Interfacial Properties and Microfailure Mechanisms of Electrodeposited Carbon Fiber/epoxy-PEI Composites by Microdroplet and Surface Wettability Tests

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Microdroplet 시험법과 Surface Wettability 측정을 이용한 전기증착된 탄소섬유 강화 Epoxy-PEI 복합재료의 계면물성과 미세파괴 메카니즘

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KEY WORDS: fracture toughness, microdroplet test, wettability, electrodeposition (ED) microfailure mode, interfacial shear strength (IFSS)

ABSTRACT

Interfacial properties and microfailure modes of electrodeposition (ED) treated carbon fiber reinforced polyetherimide (PEI) toughened epoxy composite were investigated using microdroplet test and the measurement of surface wettability. As PEI content increased, Interfacial shear strength (IFSS) increased due to enhanced toughness and plastic deformation of PEI. In the untreated case, IFSS increased with adding PEI content, and IFSS of pure PEI matrix showed the highest. On the other hand, for ED-treated case IFSS increased with PEI content with rather low improvement rate. The work of adhesion between fiber and matrix was not directly proportional to IFSS for both the untreated and ED-treated cases. The matrix toughness might contribute to IFSS more likely than the surface wettability. Interfacial properties of epoxy-PEI composite can be affected efficiently by both the control of matrix toughness and ED treatment.

Nomenclature

τ	: Interfacial shear strength (IFSS)
α, β	: Scale and shape parameters in Weibull distribution
K_{IC}	: Fracture toughness
γ_c	: Critical surface tension
γ_s	: Surface free energy of Solid
γ_s^p, γ_s^d	: Polar and dispersive surface free energy
W_a	: Work of adhesion

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1. INTRODUCTION

Thermosetting epoxy resin has been widely used as one of the most important matrix for fiber reinforced composites. Epoxy resin has many good mechanical and thermal properties such as high tensile strength and modulus, dimensional and thermal stabilities, excellent chemical resistance and fatigue properties. These properties in an epoxy resin require a high crosslinking density, which usually results in a brittle failure behavior.

Toughened epoxy matrix using liquid reactive rubber has been reported widely [1,2]. However, the toughness improvement in most of rubber modified thermosetting systems results in a significant decrease in the glass transition temperature, T_g, stiffness and strength of the cured thermosetting resin. High performance thermoplastics, such as poly(ethersulfone) (PES), PEI, polycarbonate and poly(phenyleneoxide) (PPO), or a combination of rubber and thermoplastics, are commonly added to thermosetting resins as processing modifiers

and they increased the fracture toughness without reducing thermal and mechanical properties [3,4]. Partridge *et al.* investigated the possibility for improving the toughness using a commercial grade PEI to toughen difunctional epoxy resin [5]. It showed that the stress transfer from the matrix to fiber in epoxy-PEI composites occurred efficiently because of homogeneous phase separation with PEI particles in epoxy matrix.

In this work, PEI content was controlled to improve the toughness of epoxy matrix. The interfacial properties and microfailure modes of ED-treated carbon fiber reinforced toughened epoxy-PEI composites were investigated using micromechanical and surface wettability tests. Surface energies and morphological results were correlated with IFSS.

2. EXPERIMENTAL

2. 1. Materials

Carbon fiber (Mitsubishi, Chemical Co., Japan) as a reinforcing material was used, and average diameter was about 18 μm. A difunctional epoxy resin (YD-128, Kukdo Chemical Co., Korea), diglycidylether of bisphenol-A (DGEBA) was used as a main matrix resin and nadic methyl anhydride (NMA, Kukdo Chemical Co., Korea) and benzyldiethylamine (BDMA) were used as a curing agent and a catalyst, respectively. A commercial grade of PEI (Ultem 1000, General Electric Co.) was used as a thermoplastic modifier. *N*-methyl-2-pyrrolidinone (NMP) was used for a solvent of PEI. Polybutadiene maleic anhydride (PBMA, Polyscience Inc.) was used as a coupling agent to improve IFSS by ED treatment [6].

