양극산화 처리된 탄소섬유 강화 복합재료의 기계적 계면물성

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Mechanical Interfacial Properties of Anodically Oxidized Carbon Fibers-reinforced Composites

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Key Words : carbon fibers-reinforced composites, anodic oxidation, surface properties, crack resistance

ABSTRACT

In this work, the effect of anodic oxidation on surface characteristics of high strength PAN-based carbon fibers is investigated in terms of surface and mechanical interfacial properties of the composites. As a result, the acidity of carbon fiber surfaces is increased, due to the development of oxygen functional groups in the presence of anodic oxidation. Also, it is found that the critical stress intensity factor (K_{IC}) is improved in the oxidized fibers-reinforced composites, which can be attributed to the good wettability between fibers and epoxy resin matrix.

1. INTRODUCTION

Carbon fiber composites are suited to applications where strength, stiffness, light weight, and creep resistance properties are critical requirements. Two major areas of carbon fiber applications, in general engineering and transportation, which include engineering components, such as bearing, gears, cams, and automobile bodies[1,2]. Carbon fibers, when used without surface treatment, produce composites with low interlaminar shear strength (ILSS). This has been attributed to weak adhesion and poor bonding between fibers and matrix. Thus, all the carbon fibers are given a surface treatment. These treatments increase the surface active sites and then improve bonding between the fibers and the resin matrix. This tends to increase the wettability of carbon fiber and to enhance the ILSS of the composites. Surface treatments can be classified into oxidative and nonoxidative methods. Oxidation treatment involve gaseous oxidation, liquid-phase oxidation carried out chemically or electrochemically, and catalytic oxidation[1,3,4].

In this work, we discuss the surface characteristics of carbon fibers, by anodic oxidation, and their effect on mechanical interfacial properties of the resulting composites are also discussed.

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2. EXPERIMENTAL

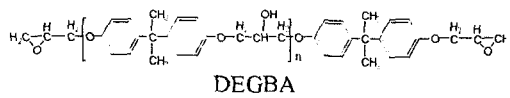
2.1 Materials and Sample Preparation

The fibers used in this work were polyacrylonitrile (PAN)-based carbon fibers (12K, TZ-307) manufactured by Taekwang of Korea. The anodic oxidation of carbon fibers was carried out with a constant rate (1 $m.min^{-1}$) in a laboratory pilot system. The current density was varied with 0, 0.2, 0.4, 0.8, and 1.6 Am^{-2}. The length of immersed fiber was 0.23 m, and the electrolyte used was 10 wt% phosphoric acid solution. The anodized carbon fibers were rinsed in a Soxhlet extractor with acetone for 2 h to remove surface impurities or residual oxides, and then dried.

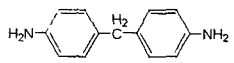
The epoxy resin used as a matrix was diglycidylether

of bisphenol-A (DGEBA, YD-128 supplied from Kukdo Chem. Co. of Korea). Epoxide equivalent weight was 185-190 $g.eq^{-1}$ and the viscosity was 11500-13500 cps at 25℃. Diaminodiphenylmethane (DDM, purchased from Aldrich Co.) was selected as a hardener and methylethylketone (MEK) was used to reduce the high viscosity of DGEBA. The chemical structures of DEGBA and DDM were shown in Figure 1.

Unidirectional carbon fibers-epoxy matrix composites were prepared by continuous impregnation of the fibers using a drum winding technique for manufacturing prepregs with subsequent hot-pressing. Specimens were prepared from laminates composed of 22 plies and fabricated in a hot-press at 150 C and 7.4 MPa for 150 min with a vacuum bagging method. The fiber volume fraction of bulk specimens was about 50% (±2%), and the specimens were cut into test specimens to carry out



DEGBA



DDM

Figure 1. Chemical structures of DEGBA and DDM.

mechanical testings.

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(5).

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

The X-ray photoelectron spectroscopy (XPS) experiment was performed using a VG Scientific ESCA LAB MK-II spectrometer equipped with a Mg-K α X-ray source. The base pressure in the sample chamber was controlled in the range of 10^{-8} to 10^{-9} torr. Also, the morphology of the fiber surfaces was analyzed by scanning electron microscope (SEM, Model JEOL JSM-840A).

2.3. Mechanical properties

Critical stress intensity factor (K_{IC}) of the composites was determined by Instron model loyd LR-5K mechanical tester according to the ASTM E-399. A span-to-depth ratio of 4:1 and cross-head speed of 0.12 $m.h^{-1}$ were used.

