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Improvement of CF/ABS Composite Properties by Anodic Oxidation of Pitch based C-type Carbon Fiber

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Abstract

The surface treatment of C-type isotropic pitch-based carbon fiber was carried out by anodic oxidation in 5 wt% NH_4NO_3 electrolyte. The changes of fiber surface and carbon fiber/ABS resin composites were characterized by SEM, XPS and mechanical properties test. The oxygen functional groups on the surface, such as hydroxyl (-C-OH), carboxyl (-COOH) groups etc., increased after oxidation. Tensile strength, flexural strength and modulus of carbon fiber/ABS composites were also enhanced. However, the impact strength decreased with the improvement of the surface adhesion between CF and matrix.

Keywords : *Carbon Fibers, Anodic Oxidation, Composite, Surface Functional Groups*

1. Introduction

Mechanical properties of composites primarily depend on the interfacial bonding strength between carbon fiber (CF) and matrix. The interfacial bonding can be improved by increasing the chemical bond or extending the contact area between carbon fiber and matrix. Many papers [1-4] have reported the liquid phase surface treatment on CF. Most of them studied the effect of acid concentration and the treatment time, and found that both the surface functionality and the surface area increased on oxidation. However, an increase in oxidation time and acid concentration resulted in the tensile strength decrease, because the less crystallized regions were more reactive toward acid and the surface of untreated fibers were pitted and fragmented by the acidic solution. The possibility of oxidation of carbon fibers in electrolytic baths of acid and alkaline aqueous solution has been indicated [5, 6] and industrially used. The electrochemical oxidative treatment offers more control over surface chemistry and can allow continuous processing of the carbon fiber. Fukunaga [7] and Park [8] have reported that the oxygen functional groups on the CF surface increased by anodic oxidation, thus giving rise to higher ILSS value of the resulting composite than untreated one's. It has been proved in our previous researches [9, 10] that the anodic oxidation, especially NH_4NO_3 electrolyte oxidation, of carbon fiber can also enhance the interfacial adhesion strength between fiber and matrix effectively. Many references [11, 12] showed that non-circular CF has higher tensile strength and modulus than regular round CF since the more surface area on the non-circular CF can improve the interfacial bonding between fiber and matrix. Ryu [13] also reported that pitch-based C-type carbon fiber shows about 7% higher tensile strength and 13% tensile modulus than regular round CF. Nevertheless, it is necessary to augment the oxygen functional groups such as C-OH, C=O, COOH on the surface of non-circular CF by proper anodic oxidation.

In the present work, the anodic oxidation of C-type pitch-based carbon fibers was carried out. The effects of surface treatment on C-type CF itself and the resulting interface between fiber and ABS matrix were analyzed. The fracture mechanism for both untreated and treated C-type CF reinforced ABS composites were studied by SEM and XPS.

2. Experimental

2.1. Materials

The C-type isotropic petroleum pitch-based carbon fibers were prepared by Chungnam National University, Korea [13]. Table 1 shows the physical properties of the isotropic pitch based C-type fibers. The ABS resin (GN095-15-150-2, LanZhou Chemical Industrial Co. China) was used as a matrix. According to our previous study, 5 wt% NH_4NO_3 was recommended to be a proper electrolyte [9].

Table 1. Physical properties of the C-type fibers [13]

Precursor	Tensile strength (Gpa)	Tensile modulus (GPa)	Density (g/cm^3)	Diameter (μm)
Isotropic pitch	1.02	62	1.65	8.0

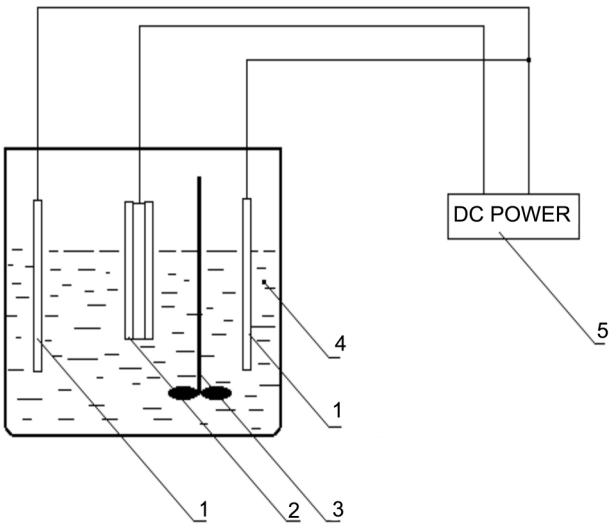

Fig. 1. Schematic view of anodic oxidation apparatus. (1) Graphite electrode (2) Carbon fiber anode (3) Stirrer (4) NH_4NO_3 solution (5) DC power.

