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Effect of acidic anode treatment on carbon fibers for increasing fiber-matrix adhesion and its relationship to interlaminar shear strength of composites

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An anodic surface treatment of PAN-based carbon fibers has been studied in increasing the surface functional groups on fibers, resulting in increasing composite mechanical behavior. With a viewpoint of acid-base interaction chemistry, the 10 wt% phosphoric acid solution is selected for the electrolyte. As an experimental result, very low electric current densities, such as 30–300 μA·m^{-2}, are need for the changing of morphological and mechanical properties. According to FT-IR and XPS measurements, it reveals that the oxygen functional groups on fibers are largely dominated in ILSS of the composites, whereas the nitrogen functional groups are not affected in this system. Also, it is found that a moderate 70 μA· m^{-2} treatment on fibers seems promising to assess the improving of the physical and mechanical properties. © *2000 Kluwer Academic Publishers*

1. Introduction

It is well known that the surface or interface properties of carbon fibers play an important part in their real composite materials involving an organic matrix, since load stress transfers from one matrix to the other via the fiber. For example, the interlaminar shear strength (ILSS) of composites is improved when the fibers are given treatments that increase surface functional group and roughness. Various methods used to modify the surface properties of the fibers are largely introduced in terms of gaseous oxidation [1–4], liquid phase oxidation [5–8], whiskerization [9], carbon and polymer coatings [10–12] anodic liquid treatment appears to be one of the most flexible and promising liquid phase oxidation in the uniform and continuous processes. However, the fiber surface areas measured by BET nitrogen adsorption [13] do not practically change after treatments [14, 15]. Therefore, it is assumed that the surface treatment is greatly resulted in improving the functional group or specific (or polar) component of the surface free energy on the fibers [16–18].

Meanwhile, numerous electrochemical surface treatments in basic electrolytes such as amines [6], diammonium hydrogen phosphate [17], sodium hydroxide [5, 18–20] have been studied in increasing oxidized functional groups on carbon fibers. Recently, Fowkes [16] and Park *et al.* [18, 21] proposed the exothermic energy term for acid-base interaction base on Gutmann's acceptor and donor number [22] between two unidentical solid surfaces in a composite system. These data [21] suggest that both PAN-based carbon fiber and amine-based epoxy resin surfaces might have a tendency of basic characteristic due to presence of electron donor molecule or group. And it is accepted that these functional groups are greatly dependent on the manufacturing temperature of carbon. When the temperature is higher than 800 °C, the functional groups are more stable and increase the basic oxides [23].

The objective of the present work is to study the effect of acidic anodic surface treatment on fibers in increasing the surface reactivity and to investigate the role of acid-base interaction between fibers and epoxy matrix resin, together with the results obtained from the composite mechanical technique.

2. Experimental

2.1. Materials and sample preparation

The fiber used in this experiment were untreated and unsized polyacrylonitrile (PAN)-based carbon fibers (12000 monofilaments), TZ-307 manufactured by Taekwang of Korea. A typical tensile modulus for these fibers was about 245 GPa. The specific surface area measured by nitrogen adsorption at 77 K was 0.7 m^2·g^{-1}. The linear mass was equal to 0.198 g·m^{-1}. The laboratory pilot plant on the anodic treatment of carbon fibers is schematically illustrated in Fig. 1. The length of electrolytic treatment bath was 0.23 m. The electrolyte used was 10 wt% phosphoric acid with a constant rate. The detailed experimental conditions

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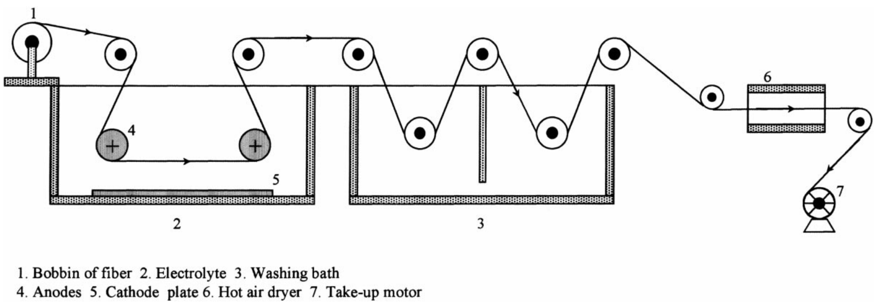


Figure 1 Schematic representation of the continuous oxidation process.

are listed in Table I. The anodized carbon fibers were washed in a Soxhlet extractor for 2 hours to remove surface impurities or residual oxides and then were dried before spectroscopic, microscopic, and mechanical analyses.

