# A Gradient Anodic Oxidation Method for Treating Polyacrylonitrile-Based High-Modulus Carbon Fibers

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**ABSTRACT:** We describe a gradient anodic oxidation method. Polyacrylonitrile-based high-modulus carbon fibers were treated by the conventional and gradient anodic oxidation methods. The results show that the carbon fibers treated by the gradient method possessed a more stable tensile strength, larger NaOH uptake, shallower striations, flatter fracture surface of composites, and better interlaminar shear strength compared to those treated by the conventional method. This indicated that the gradient method was more effective in restricting the etching reaction and improving the adhesion between the carbon fibers and matrix, and we give a suggested explanation of the mechanisms. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 1059–1066, 2011

**Key words:** electrochemistry; fibers; interfaces; surface modification

## INTRODUCTION

Carbon fibers possess excellent mechanical properties for composite reinforcement.[1,2] However, the efficient translation of these outstanding mechanical properties into usable composite structures depends, in part, on the fiber–matrix interlaminar shear strength (ILSS).[3,4] However, because most carbon fiber surfaces consist of a large number of graphitic basal planes, they do not possess good wettability to matrices and produce composites with low ILSS.[5,6] To improve the wettability and adhesion of carbon fibers to matrices, various oxidative techniques have been applied,[7–15] such as anodic oxidation, plasma treatment, and solution and gas-phase oxidation. Among these methods, anodic oxidation method is effective in improving the shear properties of carbon-fiber/resin composites and is preferred because it allows the continuous processing of the carbon fibers.[16–18]

However, some researchers reported that the anodic oxidation method was less effective when applied to highly graphitized surfaces and that the level of adhesion of high-modulus (HM) carbon fibers treated by the conventional method to matrices still remained low and could not meet the requirements of application.[19,20] Therefore, in the case of the HM carbon fibers, it is necessary to seek a feasible alternative to the conventional anodic oxidation method.

In this study, we improved the conventional anodic oxidation method and used a new gradient anodic oxidation method to increase the adhesion of polyacrylonitrile (PAN)-based HM carbon fibers to resin. We report the effects of the new method here.

## EXPERIMENTAL

### Materials

PAN-based HM carbon fibers in this study were manufactured by the Institute of Coal Chemistry, Chinese Academy of Sciences (Taiyuan, China). The mechanical properties of the carbon fibers are shown in Table I.

### Surface treatment of the carbon fibers

The apparatus used for continuous surface treatment are shown in Figure 1. Figure 1(a) shows the conventional anodic oxidation apparatus. We improved the apparatus as shown in Figure 1(b) (the cathode was inclined; this was named the *gradient anodic oxidation method*), in which carbon fibers were at an angle (ca. 6°) with the cathode. Both methods were used to treat the carbon fibers. During the treatment, carbon fibers supplied continuously from a creel stand were immersed in a vessel with 2 mol/L

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**TABLE I**
**Mechanical Properties of the Carbon Fibers**

| Filaments in a bundle | Tensile strength (GPa) | Young's modulus (GPa) | Volume density ($g/cm^3$) | Diameter (μm) | Strain (%) |
|---|---|---|---|---|---|
| 3000 | 2.97 | 351 | 1.784 | 6.50 | 0.857 |

$NH_4HCO_3$ solutions at a rate of 0.5 m/min. The current density was varied from 0 to 42 $A/m^2$. After the anodic oxidation, the carbon fibers were rinsed in distilled water and dried at 120°C before they were used as specimens for surface analysis and fragmentation testing.

