Interfacial Properties and Residual Stress of Carbon Fiber/Epoxy-AT PEI Composite with Matrix Fracture Toughness using Microdroplet Test and Electrical Resistance Measurements

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Microdroplet 시험법과 전기저항 측정을 이용한 탄소섬유 강화 Epoxy-AT PEI 복합재료의 수지파괴인성에 따른 잔류응력 및 계면물성

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KEY WORDS: fracture toughness, microdroplet test, interfacial shear strength (IFSS), thermal expansion coefficient (TEC), electrical resistivity, cyclic stress and strain test

ABSTRACT

Interfacial and electrical properties for the carbon fiber reinforced epoxy-amine terminated (AT) PEI composites were performed using microdroplet test and electrical resistance measurements. As AT PEI content increased, the fracture toughness of epoxy-AT PEI matrix increased, and IFSS was improved due to the improved toughness and energy absorption mechanisms of AT PEI. The microdroplet in the carbon fiber/neat epoxy composite showed brittle microfailure mode. At 15 wt% AT PEI content, ductile microfailure mode appeared because of improved fracture toughness. After curing, the changes of electrical resistance (ΔR) with increasing AT PEI content increased gradually because of thermal shrinkage. The matrix fracture toughness was correlated to IFSS, TEC and electrical resistance. In cyclic strain test, the maximum stress and their slope of the neat epoxy case were higher than those of 15 wt% AT PEI. The results obtained from electrical resistance measurements under curing process and reversible stress and strain were consistent well with matrix toughness properties.

Nomenclature

τ	: Interfacial shear strength (IFSS)
K_{IC}	: Fracture toughness
ΔR	: Change of electrical resistance
$\Delta\rho$	: Change of electrical resistivity
L_{ec}	: Electrical Contact length
TEC	: Thermal expansion coefficient

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1. INTRODUCTION

Toughened epoxy matrix using liquid reactive rubber has been reported widely [1,2]. However, the improved toughness 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. They increased the fracture toughness without reducing thermal and mechanical properties [3-5].

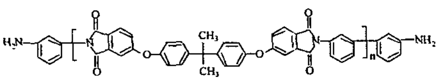
The electro-micromechanical technique had been studied as an economical and new nondestructive evaluation (NDE) method for curing monitoring, stress or strain sensing, characterization of interfacial properties, and nondestructive behavior because conductive fiber can act as a sensor in itself as well as a reinforcing fiber [6,7]. Residual stress in fiber-reinforced composite occurred during curing process due to the thermal contraction of the matrix or the difference in thermal expansion coefficient (TEC) between fiber and matrix. The effect of residual stress is reflected in the mechanical performance of cured composite [8].

In this work, interfacial properties, microfailure modes and cure monitoring of carbon fiber reinforced amine terminated (AT) PEI toughened epoxy matrix composite were investigated using micromechanical test and electrical resistance measurement. The changes of electrical resistance under cyclic stress/strain and during curing process were correlated with matrix toughness.

2. EXPERIMENTAL

2. 1. Materials

Two kinds of carbon fibers as reinforcing materials were used, and their average diameters were about 18 μm (Mitsubishi, Chemical Co., Japan) and 8 μm (Taekwang Co., TZ-307, Korea), respectively. 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) was used as a curing agent. Synthesized AT PEI using a commercial grade of PEI (Ultem 1000, General Electric Co.) was used as a thermoplastic modifier. Chemical structure of AT PEI is as follows:



(1)

2. 2. Methodologies

2.2.1. Specimen Preparation: The fracture toughness of the cured epoxy-AT PEI matrix was measured by three point bending test based on ASTM E 399 [9] using universal testing machine (UTM, Lloyd Instrument Co., U.K.). The specimens for fracture toughness test were precured for each 2 hours at 80°C and 120°C in a vacuum oven. After eliminating vacuum, it was postcured finally for 12 hours at 140°C. 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:

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

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.

2.2.2. IFSS Measurement: The carbon fiber with 18 μm diameter was fixed with regularly separated distance in a steel frame. Microdroplets of neat epoxy and epoxy-AT PEI matrix were formed on each fiber axis using carbon fiber of 8 μm in diameter. Microdroplet specimens were cured with above same curing steps.

Figure 1(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,

$$\tau = \frac{F}{\pi D_f L} \qquad (3)$$

where D_f and L are fiber diameter and fiber embedded length in the matrix resin, respectively.

