Grafting of Polystyrene-b-Poly(2-hydroxyethyl methacrylate) onto Carbon Fiber

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Carbon fiber (CF) was subjected to oxidation and acyl chlorination, resulting in CF functionalized with acyl chloride (CF-COCl). The block copolymer polystyrene-b-poly (2-hydroxyethyl methacrylate) (PSt-b-PHEMA) was synthesized by atom-transfer radical polymerization (ATRP). According to the reaction between hydroxyl groups of block copolymer and acyl chloride groups on CF, the block copolymer was successfully grafted onto the surface of CF. Fourier-transform infrared spectra (FTIR), Gel permeation chromatography (GPC) were used to determine the chemical structure and molecular weight of block copolymer; Fourier transform infrared spectroscopy-attenuated total reflection (FTIR-ATR), Scanning electron microscopy (SEM) and thermal gravimetric analyses (TGA) were used to determine the chemical property and structure of grafted CF.

Keywords: carbon fiber, grafted, block copolymer, atom-transfer radical polymerization

1. Introduction

Carbon fibers have been widely used for reinforcement in structural composite materials due to their outstanding properties, such as high modulus, high tensile strength, low density and a chemical inertness (1–4). The mechanical properties of carbon fiber (CF) composites are considered to depend not only on the mechanical properties of the matrix or CF, but also on the properties of interfacial regions between the CF and matrix. These mechanical properties of such composite materials are achieved only through optimal stress transfer from the matrix material to the fiber reinforcement. Therefore, it is necessary to modify the nonpolar CF to achieve good interfacial adhesion in many cases.

Various conventional methods of surface modification can be applied to CF, such as sizing, plasma treatment and different oxidizing methods (5–9). Most of these surface treatments produce mainly functional groups like carboxyl and hydroxyl, which can improve the interfacial adhesion between fibers and resins. But the effect of these conventional surface treatments on improving interfacial adhesion is not very obvious, especially to non-polar resin. Grafting of polymer onto inorganic fiber has been widely investigated for many years. Many researchers have observed the improvement of interfacial adhesion in grafted CF composites (10–13). In a previous study (14), it was shown that the presence of high molecular weight polymer at the fiber-matrix interphase did significantly improve the interfacial adhesion. In fact, grafting block copolymer is a kind of macromolecular coupling agent, which acts as a molecular bridge at the interface between the inorganic fiber and organic matrix. However, because of the molecular weight polydispersity of grafting polymer, there are lower molecular weight polymers grafting to the interface. They will lead to reduction in the interfacial adhesion (15,16). Therefore, it is expected that grafting of polymer chains of appropriate molecular weight to the reinforcing fiber surface would result in formation of strongly bonded chains at the interface.

To date, polymers made from different monomers have been successfully grafted onto the surface of CF by means of "grafting from" or "grafting to" method (17–20). The "grafting from" method has been developed for surface-initiated radical (21), cationic (22) or anionic polymerization (23), etc. on CF surfaces. However, the molecular weight and molecular weight distribution of grafting polymers on CF by "grafting from" are difficult to be measured or controlled. The "grafting to" method is the most widely used process for polymer-grafting carbon fibers. Generally, the "grafting to" method means the ready-made polymers with reactive end groups react with the functional groups on CF surfaces. However, the long polymer chain, with just

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one reactive group, is difficult to react with the functional groups on CF. Comparing with "grafting from" method, the grafting density in "grafting to" method is relatively lower. Therefore, in the present work, the block copolymer polystyrene-b-poly(2-hydroxyethyl methacrylate) (PSt-b-PHEMA) with many reactive hydroxyl groups was synthesized by using atom-transfer radical polymerization (ATRP). According to the reaction between hydroxyl of block copolymer and acyl chloride on CF, the block copolymer was grafted onto the surface of CF. Because the grafting polymer chain contained many hydroxyl groups, it was easy to react with the functional groups on CF. As the "grafting to" method was adopted in the grafting course and the block copolymer was synthesized by ATRP, the molecular weights of grafting polymer were easily controllable and measurable.