### Tensile strength of the carbon fibers

The effect of the treatment on the tensile strength and Young's modulus of carbon fibers was determined with an AG-1 type universal material tester (Shimadzu Co., Ltd., Kyota, Japan), in which the crosshead speed was 10 mm/min and the gauge length was 20 mm. Carbon fiber specimens were taken from different sections of the treated fiber. A single carbon fiber was glued onto a paper frame with adhesive and cured for 24 h. For each fiber tested, the tensile strength and Young's modulus were calculated with eqs. (1) and (2),[21] respectively:

$$\sigma_f = F/A_f \quad (1)$$

$$E = (F/A_f)/(\Delta L/L_0) \quad (2)$$

where $\sigma_f$ is the tensile strength (MPa), $F$ is the tensile force at break (N), $A_f$ is the fiber cross-sectional area ($mm^2$), $E$ is Young's modulus (MPa), $L_0$ is the original length of the fiber, and $\Delta L$ is the change in the length of the fiber when it is subjected to an applied stress. All measurements were repeated on at least 25 different samples of treated fibers to obtain a statistical average. The errors presented are standard errors.

### ILSS

The carbon fibers were unidirectionally impregnated with epoxy resin E-44, diethylenetriamine, and acetone at 10, 3, and 15 parts by weight, respectively. The samples were cured at 120°C for 0.75 h and postcured at 180°C for 2 h. Samples for testing were cut to approximately $25 \times 6 \times 3$ $mm^3$ with the fibers aligned longitudinally. The adhesive strength between the fibers and epoxy resin was evaluated from ILSS with the three-point bending test at a constant crosshead speed of 2 mm/min. The measurements were repeated on at least 15 different samples of treated fibers to obtain a statistical average. The errors presented are standard errors.

### NaOH uptake

An NaOH solution (1–2 mM) was prepared with boiled distilled water to remove dissolved carbon dioxide. Approximately 1 g of carbon fiber was immersed in 25–50 mL of NaOH solution in a plastic vial for 24 h. The change in the NaOH concentration was measured with a pH meter (Ion Analyzer 250, Corning).

### Fiber surface morphology

To show eventual changes in the surface morphology of the fibers and fracture surface of composites, all samples were analyzed with a JEOL JSM-35C scanning electron microscope (Japanese Electronic Optics Co., Tokyo, Japan).

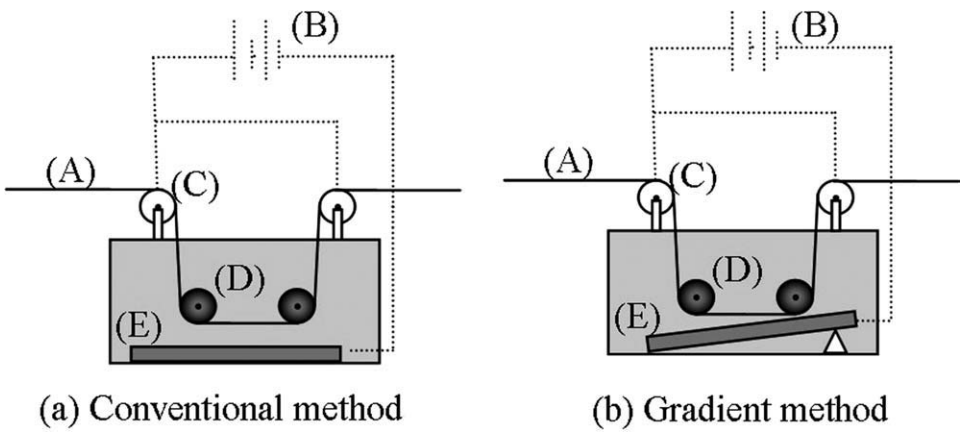



**Figure 1** Apparatus for anodic oxidation by (a) the conventional method and (b) the gradient method: (A) carbon fibers, (B) power supply, (C) anode, (D) electrolyte, and (E) cathode.