2.2. Experimental Apparatus

Fig. 1 shows the schematic view of anode oxidation apparatus. Chopped carbon fiber in a double glazed PVC cylinder was used as the anode and graphite electrode was used as the cathode. There are many ϕ 6 mm holes uniformly distributed on the cylinder surface through which the electrolyte can be permeated into the cylinder [9]. The chopped carbon fiber was packed between cylinders, and the packing density was 0.5 g/cc.

CF/ABS composite pellets were manufactured by following the previous method [9]: blending 20 wt% of anodic oxidized isotropic pitch-based C-type chopped carbon fiber to 80 wt% ABS resin and extruding it through a screw extruder at the rate of 25 rpm, 180~200°C. Then the extruded sticks were injected to get proper size pellets using SJ-20 type injector at 180~200°C, 60-150 MPa injection pressure. As-received carbon fiber was also used for comparison of it with anodic oxidized fiber.

2.3. Analysis

Tensile and flexural property of composite sticks were measured according to ASTM 638 (sample size: 60 mm × 3.0 mm × 2.8 mm) and GB1042-79 (sample size: 60 mm × 12.6 mm × 1.9 mm). Non-notched impact and notched impact property were tested according to GB1043-79 (sample size: 60 mm × 5.9 mm × 3.9 mm) and GB1043-80 (sample size: 60 mm × 12.6 mm × 3.9 mm).

Changes of O_{1S}/C_{1S} and functional groups were detected by XPS (XSAM 800, KRATOS Co.) with a monochromatic X-ray source in a vacuum of 10^{-8} torr. The XPS data were fitted using a Gaussian-Lorentzian function and linear background subtraction was used to deconvolute the XPS peaks. Atomic ratios were calculated from XPS spectra after correcting the relative peak areas by sensitivity factor based on the transmission characteristics. The surface of carbon fiber and notch assault fractured surfaces of CF/ABS composites were observed by SEM (Cambridge S-250 Scanning Electron Microscope) to examine the fractography of the composites and adhesion between carbon fiber and ABS resin.

Table 2. Changes of O_{1S}/C_{1S} and functional groups under different anodic oxidation conditions

	I	II	III	IV
Concentration (wt %)	(as-received)	5	5	7
Current intensity (A)		0.6	0.8	1.2
Oxidation time (sec)		120	120	180
O_{1S}/C_{1S}	5.40	6.48	9.20	17.60
N_{1S}/C_{1S}	–	1.30	1.50	1.50
C-C (284.5 ev)	69.87	73.69	73.85	71.27
C-OH (286.1 ev)	19.38	13.76	15.07	15.28
C=O (287.6 ev)	5.06	6.2	7.72	5.82
C-OOH (289.3 ev)	5.24	6.35	3.35	7.64

3. Results and Discussion

3.1. Effects of anodic oxidation on surface functional groups of C-typed carbon fiber

Table 2 and Fig. 2 show the effect of anodic oxidation conditions on the change of O_{1S}/C_{1S}, N_{1S}/C_{1S} ratios and functional groups. The peak deconvolutions of the surface oxidized carbon fiber obtained from XPS analysis were different from the oxidation conditions. The carbon 1s electron binding energy corresponding to graphitic carbon was refer-

