탄화규소의 첨가가 탄소섬유 강화 복합재료의 열안정성 및 기계적 계면특성에 미치는 영향

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Influence of SiC on Thermal Stabilities and Mechanical Interfacial Properties of Carbon Fibers-reinforced Composites

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Key Words : carbon fibers-reinforced composites, SiC, surface properties, mechanical interfacial preperties

ABSTRACT

In this work, the effect of chemical treatments on surface properties of SiC was investigated in mechanical interfacial properties of carbon fibers-reinforced composites. The surface properties of the SiC were determined by acid/base values and contact angles. The thermal stabilities of carbon fibers-reinforced composites were investigated by thermogravimetric analysis (TGA). Also, the mechanical interfacial properties of the composites were studied in interlaminar shear strength (ILSS) and critical strain energy release rate mode II (G_{IIC}) measurements. As a result, the acidically treated SiC (A-SiC) had higher acid value than that of untreated SiC (V-SiC) or basically treated SiC (B-SiC). According to the contact angle measurements, it was observed that chemical treatments led to an increase of surface free energy of the SiC surfaces, mainly due to the increase of the specific (polar) component. The mechanical interfacial properties of the composites, including ILSS and G_{IIC}, had been improved in the specimens treated by chemical solutions. These results were explained that good wetting played an important role in improving the degree of adhesion at interfaces between SiC and epoxy resin matrix.

1. INTRODUCTION

Carbon fibers composites are fitted to applications where strength, stiffness, lightweight, and creep resistance properties are critical requirements. Two major areas of carbon fiber applications are high technology part, which includes aerospace and nuclear engineering, and the general engineering and transportation part, which includes engineering components such as bearing, gear, cams, and automobile bodies[1-3].

The reinforcement of polymer matrix by particulate fillers has been studied in depth in numerous investigations, and it is generally accepted that this phenomenon is, to a large extent, dependent on the physical interactions between the filler and matrix, which can determine the degree of adhesion at interfaces. Generally, it is dependent on the active functional groups, surface energy, and energetically different crystallite faces of the filler surfaces[4-8].

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SiC powders are effective filler materials to introduce high thermal and mechanical properties in a composite system, due to their superior heat and abrasion resistance. Surface treatment, such as acid or base treatment of SiC is one of useful methods to donate active sites (active functional groups) on the surfaces of bulk materials, which is attributed to the increase of the adhesion at interfaces by so-called acid-base interaction with matrix[9-10].

In this work, carbon fibers-reinforced epoxy matrix composites are prepared, and chemically treated SiC are used as filler materials to enhance heat resistance and mechanical interfacial properties. The main purpose of this work is the understanding the influence of chemical treatments of SiC on the changes of physicochemical properties and mechanical interfacial properties in composite system.

2. EXPERIMENTAL

2.1 Materials and Sample Preparation

The reinforcement materials were continuous polyacrylonitrile (PAN)-based carbon fibers (12 K, TZ-307) manufactured by Taekwang of Korea. Epoxy resin, YD-128 supplied from Kukdo Chem. Co. of Korea, was used as the polymeric matrix. For enhancing thermal properties of composites, SiC was used as filler materials, which size was smaller than 7 ㎛. The samples, donated V-SiC, A-SiC, and B-SiC, were prepared from 0.1 N H_3PO_3, 0.1 N KOH, and C_6H_6 for modification of the SiC surfaces. Prior to use of the surface following analysis, residual chemicals were removed by Soxhlet extraction (boiling with acetone at 80℃ for 24h). Finally, the SiC were washed several times with distilled water and dried in a vacuum oven at 90℃ for 12h.

The composite preparations were done by filament winding, where the carbon fiber roving, before being wound up on the mandrel, was continuously soaked in the epoxy matrix bath, and SiC powder were well-dispersed in epoxy matrix. Specimens were prepared from laminates composed of 22 plies and fabricated in a hot-press at 150℃ and 7.4 MPa for 150 min with a vacuum bagging method.

2.2. Surface properties

The surface property changes of the carbon fibers before and after anodic oxidations were characterized by the following techniques;

The potential chemical activity of surface functional groups on anodized fibers can be determined by measuring the pH according to the ASTM E-70 and by measuring acid-base values using the Boehm's method on the basis of adsorption of 0.1 N NaOH and HCl standard solutions.

The FT-IR instrument used was a Hartman & Brawn Model Bomen MB 102 Spectrophotometer. The scan range was 400 to 4000 cm^{-1}.