## 2. Experimental

2.1. *Materials*

Carbon fibers were obtained from Toray Co. Ltd. They were cut into about 5 mm lengths, and were extracted with acetone in a Soxhlet apparatus for 9 h to remove any sizing agent or impurity materials. This process was repeated three times rinsing with new acetone, then followed by vacuum drying at 80°C overnight before use. Ethyl 2-bromoisobutyrate (EBriB) and N,N,N′,N″,N″-pentamethlydiethylenetri-amine (PMDETA) were purchased from Acros and used as received. Hydroxyethyl methacrylate (HEMA) was purchased from Aldrich, the inhibitor was removed by passing a column of alumina and distilling in vacuum. Thionyl chloride was obtained from Shanghai Reagent Co. without purification. Styrene was first filtered through an alumina column to remove the inhibitor, and then the monomer was distilled under reduced pressure before use. Copper bromide (CuBr) was washed with acetic acid, followed by methanol to remove impurities. 2,2′-Bipyridine (bpy) was recrystallized several times from acetone and dried in vacuum before use. N,N-Dimethylacetamide (DMAc) was dried over BaO, and then distilled under reduced pressure. Dioxane and tetrahydrofuran (THF) were previously dried over CaH_2 and distilled under reduced pressure, and then kept in the presence of a 4Å molecular sieve to eliminate any traces of water before use.

2.2. *Synthesis of PSt-b-PHEMA*

The block copolymer was synthesized by using atom-transfer radical polymerization which is described in Scheme 1. The macroinitiator PSt-Br was synthesized as follows. The polymerization was conducted in a sealed flask. CuBr, PMDETA ligand, styrene monomer, and EBriB initiator were added to the sealed flask, the mixture was degassed by three freeze–pump–thaw cycles, sealed under pure nitrogen, and placed in a preheated oil bath. After a definite time, the flask was opened and THF was added to the sample to dissolve the polymer. The mixture was then passed through neutral alumina column to remove the used ATRP catalyst. The final pure product was obtained after precipitation and dried under vacuum. The procedure of the block copolymerization was similar to that of the homopolymerization as described earlier except the macroinitiator PSt-Br and ligand bpy. HEMA was added together with the catalyst (CuBr/bpy) at first, and then the PSt-Br dissolved by anhydrous DMAc was added by a syringe technique. The flask was immersed in an oil bath at 50°C immediately and kept stirring for 20 h. At the end of the reaction, the mixture was diluted with DMAc and passed through a neutral alumina column in order to remove the spent ATRP catalyst. The crude product was obtained after precipitation. To remove the unreacted PSt, the crude product was immersed in toluene under stirring at room temperature for 6 h, followed by filtrating. This process was repeated three times, and the final product was obtained after drying under vacuum.

2.3. *Oxidation of CF*

The carbon fibers were divided into two parts, which were treated by the same course in the study except oxidation hours. One part was oxidized for 5 h and the other was oxidized for 24 h. A typical example was given as follows. A 250 ml flask charged with 1.108 g of crude carbon fibers and 100 ml of 60% HNO_3 aqueous solution was sonicated in a bath for 30 min. The mixture was then stirred for 24 h under reflux. After the mixture was cooled to room temperature, it was diluted with 400 mL of deionized water and then vacuum filtered through a filter paper. The solid was washed with deionized water until the pH value of the filtrate was 7. The filtered solid was then dried under vacuum for 48 h to give about 0.856 g of carboxylic acid-functionalized CF (CF-COOH). The CF-COOH was the
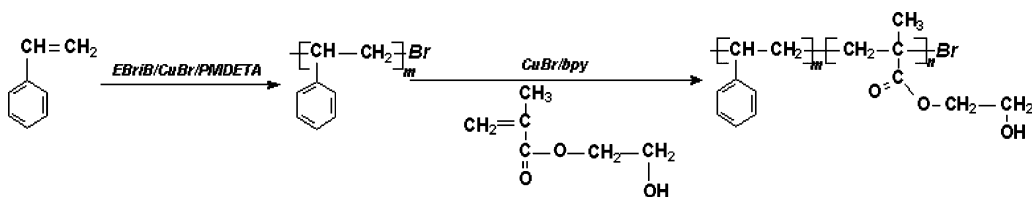
Sch. 1. Synthesis route of the PSt-b-PHEMA.
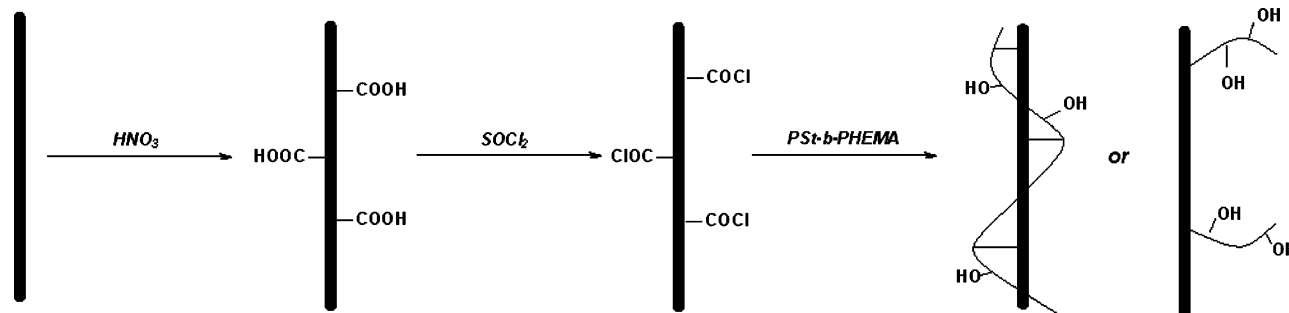
Sch. 2. Schematic illustration for the grafting of CF.

