

Surface-initiated atom-transfer radical polymerization (SI-ATRP) of methyl methacrylate from carbon fibre

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Abstract: Surface modification of carbon fibre (CF) by well-defined polymer brushes was carried out using the 'grafting from' method. Poly(methyl methacrylate)-grafted carbon fibre (CF-PMMA) was successfully prepared by surface-initiated atom-transfer radical polymerization (SI-ATRP) of methyl methacrylate (MMA) from the macro-initiator, bromo-acetic ester-modified carbon fibre (CF-BrA), with the complex of 1,10-phenanthroline and Cu(I)Br as catalyst. The percentage of grafting (PG%) and the conversion of monomer (C%) increased linearly with increasing of polymerization time, and reached 24.0 % and 6.7 %, respectively, after a polymerization time of 6 h, calculated from the elemental analyses (EA). The structural and surface morphological analyses were conducted with Fourier-transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM).

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Keywords: surface-initiated; atom-transfer radical polymerization; grafting from; carbon fibre; poly(methyl methacrylate)

INTRODUCTION

Carbon fibre (CF) is well known as an industrially important carbon-based material.¹ It has the desirable properties of high temperature resistance, high modulus, extremely high strength, low density, and chemical resistance. Therefore, CF is widely used as a reinforcing fibre in fibre-reinforced plastics (FRP). The mechanical properties of FRP are considered to depend not only on the mechanical properties of the polymer matrix, but also on the properties of the interfacial regions between the CF and the matrix polymer.

The chemical and physical modifications of CF surfaces, therefore, have been extensively studied. The chemical modification of surfaces is permanent, but physical modification is temporary. Among the permanent chemical modifications, the surface grafting of polymers, ie chemical binding of polymers onto CF surfaces, interests us for use in designing new functional carbon materials which have enhanced properties such as electro-conductivity, heat resistance and chemical resistance, and of grafted polymers, such as photosensitivity, curing ability, bioactivity and pharmacological activity.²

However, at the surface of CF, the concentration of, oxygen-containing functional groups such as

carboxyl (COOH), carbonyl (CO) and hydroxyl (OH) is known to be low.³ The surface grafting of polymers onto CF surfaces has thus rarely been achieved. The introduction of functional groups using conventional organic reactions, such as oxidation,⁴ plasma treatments⁵ and electrophilic substitution reactions to polycondensed aromatic rings of the surface, has therefore been necessary.⁶

The 'grafting to' method is the most widely used process for polymer-grafted carbon fibres (PCFs). The ready-made polymers with reactive end groups react with the functional groups on the CF surfaces.^{7–9} Recently, the 'grafting from' method has been developed for the surface-initiated radical,¹⁰ cationic¹¹ or anionic polymerization¹² on CF surfaces. However, a mass of free non-grafted polymer were produced.

In the present work, poly(methyl methacrylate)-grafted carbon fibre (CF-PMMA) was successfully prepared by surface-initiated atom-transfer radical polymerization (SI-ATRP) of methyl methacrylate (MMA) from initiator-modified CF surfaces. Compared with the reported methods, the percentage of grafting (PG%) of the PCF and the molecular weights of the grafted polymer were easily controllable because it was a controlled/'living' radical polymerization process (Scheme 1).¹³

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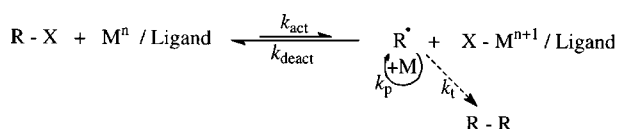
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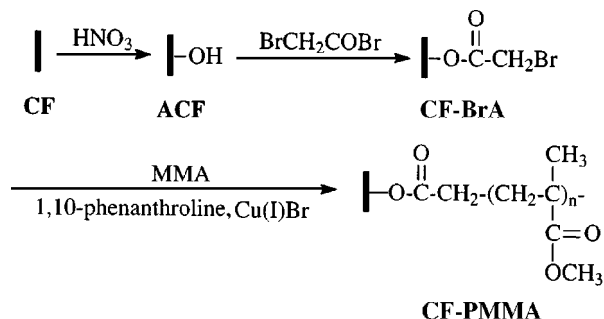
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Scheme 1. Mechanism of atom-transfer radical polymerization (ATRP).



