Effect of MWCNTs Irradiation Grafting Treatment on the Surface Properties of PBO Fiber

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ABSTRACT: The aim of this article is improved the surface properties of Poly[*p*-phenylenebenzobisoxazole] (PBO) fiber with epichlorohydrin hybridized carboxylic multi walled carbon nanotubes (MWCNTs-Ecp) grafting by using γ-ray irradiation technology. The surface chemical properties, the surface morphology, the amount of the grafted MWCNTs on PBO fiber and the surface free energy of PBO fibers have been analyzed. The results show that MWCNTs-Ecp have been grafted on the surface of PBO fiber by γ-ray irradiation treatment. The surface chemical inertness and the surface smoothness of PBO fiber are significantly improved by grafting MWCNTs-Ecp chains, the amount of the grafted MWCNTs on PBO fiber is about 11.9%, and the surface free energy of PBO fiber has an increase of 42.6% by generating some active groups such as —COOH, —OH, and —C—Cl on the surface of PBO fiber. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 3455–3459, 2011

Key words: MWCNTs; PBO fiber; irradiation grafting; surface properties

INTRODUCTION

Carbon nanotubes (CNTs) have attracted a great deal of scientific interest as advanced materials due to its high modulus and tensile strength.[1–3] Both multiwalled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs) have numerous potential applications. In particular, a number of efforts have been made to develop high performance polymeric materials based on the MWCNTs with the benefit of nanotechnology.[4–6]

PBO fiber has high tensile strength and high tensile modulus with a low density, which results in exceptionally high specific mechanical properties.[7] Therefore, PBO fiber is a good candidate as the reinforcement in advanced polymer composites. However, the adhesion between PBO fiber and resin matrix in composite is very poor due to the surface of PBO fiber is relatively smooth and chemically inactive.[8] It is widely known that the interface property influences the mechanical behavior of fiber reinforced composites. Theoretical and experimental studies have shown that the effectiveness of the reinforcement fiber is dependent on the efficiency of stress transfer between the matrix and the fibers.[9] Poor interface adhesion property of PBO fiber composites results in limiting application. Therefore, several surface modification processes have been proposed for various fibers, including plasma, electron beam, chemicals, electrolytic oxidation, γ-ray irradiation, and coupling agents.[10]

In recent years, γ-ray irradiation technology is being extensively investigated as a means of altering surface properties of materials for its unique advantages, such as high efficiency, save energy and protects the environment. The surface performance of PBO fiber can be improved by grafting epichlorohydrin and the interface shear strengths (IFSS) of the PBO fiber/epoxy composite increased effectively by mutual radiation grafting method.[11] Therefore, γ-ray irradiation technology can be used in the applications for fiber modification.

In this study, MWCNTs-Ecp are used as grating mediators, PBO fiber is irradiated by mutual radiation grafting method with a solution of MWCNTs–Ecp and acetone. The effect of MWCNTs–Ecp irradiation treatment on the surface properties of PBO fiber are investigated by X-ray photoelectron spectroscopy (XPS), Thermogravimetric analysis (TGA), surface free energy analysis, atom force microscopy (AFM) and scanning electron microscopy (SEM).

EXPERIMENTS

Materials

The PBO fiber is provided by Harbin Institute of Technology. Its average diameter is 13.5 μm. The

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measured tensile strength and module are about 4.5 GPa and 200 GPa, respectively. Epichlorohydrin, analytically pure, is provided by Tianjin Tiantai Fine Chemicals Co. Ltd. Carboxylic multi walled carbon nanotubes (MWCNTs-COOH) is provided by Shenzhen Nanotech Port Co. Ltd, and carboxyl ratio is 2.5 wt % (The rate of surface carbon atom: 8–14 mol %). Acetone, analytically pure, is provided by Tianjin Chemical Reagent Plant.

Preparation of hybridization MWCNTS solution for grafting medium

MWCNTs-COOH and epichlorohydrin were mixed according to the ratio of 1 : 70 by weight. The mixture was dispersed by using ultrasonic for 2 h at 25°C. The hybridization reaction between MWCNTs-COOH and epichlorohydrin was carried out under ultrasonic for 5 h at 120°C, and the product of hybridization reaction of MWCNTs-COOH and epichlorohydrin (denoted as MWCNTs-Ecp) are obtained. Then the MWCNTs-Ecp were thoroughly washed with acetone at least four times and dried in vacuum oven at 60°C in vacuum oven for 2 h. The dried MWCNTs-Ecp was mixed with acetone according to the ratio of 1 : 100 by weight under ultrasonic for 4 h at 25°C, and a homogeneous solution of MWCNTs-Ecp was obtained for grafting medium.