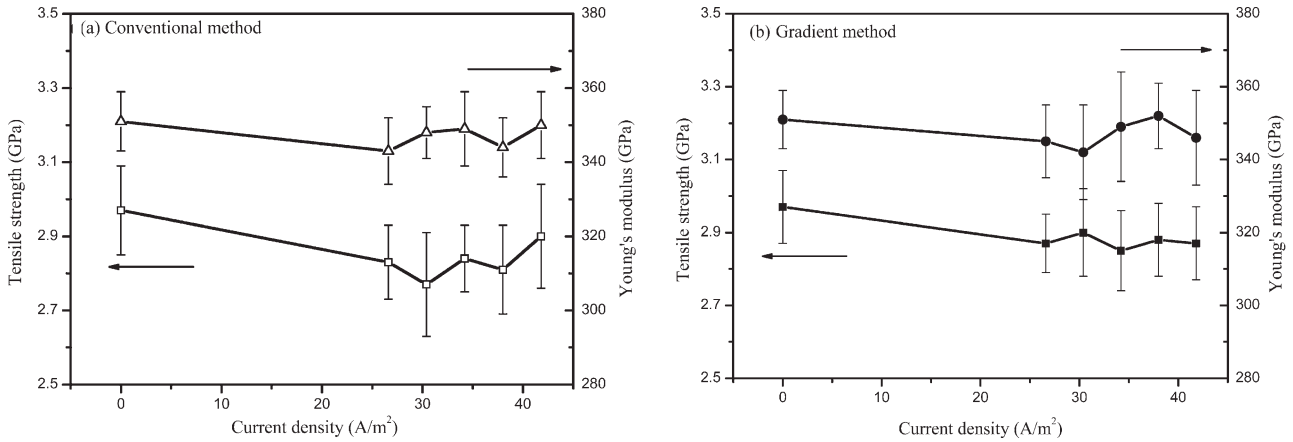



**Figure 2** Effect of the current density on the mechanical properties of the HM carbon fibers: (a) the conventional method and (b) the gradient method.

### Contact angle measurement

Contact angle measurement was performed to determine the wettability of the fiber surface with the sessile drop technique, in which the shape of the distilled water droplets attached to the fibers was recorded as digital images taken by an optical contact angle meter system (OCA 40, Dataphysics Instruments GmbH, Stuttgart, Germany). Each contact angle reported is an average of at least 20 different measurements, and at least five fibers were used. The single fiber specimens were fixed by an adhesive tape on a frame with a certain amount of tension, and the length of the fiber was about 2 cm. The water droplets were sprayed onto the single fiber during the test.

## RESULTS AND DISCUSSION

### Mechanical properties

The effect of the current density on the mechanical properties of HM carbon fibers is shown in Figure 2. It is well known that tensile strength is influenced by surface defects and that Young's modulus is related to crystallite size and preferred orientation. During the anodic oxidation process, the reactions only occur on the surface of carbon fibers; this may lead to the formation of some defects and does not change the crystallite size and preferred orientation.[19] Therefore, the curves showed that current density had a small effect on the change in Young's modulus but had a significant effect on the decrease of tensile strength. A closer look at the curves showed that the difference between two methods was clear. In the case of the conventional method, the tensile strength of the carbon fibers changed obviously with the increase in current density. At a current density of 30.4 $A/m^2$, the tensile strength decreased by 6.7%. The decrease in the tensile strength may have been due to surface defects that were introduced by a serious oxidation reaction and etching reaction. The following increase in the tensile strength may have resulted from the decrease of fiber diameter. In the case of the gradient method, the decrease of the tensile strength was very slow. At the same current density (30.4 $A/m^2$), the tensile strength decreased only by 2.4%. It was clear that the improvement in the anodic oxidation apparatus effectively restricted the reduction in the tensile strength.