Contact angles were measured using the sessile drop method on a Rame-Hart goniometer. About 5 ㎕ of Wetting liquid was used for each measurement at 20℃. The test liquids used were deionized water, diiodomethane, and ethylene glycol. For this work the surface free energies and their components for the wetting liquids are listed in Table 1.

Table 1 Surface Free Energy Characteristic of the Testing Liquids, Measured at 20℃

[unit: mJ/m^2]

	γ_L^L	γ_L^{SP}	γ_L
Water	21.8	51.0	72.8
Diiodomethane	50.4	0.38	50.8
Ethylene glycol	31.0	16.7	47.7

2.4. Thermal Stabilities and Mechanical properties

To investigate the thermal stability of the composites, themogravinetric analysis were performed in nitrogen using a TGA 951 Du Pont thermal analysis at a heating rate of 10°C/min from room temperature to 850°C

Mechanical interfacial properties of the composites were investigated using two types of testing method, namely interlaminar shear strength tests (ILSS) and critical energy release rate mode II (G_{IIC}). ILSS of the composites was determined by Instron model loyd LR-5K mechanical tester according to the ASTM D-2344. A span-to-depth ratio of 4:1 and cross-head speed of 2.0 $mm.min^{-1}$ were used. G_{IIC} in end-notch flexure (ENF) tests was conducted by cross-head speed of $1mm.min^{-1}$ according to the ASTM D-5528 (span-to-depth ratio = 4:1).

3. RESULTS AND DISCUSSION

3.1 Surface properties

Figure. 1 shows FT-IR spectra obtained by the KBr

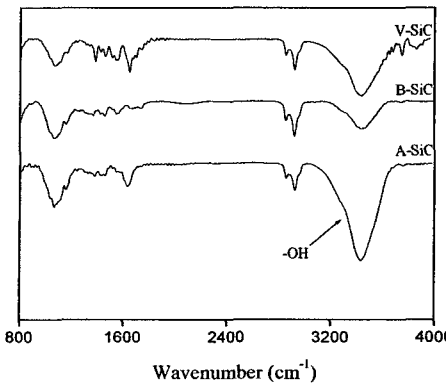

Fig. 1 IR spectra of V-SiC, B-SiC, and A-SiC..

Table 2 pH and Acid-base Values of Chemical treated SiC Powder

[unit: meq/g]

	pH	Acid values	Base values
V-SiC	8.01	15.3	20.2
A-SiC	5.04	62.1	19.2
B-SiC	8.05	14.2	22.1

pellet technique of the chemically treated SiC. It is well known that the position of the band for free hydroxyl groups is normally observed around 3500 cm^{-1}. In Figure. 1, it is found that OH band of A-SiC is dramatically increased after acidic treatment compared with V-SiC. However, that of B-SiC is even decreased. This result indicates acidic treatment on SiC is more effective in producing oxygen containing surface function groups on the surfaces of SiC than basic treatment.

Surface acidity of the SiC treated by chemicals was confirmed by Bohem's titration method and listed in Table 1. It is shown that B-SiC shows slight basic value, but A-SiC does strong acidic value. This result is corresponded with that of Figure.1, so it means that acidic treatment severely treated the surface of SiC and changed the surface structures. It is well known that epoxy matrix shows slight basic value. It is then expected that highly acidically treated SiC can have higher adhesion strength with basic epoxy matrix than that of basically treated B-SiC or V-SiC.

Figure. 2 shows the surface free energies following each treatment. It is found that the polar component (γ_L^{SP}) of A-SiC is strongly increased after acidic treatment, whereas that B-SiC is slightly decreased. However, dispersive components are not changed in cases of B-SiC and A-SiC. This result means that the chemical treatments only affects on the surface polar component, resulting in the increase of surface free energy of treated SiC.

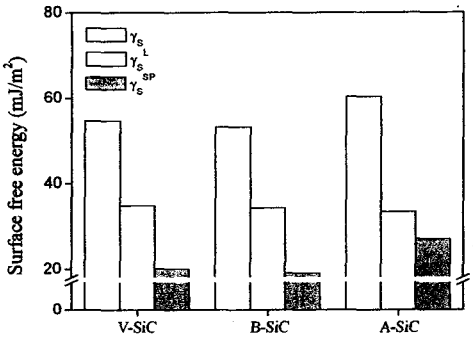

Fig. 2 Variation of the surface free energy of V-SiC, B-SiC, and A-SiC.