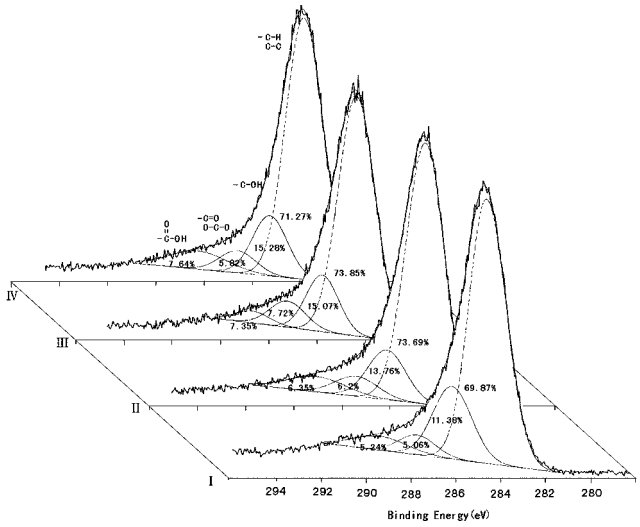

Fig. 2. High resolution XPS C_{1S} spectra of anodic oxidized carbon fibers. (I) as-received carbon fiber, (II) conc. 5%, current 0.6A, time 120s, (III) conc. 5%, current 0.8A, time 120s, (IV) conc. 7%, current 1.2A, time 180s.

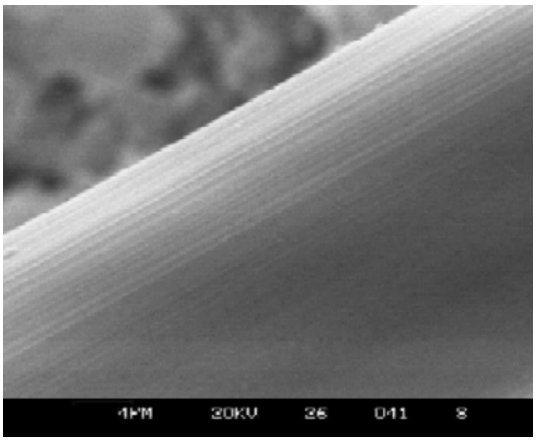

Fig. 3. SEM photograph of non-treated carbon fiber surface.

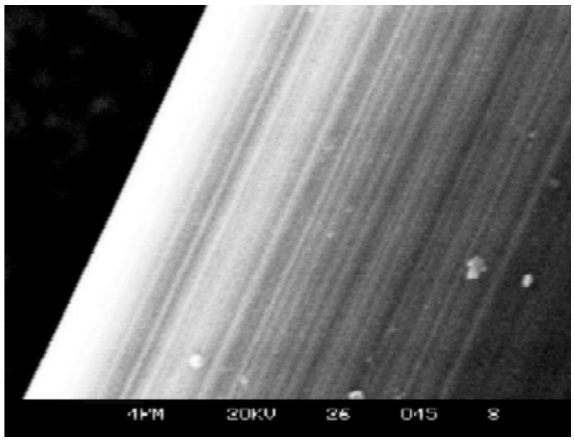

Fig. 4. SEM photograph of anodic oxidation carbon fiber surface. (Condition: conc. 7%, current 1.2A, time 180s).

enced at 284.6 eV for calibration. All the C_{1S} peaks fitted were shifted to higher binding energies about 1.2, 2.2, and 4.0 eV, respectively as well as Pittman's improper and vague expression [2, 3]. The anode oxidation gave rise to the increase of O_{1S}/C_{1S} ratio and the functional groups of C=O and C-OOH, but decrease of C-OH radical. It is difficult to correctly explain why the amount of C-OOH radical decreased at 0.8 A, 120 sec. and increased again at 1.2 A, 180 sec. Sherwood and coworkers [6] have reported that both oxygen- and nitrogen-containing functionalities increase after the anodic oxidation; while short time oxidation produce mainly C-OH groups and few C-OOH, but C=O type of functional groups are generated predominantly for a long time oxidation. However, their results were also fluctuated. It is clear that the amount of generated oxygen-containing groups depends on oxidation time and the kind of fibers. In this experiment, N_{1S} was also detected. It is believed by the decomposition of some electrolyte. Too strong current and too long time oxidation were not effective because of decreasing the carbon-oxygen groups. Neffe *et al.* [14] have reported the observation of cracks on the carbon fiber skin with excessive electrochemical oxidation. There were no cracks on carbon fibers in this oxidation conditions indicating that NH_4NO_3 is a proper electrolyte for anodic oxidation [9].

Fig. 3 and Fig. 4 are the SEM photographs of non-treated and anode oxidized carbon fiber surfaces, respectively. Photograph of the non-treated carbon fiber shows smooth surface. On the other hand, the surface of fiber was notched uniformly under the optimum condition of anodic oxidation. Sherwood [6] also reported that electrochemical oxidation increased surface activity by generating more surface area *via* the formation of ultramicropores, and by introducing polar oxygen-containing groups over this extended porous surface. However, there are no pits and fragments on anodic oxidized carbon surface.