Scheme 2. The synthetic route to the CF-BrA and CF-PMMA.

EXPERIMENTAL

Materials and reagents

The CF used was purchased from the Lanzhou Carbon Factory, Lanzhou, China. MMA (AR) was from Tianjin Chemical Co., China, and purified by vacuum distillation before use. Bromoacetyl bromide was of analytical reagent grade from Acros Organics (Phillipsburg, NJ, USA). Both 1,10-phenanthroline and Cu(I)Br (Tianjin Chemical Co., Tianjin, China) were analytical reagent grade and were re-crystallized from ethanol before use. Tetrahydrofuran (THF) and other solvents used were all analytical reagent grade from Tianjin Chemical Co., China, and were used without further purification. Distilled water was used throughout.

Preparation of functionalised CF

The CF was washed with acetone and then chemical oxidized by boiling in 60 % HNO₃ solution for 10 h.⁴ The activated carbon fibre (ACF) was dried at 100 °C after being washed to neutral with water.

The hydroxyl groups on the surface were then reacted by immersing 5.0 g of the ACF in a solution containing bromoacetyl bromide (400 mg, 2.0 mmol), triethylamine (222 mg, 2.2 mmol) and a catalytic amount of 2-dimethyl aminopyridine (DMAP) in THF (20 mL) as reported previously.¹⁴ The reaction proceeded at room temperature for 1–24 h. The bromo-acetic ester-modified carbon fibre (CF-BrA) was thereafter thoroughly washed with dichloromethane and ethanol and then dried under vacuum at 40 °C. The CF-BrA was also ultrasonicated for 3 min each time in both solvents. The preparation process is shown in Scheme 2.

SI-ATRP of MMA

The grafting was accomplished by immersing the CF-BrA into the reaction mixture containing MMA (20 mL), Cu(I)Br (172.1 mg, 1.2 mmol) and 1,10-phenanthroline (432 mg, 2.4 mmol). The SI-ATRP

proceeded at 70 °C for 6 h with magnetic stirring. N₂ was bubbled throughout the polymerization period. Samples of the CF were taken out after a certain polymerization time. The products were subjected to intense washing, by toluene, ethanol and water. Ultrasonication was used in combination with all three solvents. The CF-PMMA obtained was then dried under vacuum at 40 °C.

Analysis and characterization

Elemental analysis (EA) of C was performed on an Elementar Vario EL instrument. A Bruker IFS 66 v/s infrared spectrometer was used for the Fourier-transform infrared (FTIR) spectroscopy analysis. X-ray photoelectron spectroscopy (XPS) was performed using a PHI-5702 multi-functional spectrometer with pass energy of 29.35 eV and an Mg K α line excitation source. The binding energy of C 1s (284.6 eV) was used as a reference. The surface morphologies of the CF-PMMA were characterized with a Philips XL-20 scanning electron microscope (SEM) (Philips Co., The Netherlands).

The PG% and the conversion of MMA (C%) were calculated according to the following relationships from the results of carbon elemental analyses:

$$\begin{aligned}
 \text{PG\%} &= \frac{\text{grafted PMMA (g)}}{\text{CF charged (g)}} \times 100 \% \\
 \text{C\%} &= \frac{\text{total PMMA (g)}}{\text{monomer charged (g)}} \times 100 \%
 \end{aligned}$$

RESULTS AND DISCUSSION

SI-ATRP processes had been used successfully for the preparation of well-defined structural polymer-grafted nanoparticles,¹⁵ films,¹⁶ carbon nanotubes¹⁷ and carbon black.¹⁸ To our knowledge, it had not been used for polymer modification of CF. This may be a result of the small amount of surface functional groups.³