CF oxidized for 24 h except for those especially labeled in this passage. The carboxyl groups on the surface of CF were quantified by titration with aqueous solutions of sodium hydroxide and sodium bicarbonate, according to the literature (24). The values found for carboxyl groups contents after 5 and 24 h oxidation were 0.09 and 0.34 mmol/g, respectively.

2.4. *Grafting of PSt-b-PHEMA onto CF*

0.51 g of CF-COOH was mixed with 100 ml of thionyl chloride. This suspension was stirred at 70°C for 24 h. The residual thionyl chloride was removed by reduced pressure distillation, giving acyl chloride-functionalized CF-COCl. Typically, 3.06 g of PSt-b-PHEMA was dissolved in 180 ml of anhydrous dioxane. Then, CF-COCl and 180 ml anhydrous dioxane dissolved with the block copolymer aforementioned were placed in a dried flask. The flask was then degassed under vacuum and filled with pure nitrogen. The flask was immersed in an oil bath immediately and kept stirring at 90°C for 24 h under dry nitrogen atmosphere. After soxhlet extraction and filtration steps, the resulting solid was dried overnight in vacuum, obtaining CF functionalized block copolymer. A typical grating procedure is described as Scheme 2.

2.5. *Characterization*

Fourier-transform infrared (FTIR) spectra of products were recorded on a Nicolet Magna-IR 380 spectrophotometer. Scanning electron microscopy (SEM) analysis was performed on a SEM (JSM-6360LV) electron microscope at 20 kV. The thermogravimetric analysis (TGA) was carried out with a TA SDT-Q600 thermal analyzer at a heating rate of 10°C/min in nitrogen flow (20 mL/min). The molecular weight and its distribution of the macroinitiator PSt-Br and PSt-b-PHEMA were determined by multi-detectors GPC equipped with a DAWN HELEOS static laser scattering detector and an Optilab Rex refractive index detector, which was produced by Wyatt Technology Corporation. GPC was performed in THF at a flow rate of 1.0 mL/min.

3. Results and discussion

3.1. *Characterization of block copolymer*

FTIR spectrum of the block copolymer PSt-b-PHEMA is shown in Figure 1. The absorption band at 1727 cm^{-1} is the characteristic peak of C=O groups of PHEMA. Another characteristic absorption peak at 3424 cm^{-1} is the hydroxyl groups of PHEMA. The adsorption bands at 1602, 1942 and 1452 cm^{-1} and the double peaks of 749 and 698 cm^{-1} are the characteristic bands of PSt. These results show that the block copolymer is composed of PSt and PHEMA. The molecular weights and molecular weight distributions of macroinitiator PSt-Br and block copolymer are listed in Table 1. The molecular weights of block copolymers are higher than those of the macroinitiators (PSt–Br) and the molecular weight distributions are narrow. Both GPC traces of the block copolymer and macroinitiator in Figure 2 are monomodal, and the peak of block copolymer is shifted toward higher molecular weight position. The result for block copolymer in Figure 2 shows that the extension time is smaller than that of the macroinitiator. This indicates that PSt–Br can initiate HEMA monomers to synthesize some kinds of block copolymer.

