount of polar group in polyimide. Though these effects are observed for the epoxy resin containing no curing agent, similar effects can be expected commonly for the cured epoxy resin. If CF–S is used in place of CF–P_2, such interaction as the case of CF–P_2 can hardly be expected to arise between the sizing agent and matrix resin by taking into account the composition of the sizing agent as shown in Figure 2. Furthermore, the sizing agent can hardly be expected to remain on the fiber surface unchanged when the matrix resin is applied on the fiber. Therefore, it can be considered that the strengthening of the interaction between the fiber and matrix cannot be attributed to the sizing agent rather than to the polyimide resin.

Thus, the difference between the matrix–reinforcement interaction for composites reinforced with carbon fiber coated with polyimide resin and non-polyimide-treated fiber, which is assumed from the mechanical properties, can be supported qualitatively by the FT-IR study.

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