

Surface Modification of Carbon Fiber by Redox-Induced Graft Polymerization of Acrylic Acid

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ABSTRACT: Carbon fibers were modified by graft polymerization with acrylic acid (AA) using $\text{KMnO}_4/\text{H}_2\text{SO}_4$ redox-induced system. The carbon fibers were characterized using scanning electron microscopy (SEM), Fourier transform infrared spectroscopy, and X-ray photoelectron spectroscopy. After grafting, the absorbability of treated fibers might be enhanced and more pieces of tiny fragments stuck to the fiber surface. It was confirmed that grafting AA led to a remarkable increase in oxygen-containing functional groups of fiber surface. An about twofold

increase in retained surface carboxylic acid groups occurred. The adhesion between carbon fiber and epoxy matrix was inspected by interlaminar shear strength and SEM. It was noted that the functionalized grafting coating of fiber surface gave rise to a strong interfacial bond, with little debonding. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 1887–1892, 2008

Key words: fibers; composites; surfaces; interfaces; graft copolymers

INTRODUCTION

The unique combination of physical and chemical properties of carbon fibers has led to their widespread application in different fields of industry, machine, and sport.^{1,2} Over the last four decades, carbon fibers have emerged as the main reinforcement filler for high-performance polymer matrix composites.³ However, the smooth and inertness characteristics of carbon fiber surface usually result in inferior wettability and weak adhesion between the fibers and resin, which implies that an effective fiber-matrix adhesion should not be expected. The several methods developed for the surface modification of carbon fibers include thermal treatment,⁴ wet chemical or electrochemical oxidation,^{5,6} plasma treatment,⁷ gas-phase oxidation,¹ ultrasonic bombardment,⁸ rare earth treatment,⁹ coating treatment,¹⁰ irradiation treatment,¹¹ and so on. However, these methods have the drawback that it is difficult to use for applications because of its higher facilities, high energy consumption, environmental pollution, and high maintenance cost, in spite of improved interfacial adhesion force of the final composites.

Acrylic acid (AA), which is a vinyl monomer, possesses some unique characteristics and the polymers derived from it find many commercial applications. Furthermore, grafting of AA onto different types of

natural polymers is reported to have wide range of application in various fields.^{12–14} For example, AA was grafted onto guar gum initiated by vanadium-mercaptoposuccinic acid redox pair, onto the linen surface induced by DBD in air and onto macroporous polyacrylamide gel initiated by potassium diperiodatocuprate. Therefore, an attempt has been made to graft AA onto carbon fiber surface by the redox-induced reaction of $\text{KMnO}_4/\text{H}_2\text{SO}_4$ to improve the physicochemical properties of carbon fiber surface. In addition, this type of initiator was convenient, low-cost and environment-friendly, compared with other initiator systems.

In this work, carbon fibers were modified by the free-radical polymerization method and AA was grafted onto carbon fiber surface. The initiator was produced by the redox-induced reaction of $\text{KMnO}_4/\text{H}_2\text{SO}_4$. On the basis of the measurement and analysis of the scanning electron microscopy (SEM) images and Fourier transform infrared (FTIR) spectrum results, the surface physical and chemical characteristics of modified carbon fibers were characterized, and the composition changes of the fiber surface were analyzed by X-ray photoelectron spectrometry (XPS). The effectiveness of improving the interfacial adhesion of composites was evaluated by interlaminar shear strength (ILSS) and SEM.

EXPERIMENTAL

Materials

The reactants, AA, sulfuric acid with the concentration of 98% and potassium permanganate were

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obtained from Tianjin Chemical Company. Solvents and reagents were reagent-grade. AA was not purified before the use as reactant. The polyacrylonitrile-based continuous carbon fibers investigated in current studies were provided by Institute of Coal Chemistry, Chinese Academy of Sciences. The linear mass is $0.0638 \text{ g} \cdot \text{m}^{-1}$, the equivalent diameter of fiber is $7.6 \text{ } \mu\text{m}$, and a fiber bundle consists of 1×10^3 monofilaments.

