MECHANICAL AND INTERFACIAL PROPERTIES OF CARBON FIBER MODIFIED BY ELECTROCHEMICAL OXIDATION IN (NH_4HCO_3)/ ($(NH_4)_2C_2O_4$•H_2O AQUEOUS COMPOUND SOLUTION

Yuli Tian, Jie Liu, Jieying Liang, Zhaokun Ma*

Key Laboratory of carbon fiber and functional polymers, Mini stry of Education, Beijing University of Chemical Technology, Chao-Yang District, Beijing 100029, China

Introduction

In recent decades, carbon fibers (CFs) have been widely used as reinforcement in high-performance composite because of its preeminent mechanical strength, low density and thermo and chemical stability. Although CFs has such good performance, its inert surface makes itself only possessing lower interfacial bounding strength with sounding polymer matrix if without surface treatment. This leads to low mechanical properties of the resulting composites. Therefore surface treatment need to be introduced into the manufacture process of carbon fibers to enhance the interfacial bounding strength between carbon fibers and resin matrix, finally improve the properties of CFs/resin composites. The present surface treatment methods include electrochemical oxidation treatment, plasmas treatment, gas/liquid phase oxidation, coating treatment and so on. For being relatively simple to control and allowing the continuous processing of CFs, electrochemical oxidation treatment is the most effective technique with utility values among these treatment methods. However, this technique has a confirmed disadvantage that the treatment process will reduce the tensile strength of CFs while it increases the interfacial bounding strength between CFs and resin matrix [1-2,4].

In this research, ammonium oxalate monohydrate was added to basic ammonium bicarbonate electrolyte aqueous solution. Treating the CFs with the compound electrolyte solution brought about improving the tensile strength and interfacial bounding strength simultaneously. Then the effects of the mixture ratio about compound electrolyte solution on the chemical states and crystallites structure of carbon fibers of carbon fibers surface was analyzed by XPS, XRD and Raman spectra. Furthermore, the relationships between these effects and properties changes of carbon fibers were also discussed

Experimental

An un-sized PAN-based CFs with 3000 filaments per tow was supplied by the Jilin Carbon Co., Ltd. (Jilin, China). The ammonium bicarbonate (NH_4HCO_3) and the ammonium oxalate monohydrate ($(NH_4)_2C_2O_4$•H_2O) served for electrolytes were respectively purchased from Beijing Chemical Reagents Co. (Beijing, China) and Chemical Co., Ltd. (Shantou, China).

Based on previous researches [1~3], we selected 0.6mol/L NH_4HCO_3 aqueous solution and 0.5mol/L $(NH_4)_2C_2O_4$•H_2O aqueous solution as components of the compound electrolyte solution. For the sake of convenience, the above two solutions were named as A solution (NH_4HCO_3) and B solution ($(NH_4)_2C_2O_4$•H_2O) respectively. The samples discussed in this paper were treated at 30℃ by electric current of 1.3mA/cm^2 and treatment time of 104s. According to treated in different volume ratio of A and B solutions, the samples were named Treated I (A to B is 1 to 1), Treated Ⅱ(A to B is 1 to 2) and Treated III (A to B is 2 to 1).

The tensile strength (TS) of CFs was evaluated according to ASTM D4018-99. The specimens were tested by universal testing machine (model 5567, Instron Corp., Canton, MA) at a crosshead speed of 10.0mm/min with gage length of 150mm. 8 specimens were tested for each type of CFs. The interlaminar shear strength (ILSS) of carbon fibers refine plastic was measured by a three point short beam bending test method according to ASTM D2344 in this study. The specimens with the slenderness ratio of 5/1 were tested by universal testing machine (model 5567, Instron Corp., Canton, MA) at a crosshead speed of 2.0 mm/min; and 10 specimens were tested for each type of CFs.The chemical elements and function groups on the surface of the fibers were analyzed by X-ray photoelectron spectroscopy (XPS) which used a Therm VG Escalab 250 XPS operating at the MgKα radiation of 1253.6 eV. The crystallites structures of the fibers were analyzed by a Rigaku D/max 2500 X-Ray diffractometer (XRD) and a Renishaw RM2000 Raman spectrometer (Raman).

Results and Discussion

The performances of CFs before and after treatment in Table 1 indicated that the electrochemical oxidation in compound electrolyte resulted in substantial improvements on both TS and ILSS, especially for Treated I which tensile strength increased by17.7% and ILSS increased by 14.5% simultaneously.

Table 1. The TS and ILSS for the CF before and after electrochemical oxidation treatment (CV is Coefficient of Variance)

Sample	TS		ILSS	
	(Gpa)	CV(%)	(Mpa)	CV(%)
Untreated	2.75	6.7	74.5	1.3
Treated I	3.22	6.0	85.3	1.7
Treated II	2.96	6.2	80.1	1.5
Treated III	2.53	7.5	85.5	1.5

Electrochemical oxidation treatment could introduce active function groups such as oxygen-containing and nitrogen-containing functional groups to increasing the surface polarity and create more sites for hydrogen bonding. The XPS was employed to estimate the elemental contents of carbon (~285eV), oxygen (~533 eV) as well as nitrogen (~400 eV) of carbon fibers surface before and after treatment, the results are shown in Table 2. It was evident that the content of oxygen on the fiber surface increased by about 2~5 percentages through the electrochemical oxidation; the nitrogen elemental content

increased by 0.1~1 percentage except Treated II sample. For Treated I, its oxygen content was 15.11%, improving by 5 percentages; and its nitrogen content only was 1.16%, changing little against untreated sample (0.99%). For Treated III, its oxygen content only improved by 2 percentages, which was the lowest among the three treated samples, however its nitrogen content increased almost twice compared with the untreated CFs. Therefore, the improvement of ILSS obviously causes by interaction effects of oxygen-containing and nitrogen-containing functional groups on carbon fibers surface.

