

EFFECT OF CARBON FIBER SURFACE PROPERTIES ON FIBER-MATRIX ADHESION OF THE COMPOSITES

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Abstract : Electrochemical surface treatment of PAN-based carbon fibers in acidic electrolyte has been studied in increasing the surface functional groups on fiber surfaces for the improvement of fiber-matrix adhesion of the resulting composites. According to the FT-IR and XPS measurements, it reveals that the oxygen functional groups on fibers are largely influence on the composite mechanical behaviors, whereas the nitrogen functional groups are not affected in the system. In this work, a good correlation between surface functionality and mechanical properties is established.

1. Introduction

It is well known that the surface or interface properties of carbon fibers play an important role in their real composite materials, since load stress transfers from one matrix to the fiber. Also, it is accepted that the interfacial adhesion between fibers and matrix depends, to a large extent, on the surface area, functionality, and wettability of carbon fiber surfaces [1]. In this respect, surface treatment is effective to increase the number of functional groups on the carbon fiber surfaces and to improve adhesion with matrix materials [2].

In the early 1960s, Fowkes [3] interpreted the work of adhesion according to the acid-base interactions as Lewis acid-base interactions. Recently, Fowkes [4] and Park *et al.* [5] proposed the enthalpy approaches based on the acid-base interactions between two unidentical solid surfaces in a composite system. These data [5] suggested that both PAN-based carbon fibers and amine-based epoxy resin surfaces might have a tendency of basic characteristic due to presence of electron donor molecules or groups. With a point of view, the anodic

oxidation for increasing electron acceptor molecules or groups was performed to modify the carbon fiber surface with acidic electrolyte in this work.

The aim of this work is to study the effect of acidic anodic surface treatment on the fiber surface properties and to investigate the relationship between surface properties and mechanical behaviors following the acid-base interaction between fibers and epoxy resin.

2. Experimental

2.1 Materials and Sample Preparation

The fibers were polyacrylonitrile (PAN)-based carbon fibers (12K, TZ-307) manufactured by Taekwang of Korea. The anodic surface treatment of carbon fibers was carried out with a constant rate ($1 \text{ mm} \cdot \text{min}^{-1}$) in a laboratory pilot system, 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 were dried.

Epoxy resin used in 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 °C. Diaminodiphenylmethane (DDM) was selected as a hardener and methylethylketone (MEK) was used to reduce a high viscosity of DGEBA.

Unidirectional carbon fibers-epoxy composites were prepared by continuous impregnation of the fibers using a drum winding technique. 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% ($\pm 0.2\%$).

2.2 Surface and Mechanical Properties

The potential chemical activity of surface functional groups on anodized fibers may be determined by measuring the pH according to ASTM E-70 and by measuring acid-base values using Boehm's method [6] on the basis of adsorption of 0.1N NaOH and HCl standard solutions.

Also, Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS, or ESCA) were applied to investigate the surface property changes of the carbon fibers treated by anodic oxidation.

Interlaminar shear strength (ILSS) of the composites was determined by Instron 1121 according to ASTM D-2344. A span-to-depth ratio of 4:1 and cross-head speed of 2 mm.min⁻¹ were used.

The critical stress intensity factor (K_{1C}) in three-point bending tests were conducted at cross-head speed of 1 mm.min⁻¹ according to the ASTM E-399 (span-to-depth ratio = 4:1).

3. Results and discussion

3.1 Surface properties

Table 1 shows the experimental surface properties of

the carbon fibers treated by anodic treatment 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. As mentioned above, 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.

Fig. 1 shows the FT-IR spectra of anodized carbon fibers as a function of current density. As seen in Fig. 1, the bands occurred at 3450, 1635, and 1200-1050cm⁻¹ are respectively, attributed to the O-H stretching mode of hydroxyl group, to the C=O of carboxyl/ester groups, and C-O of hydroxyl/ether groups increases with increasing the current densities of the treatments up to 0.2 - 0.4 A.m⁻², then a marginal decrease in surface functionality is observed for the strong current densities used in this work.

Meanwhile, it is well known that XPS is a very useful apparatus in determination of chemical compositions of the carbon fiber surfaces [7]. As shown in Table 2, the amounts of surface oxygen groups increase with increasing the current densities of the treatments up to 0.4 A.m⁻², whereas nitrogen groups are not influenced on the current evolutions. This is resulted in increasing the surface acidity or hydroxyl and carboxyl groups on the fibers anodized in phosphoric acid solution, as mentioned above in FT-IR data.

From the results of Tables 1 and 2, it is expected that increase of surface functionality of the fibers plays an important role in improving the degree of adhesion at interfaces between the anodized fibers and the epoxy resin matrix [8].

3.2 Mechanical properties

It is generally accepted that the mechanical properties of composites depend strongly on the degree

of adhesion at interfaces between fibers and matrix. Meanwhile, for the interfacial mechanical properties of composites, ILSS and critical stress intensity factor (K_{Ic}) were calculated by the following Eqs. (1) and (2).

$$ILSS = \frac{3P}{4bd} \quad (1)$$

$$K_{Ic} = \frac{PL}{bd^{3/2}}Y \quad (2)$$

where, P is the load at moment of break, b and d the specimen width and thickness, respectively, L the span between the supports, Y the geometric factor described in ASTM E-399.