The carbon fibers were washed with acetone for 12 h, and then vacuum dried. Dry carbon fibers ($\sim 50 \text{ g}$) were immersed in mixed solution containing sulfuric acid and AA solution. After 10 min, the reaction was initiated by addition of KMnO_4 solution. The KMnO_4 solution was put in mixed solution dropwise and slowly and the mixed solution was kept colorless during the addition of KMnO_4 . The mixed solution system was then heated for 4 h. The grafted carbon fibers were taken out and carefully washed with warm water removing any remaining homopolymer. The washed carbon fibers then were vacuum dried at 80°C for 6 h.

Epoxy resin, curing agent, and accelerating agent were mixed at 50°C and the mixed epoxy resin was coated onto the unidirectional fiber bundle to manufacture prepreg in the manual way. And then the prepreg was paid unidirectionally into a mold at 60°C . The mold was closed and operated according to the following technique. The prepreg was pressed and cured under 5 MPa pressure for 2 h at 90°C , under 10 MPa pressure for 2 h at 120°C , and under 10 MPa pressure for 4 h at 160°C by hot-press machine and we could obtain composites with fiber mass fraction of $64 (\pm 2\%)$.

Measurements

The FTIR spectrum of the carbon fiber was obtained from 4000 to 400 cm^{-1} using a Nexus 670 Fourier Transform Infrared Spectrometer. Pellets in KBr with a sample concentration of $5 \times 10^{-1} \text{ wt } \%$, weighing 110 mg and 12 mm in diameter, were used. The spectra shown were the result of coadding 200 interferograms obtained at a resolution of 4 cm^{-1} and normalized to 1 mg cm^{-2} . Surface characterization was examined using FEI SIRION 200 SEM. The carbon fiber and composite fracture samples for SEM, 2 cm in length, were stuck on the aluminum plate. All samples on plate were gold coated using a sputter coater prior to examination. Electron Spectroscopy for Chemical Analysis (ESCA) (Lab220i-XL made in V. G. Scientific Company, U.K. and equipped with a $\text{Al K}\alpha$ (1.25 keV) radiation source generated at 12 kV and 20 mA) was used to determine composition of fiber surface. The C_{1s} peak of each carbon fiber sample was analyzed using a peak synthesis procedure, which combines Gaussian and Lorentzian functions.

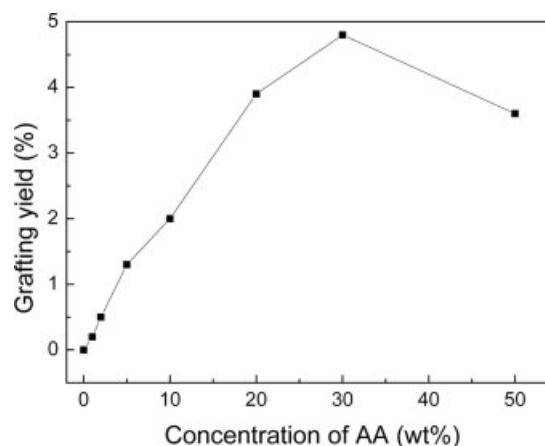


Figure 1 Effect of AA concentration on grafting yield, reaction conditions: KMnO_4 concentration $0.076 \text{ wt } \%$, H_2SO_4 concentration $0.2 \text{ wt } \%$, and 60°C .