Epoxy resin used in this study 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 density was 1.16 g·m^{-3} at 25 °C. Diaminodiphenylmethane (DDM) purchased from Aldrich Chem. Co. was selected as a hardener and methylethylketone (MEK) was used to reduce a high viscosity of DGEBA. DGEBA and DDM structures are shown in Fig. 2.

The composite laminates were prepared by the prepreg method. Individual prepregs were first made by uniformly mixing fibers and the epoxy resin of a controlled composition by a drum-winding machine. The eighteen plies of resin impregnated carbon fiber prepreg were fabricated in a hot-press at 7.4 MPa at 150 °C for 150 min with a vacuum bagging method. The bulk fiber volume fraction and thickness of the composites were about 50% (±2%) and 4 mm (±0.2 mm), respectively.

2.2. Spectroscopic and microscopic analyses, and mechanical properties

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

TABLE I Experimental condition of anodic oxidation for carbon fibers

Conc. of electrolytes	10 wt% H_3PO_4
Temperature	25 °C
Oxidation rate	1 m·min^{-1}
Current density	0 to 300 μA·m^{-2}

The X-ray photoelectron spectroscopy (XPS, also known as electron spectroscopy for chemical analysis, ESCA) experiment was performed on an ESCA LAB MK-II (VG Scientific Co.) equipped with a magnesium x-ray source. The base pressure in the sample chamber was controlled in the range of 10^{-8} to 10^{-9} torr.

The morphology of the fibers was analyzed by using Scanning electron microscopy (SEM 515, Phillips Co.). Measured surfaces were coated with gold for the microscopy.

ILSS of the composites determined using an Instron 1121 according to ASTM D2344 was calculated by the following Equtaion 1. A span-to-depth ratio of 5 : 1 and a cross-head speed of 2 mm·min^{-1} were used.

$$\mathrm{ILSS} = \frac{3}{4}\frac{F}{bd} \tag{1}$$

where, F is the load at the moment of break (N), b the width of the specimen (m), and d the thickness of the specimen (m).

3. Results and discussion

Fig. 3 shows the FT-IR spectra of anodized carbon fibers in phosphoric acid solution as a function of current density. As seen in Fig. 3, the bands occurred at 3450, 1635, and 1200–1050 cm^{-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 [24] increases with increasing the current densities of the treatments up to 70–130 μA·m^{-2}, resulting in improving of surface functionality on the fiber anodized. While, the functional groups, including especially carboxyl groups, decrease at the higher current densities. This may be explained that carboxyl groups resulted in the irreversible ionization mechanism [25] are separated to the free carboxyl

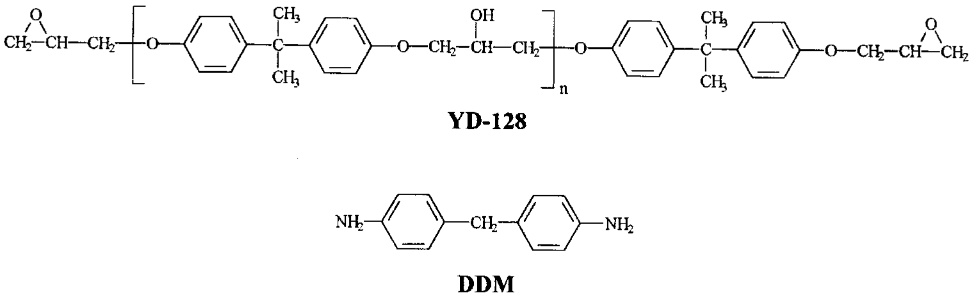


Figure 2 Chemical structure of the DGEBA and DDM.