Table 2. Contents of elements on the surface of the CFs

Sample	C_{1s}(%)	O_{1s}(%)	N_{1s}(%)
Untreated	88.89	10.12	0.99
Treated I	83.72	15.11	1.16
Treated II	85.34	13.79	0.86
Treated III	85.29	12.74	1.96

From XRD analysis (Table 3), It was evident that the average interplanar spacing "d" values and crystallite thickness parameter "Lc" values remained approximately after the treatment while the crystallite size parameter "La" decreased by 23%~27%. It is well known that smaller crystallites create additional crystalline impingements and boundaries that could reduce the residual stress caused by anisotropic crystallites near their boundaries. Therefore, additional energy was required for the cracks to grow across those boundaries, and the CFs was strengthened. Furthermore crystallites with smaller size also possessed more carbon atoms at edges, which could be readily converted into active functional groups, resulting in the improvement of ILSS. The tensile strength and ILSS of Treated I and Treated II samples were consistent with the above regularity. But for the sample of Treated III, it was a little different. After treatment, the tensile strength of Treated III decreased because the ordered layer that top of CFs was peeled off exposing the disorder and weak inner structure, which created new cracks and lead to fracture of CFs. In order to confirm this guess, Raman spectra were used to analysis the ordered degree of CFs surface before treatment and after treatment.

Table 3. The "d", "L_a", and "L_c" of CFs

Sample	(1,0,0)		(0,0,2)	
	d(Å)	La(Å)	d(Å)	Lc(Å)
Untreated	2.068	23.39	3.505	14.52
Treated I	2.088	17.12	3.503	14.24
Treated II	2.062	18.03	3.511	14.23
Treated III	2.087	17.85	3.481	14.28

The wave numbers of three bands and the calculated values of "I_D/I_G" acquired from Raman spectra are shown in Table 4. In regard to the ordered degree, the smaller R ($R=I_D/I_G$) value represented that the carbon fibers possessed more ordered structure and vice versa. For Treated I (tensile strength increased by 17.1%) and Treated II (tensile strength increased by 7.5%), their R value both were smaller than that of untreated sample. This indicated that the structurally ordered outside region of CFs after the treatment was improved; and the etching effects was not enough excessive to destroy the surface layer of carbon fibers. However, the R value of Treated III sample (tensile strength decreased by 8%) was higher than untreated sample. It was evident that in-depth oxidation may peel off the ordered crystallites layer; as a result, disorder structure inside the CFs may expose and create new cracks, then reduce the tensile strength of CFs.

Table 4. Wavenumbers of D and G bands and the calculated values of "I_D/I_G" acquired from CFs

Sample	D /cm^{-1}	G/cm^{-1}	A /cm^{-1}	$R=I_D/I_G$
Untreated	1351	1601	1533	2.30
Treated I	1352	1601	1536	2.27
Treated II	1348	1602	1537	2.23
Treated III	1352	1600	1537	2.43

Conclusions

In this study, the tensile strength of CFs increased by 17.1%, and the ILSS improved by 14.5% by electrochemical modification in 0.6mol/L NH_4HCO_3 and 0.5mol/L $(NH_4)_2C_2O_4 \cdot H_2O$ composite aqueous solution. First of all, the contents of oxygen-containing functional groups and nitrogen-containing functional groups increased after electrochemical oxidation treatment, which improves the chemical activity between CFs and resin matrix. Secondly, the crystallites size decreased by 23% ~ 27%, which was benefit to improve tensile strength and interfacial bounding strength. However the tensile strength increasing also lies on the oxidized etching degree beside grain refining effect. Suitable etching can increase the tensile strength; while the excessive etching peels off the ordered region and exposes the inner disorder region, decreases the ordered degree of carbon fiber surface, creates new cracks, and then leads to lower tensile strength.

Acknowledgment. The authors thank the supports from the National Natural Science Foundation of China (Grant No.: 50333070 and 50673011), the National High Technology Research and Development Program of China ("863 Program", Grant No.: 2006AA06Z382), and the National Basic Research Program of China ("973 Program", Grant No.: 2006CB605304).

References

[1] Guo Y, Liu J, Liang J, Surface state of carbon fibers modified by electrochemical oxidation. J. Mater. Sci. Technol 2005; 21: 371-375.
[2] Guo Y, Liu J, Liang J, Effect of electrochemical modification on the surface state of PAN-based carbon fibers. Acta Materiae Compositae Sinica (in Chinese) 2005; 22:6-10.
[3] Liu J, Guo Y, Liang J. DMTA study on electrochemical oxidation effect of carbon fibers surface. Acta Materiae Compositae Sinica (in Chinese) 2004; 21: 40-44.
[4] Montes-Morán M.A., Gauthier W, Martínez-Alonso A., Tascón J.M.D. Mechanical properties of high-strength carbon fibres. Validation of an end-effect model for describing experimental data. Carbon 2004; 42(7): 1275-1278.