γ-ray irradiation treatment

PBO fiber was washed repeatedly with acetone for 72 h, and then dried in vacuum oven at 60°C for 3 h. Some of the fibers served as the surface modification, and some served as control fiber samples.

PBO fiber was irradiated in mutual radiation grafting method with the solusion of MWCNTs-Ecp by using ^{60}Co source of energy 1.17–1.33 MeV and intensity 1.5 × 104 Ci. The irradiation dose rate was 6.0 kGy h^{-1} and the total irradiation dose was 60 kGy. Before irradiation treatment, the dried fiber was placed in a glass vessel, from which the air was purged, and then the solution of MWCNTs-Ecp as grafting medium was introduced into the glass vessel to immerse the fiber. After irradiation treatment, the fiber was removed from the grafting solution, washed repeatedly with acetone for 48 h, and then dried in vacuum oven at 60°C for 4 h.

Analysis of fiber surface chemical composition and structure

Surface chemical analysis of PBO fiber before and after irradiation treatment were carried out by X-ray photoelectron spectroscopy (XPS) on a PHI5700 X-ray photoelectron spectrometer using the monochromatized Al K-X-ray source (1486.6 eV photons) at a constant dwell time of 100 ms and a pass energy of 40 eV. The anode voltage was 15 kV and the anode current was 10 mA. The pressure in the analysis chamber was maintained at 5.0×10^{-8} Torr or lower during each measurement. Different functional groups were evaluated by curve fitting of C1s spectra using Caussian-Lorentzian distribution.

Analysis of microscopic surface topography

Analysis of microscopic surface topography of PBO fibers was carried out with a Solver P47-Atomic Force Microscopy (AFM) (Russian NT-MDT company) and scanning electron microscopy (SEM) (*S*-4800, Hitachi, Japan). The mean roughness was calculated by eq. (1).[12]

$$R_{mean} = \frac{1}{N_x N_y} \sum_{i=1}^{Nx} \sum_{j=1}^{Ny} Z_{ij} \tag{1}$$

where, R_{mean} is the mean roughness; N_x and N_y are the point numbers in the direction of X coordinate and Y coordinate, respectively; Z_{ij} is the height at the ij point.

Analysis of grafting amount of MWCNTS on fiber surface

Thermogravimetric analysis (TGA) were performed with a DuPont Instruments TGA 2950 thermobalance, controlled by a TC10A microprocessor. Samples were heated at 10°C/min under a nitrogen flow of 40 mL/min.

Contact angle measurement and surface free energy calculation

The contact angle (θ) is an important factor in the analysis of surface free energy (γ_f^T), and its dispersive component (γ_f^d) and the polar component (γ_f^p) of fiber. We measured the contact angles on PBO fibers using both for second vaporized water ($\sigma^d = 21.8$, $\sigma^p = 51.0$) and normal octane ($\sigma^d = 21.8$, $\sigma^p = 0$) by Dcat21 surface/interfacial tension apparatus from Germany Dataphysics Company. The dynamic contact angle was used to calculate the fiber surface free energy according to Kealble eq. (2).[13]

$$\begin{aligned} \gamma_1^T(1+\cos\theta) &= 2(\gamma_1^p\gamma_s^p)^{1/2} + 2(\gamma_1^d\gamma_s^d)^{1/2} \\ \gamma_f^T &= \gamma_f^d + \gamma_f^p \end{aligned} \tag{2}$$

Where γ_f^T, γ_f^d, and γ_f^p are the total surface free energy, dispersive component energy, and polar component energy of the fiber, respectively. γ_1^T, γ_1^d and γ_1^p are the surface tension of an immersion

TABLE I
Element Content of PBO Fiber Surface Before and After MWCNTs Grafting (wt %)

Element	Control PBO fiber	MWCNTs-Ecp-g-PBO fiber
C	77.98	84.98
O	15.72	9.12
N	6.31	5.70
Cl	0	0.20

liquid and its dispersive and polar component, respectively.

RESULTS AND DISCUSSIONS

The surface atom compositions of the control and the irradiated PBO fibers by XPS are given in Table I. The control samples represented the results from the initial cleaned and vacuum oven-dried fiber samples, without any treatment. Noticeable changes are observed with the surface atom compositions, carbon element content of the irradiated fiber has increased by of 8.9% comparing with the control fiber, and polar chlorine element appears at the meantime.