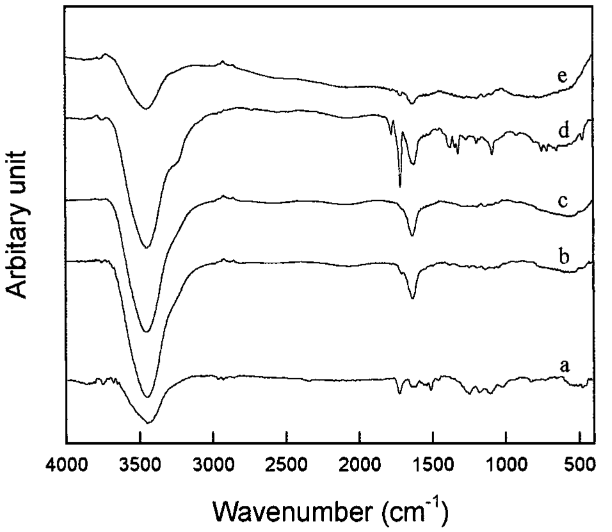


Figure 3 FT-IR spectra of carbon fibers studied (a: as-received, b: 30, c: 70, d: 130, and e: 300 μA·m^{-2}).

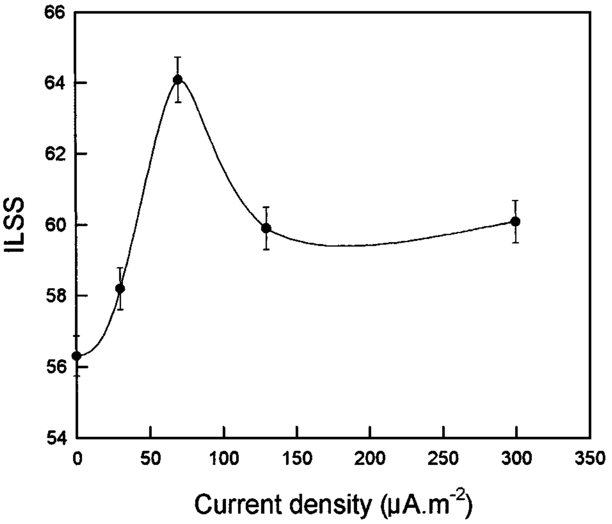
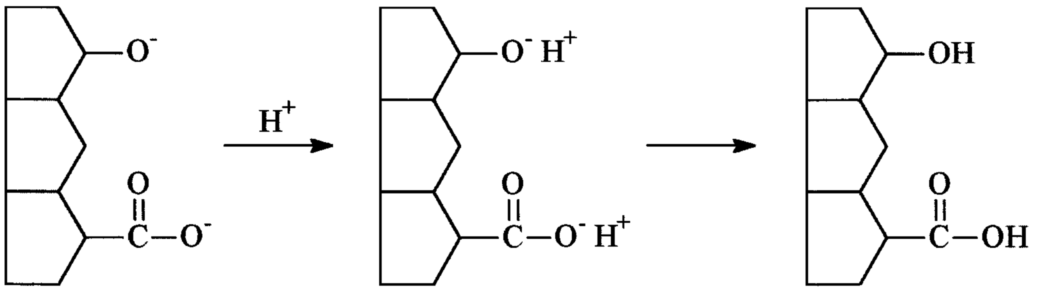


Figure 4 Evolution of ILSS as a function of the electric current density studied.

groups by reactive phosphoric acid solution. This is also due to the presence of the flexible and powerful interactions between basic carbon and acidic solution, in spite of very low current densities studied (30–300 μA·m^{-2}) as compared with those of experimental conditions widely elucidated in mA·m^{-2} or A·m^{-2} in basic solutions [5, 6, 17–20].

Meanwhile, it is well known that XPS is a very useful apparatus in determination of chemical compositions of the carbon fiber surfaces [26–29]. As shown in Table II, the amounts of surface oxygen groups increase with increasing the current densities of the treatments up to 70 μA·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, expected as:



Therefore, it is clearly expected that the increasing of oxygen functional groups on the fibers plays an important role in improving the degree of adhesion at interfaces between fibers and epoxy resin matrix, and the ILSS of the resulting composites.