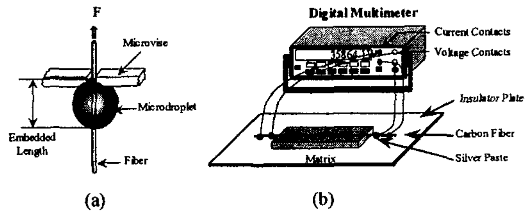


Fig. 1 Schematic diagram for (a) microdroplet test and (b) electrical resistance measurements

2.2.3. Measurement of Electrical Resistance: Figure 1 (b) shows scheme for electrical resistance measurements of carbon fiber/epoxy-AT PEI composite. While curing process was in progress and cyclic load was applied, the electrical resistance was measured using a HP34401A digital multimeter. For the electrical resistance measurements under cyclic load, strain-stress curves were measured by mini-UTM (Hounsfield Test Equipment Ltd., U.K.). Testing speed and load cell were 0.5 mm/minute and 100 N, respectively. The calculation method of electrical resistivity, ρ is as follows:

$$\rho = \left(\frac{A}{L_{ec}}\right) \times R \qquad (4)$$

where R is the electrical resistance, A is the cross-section area of conductive fiber, and L_{ec} is the electrical contact length between voltage contacts.

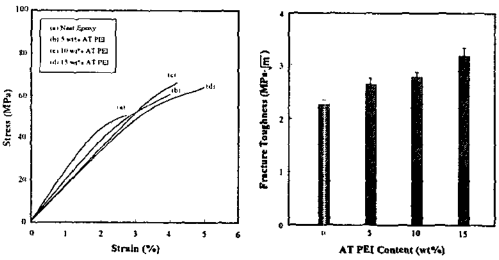
3. RESULTS AND DISCUSSION

3.1. Mechanical Properties of Fiber and Matrix:

Figure 2 shows SEM photographs for epoxy-AT PEI matrix with AT PEI content for (a) 5 wt% AT PEI, (b) 10 wt% AT PEI and (b) 15 wt% AT PEI. Epoxy-AT PEI matrix appeared many AT PEI phases in the epoxy matrix, and AT PEI particles were microspherical shape. It could be due to the difference in surface energy or hydrophilicity between epoxy and PEI matrices. AT PEI microspheres were spread uniformly in epoxy resin, and both relative contents and size of AT PEI microsphere increased with increasing initial blending PEI content. Several parameters, i.e. the content, size and shape of AT PEI particle might affect on mechanical properties of epoxy-AT PEI matrix, such as toughness, tensile strength and modulus.

(a) (b) (c)

Fig. 2 SEM photographs for epoxy-AT PEI matrix with AT PEI content.



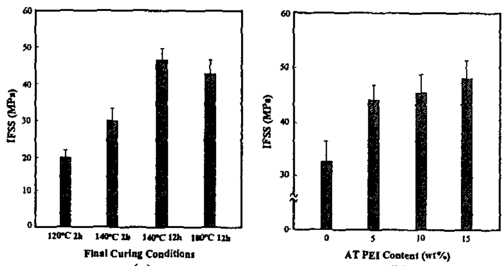
(a) (b)

Fig. 3 (a) Stress-stain curves and (b) fracture toughness of epoxy-AT PEI matrix with AT PEI content.

Mechanical properties of AT PEI modified epoxy matrix were compared to matrix toughness. Figure 3(a) shows the mechanical properties of epoxy-AT PEI matrix and their stress-strain curves. Tensile strength and elongation were improved with increasing AT PEI content by the general rule of mixture, whereas Young's modulus decreased. Figure 3(b) shows the matrix fracture toughness of epoxy-AT PEI matrix. The fracture toughness was improved gradually with increasing AT PEI content. These results were consistent with stress-strain curves in Figure 3(a). Microcracks could be propagated easily through brittle matrix, whereas ductile matrix could blunt crack propagation. At 15 wt% AT PEI, the fractured surface appeared tougher than the case of 5 wt% AT PEI content showing more likely smooth surface. The morphological change of fracture surface indicated improving fracture toughness by adding AT PEI content.