3.2. Effect of anodic oxidation conditions on mechanical properties of C-type CF/ABS composites

Table 3 shows the effect of anode oxidation conditions on mechanical properties of C-type CF/ABS composites. The tensile strength and flexural strength of pure ABS sample stick were 45 MPa and 90.5 MPa, respectively. They increased up to 57.7 MPa and 120.87 MPa by blending 20 wt% of as-received C-type chopped carbon fibers. On the other hand, the impact strength of composite decreased with the addition of isotropic pitch-based chopped carbon fibers. But anodic oxidation of carbon fiber did not affect the impact strength of composite. In case of general carbon

Table 3. Effect of anodic oxidation conditions on mechanical properties of C-type CF/ABS resin composites

Oxidation conditions	Tensile strength (MPa)	Modulus of elasticity (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)	No-notch impact strength (kJ/m^2)	Notch impact strength (J/m)
Pure ABS*	45.00	0.73	90.50	2.60	26.49	130.0
I (as-received)	57.7	0.78	120.87	5.62	9.53	37.2
II	65.1	0.83	122.77	5.65	9.30	34.3
III	66.1	1.00	134.6	5.97	9.00	36.5
IV	68.3	1.22	135.3	6.15	9.70	35.7

*mechanical properties of ABS resin composite without chopped carbon fiber

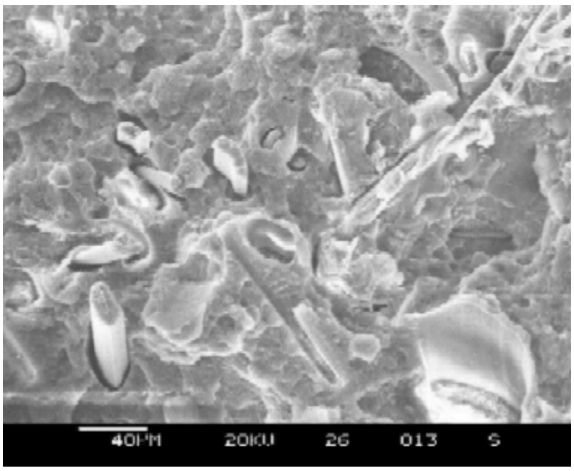

Fig. 5. SEM micrograph of impact fracture of as-received C-type CF/ABS composite.

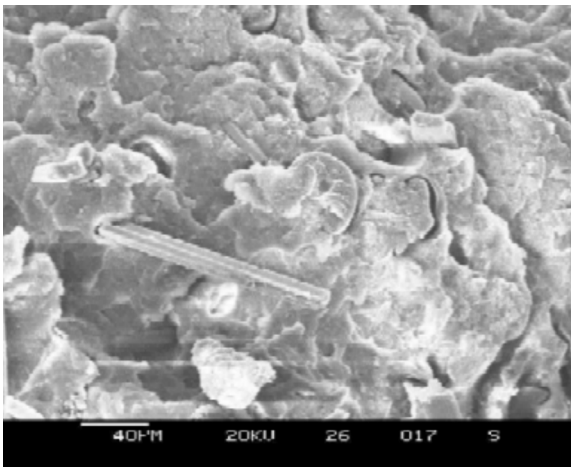

Fig. 6. SEM micrograph of impact fracture of anodic oxidized C-type CF/ABS composite (Condition: conc. 7%, current 1.2A, time 180s).

fibers, optimum oxidation conditions were 0.8 A current density and 120 sec. oxidation time in 5 wt% NH_4NO_3 electrolyte [9]. For C-type carbon fibers, the optimum conditions were extended to 1.2 A and 180 sec. The mechanical properties of composite increased about 18% in tensile strength and 9.4% in flexural modulus by the anodic oxidation of carbon fiber. This increment is similar to the case of general carbon fibers. Park [8] reported that very low electric current density, such as 30~300 $mA \cdot m^{-2}$, are needed for morphological change of fibers in 10 wt% phosphoric acid electrolyte. He has mentioned that the imrovement of fiber-matrix is caused by the increase of oxygen-containing functional groups and surface area on carbon fibers. He also mentioned that the nitrogen functional groups did not affected the mechanical properties of composite.