The evolution of ILSS of the composites versus the current density studied is shown in Fig. 4. As a result, it is noted that a maximum strength value is found about 64 MPa at the anodic treatment of 70 μA·m^{-2}. Also, a good linearity between O_{1S}/C_{1S} ratio of the fibers and ILSS of the composites is shown in Fig. 5, when the O_{1S}/C_{1S} ratio of the fibers is considered in this system. As mentioned above, this is a consequence of the improving of acidic oxygen functional groups on fibers, resulting in growing fiber-matrix physical adhesion of the composites although, in the case of strong anodic treatments, it is also able to induce degradation according to irreversible ionization mechanism.

It is generally accepted that the moderate surface treatments do not lead to essential morphological changes to their surfaces [1]. Fig. 6 shows the SEM photographs of the carbon fibers with and without anodic surface treatments. The axial striations from

TABLE II Chemical composition of anodized carbon fiber surfaces from XPS analysis

Current density	C_{1S}		N_{1S}		O_{1S}		
(μA·m^{-2})	E_b (eV)	AT (%)	E_b (eV)	AT (%)	E_b (eV)	AT (%)	O_{1S}/C_{1S}
0	284.7	74.3	400.7	1.4	532.5	24.3	0.327
30	284.7	73.5	400.9	1.4	533.9	25.1	0.342
70	284.6	68.8	400.3	0.7	532.3	30.6	0.445
130	284.6	72.1	400.8	1.4	532.6	26.5	0.368
300	284.7	69.7	401.0	1.5	532.8	28.9	0.414

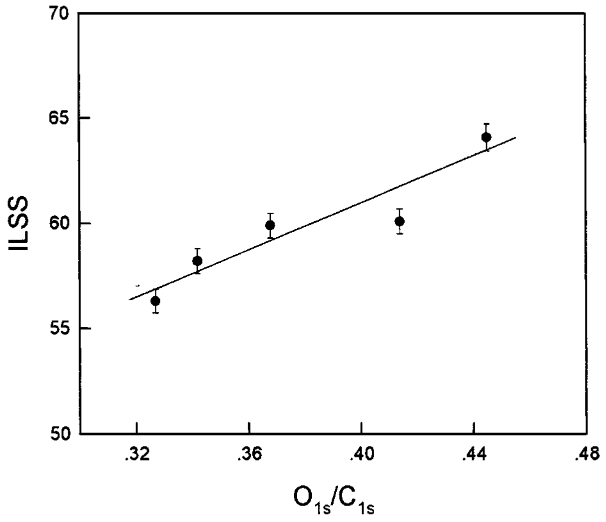
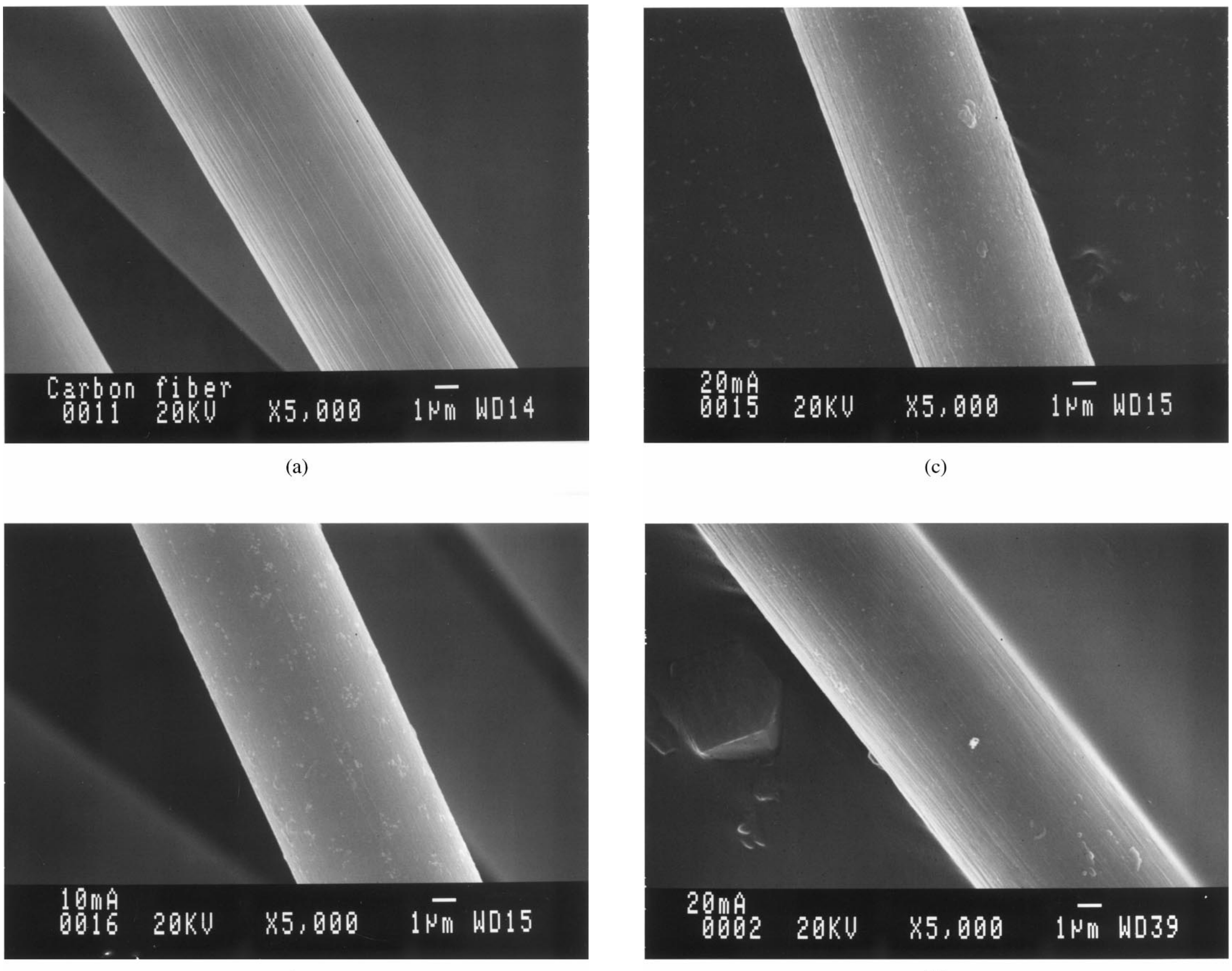