The intensity contribution of each functional component peak was estimated by a computer simulation.¹⁵ The ILSS of composites was measured by short-beam bending test according to ASTM D-2344 using an Instron 1125. A span-to-depth ratio of $5 : 1$, cross-head speed of $2 \text{ mm} \cdot \text{min}^{-1}$, and sample thickness of 2 mm were used. Flexural properties of composites were determined according to ASTM D-790 ($L/d = 15$; cross-head speed = $1.5 \text{ mm} \cdot \text{min}^{-1}$). Tensile tests were carried out, following ASTM standard D3039-94 at a cross-head speed $2 \text{ mm} \cdot \text{min}^{-1}$. More than eight specimens were tested for each of the composites studied and the average value was taken in the present work studied. The grafting yield (degree of grafting) was calculated using the eq. (1):

$$\text{Degree of grafting (\%)} = [(W_g - W_0)/W_0] \times 100 \quad (1)$$

where W_0 denotes the weight of the blank carbon fiber and W_g presents the weight of the fiber after treatments.

RESULTS AND DISCUSSION

Effect of grafting conditions

Figure 1 shows the effect of AA concentration on grafting degree. It was clearly indicated that the grafting yield of AA increased as the concentration of AA increased under low concentration condition and reached maximum at AA concentration of about $30 \text{ wt } \%$. Nevertheless, the grafting yield of AA decreased as the AA concentration exceeded $30 \text{ wt } \%$ indicating that the copolymerization of AA did harm to the grafting between carbon fiber and AA. The graft degree of AA onto carbon fibers increased slightly with increasing the reaction temperature from 20 to 90°C . However, the temperatures above

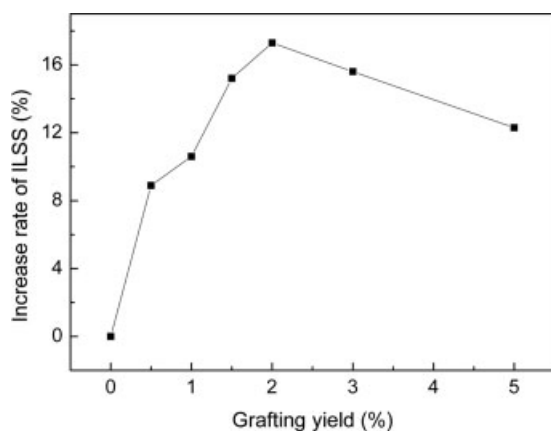


Figure 2 Effect of grafting yield on increase rate of ILSS, reaction conditions: KMnO_4 concentration 0.076 wt %, H_2SO_4 concentration 0.2 wt %, and 60°C .

60°C were considered inappropriate for AA grafting to carbon fiber due to the increasing copolymerization of AA. The ILSS of grafted carbon fiber composites increased with increasing KMnO_4 and H_2SO_4 concentrations leveling at about 0.076 and 0.2 wt %, respectively. The increase rate of ILSS of treated carbon fiber composites increased nearly linearly with increasing in grafting yield up to 2% and then started to decline at grafting yield 3–5% (Fig. 2). This may be due to the fact that the AA homopolymer stuck onto fiber surface and was not removed during washing process. Therefore, the optimum reaction conditions of 60°C temperature and 10 wt % AA concentration were selected for further experiments.

Surface topography of carbon fibers

The SEM images of untreated and AA treated carbon fibers are shown in Figure 3(a,b), respectively. Remarkable differences in micrographs can be observed on untreated and treated carbon fibers. It was shown that the surface of untreated carbon fiber seemed to be relatively smooth and a few narrow grooves or channels that parallel distributed along with the longitudinal direction of fiber were characteristic of the surface.¹⁶ After grafting, many acrylic copolymer pieces of tiny fragments stuck to the fiber surface, which suggested that the absorbability of treated fibers might be enhanced to some extent. Therefore, interfacial adhesion between grafted fibers and matrix resin may be enhanced by increasing the surface activity which may provide more effective wetting between the fiber and the matrix.

