

Synthesis and characterization of carbon fibers functionalized with poly (glycidyl methacrylate) via atom transfer radical polymerization

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Abstract. In this work, polyacrylonitrile (PAN)-based carbon fibers (CF) were chemically modified with poly (glycidyl methacrylate) (PGMA) via atom transfer radical polymerization (ATRP) to improve the interaction between the CF and polymer matrix. The FT-IR, TGA, and XPS were used to determine the chemical structure of the resulting products and the quantities of PGMA chains grafted from the CF surface. The experimental results confirm that the CF surface was functionalized and glycidyl methacrylate was graft-polymerized onto the CF, and the grafting content of polymer could reach 10.2%.

1. Introduction

In the past decade, the carbon fibers (CF) have attracted considerable attention because of their high mechanical properties, excellent high thermal stability and light weight, which have been used in a variety of fields [1-4]. Even though the carbon fibers possess these excellent properties, they are poor wetted by resins because of their smooth surface and inertness characteristics, resulting in a low interlaminar shear strength of composites [5-7].

Therefore, various methods have been developed for surface modification of CF with functional groups or polymers mainly to overcome this problem and improve the compatibility between CF and polymer matrix [8-10]. These methods include plasma treatment, electrochemical method, wet chemical, surface grating, thermal treatment and so on [11-15].

Among these methods, the functionalization of the CF with polymer is an effective method. It can be accomplished by many different approaches, including conventional free radical polymerization, cationic, anionic, esterification reaction and controlled radical polymerization [16, 17]. In those methods, the ATRP has become an important method to modify the CF surface with polymer chains because of its good controllability over the molecular weight and molecular weight distribution of the grafting polymers. Furthermore, the experimental condition of ATRP is not stringent, and a large numbers of monomers can be used in this method [18-20]. Herein we present a method of grafting

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poly (glycidyl methacrylate) onto the CF surface via ATRP. The introduction of polymers onto the CF surface can improve the compatibility between CF and resins, which results in high interfacial properties of the CF reinforced composites.

2. Experimental

2.1. Materials

The PAN-based carbon fibers were purchased from Hexcel Corporation, and the diameter of fiber is between 5 and 10 μm . The carbon fibers were cleaned by ethanol and acetone in turn, and then were dried for overnight at 60°C. Glycidyl methacrylate (GMA) was purchased from Shanghai Reagents Company and was purified under reduced pressure to remove the polymerization inhibitor. Thionyl chloride, 2-bromoisobutyryl bromide (BIBB), N, N, N', N'', N''-pentamethyldiethylenetriamine (PMDETA), N, N-dimethylformamide (DMF), and diethylenetriamine (DETA) were purchased from Shanghai Chemical Company. All other reagents used in this study were obtained from commercial sources and used as received.

2.2. Immobilizing the ATRP initiators onto the carbon fibers

The carbon fibers were first treated with a 70% nitric acid that was stirred for 1.5h at 115°C. Then the resulted CF was washed with diluted water and dried for 24 h at 70°C. In the next step, the acid-treated carbon fibers were reacted with excess thionyl chloride at 70°C for 36 h. The resulted acyl-derivated carbon fibers (CF-COCl) were washed with tetrahydrofuran (THF) and dried for overnight at 40°C. The CF-COCl was then put in an excess amount of DETA at 80°C for 36h, and washed with ethanol and dried at 90°C for 24 h. The resulted products were amine treated carbon fibers (CF-NH₂). Finally, the CF-NH₂ was reacted with BIBB at room temperature. After 48 h, the resulted products were washed with a solution of acetone/distilled water (1:1 v/v). The black final product (termed CF-Br) was dried at 60°C for overnight.

2.3. Synthesis of carbon fibers grafted with PGMA via ATRP

The carbon fibers grafted with PGMA were prepared by using ATRP method. The CF-Br, GMA, CuBr, PMDETA and DMF were added into a dried flask. The flask was degassed and sealed under vacuum. The sealed flask was then immersed in an oil bath at 80°C for 6 h. The reaction mixture was then intensively washed with ethanol and acetone (sequentially) and dried in an oven at 25°C for overnight. The final products were the carbon fibers grafted with PGMA (CF-PGMA). Figure 1 shows the procedure of grafting PGMA chains onto the CF via ATRP.