3.2. *Characterization of the grafted CF*

Scheme 2 just illustrates the synthesis route of grafting PSt-b-PHEMA onto CF, does not mean that there is only one grafting structure on the CF. The probability of grafting polymer onto CF is increased due to many hydroxyl groups on the block copolymer chain, but the hydroxyl groups of block copolymer will lead to several structures of the product obtained. There are two structures in the grafting course apparently. The first, when one hydroxyl group of block copolymer reacted with acid chloride group, the polymer chain was grafted on CF and the other hydroxyl groups no more reacted with acid chloride group. The second, several hydroxyl groups of one block copolymer chain reacted with acid chloride groups on the same CF and several chemically bonded structures were produced between the CF and grafting polymer chain like Scheme 2 illustrating.
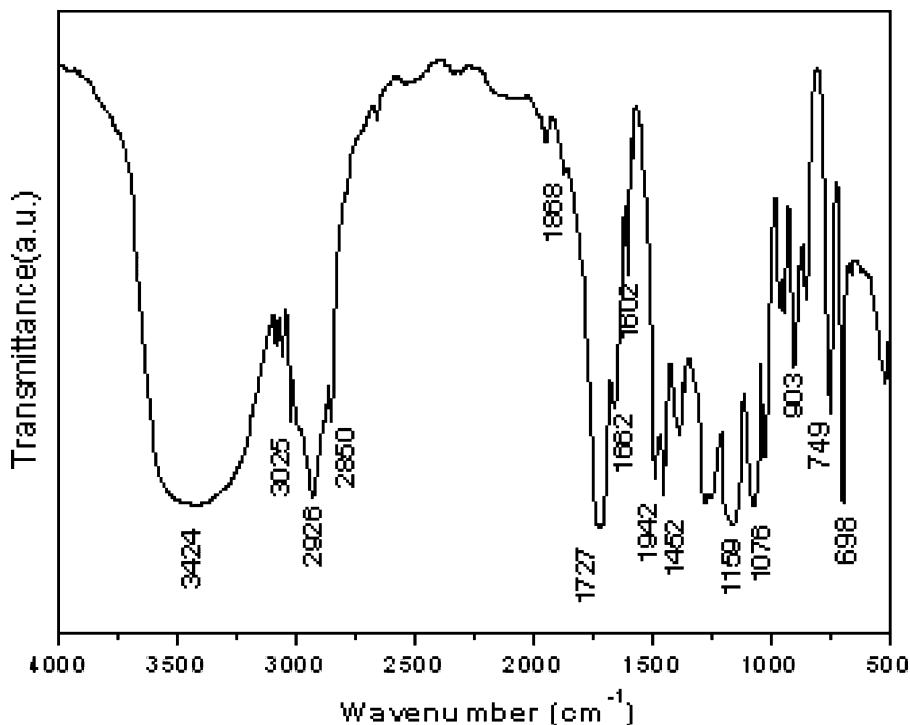
Fig. 1. FTIR spectra of PSt-b-PHEMA.

Does any other grafting structure exist, for example, different carbon fibers linked by one polymer chain through the reaction between hydroxyl and acid chloride? Generally, this crosslinking of neighbor carbon fibers is considered to be non-existent or negligible. Firstly, after the block copolymer is grafted on one CF, steric hindrance will make the hydroxyl groups difficult to react with the acid chloride groups on other carbon fibers. In much of the literature about functionalization of CNT and CNF (25–28), the reaction between hydroxyl groups on CNT and acid chloride group on other CNT is considered to be non-existent or negligible. Secondly, the length of CF is about 5 mm and the diameter of CF is about 5–10 μm. So, it is very difficult for such large carbon fibers to be interlinked by the small polymer chain. Whichever grafting structure occurs in the grafting course, the interfacial adhesion between fibers and resins can be improved as long as the macromolecular chain is grafted on the CF.

