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The effect of thermoplastic coating on the mechanical properties of woven fabric carbon/epoxy composites

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The effect of a polyetherimide (PEI) coating on the mechanical properties of woven fabric carbon/epoxy composites was investigated by thermal mechanical analysis, fractographical analysis and mechanical properties measurements. PEI coating enhanced the mechanical properties of carbon/epoxy composites mainly through the improvement of matrix properties. This was because most of the PEI coated on the carbon fiber diffused into the bulk of epoxy matrix due to its good miscibility with epoxy resin. As for mechanical properties of woven fabric carbon/epoxy composites, the extent of improvement by PEI coating highly depended on the applied stress state. Among the mechanical properties, mode II delamination resistance of carbon/epoxy composites showed the highest increment because matrix shear property played an important role in delamination resistance of woven fabric carbon/epoxy composite. Because of the woven geometry of carbon fiber, the improvement in impact property of carbon/epoxy composite was trivial except the large amount of PEI coated case.

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1. Introduction

Carbon/epoxy composites have been well known for their excellent properties, such as high specific strength and modulus, good chemical resistance and thermal property. Owing to these excellent properties, carbon/epoxy composites compete with metals in military and civilian aircraft industries [1–3]. However, carbon/epoxy composites have major drawback of brittleness and this drawback should be overcome to enlarge their applications [3].

In the past decades, the toughness improvement of carbon/epoxy composites has become an important research objective in thermosetting polymer composite sciences. The toughness improvement of carbon/epoxy composites has been carried out by various methods such as matrix toughening method, interface control and so on [5–10]. Among them, fiber coating method has been received considerable interest because it has several advantages over the other methods [11].

In fiber coating methods, the selection of coating materials is the most important factor in determining the final properties of polymeric composites. Properly selected coating materials can simultaneously enhance the impact resistance and mechanical strength of composites. In addition, coating materials act to protect the filaments and healing flaws [12]. In composite materials, rubbery fluid, liquid rubber, and ductile thermoplastic have been commonly used as coating materials. Although the selection of proper coating materials for a specific composite is very important factor, the selection guide is still arbitrary.

When the high specific strengths and moduli of polymer composites are needed, high performance thermoplastics are generally preferred to use as coating materials instead of rubber materials. Polyetherimide (PEI) has received public recognition about its effectiveness in toughness improvement of epoxy resin due to its excellent fracture toughness compared with epoxy resin [13–15]. Recently, PEI was introduced to carbon/epoxy composites. Woo *et al.* introduced PEI powders into the interlayer between unidirectional carbon/epoxy prepregs [16, 17]. They reported that the strain energy release rate (G_{IIc}) of carbon/epoxy composite increased four times by addition of PEI.

The purpose of this study is to investigate the effect of PEI coating on the mechanical properties and interphase of woven fabric carbon/epoxy composites. In this research, we performed the dynamic mechanical thermal analysis to evaluate the interphase properties of woven carbon fabric composites. Fractographical analysis and mechanical properties measurement of PEI coated carbon fabric/epoxy composites were also carried out. In addition, the relationship between the surface coating of carbon fiber and the mechanical properties of the composites was studied.

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TABLE I Typical properties of carbon fiber[a] [22]

Number of filament per bundle	Tensile strength (GPa)	Tensile modulus (GPa)	Ultimate strain (%)	Density (g/cm^3)
3 k	3.53	230	1.50	1.77

[a] Trade name: Torayca T300.

2. Experimental

2.1. Materials

Carbon fiber used in this study was plane fabric type Torayca T300. The basic properties of Torayca T300 are given in Table I. Carbon fiber was used after desizing. Carbon fiber was refluxed in dichloromethane for 5 days and then refluxed in distilled water for 2 days. Desized carbon fiber was dried at 120°C for more than 5 days.

N, *N*, *N′*, *N′*-tetraglycidyl-α, α'-bis-(4-amino-phenyl)-*p*-diisopropylbenzene (TGBAP) and α, α'-bis-(4-aminophenyl)-*p*-diisopropylbenzene (BAP) were used as an epoxy resin and a curing agent, respectively. These materials were supplied by Shell Chemical Co. and used as supplied without further purification. The chemical structures of TGBAP and BAP are illustrated in Fig. 1. The physical properties of these materials are presented in Table II.

Polyetherimide (PEI), used as a coating material, was supplied by the General Electric Co. The number average molecular weight ($\bar{M}_n$) of PEI was 20,000. Its structural formula is also represented in Fig. 1. Table III shows the physical properties of PEI.

TABLE II Typical properties of TGBAP and BAP

	TGBAP	BAP
Physical form	Dark solid	Free flowing solid powder
Epoxy equivalent weight	150–170	
Melting point[a]	50°C	161–164°C
Melting viscosity (110°C)[b]	1.8–2.2 Pa· s	
Equivalent weight per active hydrogen		86
T_g[c]	22.8°C	

[a] ASTM D3461, Mettler, 1°C/min.