Analysis of FTIR spectroscopy

The FTIR spectra of untreated and treated carbon fibers are shown in Figure 4. The spectra indicated

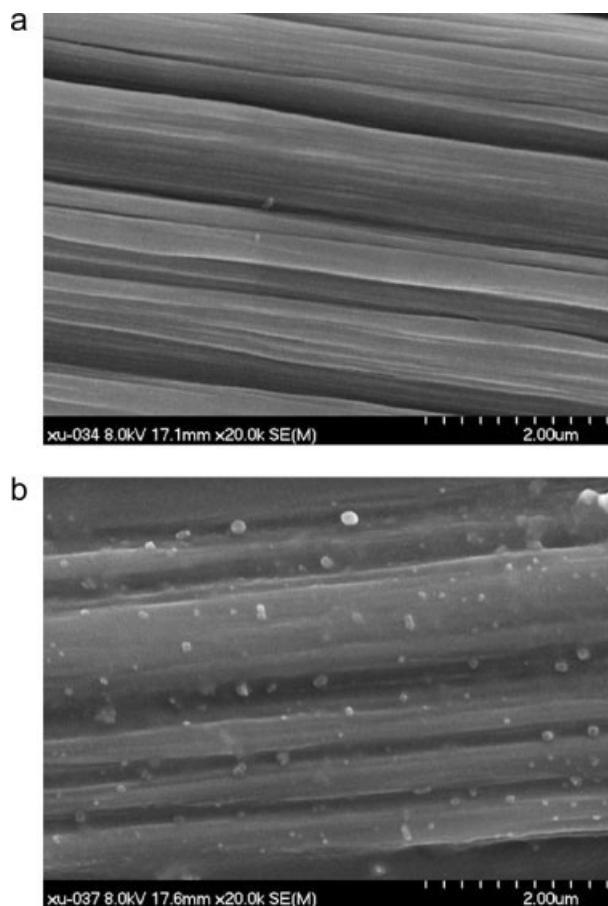


Figure 3 SEM micrographs of carbon fiber surface (a) untreated; (b) treated.

that there were no significant differences between fresh and treated fibers in the major bands. The 3203, 1682, and 1450 cm^{-1} bands in Figure 4 were the characteristic absorption of carboxyl in carbon

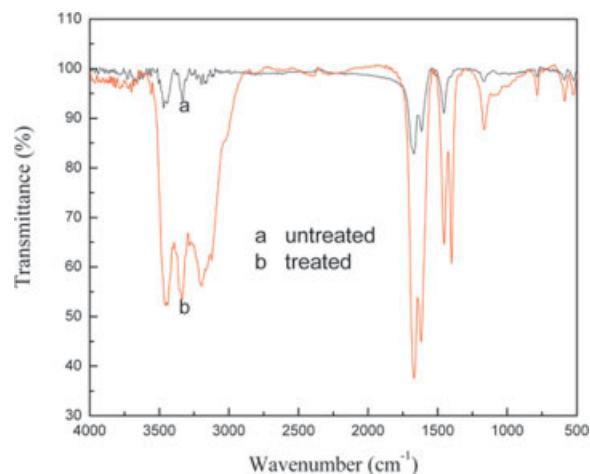


Figure 4 FTIR spectra of untreated and treated carbon fibers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
Variation of Surface Composition of the Carbon Fibers Before and After Treatment

	C (%)	O (%)	O/C	Peak I	Peak II	Peak III	Peak IV
				C—C	C—OH/C—O—C	C=O	COOR/COOH
Untreated	87.39	12.61	0.14	49.7	31.9	12.9	5.5
Treated	70.93	29.07	0.41	39.1	25.4	21.4	14.1

fiber surface, and the 3340 cm^{-1} was the characteristic absorption of hydroxyl. The peaks at 3446 and 1620 cm^{-1} were due to the ether group of fiber surface.^{17–19} The only exception was the appearance of a methane band (1407 cm^{-1}) after grafting treatment, indicating AA was grafted on carbon fiber surface. However, there were noticeable differences in peak intensities, which indicated changes in the amount or concentration. After grafting, almost all the bands ascribed to the carboxyl group became strong and broadened. As indicated by the following elemental analysis (Table I), the carboxyl and ester content of fiber surface significantly increased after treatment and this fact was reflected by the increase in intensity of the O—H and C=O stretching bands in the related spectra.