### NaOH uptake

During the anodic oxidation process, active site atoms on the fiber surface are oxidized to form oxygen-containing surface groups (C—OH, C=O, COOH), and finally, some groups are oxidized to form $CO_2$. The types of oxygen functions and the simplified stepwise progression mechanism for

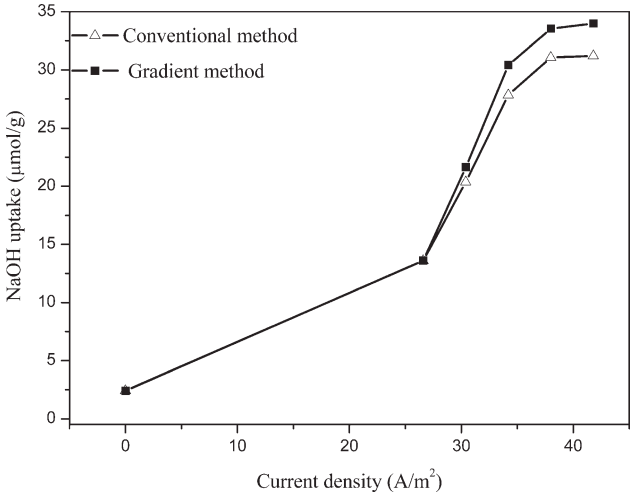



**Figure 3** NaOH uptake by anodic oxidized carbon fibers prepared continuously at different current densities.

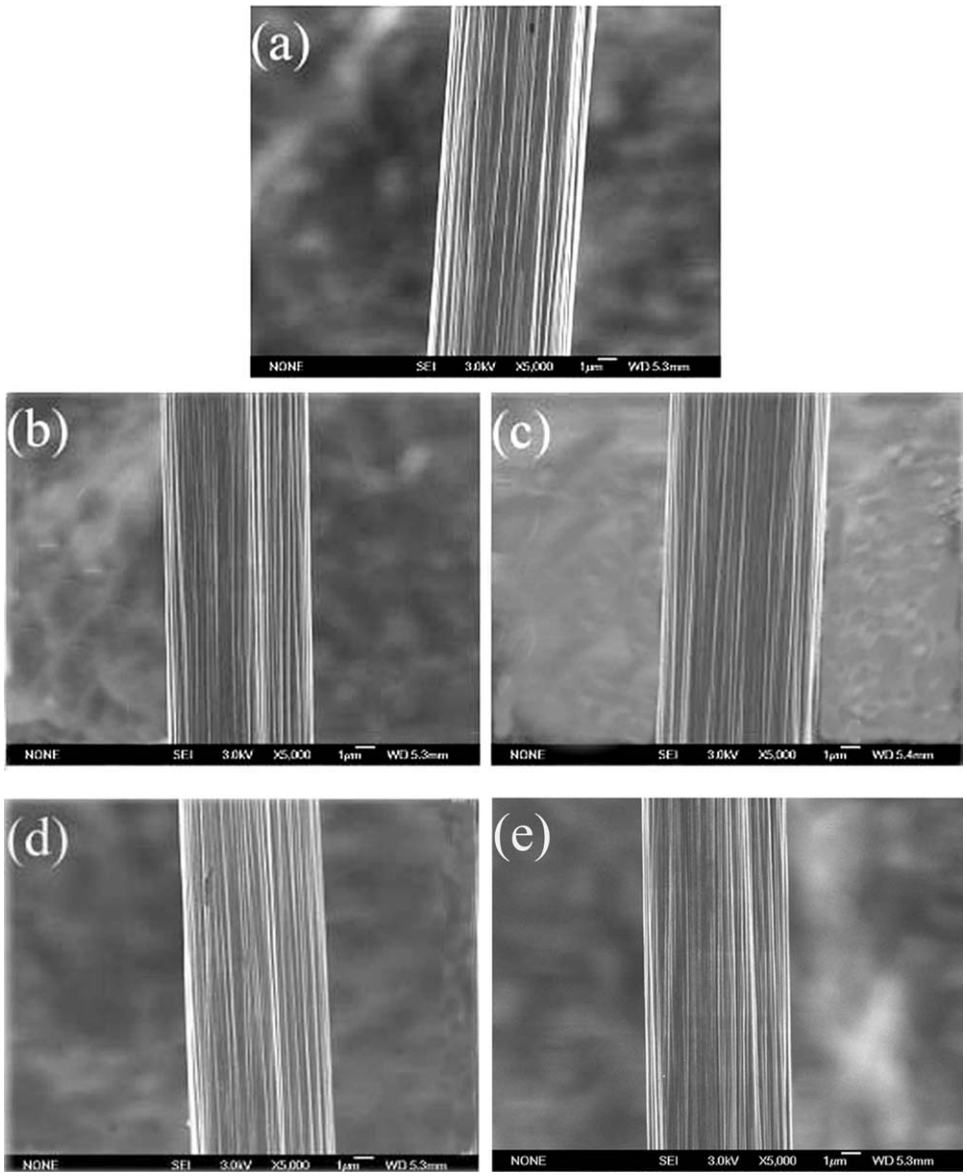
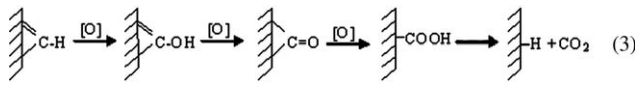