[b] Brook Field viscometer.

[c] Differential scanning calorimetry.

TABLE III Physical properties of poly(ether imide)[a] [23]

Molecular weight ($\bar{M}_n$)	20,000
Tensile strength	104.88 MPa
Flexural modulus	3.3 GPa
Flexural strength	150 MPa
Fracture energy	2.5 kJ m^{-2}

[a] Trade name: ULTEM 1000.

2.2. Surface coating of carbon fiber

Fiber coating was performed by impregnation method. 12 plies of carbon fabric whose dimension was 120 × 120 mm were dipped in the 200 ml of PEI/dichloromethane solution. The concentration of PEI solution was varied as 0.5, 1.0 and 3.0 wt%. Impregnation time was fixed at 1 hr. The impregnated fiber was dried in a fume hood for one day and then *in vacuo* at 80°C for more than 6 hrs. The amount of PEI adsorbed on carbon fiber was determined by comparing the weights of carbon fiber before and after extraction. Extraction was carried out with Soxhlet using dichloromethane as a solvent.

2.3. Prepreg and composite preparation

Carbon/epoxy prepreg was made by hand lay-up method. The resin bath was composed of TGBAP, BAP and acetone whose weight ratio was 1 : 0.45 : 2.86. Carbon/epoxy prepreg was dried in a fume hood at room

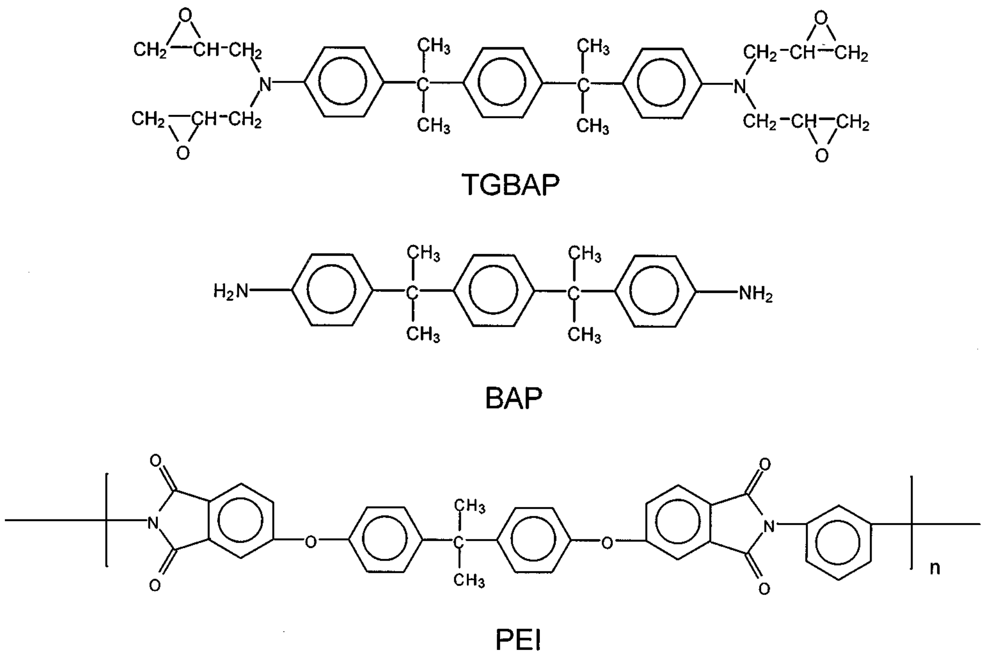

Figure 1 Chemical structures of TGBAP, BAP and PEI.

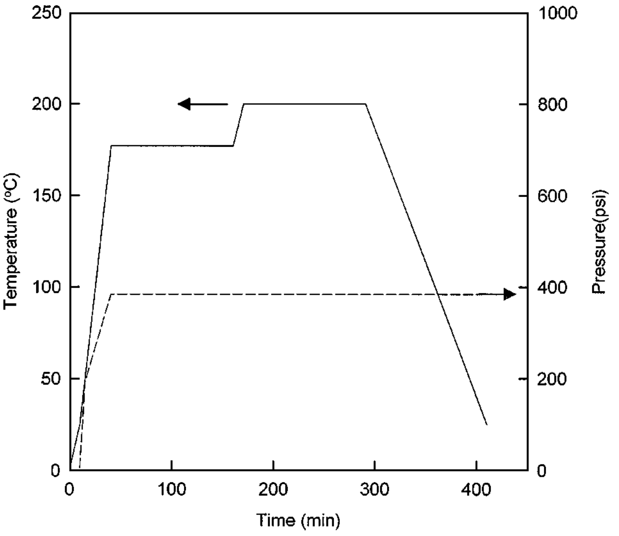

Figure 2 Manufacturing cycle of carbon/epoxy composites.

temperature for 1 day and dried *in vacuo* at 80°C for 3 hrs, consecutively.