Analysis of XPS

XPS is a very useful technique in the determination of chemical composition and functional groups of fiber surface and wide scan spectra in the binding energy range 0–1350 eV were obtained. The XPS spectra show distinct carbon and oxygen peaks, representing the major constituents of the carbon fibers investigated. The surface composition of untreated and treated carbon fibers is given in Table I. The amount of surface oxygen increased and the amount of surface carbon decreased after grafting. An about twofold increase in O/C occurred after grafting.

Figure 5(a,b) present C_{1s} envelopes for the untreated and treated fibers, respectively. Compared with the untreated carbon fibers, the component of treated carbon peak on the high energy side was well developed, which indicated that the surface of carbon fibers was distinctly aliphatic, and that on the fiber surface, lots of functional groups, such as carboxyl, carbonyl, and ester groups, increased. The carbon peaks, which were observed in the binding energy range from 280 to 295 eV, can be attributed to several carbon-based surface functional groups that have different binding energies.

The narrow scan spectra of the C_{1s} region deconvoluted into surface functional group contributions are shown in Figure 5(a,b) for the untreated and treated fibers, respectively. The percent contribution of each curve fit photopeak was estimated from

these curve fit C_{1s} photopeaks and is listed in Table I. Deconvolution of the C_{1s} spectra of carbon fibers gave four peaks designated as peak I (at 284.7–284.9 eV assigned to graphitic carbon), peak II (at 285.5–285.8 eV, carbon bonded phenolic or alcoholic hydroxyls or ether oxygen), peak III (at 286.8–286.9 eV, carbonyl carbon in ketones and quinines), and peak IV (at 288.7–289.0 eV, carboxyl functions or ester groups).^{9,20,21}

It was clear that the carbonyl in ketones and quinines (C=O) and carboxyl or ester (COOH/COOR)

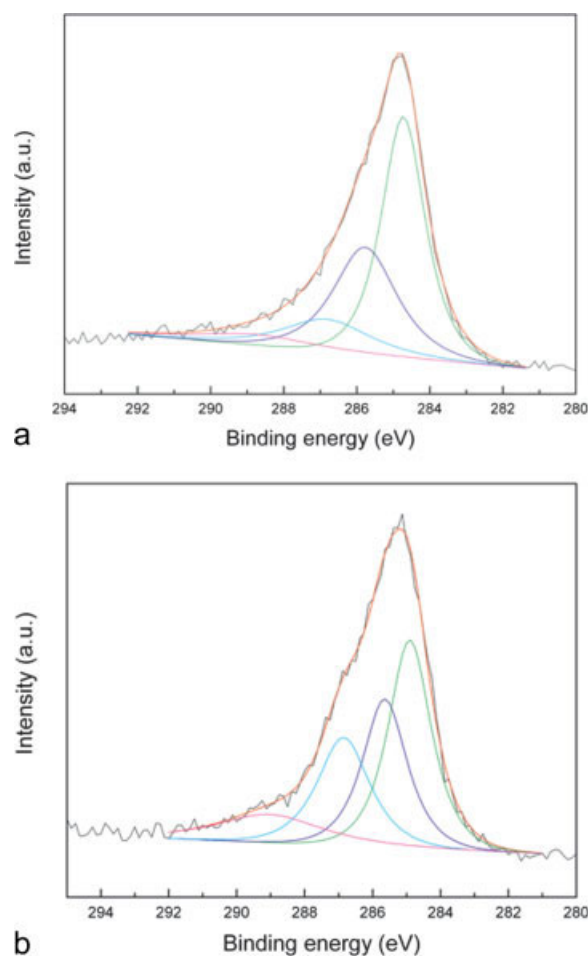


Figure 5 Resolved C_{1s} XPS spectra of carbon fibers (a) untreated; (b) treated. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