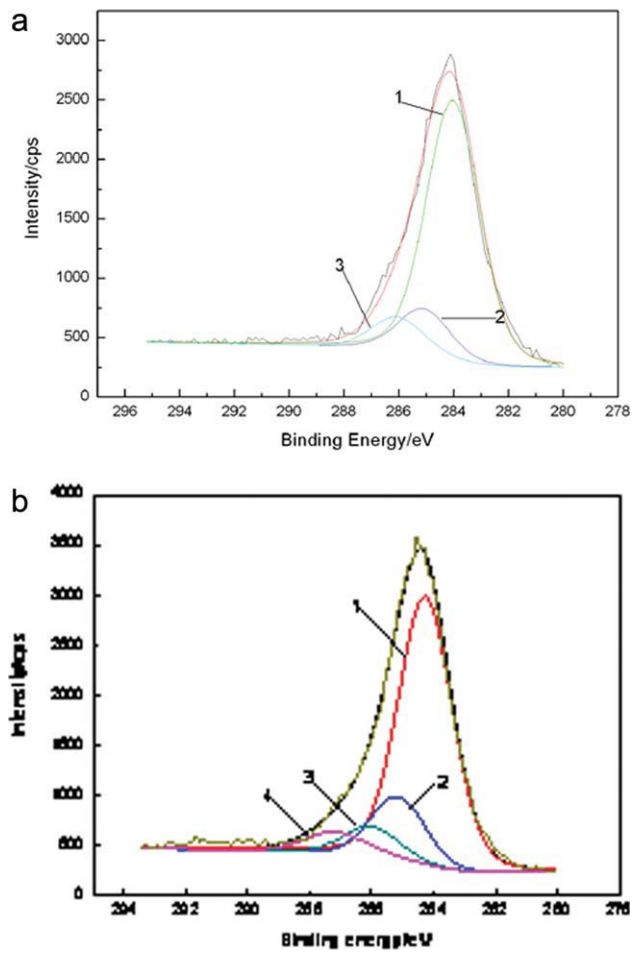

Figure 1 (a) XPS C1s spectra of control PBO fiber: (b) XPS C1s spectra of PBO fiber after MWCNTs grafting. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

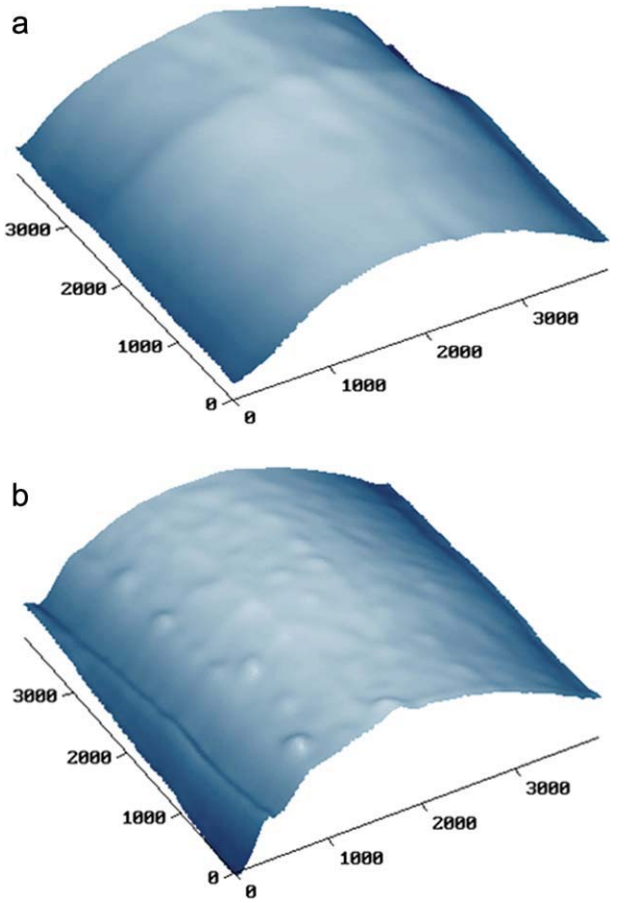

Figure 2 (a) AFM topographies of control PBO fiber: (b) AFM topographies of PBO fiber after MWCNTs grafting. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