Carbon/epoxy composites were manufactured by compression molding technique. The molding cycle is represented in Fig. 2. The specimens for mechanical tests were made with 12 plies of prepreg. In the case of ENF specimens, 25 μm thickness of polyimide film was inserted at the center of the specimen as a delamination film.

2.4. Measurements

2.4.1. Thermomechanical properties

As for woven fabric composites, the contribution of interphase to tan δ curve is larger than that of unidirectional composites due to their low matrix volume fraction. Therefore, dynamic mechanical thermal analysis (DMTA) is an effective tool to examine the interphase properties of woven fabric composites. DMTA was performed by Rheometics Scientific Co. MKIII. The measurement was carried out in bending mode with 1 Hz frequency and 5°C/min heating rate.

2.4.2. Mechanical properties

The mechanical properties of carbon/epoxy composites were measured by using an Universal Testing Machine model Lloyd LR10k. The interlaminar shear strengths (ILSSs) of composites were obtained according to ASTM 2344. In this case, the span to depth ratio was fixed at 6 and the crosshead speed was 1.3 mm/min. Considering the application fields of carbon/epoxy composites, it is apt to be under a shear stress state, so its resistance to shear stress is very important. Therefore, a mode II method, especially the ENF (end notched flexural) method was chosen for this study. Apart from unidirectional samples, fabric-reinforced composites were difficult to analyze theoretically so this structure was approximated as a crossplied structure of unidirectional form. Consequently, G_{IIc} was calculated by following equation [18].

$$G_{\mathrm{IIc}} = \frac{9a^2 P_c \delta_c}{2w(2L^3 + 3a^3)} \qquad (1)$$

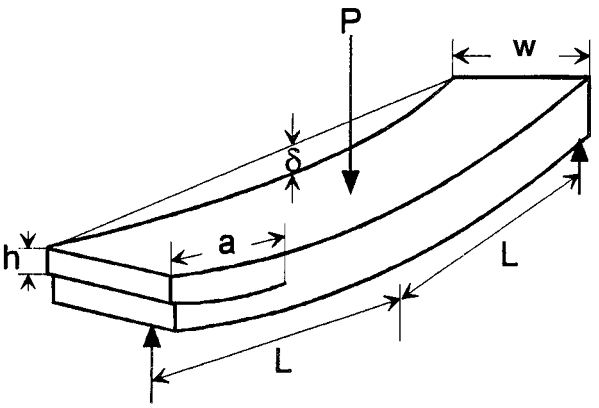

Figure 3 Schematic diagram of ENF specimen.

The terminology is explained in Fig. 3. In the ENF test, the crosshead speed was 2.5 mm/min. The detailed test method was given in reference [19, 20].

Flexural properties of the carbon/epoxy composites were measured by three-point bending tests according to ASTM D790. The specimen was machined into bars with dimensions 60 mm × 25 mm × 2.5 mm. In the flexural tests, the crosshead speed was 1.2 mm/min and the gauge length was 48 mm.

A driven dart impact tester, model Radmana ITR 2000, was used to study the impact properties of the carbon/epoxy composites. The impact velocity was controlled by compressed air at 3.12 m/sec. The diameter of the nose tip was 1.27 cm and the size of anvil was 7.5 cm. The impact energy was 156.6 J.

2.4.3. Composition of composites

The composition of carbon/epoxy composites was calculated from the equations;

$$V_f = W_f \frac{\rho_c}{\rho_f}$$

$$V_p = W_p \frac{\rho_c}{\rho_p}$$

$$V_m = W_m \frac{\rho_c}{\rho_m} = (100 - W_f - W_p)\frac{\rho_c}{\rho_m}$$

$$V_v = 100 - V_f - V_m - V_p$$

where the subscripts c, f, p, m and v represent composite, fiber, PEI, matrix resin and void respectively. V_f, V_p, V_m, V_v : volume fractions of each component W_f, W_p, W_m : weight fractions of each component ρ_c, ρ_f, ρ_p, ρ_m : densities of each component measured by picnometer

2.4.4. Fractographic analysis

Analysis of the fractured surfaces of carbon/epoxy composites was carried out by scanning electron