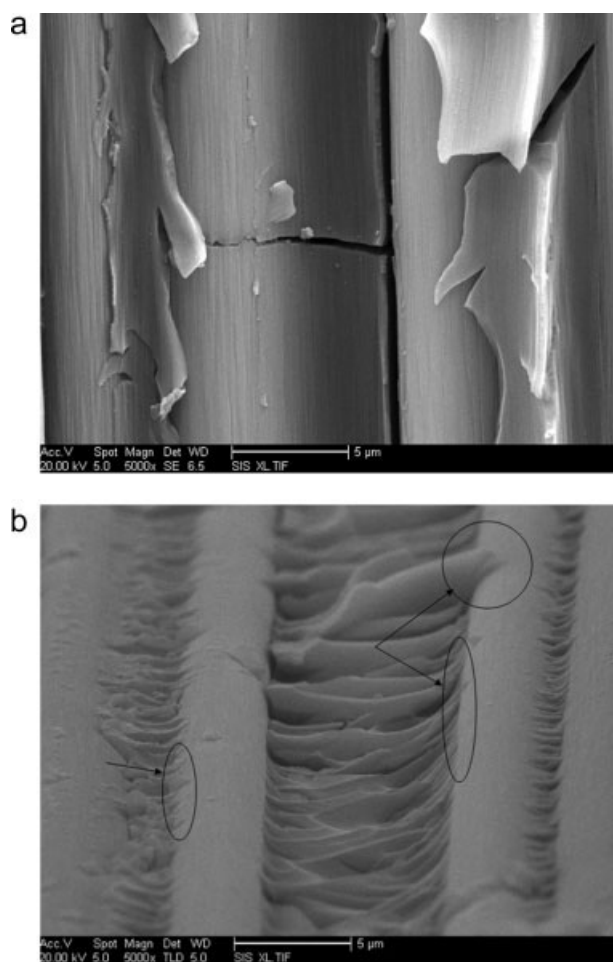


Figure 6 SEM micrographs of fractured surface of composites (a) untreated; (b) treated.

functional groups increased, and the graphitic carbon (C—C) and phenolic or alcoholic hydroxyl or ether oxygen (C—OH/C—O—C) functional groups decreased after treatment. The decrease in concentration of hydroxyl or ether groups would benefit the retained COOH functionality. The percentage of AA grafted to the carbon fiber was about 10%, according to the grafting yield of 2% onto carbon fiber surface. The residual AA solution could be used circularly.

Interfacial properties of composites

Mechanical test under interlaminar shear load indicated that the ILSS (90.6 MPa) for composites reinforced by grafted fibers was 17.3% greater than the ILSS (77.3 MPa) for composites reinforced by untreated fibers. These results were in fairly good agreement with the SEM images of fractured composite surface in Figure 6.

Figure 6(a,b) correspond to the fracture micrographs of untreated and treated fiber/epoxy composites, respectively. It was easily recognized in Figure 6(a) that untreated carbon fibers performed very

poor interface bonding with epoxy matrix. Interfacial debonding was obviously observed and no resin matrix adhered on the fiber surface. However, after grafting treatment shown in Figure 6(b), the interfacial bonding of composites appeared to have been obviously improved. The fibers were engulfed by matrix, which allowed the matrix to secure more bonds and better adhesive force between two phases. The interlocking of fiber-matrix bonding has been shown by the arrows and loops in Figure 6(b). The increase in carboxyl group amount and absorbability on fiber surface may be responsible for these results.²² The flexural strength and tensile strength of carbon fiber/epoxy composites were improved due to the increased interfacial properties. The average flexural and tensile strength of treated carbon fiber-reinforced composites were 1436 ± 62 MPa and 1622 ± 31 MPa, and the average flexural and tensile strength of untreated carbon fiber-reinforced composites were 1298 ± 58 MPa and 1586 ± 26 MPa, respectively. It is indicated that the grafting treatment by redox-induced reaction is an effective method for improving the interfacial adhesion of carbon fiber/epoxy composites.