2. 2. Methodologies

2.2.1 Specimen Preparation: Figure 1(a) shows a schematic diagram for mixing process of epoxy and PEI. The PEI was dissolved with dichloromethane for 1 hour in the mixing vessel and their concentration was about 10 wt%. This mixture was stirred with the epoxy resin for 2 hours at room temperature, and then degassed in a rotary vacuum evaporator for 24 hours at 80°C. The hardener was dissolved into the mixture to make a homogenous resin paste using a three roll mill for 1 hour. Selected two PEI contents were 5 and 20 wt% for comparison.

The fracture toughness of the cured epoxy-PEI matrix for two PEI contents was measured by three point bending test based on ASTM E 399 [7] using UTM. Figure 1(b) shows (a) the specimen dimension and (b) the testing scheme for three point bending test. The crosshead speed was 1.3 mm/minute and the span length was 40 mm. The fracture toughness, K_{IC} was calculated using the following equation,

$$K_{IC} = \left(\frac{FS}{BW^{3/2}}\right) \cdot f\left(\frac{a}{W}\right) \quad (1)$$

where F is the load, S is the span length, B and W are specimen thickness and width length. And a is the crack depth and $f(a/W)$ is a geometrical factor of the specimen.

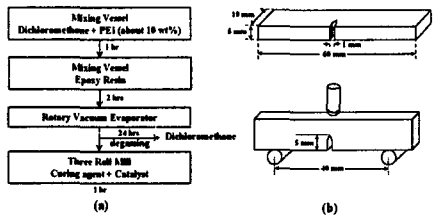

Fig. 1 Schematic diagram for (a) mixing process and (b) three point bending test.

2.2.2 IFSS Measurement: The untreated and ED-treated carbon fibers were fixed with regularly separated distance in a steel frame. Microdroplets of neat epoxy and epoxy-PEI matrix were formed on each fiber axis using carbon fiber of 8 μm in diameter. Microdroplet specimens were cured with a same curing steps. In the case of pure PEI, the formation of microdroplet by melting method was difficult due to high melt viscosity. Instead of it, pure PEI was solved in NMP and then good shaped-microdroplets were formed well on carbon fiber. Microdroplet of pure PEI resin was formed at about 350°C in a high temperature oven.

Figure 2(a) shows a schematic diagram for an experimental system for microdroplet test. The shear force at the interface was developed by applying the load. A microdroplet specimen was fixed by the microvise using a specially designed micrometer. The IFSS, τ was calculated from the measured pullout force, F using the following equation,

$$\tau = \frac{F}{\pi D_f L} \quad (2)$$

where D_f and L are fiber diameter and fiber embedded length in the matrix resin, respectively. It is assumed that there is a linear relationship between pullout force and embedded length of the fiber.

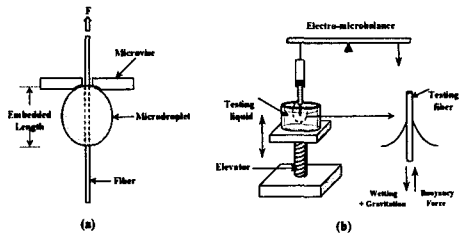

Fig. 2 Schematic diagram of (a) microdroplet test and (b) dynamic contact angle measurement.

2.2.3 Measurement of Wettability and Surface Energies: Wettability of fiber and matrix was measured by Wilhelmy plate technique [8] (Sigma 70, KSV Co., Finland). Figure 2(b) shows an experimental system for dynamic contact angle measurement. Dynamic contact angle, critical surface tension and polar and dispersive surface free energy of the fiber were measured. Used three testing liquids were double distilled water, formamide and dimethylformamide. Dynamic contact angle was measured using Wilhelmy plate method as

$$\cos\theta = \frac{M \cdot g}{\pi D \gamma_{LV}} \quad (3)$$

where M is measured force. The value of critical surface tension at $\cos\theta = 1$ was measured using Zisman plot that plotted γ_{LV} *versus* $\cos\theta$. To measure polar and dispersive surface free energies, Owens-Wendt Eq. (4) were expressed as follows:

$$W_a = 2\sqrt{\gamma_l^d \gamma_s^d} + 2\sqrt{\gamma_l^p \gamma_s^p} \quad (4)$$

where W_a is work of adhesion, γ_l, γ_l^d and γ_l^p is known for the testing liquids and $\cos\theta$ can be measured using Eq. (3). Polar and dispersive surface free energy can be measured from the slope and the intercept of the graph, where $(\sqrt{\gamma_l^p}/\sqrt{\gamma_l^d})$ and $(W_a/2\sqrt{\gamma_l^d})$ are plotted by Eq. (4).