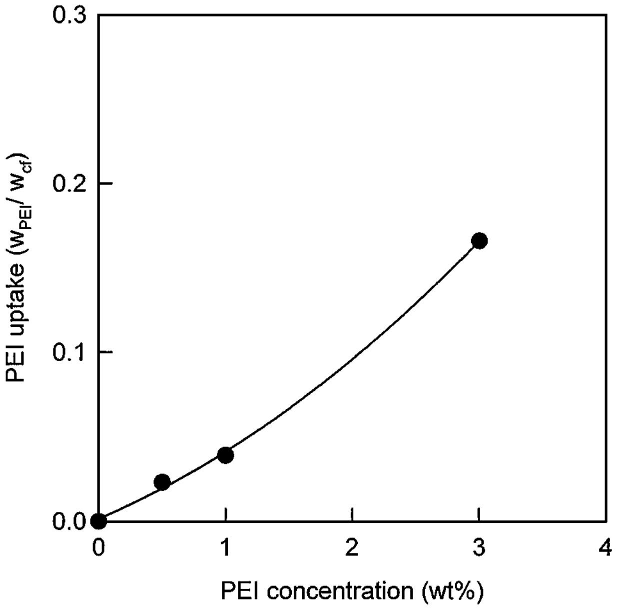

Figure 4 Real amount of PEI uptake as a function of concentration of PEI solution.

microscopy (SEM) in a model JEOL-840A. The fractured surface was gold coated with thickness of 100 Å.

3. Results and discussion

3.1. PEI coating on the carbon fabric

The coating amount of PEI depends on the concentration of PEI solution, impregnation time and the surface properties of carbon fiber. Therefore, it was necessary to measure the real amount of PEI coated on carbon fiber. The real amount of coated PEI was calculated by comparing the weight of PEI coated carbon fiber with that of PEI extracted carbon fiber. The relation between the concentration of PEI solution and the real amount of PEI uptake is given in Fig. 4. This curve shows that the PEI uptake increased remarkably with increasing concentration of PEI solution. This result was partly because the adsorption rate between the same materials was faster than that of the different ones and because solution mobility decreased as the concentration of PEI solution increased.

Fig. 5 shows the surface morphologies of desized carbon fiber and PEI coated carbon fiber. The desized carbon fiber shows many grooves and crevices, which are characteristics of T-300 grade carbon fiber. However, these morphologies were covered with PEI layer when carbon fiber was coated with PEI solution. Considering Fig. 5, carbon fiber was not coated uniformly with the PEI layer because of the heterogeneous surface properties of carbon fiber and geometrical shape of fabric structure.

3.2. Mechanical properties

3.2.1. Interlaminar shear strength

In fiber/matrix composites, the ILSS is mainly determined by the interfacial strength between fiber and matrix. As for carbon/epoxy composites, the interfacial strength between carbon and epoxy matrix has been explained by the concept of mechanical interlocking and adsorption theory [20].

The many grooves and crevices in carbon fibers, observed in Fig. 5, were known to be effective in casing mechanical interlocking [20]. Although the carbon fiber was desized, residual sizings and polar components on the carbon fiber surface made its surface hydrophilic and enhanced the wettability of the carbon fiber. Therefore, it was simply expected that ILSS values for the carbon/epoxy composite decreased monotonically with increasing amounts of PEI coating because the PEI layer covered the mechanical interlocking sites and polar components of carbon fiber.

Fig. 6 shows the ILSS of the carbon/epoxy composites as a function of PEI uptake. Unexpectedly, the reduction in ILSS was not large. This result seems to originate from the improvement in the mechanical properties of epoxy resin as a result of PEI migration into the continuous epoxy phase. This can be confirmed by the study on the interphase of carbon/epoxy composites.

Fig. 7 shows the tan δ curves of PEI-coated carbon/epoxy composites. In this study, carbon/epoxy composites, in which the fiber surfaces were coated by 0.5, 1.0 and 3.0 wt% PEI solutions, were designated as P0.5, P1 and P3. The shape of the tan δ curve for the carbon/epoxy composites changed with PEI addition and the remarkable difference in tan δ was observed at P3. It was well known that the peak temperature of tan δ curve is related to the interfacial strength of carbon/epoxy composites and full width at half maximum (FWHM) of tan δ curve is related to the molecular relaxation of the epoxy matrix. That is, a broad FWHM means that the epoxy resin has various network structures. FWHM values of carbon/epoxy composites determined from tan δ curves are summarized in Table IV. Compared with P0.5 and P1, P3 had abnormally broad tan δ shape. This implies that the PEI coating influences the cure reaction of TGBAP and BAP not only at the interphase but also in the bulk matrix regions. This was due to the good miscibility of PEI with epoxy resin and relatively large amount of PEI in P3. Table V shows the calculated composition of carbon/epoxy composites. P0.5 and P1 showed the similar amount of PEI, however