**Figure 4** SEM micrographs of untreated and treated carbon fibers: (a) no treatment, (b) the conventional method at 26.6 $A/m^2$, (c) the conventional method at 41.8 $A/m^2$, (d) the gradient method at 26.6 $A/m^2$, and (e) the gradient method at 41.8 $A/m^2$.

carbon surface oxidation in eq. (3) have been widely studied.[22–24] The amount of acidic surface function groups could be determined by NaOH uptake (Fig. 3). The curves indicated that with the increase in the current density, the amount of acidic functional groups generated on the fiber surfaces accessible to aqueous NaOH initially increased obviously and then leveled off. This was in accordance with other studies in which a saturated state in surface oxidation was reached after a short period of carbon fiber oxidation in various electrolyte systems.[25–27] The difference between the two methods was only that in the case of the gradient method, the amount of NaOH uptake was greater than in the conventional method.




### Scanning electron microscopy (SEM)

As shown by the SEM micrographs, striations existed on the surface of the unmodified HM carbon fibers [Fig. 4(a)]. These striations were typical of carbon fibers prepared from PAN precursors. When the carbon fibers were treated by the conventional method, there seemed to be a slight increase in the depth and width of striations present on the treated surfaces, especially at 41.8 $A/m^2$ [Fig. 4(c)]. However, in the case of the gradient method, no obvious

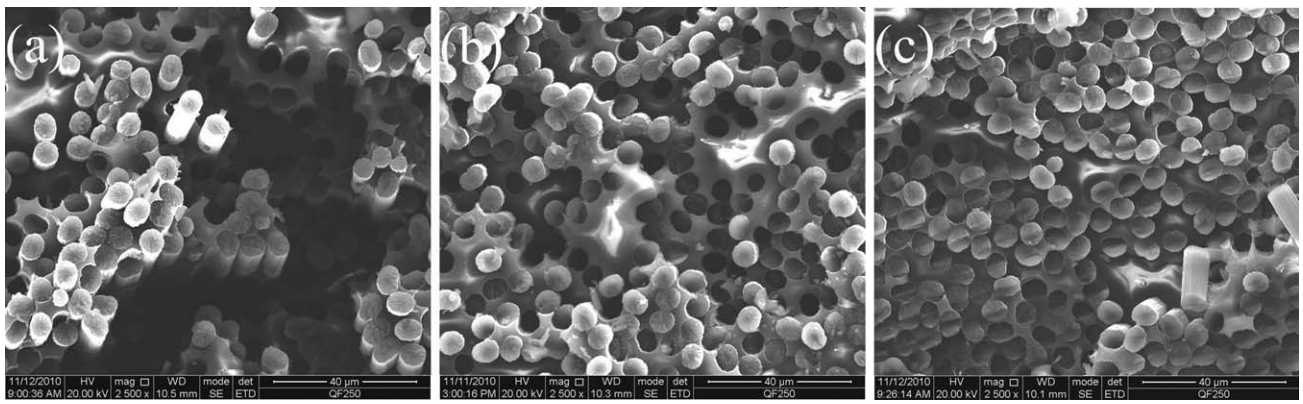



**Figure 5** SEM micrographs of fracture surfaces of the composites: (a) untreated carbon fiber/epoxy composites, (b) conventional-method-modified carbon fiber/epoxy composites at 41.8 A/m$^2$, and (c) gradient-method-modified carbon fiber/epoxy composites at 41.8 A/m$^2$.