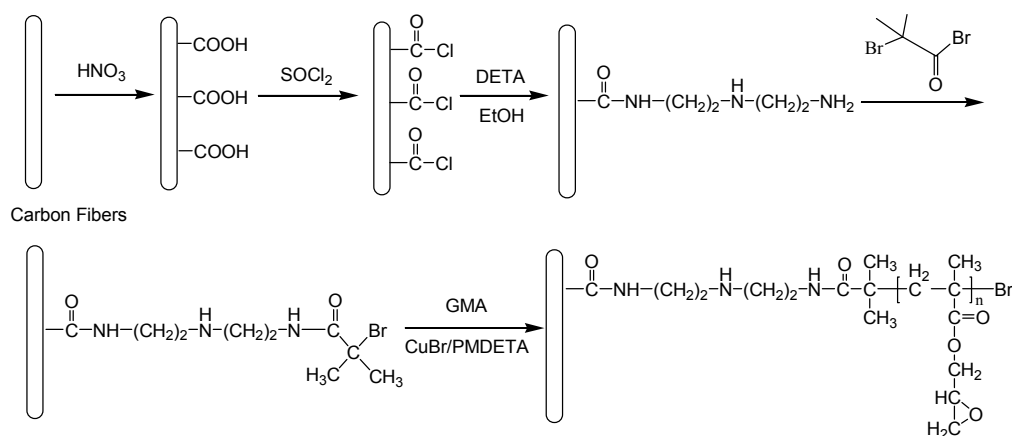


Figure 1. Synthesis of CF-PGMA via ATRP.

2.4. Measurements

Fourier transform infrared (FT-IR) spectra of the pure and functionalized CF in KBr pellets were obtained with Perkin-Elmer spectrometer at room temperature. The X-ray photoelectron spectroscopy (XPS) (monochromatized Mg ($K\alpha$) radiation) was used to characterize surface chemical compositions of different CF. Thermogravimetric analyses (TGA) were carried out using a Shimadzu TG-50 system under N_2 flow. The samples were heated from 25°C to 800°C at a rate of $20^\circ\text{C}\cdot\text{min}^{-1}$.

3. Results and discussion

3.1. Characterization of carbon fibers fixed with ATRP initiators

The carboxyl groups of the carbon fibers were treated with thionyl chloride, DETA, and 2-bromoisobutyryl bromide, then the ATRP initiators were introduced on the CF surface. The formation of CF-Br is detected by FT-IR and TGA. Figure 2 shows the FT-IR spectra of pure CF and CF-Br. Compared with the FT-IR spectrum of the pure CF, the spectrum of CF-Br clearly shows a new peak at 1720 cm^{-1} which is ascribed C=O stretching band. The occurrence of C=O peak indicates that the acylamide groups were formed through the reaction between CF- NH_2 and BIBB. The absorption at 2855 cm^{-1} and 2920 cm^{-1} ascribed to C-H of grafting organic compounds. The FT-IR results confirm that the synthesis of CF-Br is successful.

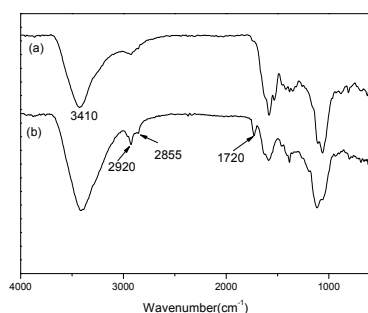


Figure 2. The FT-IR spectra of (a) pure CF and (b) CF-Br.

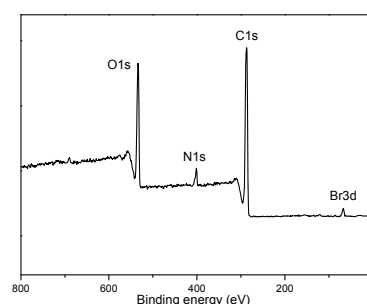


Figure 3. XPS spectrum of CF-Br.

The FT-IR results can also be confirmed by the results of XPS. Figure 3 shows the XPS spectrum of CF-Br. In this spectrum, the peaks at 530.9, 399.2, 285.3 and 69.6 eV are assigned to O1s, N1s, C1s, and Br3d, respectively. The appearance of Br3d peak in the spectrum shows that the ATRP initiators were grafted onto the CF by the reaction between CF- NH_2 and BIBB.