TABLE IV Full width at half maximum (FWHM) of PEI coated carbon/epoxy composites

Sample code	FWHM (°C)
Control	34.5
P0.5	37.3
P1	39.2
P3	70.6

TABLE V The compositions of PEI coated carbon/epoxy composites

Sample code	V_f	V_m	V_p	V_v
Control	0.665	0.323	0.000	0.012
P0.5	0.653	0.328	0.021	0.010
P1	0.650	0.300	0.035	0.015
P3	0.601	0.260	0.138	0.014

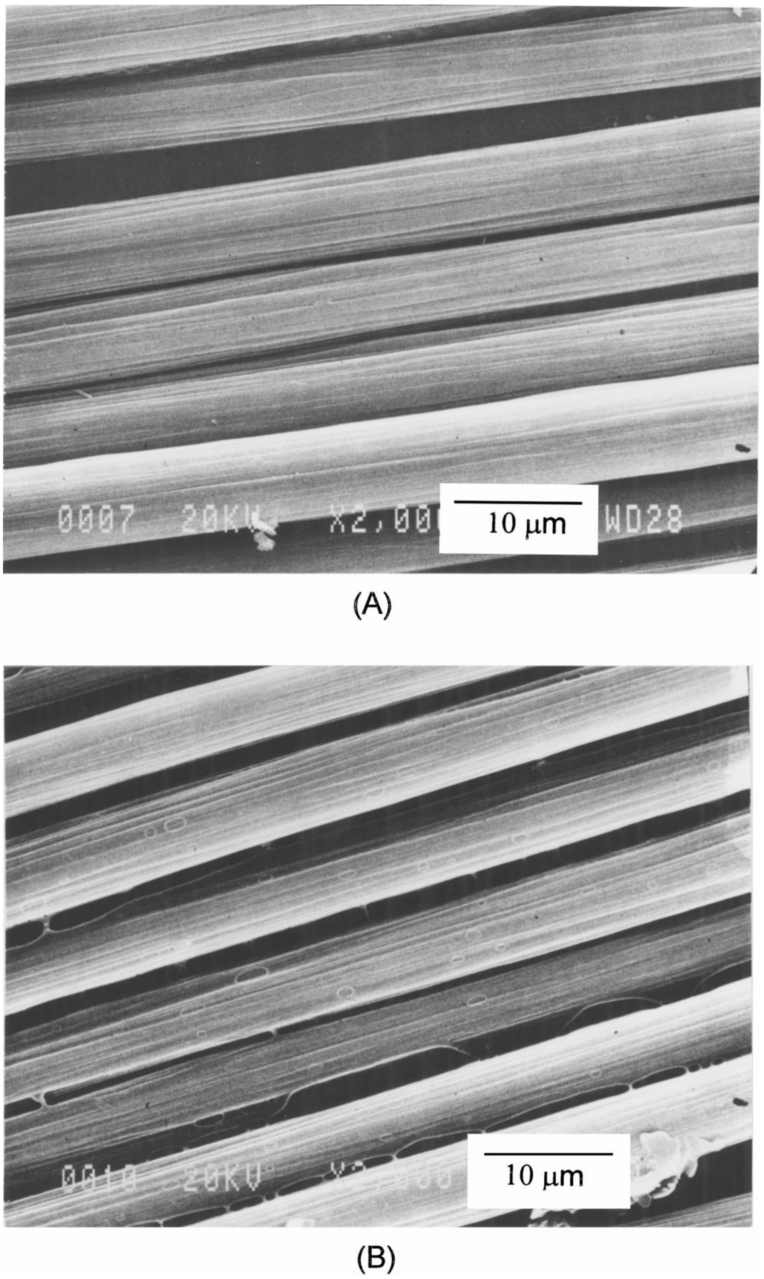

Figure 5 SEM photographs of carbon fibers; (A) untreated, (B) PEI coated (5 wt% PEI solution).

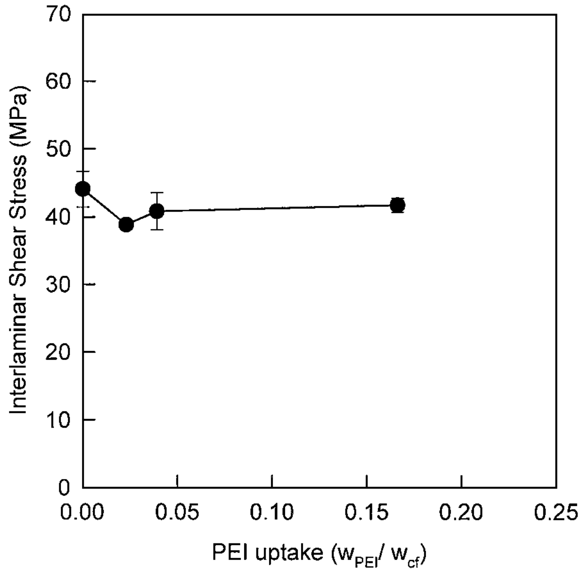

Figure 6 Interlaminar shear strengths of carbon/epoxy composites as a function of PEI uptake.