3. RESULTS AND DISCUSSION

3.1 Mechanical Properties of Fiber and Matrix: Figure 3 shows SEM photographs for epoxy-PEI matrix with PEI content for (a) 5 wt% PEI and (b) 20 wt% PEI. Epoxy-PEI matrix appeared many PEI 'island' phases in the epoxy matrix, and PEI particles were microspherical shape. PEI microspheres were spread uniformly in epoxy resin, and both relative contents and size of PEI microsphere increased with increasing initial blending PEI content. In high 20 wt% PEI case, shape of PEI particles changed from the microsphere to the rather ellipse because of geometrical effect by gravity. Several parameters, i.e. the content, size and shape of PEI particle might affect to mechanical properties of epoxy-PEI matrix, such as toughness, tensile strength and modulus.

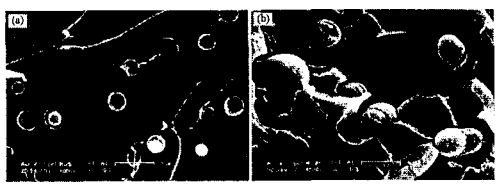

Fig. 3 SEM photographs for epoxy-PEI matrix with PEI content.

Mechanical properties of PEI modified epoxy matrix were compared with those of the pure PEI and neat epoxy matrices. Figure 4(a) shows the mechanical properties of epoxy-PEI matrix with PEI content and their stress-strain curves. Although the tensile strength was expected to increase with PEI content by the general rule of mixture, tensile strength and modulus increased for 5 wt% and then decreased. Figure 4(b) shows the fracture toughness of epoxy-PEI matrix with PEI content. The fracture toughness at 5 wt% PEI improved slightly compared to neat epoxy resin, whereas the fracture toughness improvement at 20 wt% PEI was very high and showing about 45 %. Microcrack could be propagated easily through brittle epoxy phase, whereas ductile PEI phase could blunt crack propagation. At 5 wt% PEI case, crack blunting effect might be less because the separation between PEI particles was rather far away as shown in Figure 3(a). On the other hand, at 20 wt% PEI case, crack propagation could be restricted more due to closely apart distance and large size of PEI particles in Figure 3(b). At 20 wt% PEI, the fractured surface appeared tougher than the case of 5 wt% PEI content showing more likely smooth surface. The morphological change of fracture surface indicated improving fracture toughness by adding PEI content.

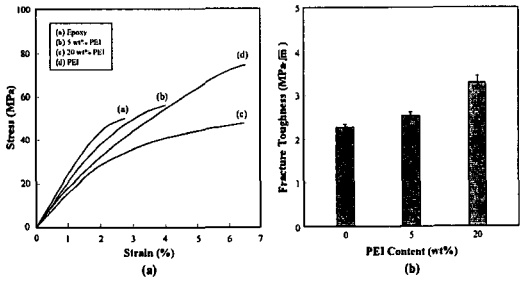

Fig. 4 (a) Stress-stain curves and (b) fracture toughness of epoxy-PEI matrix with PEI content.

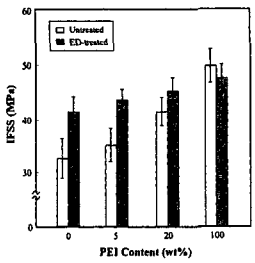

Fig. 5 IFSS of the untreated and ED-treated carbon fiber/epoxy-PEI composite.

3.2 IFSS and Microfailure Modes: Figure 5 show IFSS of the untreated and ED-treated carbon fiber reinforced epoxy-PEI composite using microdroplet test. In the untreated case, IFSS increased with adding PEI content due to the enhanced fracture toughness and energy absorption [9]. IFSS of pure PEI resin was the highest because of good wettability due to low viscosity despite

their rather weak chemical reactivity. For the ED-treated cases, they showed significant IFSS improvement compared to that of the untreated case. IFSS increased with adding PEI content, whereas the improvement percentage reduced gradually. It could be considered that chemical interactions between PBMA and epoxy matrix were more efficient than the interaction with PEI, since PEI does not contain many functional groups. IFSS between ED-treated carbon fiber and pure PEI decreased even to some degree compared to the untreated case. It might be because PBMA occurred partially thermal degradation in butadiene segments during forming a microdroplet at high temperature, 350°C.