Scheme 1 illustrates the process used to synthesize the macro-initiator. The synthesis included two major steps: chemical oxidation of the CF surfaces to introduce hydroxyl groups and attachment of bromo-acetyl

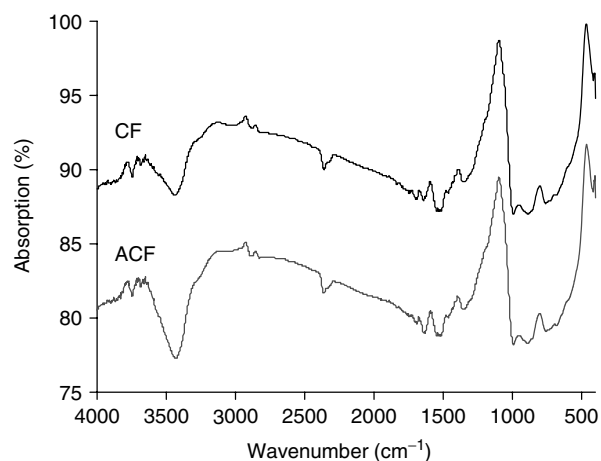


Figure 1. FTIR spectra of CF and ACF.

ester groups to the surface modified with the anchoring layer through the reaction between the hydroxyl groups introduced and bromoacetyl bromide. The reaction produced a bromo-acetic ester derivative of CF (Scheme 1). Such bromo esters are known to be effective initiators for ATRP of styrene, acrylic, and some other vinyl monomers.¹³ Therefore, the ATRP initiator, covalently anchored to the CF surfaces, was synthesized.

It was found from the FTIR spectra (Fig 1) that the band of hydroxyl groups at about 3430 cm^{-1} had been enhanced after the chemical oxidation with HNO_3 . The formation of the bromo acetic ester derivative of CF was conducted by reaction of the hydroxyl groups introduced and bromoacetyl bromide. Characterization of the macro-initiator, CF-BrA, was carried out by XPS. A surface Br element content of 4.72 % was found (Table 1) and a small Br 3d signal (70 eV) was seen in the spectrum of CF-BrA (Fig 2).

The fundamental idea of ATRP is the halogen exchange in the polymerizing system between the halogen-terminated growing polymer chain/ Cu(I)/L complex and macroradical/ Cu(II)/L complex. The kinetics of SI-ATRP of MMA were studied by monitoring the changes in the carbon element content of the CF-PMMA by EA as a function of time. To prove the controlled nature of the polymerization initiated from the surface by the CF-BrA macro-initiator, the effects of the polymerization time on the PG% and the C% were investigated (Fig 3). They increased linearly with increasing polymerization time, and reached 24.0 % and 6.7 %, respectively, after a polymerization time of 6 h, calculated from EA. The concentrations of monomer decreased slightly when the C% was low. So the PG% and the C% increased linearly with increasing polymerization time. This indicated that the proposed method has the characteristics of controlled/‘living’ radical polymerization.

No non-grafted PMMA was found in the polymerization mixture, which was because of the mechanism of the SI-ATRP. The MMA monomer had polymerized from the surface of the macro-initiator and the polymers obtained were all anchored on the surfaces of the CF. The characteristic absorption of the carbonyl group at 1730 cm^{-1} was found after the SI-ATRP of MMA, which indicated that the PMMA brushes had been successfully grafted onto the CF surfaces. XPS was used to determine the surface composition of the PMMA obtained by SI-ATRP from the functionalized CF. Figure 2(a) shows the survey scan spectra of the CF-BrA and CF-PMMA, which detected three