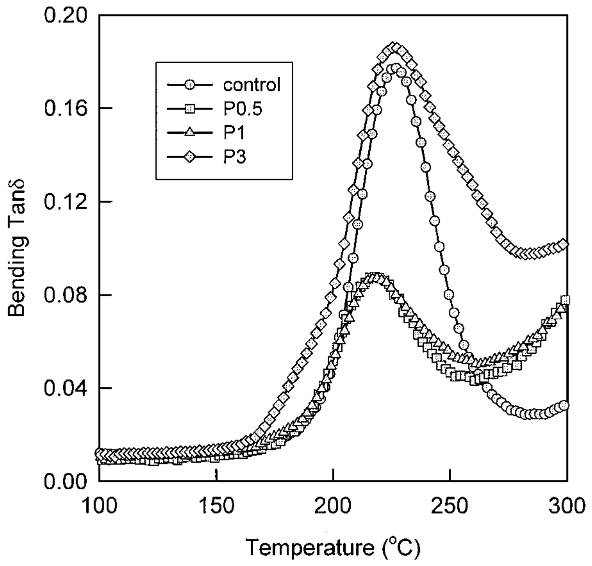

Figure 7 Bending tan δ of PEI coated carbon/epoxy composites.

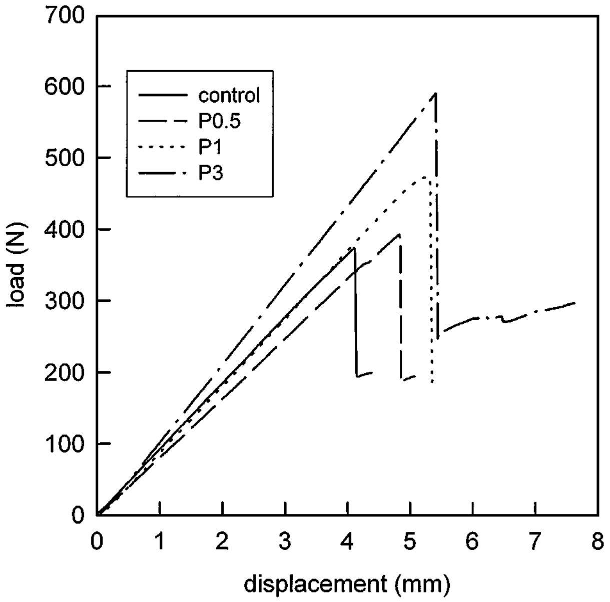

Figure 8 The loads versus displacement curves of PEI coated carbon/epoxy composites by ENF test.

P3 had six times larger PEI content than above two cases.

3.2.2. Mode II delamination

The mode II delamination of carbon/epoxy composites was tested by the ENF method. To study the effect of the PEI coating on the failure mode of the carbon/epoxy composites, the loads versus displacement curves of carbon/epoxy composites were examined. These plots are given in Fig. 8. The overall shapes of these curves showed that carbon/epoxy composites fractured in a brittle mode irrespective of the amount of PEI. However, it was obvious that the load and displacement at break point increased with increasing amount of coated PEI.

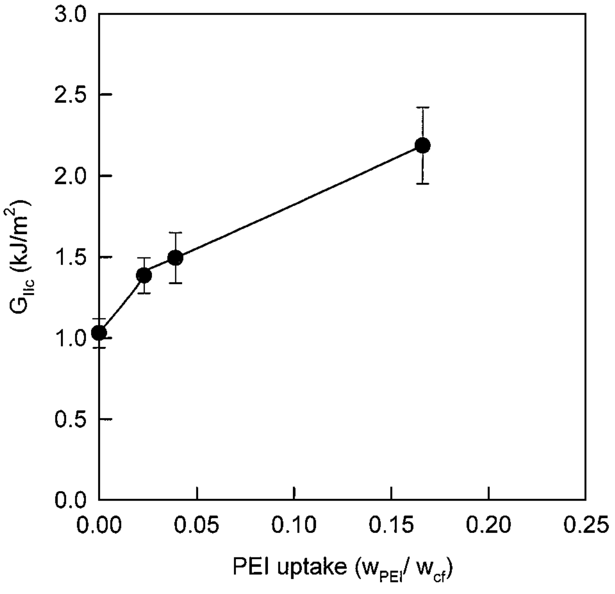

Figure 9 Strain energy release rate (G_{IIc}) of PEI coated carbon/epoxy composites as a function of PEI uptake.

Fig. 9 shows the G_{IIc} of carbon/epoxy composite as a function of PEI uptake. As expected from the load versus displacement curves, G_{IIc} values of carbon/epoxy composites simply increased with increasing amounts of PEI coating. This trend is similar to that for the case of plain epoxy resin in fact that percent increment in G_{IIc} was the largest when PEI was introduced pristine sample for the first time.