Figure 3 shows the FTIR spectra of different modified carbon fibers. In Figure 3(a), the absorption signal of carbonyl band at around 1730 cm^{-1} is scarcely detected for the crude carbon fibers except the C=C absorption band around 1660 cm^{-1}. Figure 3(b) shows the sample of CF-COOH, we also did not find that there is an obvious C=O stretch at around 1730 cm^{-1}. Figure 3(c) shows the spectrum of CF grafted by PSt-b-HEMA, the peak at 1724 cm^{-1} attributed to C=O stretch of ester group is easily found. The peaks at 1494 and 1450 cm^{-1} are the characteristic absorption band of PSt. The peaks at 2922 and 3024 cm^{-1} belong to the C–H stretch of PSt. These results clearly indicate that PSt-b-HEMA chains have been successfully grafted onto the CF.

The CF is consistent with the surface morphological analyses by SEM. A smooth surface can be seen in crude CF (Figure 4a). But for the grafted CF, there are a few polymers deposited on the fiber substrate (Figure 4b). Due to the long duration of soxhlet extraction, we assume all physisorption polymer molecules should be removed through the extraction process. But for the chemically bonded polymer molecules, it is impossible to remove the grafting polymers from the surface of CF without degrading it. So the block copolymer PSt-b-PHEMA is successfully grafted onto the CF.

The samples of carbon fibers with or with out surface modification were studied with TGA. As shown in Figure 5, the sample of crude CF is steady without significant weight

Table 1. The results of the block copolymers using PSt-Br as macroinitiator

Macroinitiatos	M'_n	2nd monomers	Block copolymers		
			M_{th}	$M_{n,GPC}$	M_W/M_n
PSt-Br	3400	HEMA	10120	9170	1.13
PSt-Br	5690	HEMA	19650	18010	1.26
PSt-Br	13510	HEMA	24520	22930	1.10
PSt-Br	15150	HEMA	32830	29890	1.18

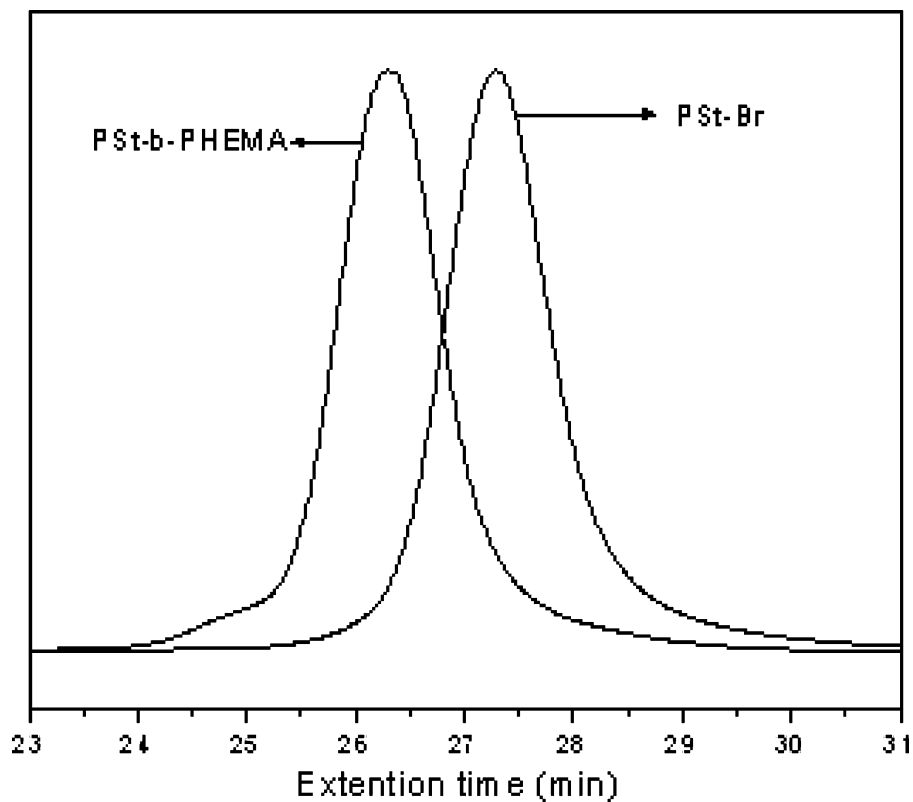M'_n: the molecular weights of PSt-Br, Determined by GPC measurement