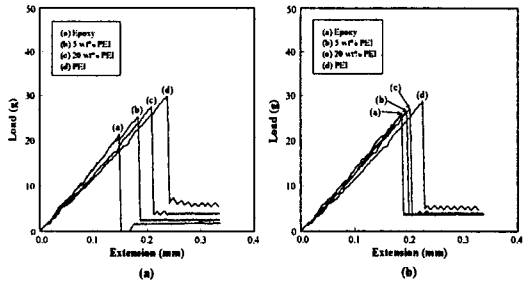

Fig. 6 Typical load versus extension curves for carbon fiber/epoxy-PEI composites for (a) the untreated and (b) ED-treated.

Figures 6 shows typical load *versus* extension curves for (a) the untreated and (b) ED-treated carbon fiber reinforced PEI-epoxy composites using microdroplet test. In the untreated case, the maximum and friction forces of neat epoxy matrix were the lowest compared with other three matrices, and the force was dropped to the almost zero level directly right after the maximum point attained due to the brittleness of epoxy matrix. On the other hand, the maximum and frictional forces increased steadily with increasing PEI content, and pure PEI matrix showed the highest maximum and frictional values. For the ED-treated case, force-length lines of neat epoxy, 5 wt% PEI and 20 wt% PEI were almost similar to each other except pure PEI case.

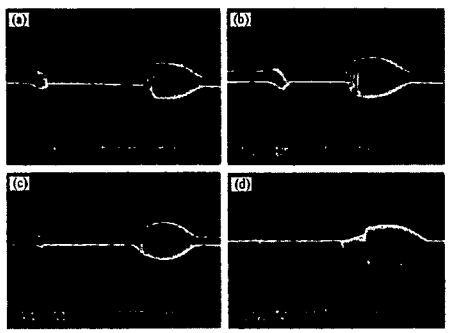

Fig. 7 Typical microfailure modes of the untreated carbon fiber/epoxy-PEI composite with PEI content.

Figures 7 shows SEM photographs of typical microfailure modes for the untreated carbon fiber reinforced epoxy-PEI composites with PEI content after the microdroplet test for (a) neat epoxy, (b) 5 wt% PEI, (c) 20 wt% PEI and (d) pure PEI. Neat epoxy microdroplet appeared brittle microfailure mode, whereas PEI microdroplet exhibited more likely plastic deformation and ductile microfailure mode. Failure mode of fracture surface was generally changed from smooth to rough and the brittle nature became tougher with adding PEI content.

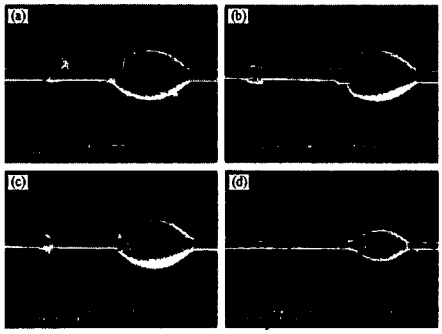

Fig. 8 Typical microfailure modes of ED-treated carbon fiber/epoxy-PEI composite with PEI content.

Figure 8 shows SEM photographs of typical microfailure modes for ED-treated carbon fiber reinforced epoxy-PEI composites with PEI content after microdroplet test for above same four matrices. Microfailure mode of ED-treated pure epoxy system showed more ductile fracture compared with the untreated case, because of the existence of the interlayer with about 1 μm in thickness. Microfailure modes for other three matrices were also similar like ductile microfailure patterns as pure epoxy case.