Although the ILSS of the carbon/epoxy composites showed a small change, the G_{IIc} values for the carbon/epoxy composites increased considerably as a result of the PEI addition. Considering the mode II stress state of woven carbon/epoxy composites, fracture mechanisms, which were restricted by woven geometry, occurred with difficulty. Therefore, their contribution to fracture toughness was trivial. In woven carbon/epoxy composite, the delamination resistance was mainly affected by the fiber/matrix interfacial adhesion and matrix shear plastics.

To confirm this, the fractured surfaces of fill yarn region of PEI coated carbon/epoxy composites were investigated and their SEM photographs are given in Fig. 10. It was difficult to observe the distinct difference at fiber/matrix interface. However, the epoxy matrix showed obviously different features. In particular, the P3 sample showed the distinct PEI domains and ductile fracture surface compared with control.

3.2.3. Flexural property

The flexural strengths and G_{IIc} values of PEI coated carbon/epoxy composites are given in Fig. 11. It can be seen that the flexural strengths and G_{IIc} values of carbon/epoxy composites showed similar trend with respect to PEI coating. However, the flexural strength of the carbon/epoxy composite was less affected by PEI coating than G_{IIc} value. This fact came from the different failure mode of carbon/epoxy composites by flexural and mode II shear tests.

Examining the flexural test, the bending crack of carbon/epoxy composite was formed at the tensile stressed side and it induced the catastrophic failure of carbon/epoxy composite through the fiber fracture and delamination. Of these two processes, fiber fracture is a more effective energy absorption mechanism than is delamination. In consequence, the enhancement of flexural strength of carbon/epoxy composite by PEI coating was smaller than that of G_{IIc}.

3.2.4. Impact properties

The impact properties of PEI coated carbon/epoxy composites were measured by the driven dart method. For a detailed investigation of the impact behavior, the impact energy was divided into initiation energy and propagation energy. In this study, propagation energy was defined as the energy consumed by the process extending from the peak position to complete perforation. Impact data for carbon/epoxy composites are given in Table VI.

As the amount of PEI coating increased, the load at break also increased. However, the increment of load