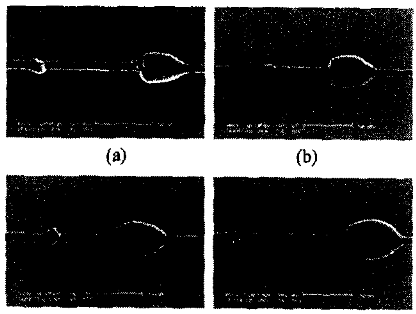
3.2. IFSS and Microfailure Modes: Figure 4 (a) shows IFSS of carbon fiber reinforced epoxy-AT PEI composite with postcuring conditions. IFSS between carbon fiber and epoxy-AT PEI matrix cured at too low or high temperature might be low because of the low cross-linking density and thermal damage. Optimum postcuring condition obtained from results of IFSS measurement was for 12 hours at 140°C.

Figure 4 (b) shows IFSS of carbon fiber reinforced epoxy-AT PEI composite with AT PEI content. IFSS increased with adding AT PEI content due to the enhanced fracture toughness and energy absorption mechanisms.



(a) (b)

Fig. 4 IFSS of carbon fiber/epoxy-AT PEI composites with (a) curing conditions and (b) AT PEI content.



(a) (b)

(c) (d)

Fig. 5 Typical microfailure modes of carbon fiber/epoxy-AT PEI composite with AT PEI content.

Figures 5 shows SEM photographs of typical microfailure modes for the carbon fiber reinforced epoxy-AT PEI composite with PEI content after the microdroplet test for (a) neat epoxy, (b) 5 wt% AT PEI, (c) 10 wt% AT PEI and (d) 20 wt% AT PEI. Neat epoxy microdroplet appeared brittle microfailure mode, whereas high content of AT 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 AT PEI content.

3.3. Results of Electrical Resistance Measurements: Figure 6 shows the changes of electrical resistance for carbon fiber/epoxy-AT PEI composite with AT PEI content during curing and after curing. As AT PEI content increased, electrical resistance after curing increased gradually. However, the change of electrical resistance for neat epoxy during holding at 120°C was the highest. The changes of electrical resistance after curing may be affected by matrix thermal shrinkage or residual stress determined by matrix toughness or flexibility, whereas the change of electrical resistance during curing may be affected by cure shrinkage. External stress induced by cure and thermal shrinkage applied to carbon fiber through matrix. The higher modulus is, the higher cure shrinkage, and the higher fracture toughness is, the higher thermal shrinkage or expansion. Therefore, electrical resistance after curing increased by combination of above two factors. The change of electrical resistance of neat epoxy during curing was the highest, whereas that after curing was the lowest. It might be because neat epoxy had the highest modulus and the lowest matrix fracture toughness among four matrix series.

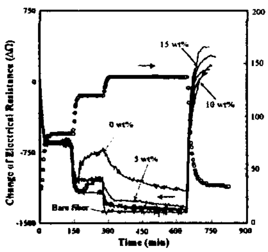


Figure 6 The changes of electrical resistance for carbon fiber/epoxy -AT PEI composite

Table 1 Mechanical, thermal and electrical properties of carbon fiber/epoxy-AT PEI composite and matrix

AT PEI Content (wt%)	Modulus (GPa)	K_{IC} (MPa·$\sqrt{m}$)	IFSS (MPa)	TEC (°C^{-1})	$\Delta R^{2)}$ (Ω)
0	2.0 (0.4)$^{1)}$	2.2 (0.1)	32.7 (7.5)	81.4	140
5	1.8 (0.2)	2.6 (0.2)	44.2 (4.5)	57.1	164
10	1.7 (0.1)	2.8 (0.1)	46.8 (6.5)	69.1	247
15	1.6 (0.2)	3.1 (0.3)	48.6 (6.6)	76.6	278

1) Standard deviation (SD)
2) After curing

Table 1 shows mechanical, interfacial, thermal, and electrical properties of carbon fiber/epoxy-AT PEI composite and epoxy-AT PEI matrix. As AT PEI content increased, modulus decreased only, whereas fracture toughness, IFSS, TEC, and electrical resistance increased gradually. These results might be consistent well with each other.