change was observed. This was in accordance with the change in the fiber tensile strength. In addition, we noted that the color of the $NH_4HCO_3$ solution turned dark at 41.8 A/m$^2$ during conventional anodic oxidation treatment process and the color became light brown under the same conditions in the case of the gradient method. The inking of the electrolyte solution was caused by colloidal degradation products.[28] This inferred that the amount of degradation products was larger in the conventional method. It seemed that the fibers treated by the conventional method suffered serious damage.

Figure 5 demonstrates the interlaminar shear damage morphology along the cross section in the carbon fiber/epoxy composites. As shown in Figure 5(a), the main failure mechanism of the untreated carbon fiber/epoxy composites was the fiber debonding. After anodic oxidation modifications, as shown in Figure 5(b,c), although some carbon fibers were separated from the matrix, a flatter cross section was observed, which indicated that stronger interfacial bonding was formed. The fracture model was changed from pure interfacial failure to combination failures of the interface and resin interlayer. When we compared Figures 5(b) and 5(c), it was clear that gradient anodic oxidation method led to a flatter cross section and fewer holes; this indicated stronger interactions of the treated carbon fibers and the epoxy resin matrix; this correlated with ILSS results (Fig. 6).

## ILSS

Figure 6 shows the effect of the current density on the ILSS of the carbon fiber/epoxy composite system. When the carbon fibers were treated by anodic oxidation, the ILSS values at the beginning increased rapidly and then leveled off; this was in accordance with other studies.[19,29] The ILSS values showed a corresponding trend with NaOH uptake, which indicated that oxygen-containing surface groups were mainly responsible for the level of matrix adhesion in the carbon fiber composites. The ILSS values of carbon fibers modified by the gradient method were much larger than that by the conventional method. In the case of the gradient method, the value of ILSS reached 83.4 GPa at 34.2 A/m$^2$, an increase of 18.3% compared to the sample treated by the conventional method. This indicated that the gradient method was more effective in improving the adhesion than the conventional method.

From these results, we observed that compared to those treated by the conventional method, the carbon fibers treated by the gradient method showed a more stable tensile strength, larger NaOH uptake, shallower striations, flatter fracture surface of composites, and better ILSS. All of these results indicate that the gradient method was more effective in improving adhesion between the carbon fibers and matrix.

When the carbon fibers were treated with a constant current density, the voltage between the carbon