XPS wide-scan C1s spectra of PBO fibers before and after irradiation are shown in Figure 1. As shown in Figure 1a, there are the characteristic group peaks of —C—C—C—, C—O— and —C=N—, these functional groups represent the surface chemistry structure of control PBO fiber. For irradiated PBO fiber in Figure 1(b), there are two new characteristic group peaks of —C—Cl and —COOH which are on the surface of MWCNTs-Ecp appeared in the C1s spectra besides the characteristic group peaks of —C—C—C—, —C—O—, —C—N—. These five group peaks represents the major surface constitute of the irradiated PBO fiber. No —COOH and —C—Cl group peak is detected from the spectra [Fig. 1(a)] on the surface of control PBO fiber. The reason may be that in the procedure of irradiation, the grafting reactions between MWCNTs-Ecp and the PBO fiber were produced by high irradiation energy, and MWCNTs-Ecp were grafted on the surface of PBO fiber, and the groups of —COOH, —OH, and —C—Cl on the surface of MWCNTs-Ecp are transferred to the

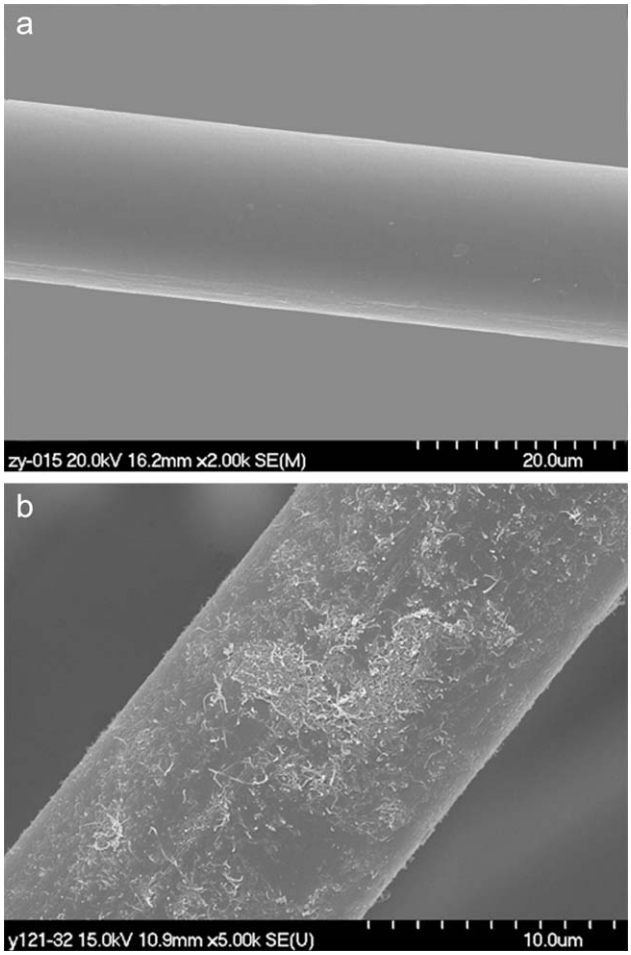

Figure 3 (a) SEM micrographs of control PBO fiber: (b) SEM micrographs of PBO fiber after MWCNTs grafting.

surface of PBO fiber with the grafting reactions between PBO fiber and MWCNTs-Ecp.

The effect of MWCNTs-Ecp grafting on the surface topography of PBO fiber is analyzed by AFM as shown in Figure 2 and SEM as shown in Figure 3. The control PBO fiber is analyzed, too. It can be found that the surface smoothness of PBO fiber has been obviously changed by grafting reactions between MWCNTs-Ecp and PBO fiber, the surface of irradiated fiber by grafting MWCNTs-Ecp becomes rougher than the control fiber, and the sizing change of the surface topography is on a microscopic scale. The roughness analysis of the irradiated and control

TABLE II
Surface Roughness of PBO Fibers Before and After MWCNTs Grafting

	Control PBO fiber	MWCNTs-Ecp-g-PBO fiber
Mean roughnees (nm)	15	60
Maximum roughnees (nm)	20	100
Area (μm^2)	16	16

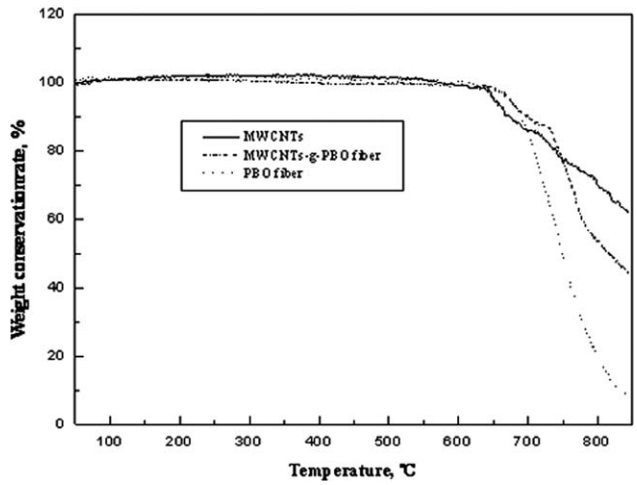

Figure 4 TGA curves of MWCNTs-Ecp, control PBO fiber and MWCNTs-g-PBO fiber.