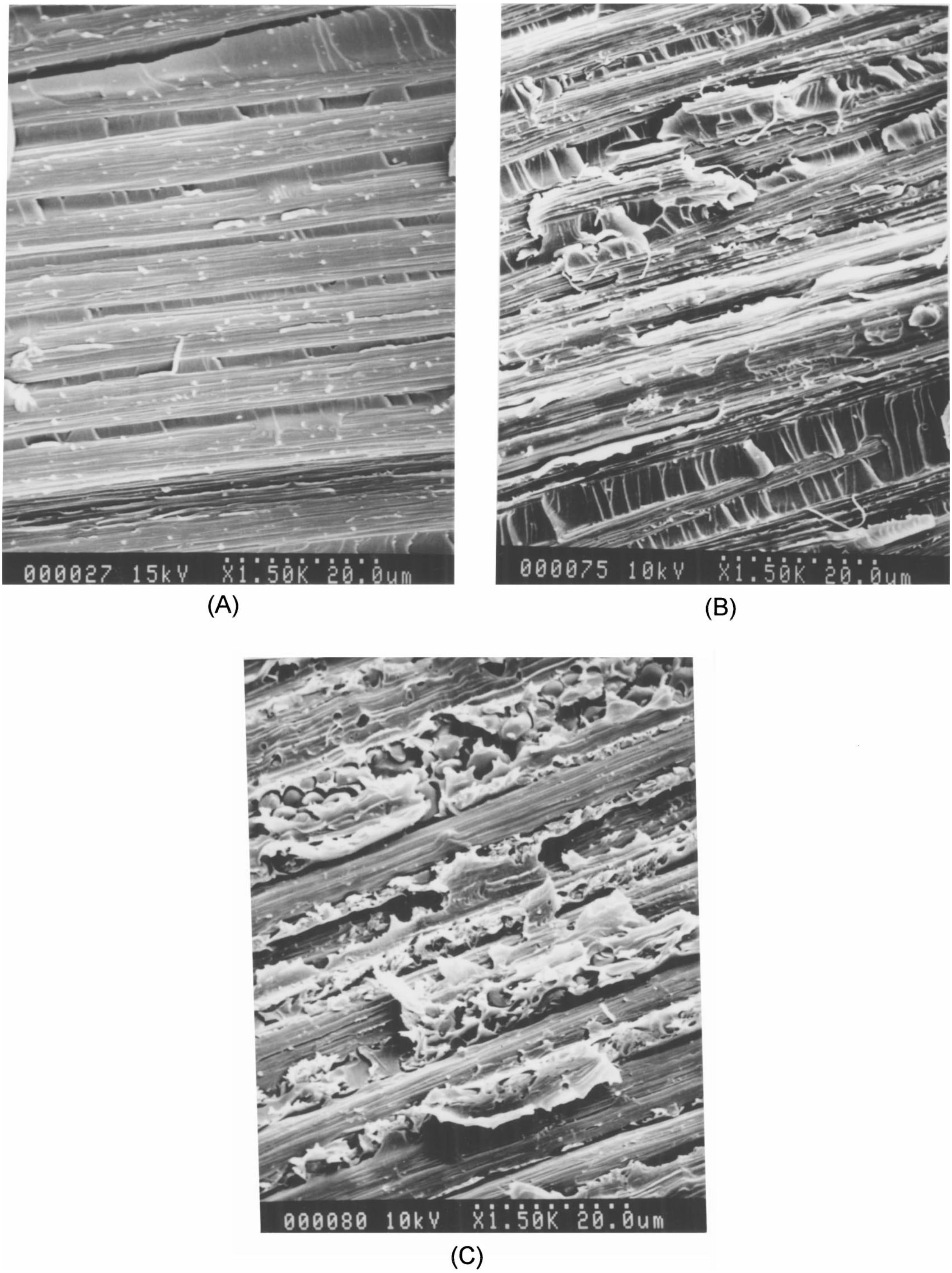

Figure 10 SEM photographs of fractured surface of PEI coated carbon/epoxy composites by ENF test.

TABLE VI Impact energy of PEI coated carbon/epoxy composites

Sample code	Load at peak (N)	Initiation energy (J)	Propagation energy (J)
Control	1640	2.39 ± 0.09	4.19 ± 0.21
P0.5	1655	2.40 ± 0.08	4.39 ± 0.18
P1	1785	2.42 ± 0.09	4.41 ± 0.22
P3	1889	2.52 ± 0.11	4.88 ± 0.24

at break was not so much except P3 case. This suggests that the matrix deformation, particularly for woven fabric type composites, was restricted by the rigid woven fiber. Therefore, the slight increase in impact properties could be explained by considering this fact. Some detail investigation about the impact behavior of PEI toughened woven carbon/epoxy composites was performed previously [21].

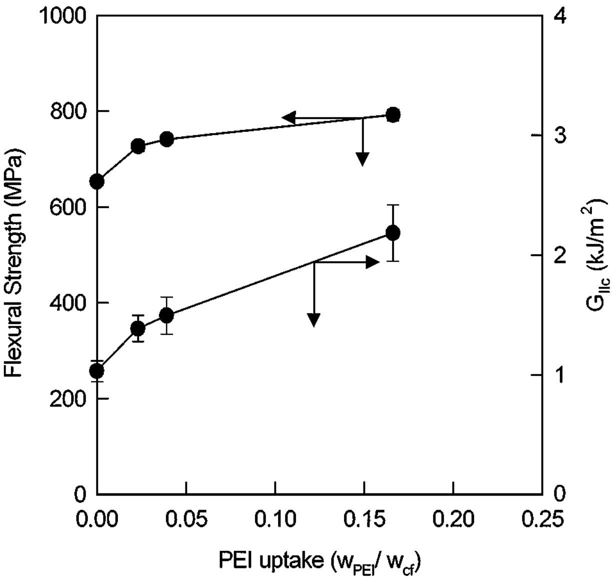

Figure 11 Flexural strengths and G_{IIc} values of PEI coated carbon/epoxy composites as a function of PEI uptake.

4. Conclusions

From this study of the effect of PEI coating on the mechanical properties of woven carbon/epoxy composites, following conclusions were obtained.

When the PEI was coated onto the woven carbon fiber, most of the coated PEI did not remain on the carbon fiber surface. PEI migrated into the bulk epoxy matrix because of its good miscibility with epoxy resin. PEI coating induced the poor interlayer structure. As the coating amount of PEI increased, epoxy bulk property became more ductile.

Interlaminar shear strengths of carbon/epoxy composites showed a little decrease due to the PEI coating. This came from the enhanced matrix properties due to the migration of PEI particles compensated for the decrement of interfacial adhesion of carbon/epoxy composites. However, delamination resistance to shear stress, flexural strength and impact resistance of carbon/epoxy composites, which were known to be largely dependent on the matrix properties, increased monotonously with increasing the PEI coating amount. In particular, the largest enhancement was observed in delamination resistance to shear stress. Judging from the above results, the PEI coating effect appeared as an improvement of the mechanical properties through modification of matrix property. Therefore, thermoplastic coating technology overcomes the disadvantage of rubber toughening and this method can provide wide range of applications for the carbon fiber composite business.

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