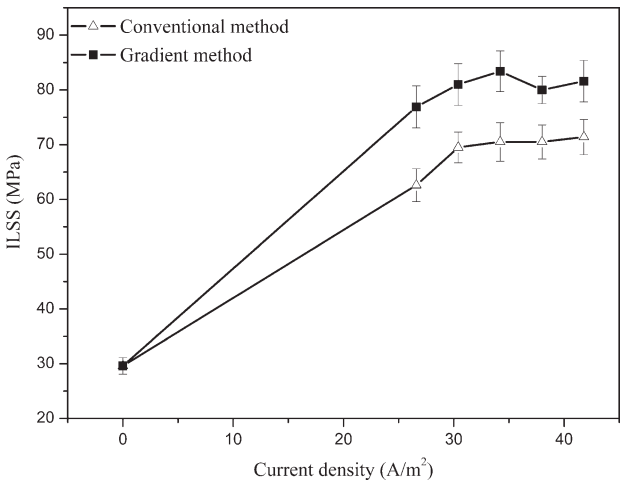



**Figure 6** Effect of the current density on the ILSS of the carbon fiber/epoxy composite system.

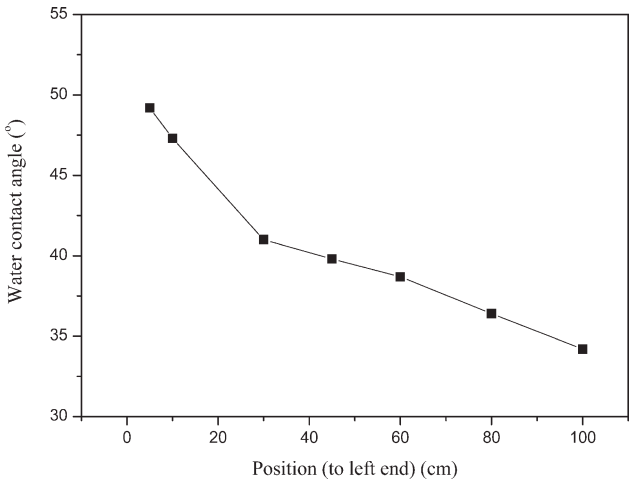



**Figure 7** Water contact angles of the treated carbon fibers at different positions (to the left end).

fibers and cathode was almost constant (at the same current density, the voltage of the gradient method was a little smaller than that of the conventional method). In the case of the conventional method, the carbon fibers were uniformly oxidized during the treatment process. However, in the case of the gradient method, because the carbon fibers approached the cathode gradually during the treatment process, the microresistance between carbon fibers and the cathode decreased gradually; this may have led to an increase in the microcurrent. Therefore, we supposed that the oxidation rate may have been gradually enhanced when the carbon fibers were treated with a constant current density in the case of the gradient method.

To verify that the oxidation rate gradually increased during the treatment process of the gradient anodic oxidation, we used the gradient anodic apparatus to treat carbon fibers discontinuously at a current density of 26.6 $A/m^2$ for 2 min. The contact angle was used to determine the change in the fiber surface wettability (Fig. 7). It was clear that the anodic oxidation method was effective in hydrophilic surface modification (the water contact angle of the untreated carbon fiber was 62°). With increasing distance to the left end [Fig. 1(b)], the water contact angles decreased continuously. It is well known that wettability is governed by both chemical composition and surface structure.[30,31] In the case of the gradient method, the surface morphology of the treated carbon fibers changed little (Fig. 4). Therefore, the increase of wettability was due to the change in the chemical composition. The gradual increase in the hydrophilicity indicated that more and more oxygen-containing functional groups were introduced with increasing distance to the left end. This result proved our previous supposition that the oxidation rate increased gradually during the treatment process of the gradient method. This method may be used to fabricate material surfaces with a surface energy gradient, which could be used in water collection and the directional movement of liquids.[32,33]

According to all of our observations, we supposed the difference between the two methods was follows. As proven by the laser Raman spectra, the surface area of the carbon fibers was occupied by chemically stable surfaces (basal planes) and easily oxidized surfaces [amorphous regions; Fig. 8(a)]. During the surface treatment, these easily oxidized