fibers from AFM images is summarized in Table II. The result indicates that the mean surface roughness value is only 15–20 nm for control PBO fiber, but for MWCNTs-Ecp-g-PBO fiber, it is become about 60–100 nm. The surface roughness of MWCNTs-Ecp -g-PBO fiber becomes fivefold of the control fiber, and the size of the mean surface roughness value is correspondence with the MWCNTs. It is further indicated that MWCNTs-Ecp have been grafted on the surface of PBO fiber by γ-ray irradiation treatment. The result indicated that MWCNTs-Ecp have been grafted to PBO fiber, and grown uniformly and densely on the surface of the fiber.

The increase of surface roughness of PBO fiber makes to the increase of the special surface area of PBO fiber, which may provide more contact points and more mechanical interlocking between the fiber and matrix. It will enhance the interfacial adhesion between the irradiated PBO fiber and matrix.

Thermal decomposition is a convincing method to determine the relative amount of grafted CNTs on polymer materials. As shown in Figure 4, the weight losses of all three materials at 650°C were not obvious, but a sever thermal decomposition of MWCNTs-Ecp appeared at the range of 650–684°C, then the decomposition rate of MWCNTs-Ecp was not changed from 684°C to 715°C. This is because that the degradation at 650°C was for molecule chains of epichlorohydrin on MWCNTs-Ecp and it is ended at 684°C, the degradation of MWCNTs started after 715°C. The weight conservation rate of PBO fiber and PBO fiber irradiated in the solution of MWCNTs-Ecp at 715°C were 88.0 wt % and 76.1 wt %, respectively. The amount of grafted MWCNTs is about 11.9 wt % according to the weight loss factor.

The contact angles of second vaporized water and normal octane on PBO fibers have been measured. It is obvious indicated that the contact angles of both

TABLE III
Surface Energy of PBO Fiber Before and After MWCNTs Grafting

Surface free energy, mJ m^{-2}	γ_f^d	γ_f^p	γ_f^T
Control PBO fiber	20.4	9.9	30.3
MWCNTs-Ecp-g-PBO fiber	20.9	22.3	43.2

second vaporized water and normal octane on MWCNTs-Ecp-g-PBO fiber are smaller than that of control PBO fiber. On control PBO fiber the contact angle of second vaporized water and normal octane are 78.6° and 20.8°, while on MWCNTs-Ecp-g-PBO fiber the values decrease to 59.1° and 16.6°, respectively. It is further indicated that the surface polarity of MWCNTs-Ecp-g-PBO fiber is improved by incorporation of MWCNTs-Ecp grafting chains.

The calculated surface free energy components are listed in Table III. The MWCNTs irradiation treatment seemed to be quite effective in the modification of the surface free energy of PBO fiber. The PBO control sample had a total surface free energy of 30.3 mJ m^{-2}. The total surface free energy of PBO fiber was increased by 42.6% to 43.2 mJ m^{-2} after the irradiation treatment. The polar component of the surface free energy is enhanced much more than the dispersive component, indicating a strong chemical interaction between PBO fiber surface molecules and the MWCNTs-Ecp, and the presence of grafting chain of MWCNTs-Ecp on the surface of PBO fiber increased the surface polarity of fiber. The surface polarity decreased the contact angle of the fiber by the solutions. Therefore, the wettability of the PBO fiber is improved, too. This result is corresponding with the ones of XPS and AFM.

CONCLUSIONS

1. MWCNTs-Ecp have been grafted on the surface of PBO fiber by γ-ray irradiation treatment. Some polar groups such as —COOH, —OH and —C—Cl on the surface of MWCNTs-Ecp are transferred to the surface of PBO fiber with the grafting reactions between PBO fiber and MWCNTs-Ecp. The grafting chains of MWCNTs-Ecp on the surface of PBO fiber can modify the surface chemical properties.
2. MWCNTs-Ecp grafted on the surface of PBO fiber have changed the fiber's surface morphology. The surface of MWCNTs-Ecp-g-PBO fiber becomes rougher with a mean surface roughness value fivefold of the control fiber.
3. The surface free energy of PBO fiber has been increased by MWCNTs-Ecp grafting chains. The surface free energy of MWCNTs-Ecp-g-PBO fiber is 43.2 mJ m^{-2}, which is 42.6% increased comparing to control PBO fiber, and moreover the polar component is enhanced much more than the dispersive component.

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