Fig. 2. GPC curves of macroinitiator PSt-Br and block copolymer PSt-b-PHEMA.
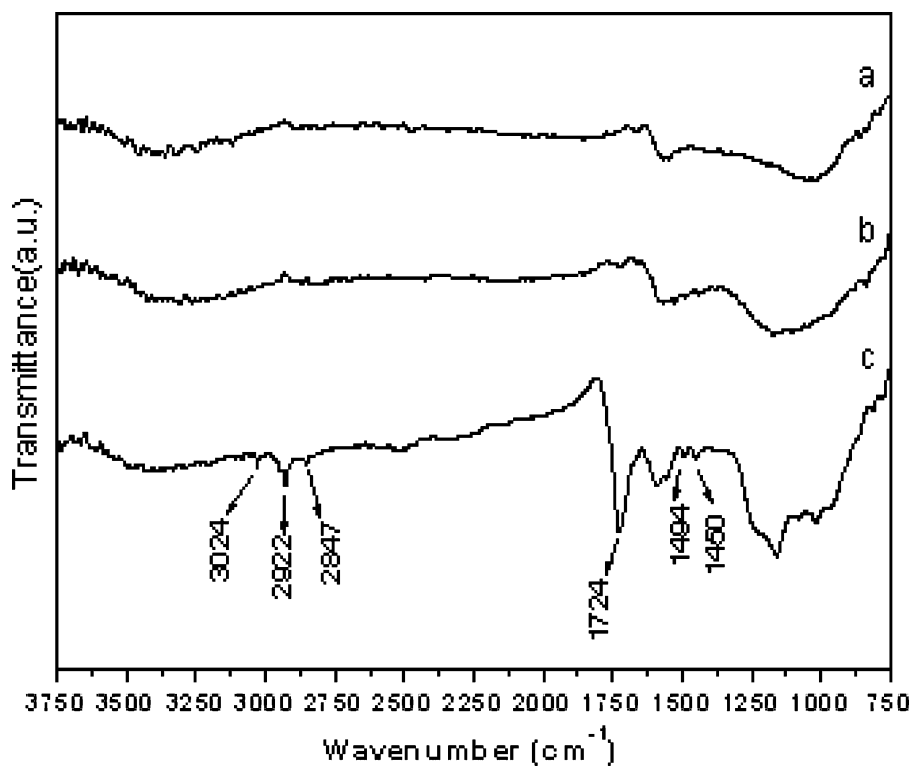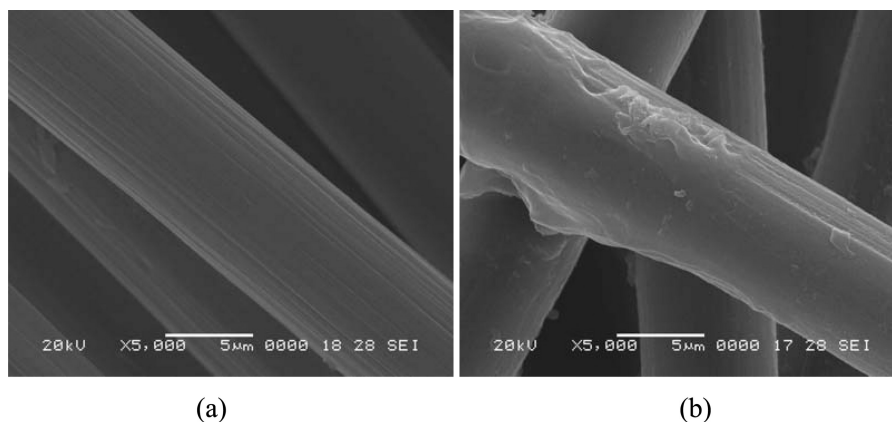

Fig. 3. FTIR-ATR spectra of (a) crude CF, (b) CF-COOH, (c) CF grafted by PSt-b-PHEMA.