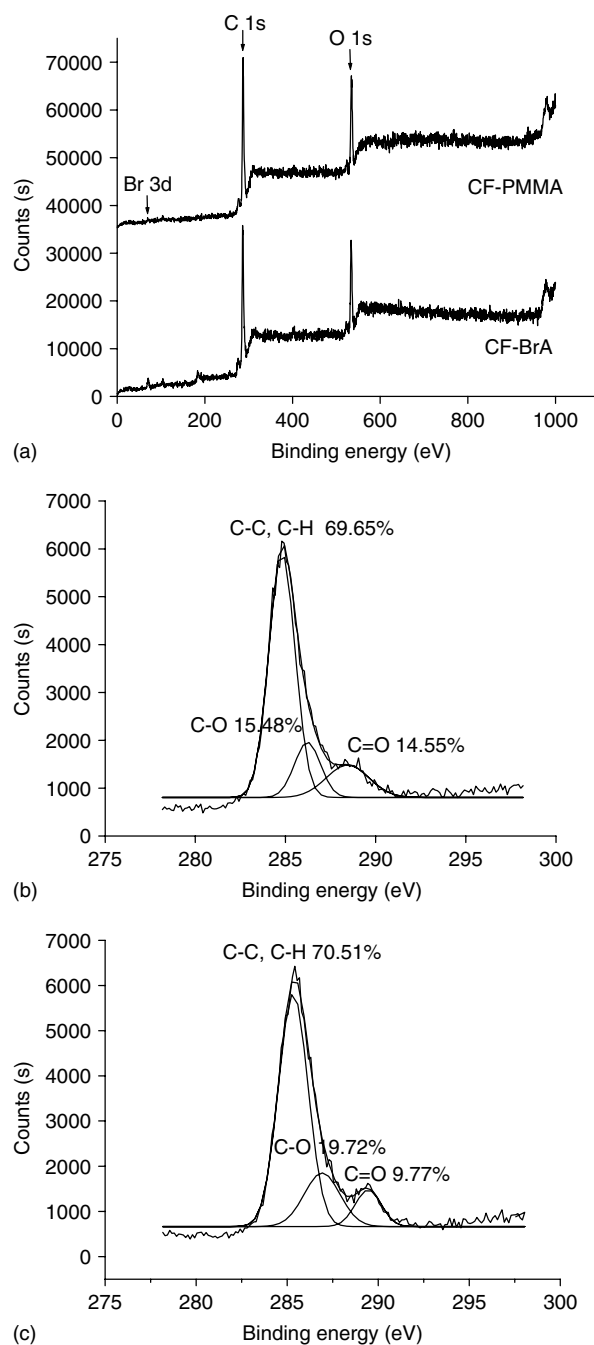


Figure 2. XPS analysis of the CF-BrA and CF-PMMA: (a) XPS survey scan spectra; (b) C 1s core-level spectrum of CF-BrA; (c) C 1s core-level spectrum of CF-PMMA.

elements: oxygen (533 eV), carbon (285 eV) and Br (Br 3d at 70 eV and Br 3p at about 290 eV). The surface element contents of C and O increased and that of Br decreased after the PMMA had been grafted (Table 1). Obviously, the reduction of the bromine signal detected on the copolymer surface was due to dilution of the active centres by MMA units.

In the C 1s core-level spectra of CF-BrA and CF-PMMA (Figs 2(b) and (c)), the same three peak components of C–C and C–H, C–O, and C=O species at 285.0, 286.5 and 288.0 eV were found, respectively. However, the peak components of C–C and C–H, and of C–O increased whereas that of C=O

Table 1. Surface composition data from XPS analysis

Sample	Surface concentration (%)		
	C	O	Br
CF-BrA	46.03	49.25	4.72
CF-PMMA	49.01	49.58	1.41