In same strain, the stress of carbon fiber/epoxy-AT PEI specimens for measuring electrical resistivity appeared differently with their mechanical properties of matrix. Figure 7 shows the changes of electrical resistivity and stress for carbon fiber reinforced (a) neat epoxy and (b) 15 wt% AT PEI specimens under 5 cyclic strains. In same strain (0.5%), maximum stress and their slope of changing electrical resistivity for neat epoxy were higher than those of 15 wt% AT PEI. This tendency could be related to their matrix modulus. Mobility of carbon fiber in neat epoxy matrix might be small due to high matrix modulus, whereas in case of 15 wt% AT PEI, mobility in the interface might be high due to high matrix toughness and low modulus. Neat epoxy with high modulus needs higher stress to reach the same strain. The change of stress and stain is correspondence with the behavior of electrical resistivity.

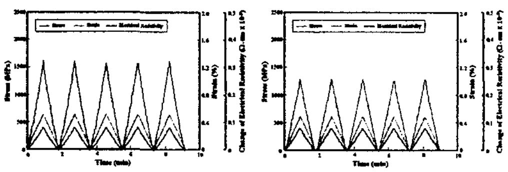


Figure 7 The change of stress and electrical resistivity for single carbon fiber/epoxy-AT PEI composite

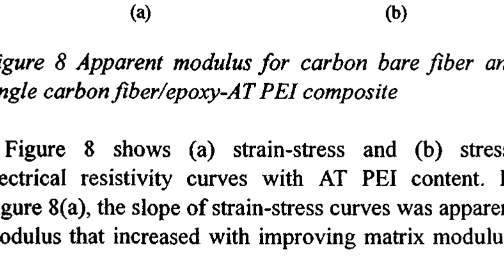
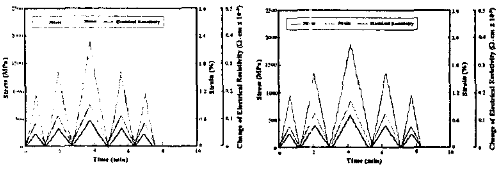


Figure 8 Apparent modulus for carbon bare fiber and single carbon fiber/epoxy-AT PEI composite

Figure 8 shows (a) strain-stress and (b) stress-electrical resistivity curves with AT PEI content. In Figure 8(a), the slope of strain-stress curves was apparent modulus that increased with improving matrix modulus. The apparent modulus means the fiber modulus embedded in the matrix in stress-strain curve comparing to a bare fiber modulus in itself [10]. The tendency of apparent modulus was consistent well with the change of electrical resistivity.

Figure 9 shows the changes of strain and electrical resistivity for (a) neat epoxy and (b) 15 wt% AT PEI under changeable stress. The strain and electrical resistivity of neat epoxy were higher than those of 15 wt% AT PEI, and the reaching time until the same stress was faster in neat epoxy case. It might be due to higher apparent modulus of composite.



(a) (b)

Figure 9 The changes of strain and electrical resistivity under changeable stress

4. CONCLUSIONS

Interfacial and electrical properties for the carbon fiber reinforced epoxy-AT PEI composites were performed using microdroplet test and electrical resistance measurement. With adding AT PEI content, the fracture toughness of epoxy-AT PEI matrix increased, and IFSS was improved due to the improved toughness. The microdroplet in the carbon fiber and neat epoxy system showed rather brittle microfailure pattern. For higher AT PEI content, ductile microfailure mode appeared. The changes of electrical resistance after curing and TEC increased gradually with increasing AT PEI content. The matrix fracture toughness was directly proportional to IFSS, TEC and electrical resistance. In cyclic strain test, the maximum stress of neat epoxy case was higher than that of 15 wt% AT PEI. It might be because of increasing matrix apparent modulus. The results obtained from measuring electrical resistance during curing process, and measurement of electrical resistivity under cyclic stress and strain were correspondence well with matrix mechanical properties such as modulus and toughness.

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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) J. M. Park, D. S. Kim, J. W. Kong, M. Y. Kim, W. H. Kim, and I. S. Park *J. Colloid Interface Sci. 2002, (In Press)*
(6) X. Wang and D. D. D. Chung, *Cem. Conc. Res.* 26, 1996, p. 1007.
(7) J. M. Park, S. I. Lee, K. W. Kim and D. J. Yoon, *J. Colloid Interface Sci.* 237(2), 2001, p. 80
(8) S. Lee and G. S. Springer, *J. Compos. Mater.* 22, 1998, p. 15.
(9) ASTM E 399 'Special requirement for the testing of bend specimens' 1998. p. 693.
(10) S. Wang, S. I. Lee, D. D. L. Chung and J. M. Park, *Compos. Interface*, 8(6), 2001, p. 453.