3. RESULTS AND DISCUSSION

3.1 Surface properties

Table 1 shows the experimental surface properties of the carbon fibers treated by anodic oxidation in aqueous phosphoric acid solution. The results of pH show that the surface properties of untreated carbon fibers are a slight excess of basic properties. This is probably due to the existence of basic groups on the fiber surfaces through high manufacturing temperature. Both the pH and the acid values of anodized carbon fibers acidify to that of the untreated fibers, and indicate that the current density of 0.4 $A.m^{-2}$ provides an optimum condition to the surface acidity of the fibers.

Figure 2 shows the FT-IR results of anodic oxidation carbon fiber specimens. As a result, the oxygen functional groups (C=O, COOH, and C-O) at 1600-1800 cm^{-1} and hydroxyl group (O-H) at 3450 cm^{-1} are increased in the anodic oxidation carbon fibers. Moreover, hydrocarbon group (CH) at 2980 cm^{-1} is degreased with increasing the current density. This result affects the surface characteristics of the fibers, resulting in improving the interfacial adhesion between the fibers and the matrix resins, due to the increase of oxygen functional groups on carbon fiber surfaces.

Meanwhile, it is well known that XPS has been used as a powerful analytical technique to evaluate the surface compositions of the carbon fibers. The surface

Table 1 pH and Acid Values of Anodized Carbon Fibers

Current Density ($A.m^{-2}$)	pH	Acid value ($mequiv.g^{-1}$)
0	7.02	15.0
0.2	6.98	35.0
0.4	6.97	65.1
0.8	6.98	32.5
1.6	6.98	36.7

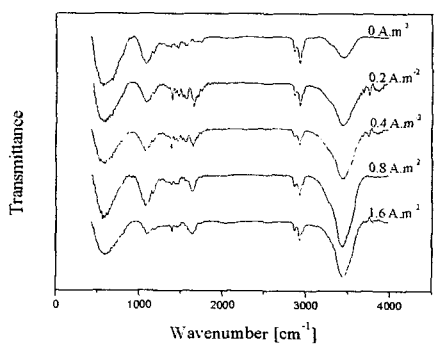


Figure 2. IR spectra of anodized carbon fibers as a function of current density.

Table 2. Chemical compositions of the anodized carbon fiber surface, measured from XPS analysis

Current density [A·m^{-2}]	C_{1S} AT[%]	N_{1S} AT[%]	O_{1S} AT[%]	O_{1S}/C_{1S}
0	74.3	1.4	24.3	0.327
0.2	73.5	1.4	25.1	0.342
0.4	68.8	0.7	30.6	0.445
0.8	72.1	1.4	26.5	0.368
1.6	69.7	1.5	28.9	0.414

compositions of the fibers for current density are summarized in Table 2. As seen in the results, the amounts of surface oxygen are increased with increasing the current density of the treatments up to 0.4 A.m^{-2}, whereas nitrogen is not largely influenced on the current density. This result suggests that the oxidation of carbon fiber surfaces occurs very rapidly in phosphoric electrolyte with low current density. This results in increasing the surface acidity or hydroxyl and carboxyl functional groups on the anodized fibers. From the results of Tables 1 and 2, the anodic oxidation in phosphoric acid electrolyte solutions plays an important role in increasing the acidic properties of the carbon fibers. Moreover, the increasing in acidic groups on the surfaces can be expected to promote the surface energy of the fibers, as well as the interfacial bonding by establishing secondary or van der Waals' forces at the interfaces between fiber and matrix.

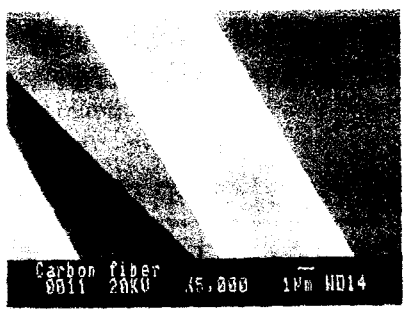
Figure 3 shows the SEM photographs of the carbon fibers with and without anodic oxidations. The axial striations from the manufacturing process are observed in the untreated fiber image. Whereas, it can be seen that the anodic surface treatment does lead to a significant change in surface morphology at the microscopic scale. Also, the photographs of Figure 3 illustrate how the smoothening of the surface occurs in the case of fibers etched in phosphoric acid with low current densities. It appears that the axial striations constitute preferential sites of attack, and largely dominate for increasing the current density.