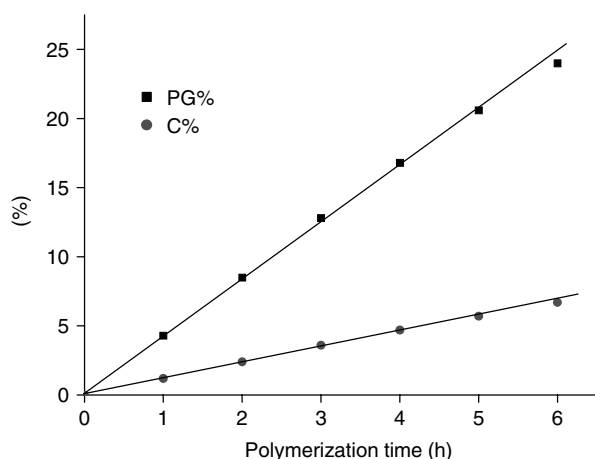


Figure 3. Effect of the polymerization time on PG% and C% of CF-PMMA.

decreased after the formation of the PMMA brushes on the CF surfaces. This may have resulted from the wrapping of the original C=O groups of the CF with the grafted PMMA brushes. This result suggests that the thickness of the grafted PMMA layer is above the probing depth of the XPS technique (about 7.5 nm in an organic matrix).¹⁹ It was consistent with the surface morphological analyses by SEM (Fig 4). The formation of the grafted PMMA layer provided a smoother surface morphology of the CF-PMMA than that of the CF-BrA.

CONCLUSION

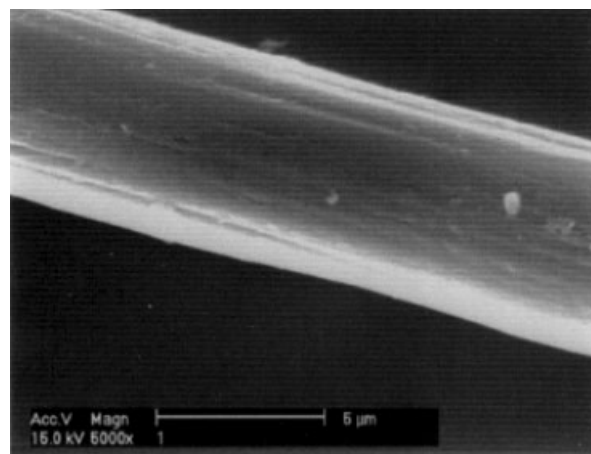
Chemical oxidized CF was successfully used for preparation of an effective macro-initiator for the synthesis of polymer brushes by ATRP initiated from the surface. The ATRP macro-initiator, CF-BrA, was synthesized on the substrate surface by the reaction between the hydroxyl groups introduced by the oxidative modification and bromoacetyl bromide. PMMA brushes were grafted from the CF surface via an SI-ATRP technique. This proposed method had the characteristics of the controlled/'living' radical polymerization. The surface element contents and the structure of the CF-PMMA were characterized by XPS. The smoother surface after the SI-ATRP of MMA, as characterized by the SEM analyses, also testified to the formation of the PMMA brushes on the CF surface.

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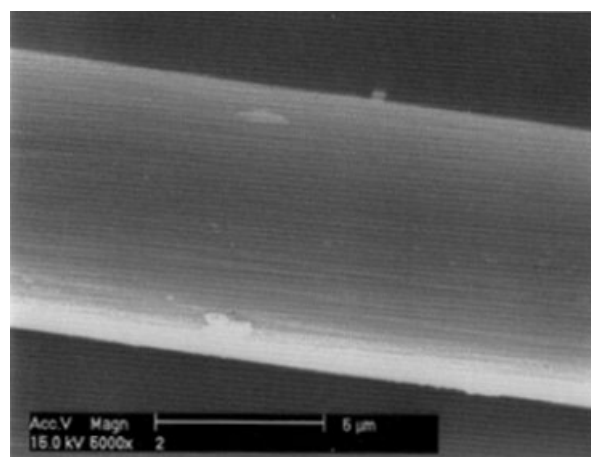
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(a)



(b)

Figure 4. SEM micrographs of (a) CF-BrA and (b) CF-PMMA.

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