Table 1 Surface free energy and critical surface tension for carbon fiber and epoxy-PEI matrix

Materials		γ_s	γ_s^d	(γ_s^p)	γ_c
		(mJ/m^2)			(dyn/cm)
Carbon Fiber	Untreated	32.6	27.9	4.7	33.3
	ED-treated	42.9	23.6	19.3	36.6
Matrix	Epoxy	35.0	28.6	6.4	35.9
	5 wt% PEI	36.3	34.3	2.0	37.0
	20 wt% PEI	36.4	34.1	2.3	37.2
	PEI	35.1	32.9	2.2	35.8

3.3 Wettability and Surface Energies: Table 1 shows the surface free energy and critical surface tension for two untreated and ED-treated carbon fibers and four matrix series. Polar surface free energy of neat epoxy was the highest compared with three other matrices because of the many high hydrophilic epoxide groups

existed in epoxy matrix. Critical surface tension and polar surface free energy of ED-treated carbon fiber were higher than those of the untreated case. It is considered that the surface of PBMA coupling agent contains hydrophilic functional groups such as carboxyl and carbonyl etc. The high polar term in the total surface free energy can be expected to contribute to good wettability and adhesion between fiber and matrix.

Table 2 Work of adhesion, W_a between carbon fiber and epoxy-PEI matrix

Work of Adhesion (mJ/m^2)	Fiber	Matrix			
		Epoxy	5 wt% PEI	20 wt% PEI	PEI
W_a	Untreated	67.5	68.0	68.3	67.0
	ED-treated	74.2	69.3	70.0	68.8

Table 2 shows the work of adhesion, W_a between the untreated and ED-treated carbon fiber and four matrix series. For the untreated carbon fiber, the four values of work of adhesion were similar within the error range. It means that thermodynamic value, W_a does not change significantly with adding PEI content. In the case of ED-treated carbon fiber, neat epoxy matrix showed some improvement, whereas other three matrices showed only slight improvement.

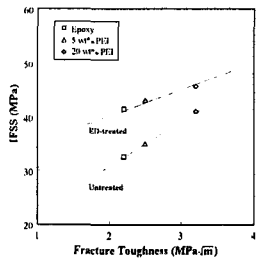

Fig. 9 Plot of IFSS versus fracture toughness for carbon fiber/epoxy-PEI composite.

Figure 9 shows the correlation of fracture toughness and IFSS for the untreated and ED-treated carbon fiber reinforced epoxy-PEI composites. Trends of fracture toughness were consistent with IFSS for both the untreated and ED-treated cases. The slope of the untreated case was higher than that of ED-treated case. As a result, IFSS may depend on strongly matrix toughness in the untreated case. On the other hand, in ED-treated case improved IFSS may be determined such as the ductile PBMA interlayer and matrix toughness.

4. CONCLUSIONS

Interfacial properties and microfailure modes for the untreated and ED-treated carbon fiber reinforced epoxy-PEI composites were performed using microdroplet and wettability tests. With adding PEI content, in the untreated case the fracture toughness of epoxy-PEI matrix increased, and IFSS was improved due to the improved toughness and energy absorption by plastic deformation of PEI. IFSS between ED-treated carbon fiber and epoxy-PEI matrix increased. The microdroplet in the untreated carbon fiber and neat epoxy system showed rather brittle microfailure pattern. For higher PEI content, ductile microfailure mode appeared because of improved fracture toughness. In the case of ED-treated, microfailure modes of four matrices were similar to each other and rather ductile fracture mode appeared because of the existence of the interlayer. The work of adhesion was not proportional directly to IFSS. The matrix toughness and energy absorption mechanism might contribute to IFSS more likely than surface wettability in this carbon fiber and epoxy-PEI matrix system.

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REFERENCES

1. A. Okamoto, *Polym. Eng. Sci.* 23, 1983, p. 222.
2. D. J. Hourston, J. M. Lane and H. X. Zhang, *Polym. Int.* 42, 1997, p. 349.
3. C. B. Bucknall, and I. K. Partridge, *Polymer* 24, 1983, p. 639.
4. M. C. Chen, D. J. Hourston and W. B. Sun, *Eur. Polym. J.* 28, 1992, p. 1471.
5. D. J.-P. Turmel and I. K. Partridge, *Compos. Sci. Technol.* 57, 1997, p. 1001.
6. J. M. Park, Y. M. Kim, K. W. Kim, and D. J. Yoon, *J. Colloid Interface Sci.* 231, 2000, p. 114.
7. ASTM E 399 'Special requirement for the testing of bend specimens' 1998. p. 693.
8. J. M. Park, and J. H. Kim, *J. Colloid Interface Sci.* 168, 1994, p. 103.
9. J. M. Park, and D. S. Kim, *Polym. Comp.* 21, 2000, p. 789.