(a)　　　　　　　　　　　　　(b)

Fig. 4. SEM images of (a) crude CF, (b) CF grafted by PSt-b-PHEMA.

loss below 600°C. On the contrary, the CF-COOH sample decomposes slowly with the increasing temperature, likely because of losing carboxyl groups on the surface of CF. But for the sample of CF grafted by block copolymer, three main weight-loss regions are found. The first weight-loss region below 200°C can be assigned to the decomposition of free carboxyl groups on the surface of CF. The rapid weight decrease in the second region (200–450°C) may be attributed to the decomposition of PSt and PHEMA. The third region (450–600°C) only shows a small weight loss which may come from the decomposition of CF. Carbon

fibers which are oxidized for 5 h have a similar course of weight loss, except that the degree of weight loss is different. Therefore, the amount of grafting block copolymer on CF can be relatively controlled by the content of carboxyl groups.

From the weight loss curves of different modified carbon fibers, we can see that the modified carbon fibers have a lower decomposition temperature than crude carbon fibers, which may come from the oxidation and grafting course. The oxygenous units and other molecule fragments generated by decomposition of grafting polymer or functional
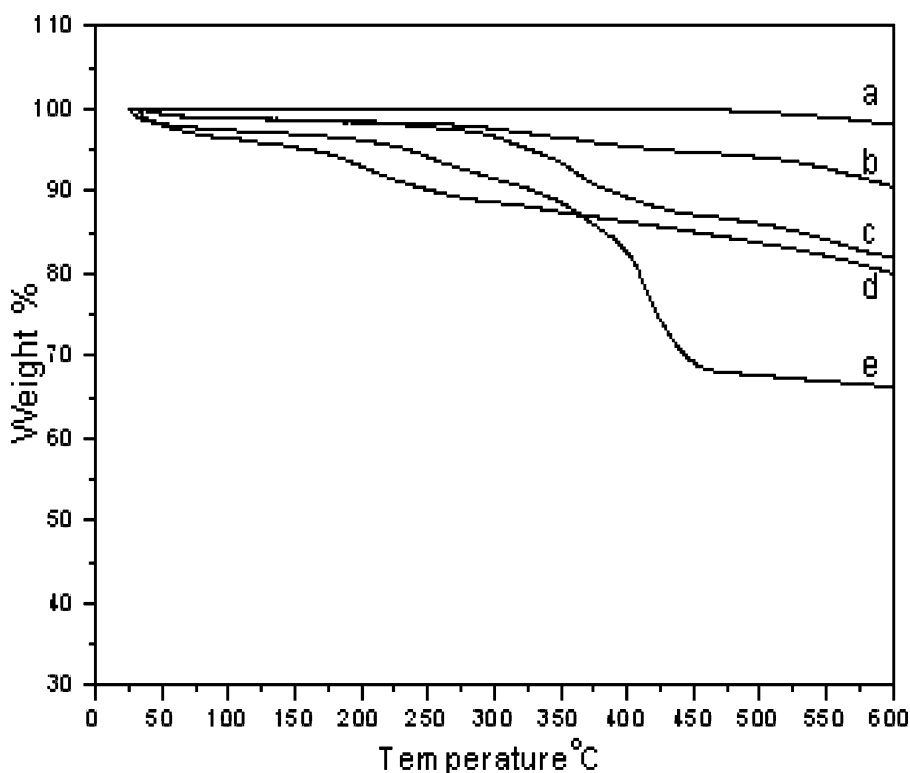
Fig. 5. TGA curves of the crude CF and modified CF. (a) crude CF, (b) CF_1-COOH (oxidized for 5 h), (c) CF_1 grafted by PSt-b-PHEMA, (d) CF-COOH (oxidized for 24 h), (e) CF grafted by PSt-b-PHEMA.

group would lower the decomposition temperature of CF, because part of these fragments or oxygenous units can couple with some outer layer carbons of CF and destroyed the relatively steady structure of CF.

4. Conclusions

The preparation of the block copolymer attached on CF was completely investigated in this work. This proposed method had the characteristics of the controlled/'living' radical polymerization. The molecular weight and molecular weight distribution of grafting block copolymer could be controlled by the ATRP. After the acyl chloride groups were introduced onto the surface of CF, PSt-b-PHEMA was successfully grafted onto the surface of CF. The realization of controlled polymerization of block copolymer onto CF will improve the application of carbon fibers, carbon nanofibers, etc. polymer composites. The relevant works are in progress and will be reported later.

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