3.1 Crack Resistance Properties

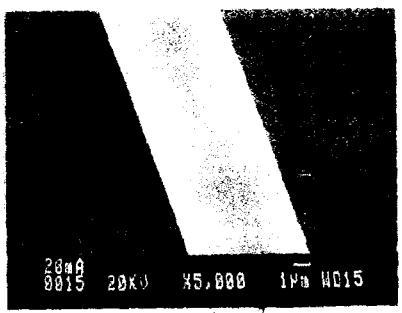
The critical stress intensity factor (K_C), which is one of the fracture toughness parameters, describes the state in the vicinity of the tip of a crack as a function of specimen geometry, the crack geometry and the applied load on the basis of linear elastic fracture mechanics (LEFM)[6]. For the SEN bending specimens, the value of K_{IC} is calculated using the Eq. (1).

$$K_{IC} = \frac{P \cdot L}{b \cdot d^{3/2}} \cdot Y \qquad (1)$$

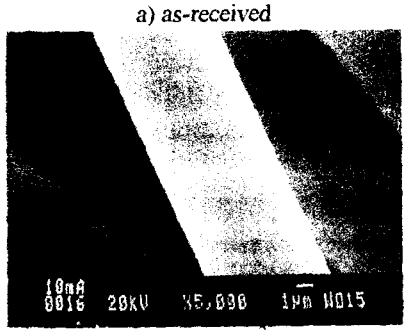
where, P is the load obtained from the load-deformation curve, L the span between the supports, Y the geometric factor described in ASTM E 399, and b and d the specimen width and thickness, respectively.



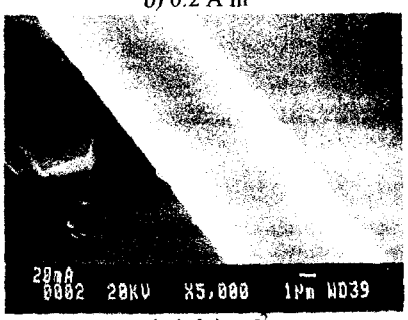
a) as-received



b) 0.2 A·m^{-2}



c) 0.4 A·m^{-2}



d) 1.6 A·m^{-2}

Figure 3 Photographs of SEM of carbon fibers made with and without anodic surface treatments.

Figure 4 shows the results for K_{IC} of the composites as a function of current density. As a result, the effect of fiber surface treatment conditions and the resulting fiber-matrix adhesion on composite mechanical properties produce noteworthy relationships. Thus, the K_{IC} increases for the degree of adhesion at interfaces. The maximum strength values of 274.1 MPa/cm$^{1/2}$ was attained at the anodic oxidation of 0.4 A.m^{-2}. Therefore, we suggest that additional energy to extend the interfacial crack at this condition is attributed to increasing the interfacial adhesion between fibers and matrix.

4. CONCLUSION

In this work acid-base interaction chemistry, an anodic oxidation of carbon fibers in acidic electrolyte solutions with low current density is performed to enhance crack resistance properties between carbon fibers and epoxy resins. According to the acid-base value and XPS measurements, it is clearly shown that the oxygen functional groups on the fibers are largely dominated in mechanical interfacial behavior of the composites, whereas the nitrogen functional groups are not affected in this system. It is also found that an anodic oxidation gives excellent crack resistance properties of the composites. From the correlation between surface acidic functionality and crack resistance properties, the 0.4 A.m^{-2} current density is the optimum condition for the present system.

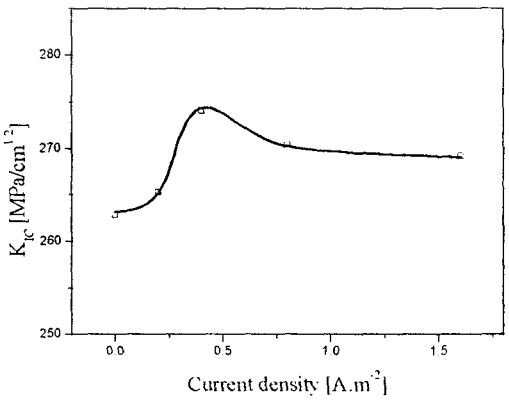


Figure 4. K_{IC} and of the composites.

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