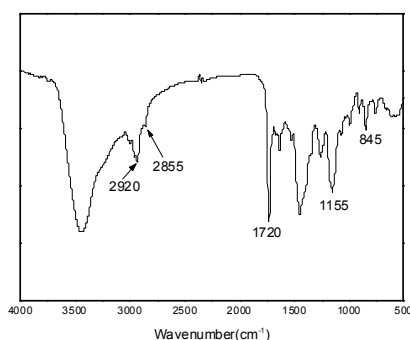


Figure 4. The FT-IR spectrum of CF-PGMA.

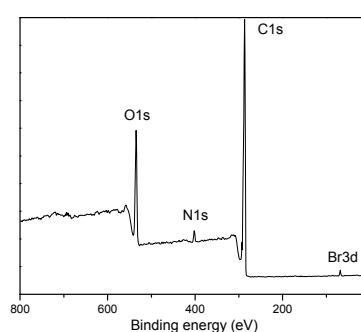


Figure 5. XPS spectrum of CF-PGMA.

3.2. Characterization of carbon fibers grafted with PGMA

After the immobilization of ATRP initiators, the monomer of GMA can be graft-polymerized onto the CF surface via ATRP. The CF functionalized with PGMA was characterized by means of FT-IR, XPS, and TGA. Figure 4 presents the FT-IR results of CF-PGMA. In this spectrum, it can be found that

there is a strong absorption band at 1720 cm^{-1} ascribed to the ester carbonyl ($\text{C}=\text{O}$), which is associated with the grafting PGMA. The bands at 2920 cm^{-1} and 1155 cm^{-1} are assigned to the C-H and C-O-C, respectively. The spectrum of CF-PGMA also shows a new band at 845 cm^{-1} , which is ascribed to the epoxy groups. The FT-IR results demonstrate that the synthesis of the CF grafted with PGMA chains was successful.

XPS was used to determine the chemical compositions of the functionalized CF surface. Figure 5 shows the XPS spectrum of CF-PGMA. As compared with the spectrum of CF-Br, the spectrum of CF-PGMA shows that the peaks corresponding to O1s, Br3d and N1s become weak. On the other hand, the peak for C1s grows strong. The XPS results further suggest that the synthesis of CF-PGMA was successful.

Thermal degradation of pure CF, CF-Br and CF-PGMA were investigated by heating up from 25°C to 800°C under N_2 flow with a heating rate of $20^\circ\text{C}\cdot\text{min}^{-1}$. The TGA results of different CF are shown in figure 6. Pure CF (figure 6a) did not present significant weight loss between room temperature and 800°C . In contrast, the CF-Br (figure 6b) shows a gradual decomposition as the temperature rises. From the TG curves it can be estimated that the weight loss in the range $30\text{--}800^\circ\text{C}$ is about 5.6%, which may be ascribed to the decomposition of the ATRP initiators immobilized onto the carbon fiber surface. The TGA curve of CF-PGMA (figure 6c) is much different to the pure CF and CF-Br. It can be found that this curve shows a major decomposition near 300°C because of the thermal decomposition of PGMA, which was grafted from the CF-Br surface. According to the TGA data, the weight fraction of PGMA on the CF surface is approximately 10.2%.

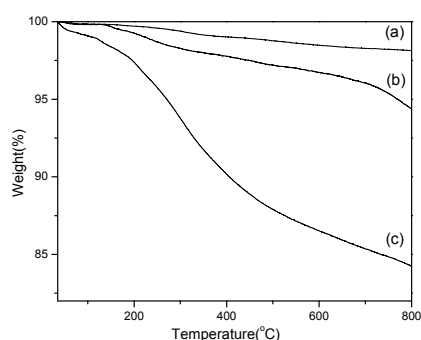


Figure 6. TGA curves of (a) pure CF, (b) CF-Br and (c) CF-PGMA.

4. Conclusion

To improve the interfacial properties between the CF and polymer resins, the monomer of glycidyl methacrylate (GMA) was graft-polymerized on the CF surface via ATRP method in this paper. The functionalized CF was characterized in terms of the XPS, FT-IR, and TGA. The experimental results confirmed that the occurrence of PGMA functionalization and the content of grafting polymer on the CF surface is about 10.2%. Therefore, this is an effective method to the preparation of the CF functionalized with polymer. It provides a potential approach for high performance composites developing.

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