Figure 5 Dependence of the ILSS of composites on the O_{1S}/C_{1S} of the fibers studied.

the extrusion process can again be seen in the untreated fiber image. As one compares the untreated and the treated fibers, it can be seen that acidic anodic oxidation does lead to a change in surface morphology at the microscopic scale. This tendency is observed that "surface smoothing" or "crystallite stacking diminishing" on fibers is largely dominated as increasing the current density. This seems to be a consequence of the surface destruction of the fibers, preferentially prismatic planes. And again suggestion can be done in the consideration of the strong decomposing interaction between basic carbon and acidic electrolyte, even if the treatments are carried out at low current densities. At the higher densities, there exists a severe structural heterogeneity, such as "micro-etching spots", aligned along the fiber axis. This may lead to enhancing the lack of overall distance for physical interaction between fibers and matrix [30], resulting in lowering the composite mechanical properties.

4. Conclusion

With a viewpoint of acid-base interaction chemistry, the effect of acidic anodic treatment on the carbon fibers has been studied in terms of spectroscopic, microscopic and mechanical techniques. Therefore, the fibers are needed to submit during their immersion in the phosphoric electrolyte with very low electric current densities. According to FT-IR and XPS measurements, it reveals that the oxygen functional groups on fibers are largely dominated in composite mechanical behavior, such as ILSS, whereas the nitrogen functional groups are not affected in this system. Also, it is found that a moderate anodic treatment on fibers seems promising to assess the changes of physical and mechanical properties.



(a)

(c)

(b)

(d)

Figure 6 SEM photographs of the carbon fibers studied: (a) untreated; (b) 30 μA·m^{-2}; (c) 70 μA·m^{-2}; (d) 300 μA·m^{-2}.

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