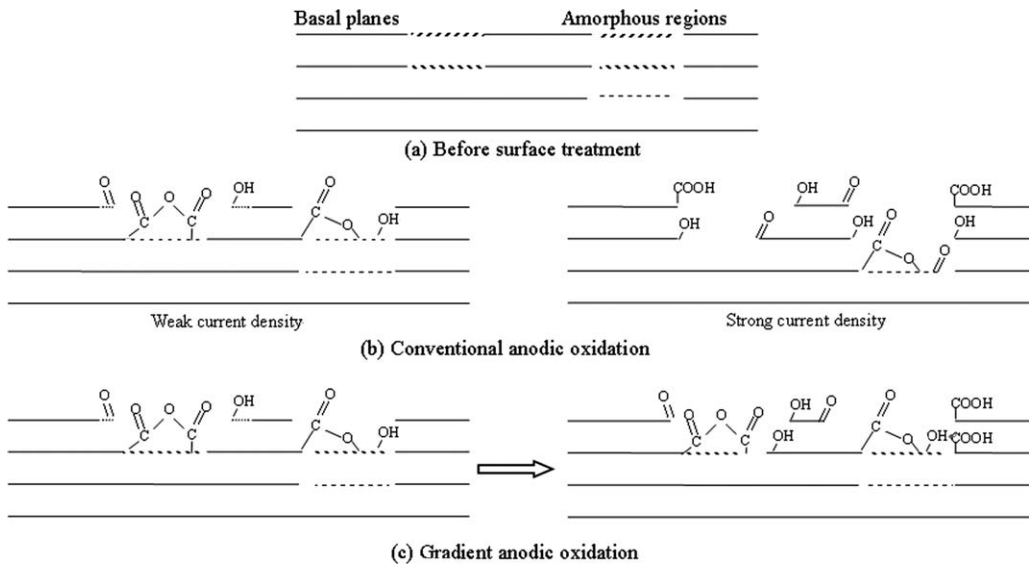



**Figure 8** Schematic models for the mechanism of anodic oxidation of carbon fibers: (a) before surface treatment, (b) conventional anodic oxidation, and (c) gradient anodic oxidation.

surfaces may have been selectively oxidized.[29] In the case of the conventional method, the current density was constant during the treatment. When the current density was weak, the oxidation and etching reactions selectively started to occur in the amorphous regions and crystallite boundaries to form some oxygen-containing functional groups. Therefore, the increases in the NaOH uptake and ILSS values were obvious. However, the increases were not continuous. When the current density was strong, the reaction extended to the crystallite regions, and more oxygen-containing functional groups were formed. As the oxidation and etching rates were fast, some partially oxidized graphitic fragments could be etched and removed as degradation products[29] [Fig. 8(b)]; this resulted in an obvious decrease in the tensile strength (Fig. 2). We also observed that the color of the $NH_4HCO_3$ solution turned dark, and the depth and width of striations present on the treated surfaces increased (Fig. 4). When the oxidation reaction and etching reaction reached a homeostasis, the ILSS values reached a constant. Therefore, it was clear that in the case of the conventional method, when the current density was weak, the increase in the ILSS value was lower. When the current density was strong, the ILSS value had a lower upper limit because of the serious etching reaction.

When the carbon fibers were treated by the gradient method, the current density gradually increased. At the initial stage, the oxidation rate was low, and some oxygen-containing functional groups were formed in the amorphous regions and crystallite boundaries. The graphitic fragments in amorphous regions may have been linked to the basal planes through esterification, anhydridation, and amidization reactions to form a chemical bond.[34,35] As the carbon fibers moved forward, the oxidation and etching rates increased gradually, and more oxygen-containing functional groups were formed. The removal of oxidized graphitic fragments also took place, but it may have been effectively restricted because of the chemical bond between the graphitic fragments and basal planes [Fig. 8(c)]. Therefore, the decrease in the tensile strength was not obvious, and the solution became light brown. The carbon fibers treated by the gradient method had higher ILSS values and NaOH uptake compared to those treated by the conventional method. When the oxidation and etching reaction reached homeostasis, the change of the ILSS values and NaOH uptake was not obvious. Therefore, it was clear that the gradient method was more effective in improving the adhesion between the carbon fibers and the matrix.

## CONCLUSIONS

An improved method for anodic oxidation was proposed. The influence of the gradient method on the tensile strength, NaOH uptake, surface morphology, and ILSS was studied. The results indicate that compared to those treated by the conventional method, the carbon fibers treated by the gradient method showed a more stable tensile strength, larger NaOH uptake, shallower striations, flatter fracture surface of composites, and better ILSS. All of these observations indicate that gradient method was more effective in restricting the etching reaction and improving the adhesion between the carbon fibers and the matrix. The reason may have been that the reaction rate increased gradually during the treatment process of the gradient method. This method may be used to fabricate material surfaces with surface energy gradients, which could be used in water collection and the directional movement of liquids.

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