3.3. Fracture surface of as-received and treated CF/ABS composite

Fig. 5 was the SEM micrograph of impact fracture of ABS composites reinforced by as-received C-type carbon fiber. It is seen that non-oxidized C-type carbon fibers has smooth surfaces to which there are no resins adhered, indicating that the interfacial adhesion between non-treated carbon fibers and ABS matrix was weak. Some fibers look like ribbon type fibers [15], but most of fibers are C-type. For the anodic oxidized C-type CF/ABS composite shown in Fig. 6 and Fig. 7, the carbon fibers were adhered with ABS resin and mainly fractured at basal planes rather than being pulled out. All these indicated that the interfacial adhesion between CF and ABS was enhanced by the anodic oxidation of carbon fiber.

From the above XPS and SEM analysis, it can be deduced that the interfacial bonding between CF and ABS was enhanced mainly by introducing polar oxygen-containing groups to carbon fiber surface in the oxidation processing,

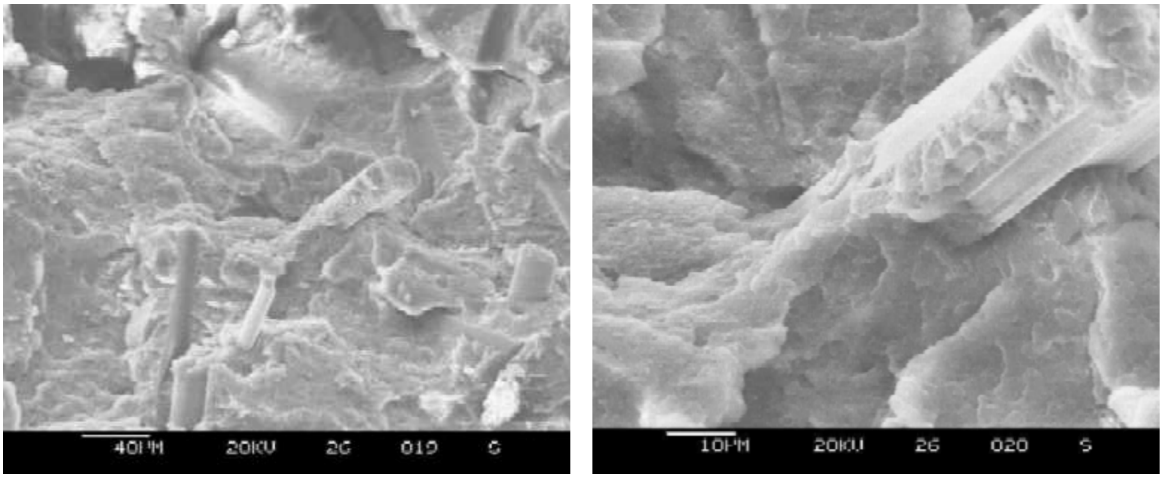

Fig. 7. SEM micrographs of tensile fracture of anodic oxidized C-type CF/ABS composite (Condition: conc. 7%, current 1.2A, time 180s).

consequently, giving rise to the increase in the tensile strength and the flexural strength of composites. However, the improvement of tensile strength and flexural strength is not much more apparent than the non-treated CF reinforcing composite, and the impact strength decreased because of the addition of isotropic pitch-based C-type chopped carbon fibers. This may be due to the lower filament strength, the larger diameter of isotropic-pitch-based C-type CF and the decrease in filament strength caused by anodic oxidation. All of these results showed that the electrolysis oxidation etching improved the interfacial adhesion and the main way of the fracture of CF/ABS composite was fiber fracture.

4. Conclusions

Proper anodic oxidation in NH_4NO_3 electrolyte increased the content of oxygen-containing functional groups such as hydroxyl (-C-OH), carboxyl (-COOH) groups and surface area on C-type petroleum pitch based carbon fibers without pits and fragments. Such functional groups have improved the interfacial adhesion between carbon fiber and ABS matrix, and consequently giving rise to the increase in the tensile strength and the flexural strength of carbon composites. However, the impact strength decreased with the improvement of the surface adhesion between CF and matrix.

Acknowledgement

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