CONCLUSIONS

Graft polymerization of AA onto the carbon fiber surface induced by $\text{KMnO}_4/\text{H}_2\text{SO}_4$ redox-induced reaction was found to be an efficient and convenient method for modifying the physicochemical properties of carbon fibers and improving the interfacial adhesion of composites.

Compared with the original carbon fiber, many acrylic copolymer pieces of tiny fragments stuck to the grafted fiber surface and an about twofold increase in O/C occurred. The carbonyl and carboxyl or ester functional groups increased, and the graphitic carbon and hydroxyl or ether functional groups decreased after treatment. After grafting, the fibers were engulfed by matrix, the strong interlocking of fiber-matrix bonding could be observed by SEM and the ILSS value of composites was enhanced by 17.3%.

References

- Xuli, F.; Weiming, L.; Chung, D. D. L. *Carbon* 1998, 36, 1337.
- Jae, W. C.; Jun, S. C.; Young, S. Y. *J Appl Polym Sci* 2002, 83, 2447.
- George, C. J.; Michael, S.; John, F. F.; Srdan, S. *J Appl Polym Sci* 2006, 101, 1477.
- Bismarck, A.; Wuertz, C.; Springer, J. *Carbon* 1999, 37, 1019.
- Fukunaga, A.; Ueda, S. *Compos Sci Technol* 2000, 60, 249.
- Sanchez-Adsuar, M. S.; Linares-Solano, A.; Cazorla-Amoros, D. *J Appl Polym Sci* 2003, 90, 2676.
- Montes-Moran, M. A.; Martinez-Alonso, A.; Tascon, J. M. D. *Compos A* 2001, 32, 361.

8. Huang, Y. D.; Liu, L.; Qiu, J. H.; Shao, L. *Compos Sci Technol* 2002, 62, 2153.
9. Xu, Z. W.; Huang, Y. D.; Song, Y. J.; Zhang, C. H. *J Rare Earth* 2007, 25, 462.
10. Fabio, L. B.; Bluma, G. S.; Marianna, G.; Jose, A. C. *J Appl Polym Sci* 1999, 74, 1424.
11. Xu, Z. W.; Huang, Y. D.; Zhang, C. H.; Liu, L.; Zhang, Y. H.; Wang, L. *Compos Sci Technol* 2007, 67, 3261.
12. Pandey, P. K.; Srivastava, A.; Tripathy, J.; Behari, K. *Carbohydr Polym* 2006, 65, 414.
13. Ghosh, P.; Das, D. *Eur Polym J* 2000, 36, 2505.
14. Ren, C. S.; Wang, D. Z.; Wang, Y. N. *Surf Coat Technol* 2006, 201, 2867.
15. Gardner, S. D.; He, G.; Pittman, C. U. *Carbon* 1996, 34, 1221.
16. Nursel, D.; Wightman, J. P. *Carbon* 1999, 37, 1105.
17. Villar-Rodil, S.; Paredes, J. I.; Martinez-Alonso, A. *Chem Mater* 2001, 13, 4297.
18. Yun-Hua, L.; Mao-Sheng, Z.; Wen-Hai, Z. *J Appl Polym Sci* 2006, 102, 646.
19. Ayustede, J.; Gandhi, M.; Sukigara, S.; Ye, H.; Hsu, C. *Biomacromolecules* 2006, 7, 208.
20. Park, S.; Kim, B. *Mater Sci Eng A* 2005, 408, 269.
21. Wan, Y. Z.; Wang, Y. L.; Li, Q. Y.; Dong, X. H. *J Appl Polym Sci* 2001, 80, 367.
22. Guduri, B. R.; Luyt, A. S. *J Appl Polym Sci* 2006, 101, 3529.