Table 3 shows the results for ILSS and K_{Ic} of the composites as the current density. As a result, the effect of treatment conditions and the resulting fiber-matrix adhesion on composite mechanical properties produce noteworthy relationships. Thus, K_{Ic} value is to increase with increasing the ILSS value for the degree of adhesion at interfaces. The maximum strength values of 64 MPa and 283 MPa $\sqrt{\text{cm}}$ are attained at the anodic treatment of 0.4 A.m². 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.

Figs. 2 and 3 show the relations between surface properties of the fibers and mechanical properties of the composites. It can be seen that both ILSS and K_{Ic} increases with increasing the acid value and O_{1s}/C_{1s} ratio. From a good linearity of the results, it is found that there is strong correlation between surface functionality and

mechanical properties. As above mentioned, this is a consequence of the improving of acidic oxygen functional groups on fibers, resulting in growing fiber-matrix physical adhesion of the composites.

4. Conclusion

The effects of surface treatment on carbon fibers have been studied in terms of the surface properties and mechanical behaviors. According to FT-IR and XPS measurements, it is concluded that the oxygen functional groups on fibers are directly correlated with the resulting composite mechanical behaviors, whereas the nitrogen functional groups are not affected in this system. From the correlation between surface functionality and mechanical properties, the 0.4 A.m² current density is the optimum conditions for this system.

5. References

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Table 1. pH and Acid-Base Values of the Anodized Carbon Fibers

Current density (A.m ⁻²)	pH	Acid value (mequiv.g ⁻¹)	Base value (mequiv.g ⁻¹)
as-received	7.02	15.0	20.1
0.2	6.98	35.0	-
0.4	6.97	65.1	-
0.8	6.98	32.5	-
1.6	6.98	36.7	-

Table 2. Chemical Composition of Anodized Carbon Fibers from XPS Analysis

Current density (A.m ⁻²)	C _{1s}	O _{1s}	N _{1s}	O _{1s} /C _{1s}
as-received	74.3	24.3	1.4	0.327
0.2	73.5	25.1	1.4	0.342
0.4	68.8	30.6	0.7	0.445
0.8	72.1	26.5	1.4	0.368
1.6	69.7	28.9	1.5	0.414

Table 3. Interlaminar Shear Stress (ILSS) and Critical Stress Intensity Factor (K_{1C}) Data of the Composites as Current Density

Current density (A.m ⁻²)	ILSS (MPa)	K _{1C} (MPa√cm)
as-received	56.3 ± 1.5	261 ± 1.3
0.2	58.2 ± 0.7	269 ± 1.7
0.4	64.1 ± 1.2	283 ± 1.3
0.8	59.9 ± 1.4	267 ± 2.0
1.6	60.1 ± 0.9	274 ± 1.0

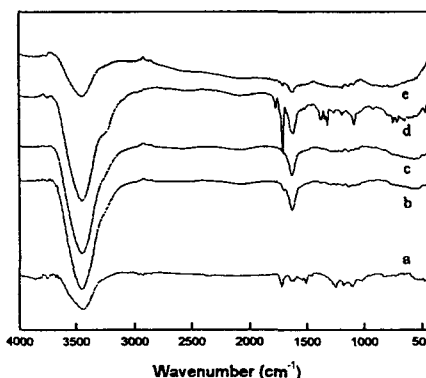


Fig. 1 FT-IR spectra of carbon fibers studied. (a: as-received, b: 0.2, c: 0.4, d: 0.8, e: 1.6 A.m⁻²)

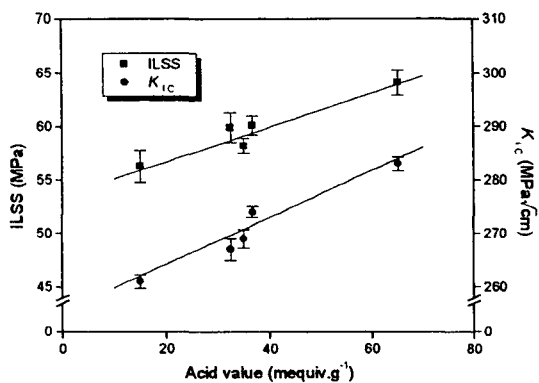


Fig. 2 Dependence of the ILSS and the K_{1C} as a function of the acid value of the fibers.

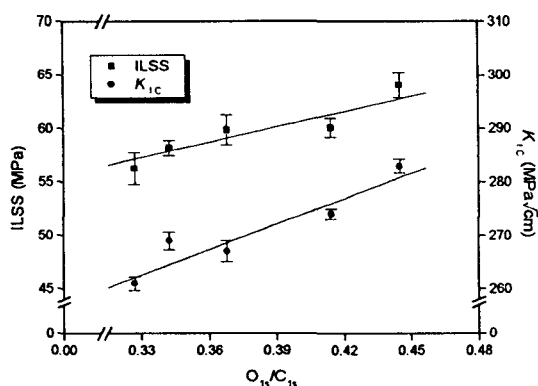


Fig. 3 Dependence of the ILSS and the K_{1C} as a function of the O_{1s}/C_{1s} ratio of the fibers.