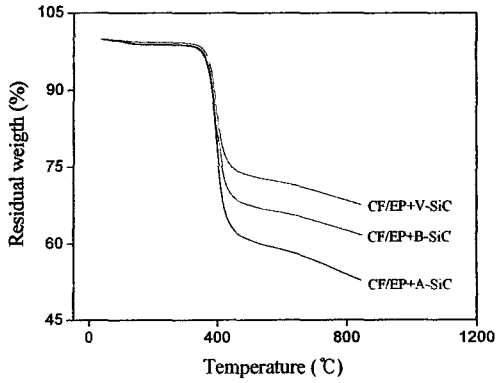

Fig. 3 TGA curves of the composites made with V-SiC, B-SiC, and A-SiC.

3.1 Thermal Stabilities and Mechanical properties

Figure. 3 is TGA results with each treatment. It is found that all samples treated show higher residual weight than that of V-SiC. This result indicates that the chemical treatment of fillers can increase the heat resistance of the composites. It is also found that A-SiC shows higher residual weight than that of B-SiC. This means that acidic functional groups on filler materials are more effective in enhancing heat resistance of the composites than basic groups. This result is probably due to the A-SiC has superior adhesion strength with basic epoxy resin by acid-base interaction.

It is generally accepted that the mechanical interfacial properties of carbon fibers-reinforced composites depend strongly on the level of adhesion between the fiber and the matrix. The degree of adhesion at the interface between a fiber and a matrix can be measured by the interlaminar shear strengths (ILSS) for the mechanical interfacial behaviors. For a rectangular crosssection of the composites, the ILSS from three-point bending tests is calculated as follow:

$$ILSS = \frac{3F}{4bd} \qquad (1)$$

where F is the rupture force, b the width of the specimen, and d the thickness of the specimen.

Expressions for the calculation of mode-II critical strain energy-release rate (G_{IIC}) are calculated by the following Eq. (2) [7]

$$G_{IIC} = \frac{9a^2 p\Delta a}{2w(2L^3 + 3a^3)} \qquad (2)$$

where, P is the load, a crack, L half-span length, and W

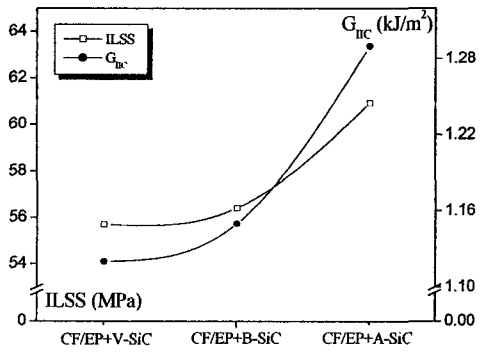

Fig. 4 ILSS and G_{IIC} of the composites made with V-SiC, B-SiC, and A-SiC

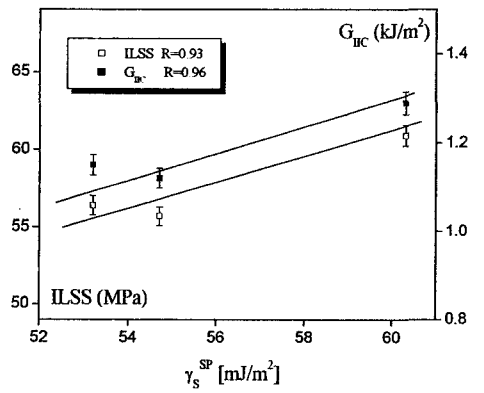

Fig. 5 Dependence of ILSS and G_{IIC} on the specific component of surface free energy

width

Two kinds of mechanical interfacial property testing methods (ILSS and G_{IIC}) are used in this work and listed in Figure. 4. It is found that all treated samples show higher mechanical interfacial properties than that of CFRP+V-SiC sample, and CFRP+A-SiC shows higher value than that of CFRP+B-SiC sample. This result indicates that the adhesion strength between fillers and matrix is strongly ruled by acid-base interaction.

Figure. 5 is the dependency of ILSS and G_{IIC} results on the polar component of SiC. It is found that the mechanical interfacial properties are highly depended on the polar component of filler materials. This result is corresponded with Figure. 1 and Table 2.

4. CONCLUSION

In this wokr, the effect of chemical treatments of SiC on thermal stabilities and mechanical interfacial properties of carbon fibers-reinforced composites was investigated. As a result, the acidically treated SiC had higher acid value than that of untreated SiC or basically treated SiC. According to the contact angle measurements, it was observed that acidically treatments led to an increase of surface free energy of the SiC surfaces, mainly due to the increase of the specific component. The mechanical interfacial properties of the composites, including ILSS and G_{IIC} had been improved in the specimens treated by acidic solution. These results were explained that good wetting played an important role in improving the degree of adhesion at interfaces between SiC and epoxy resin matrix.

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