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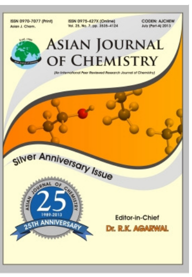

Preparation of Poly(methyl methacrylate) Functionalized Carbon Fiber *via* Reversible Addition-Fragmentation Chain Transfer Polymerization

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We report a novel method for the functionalization of carbon fiber with poly(methyl methacrylate) by using reversible addition-fragmentation chain transfer polymerization. The carbon fiber was first oxidized with a mixture of nitric acid and sulphuric acid (1:3), in order to introduce hydroxyl groups onto the carbon fiber surface. Then the reversible addition-fragmentation chain transfer agents were immobilized onto the surface of carbon fiber by chemical reaction of hydroxyl groups with silane coupling agent containing dithioester groups. Finally, the methyl methacrylate was initiated and propagated on the carbon fiber surface by reversible addition-fragmentation chain transfer. The poly(methyl methacrylate) grafted carbon fiber was characterized by FT-IR, ^{1}H NMR and TGA. The results show that the poly(methyl methacrylate) grafted carbon fiber were synthesized successfully and the graft content could reach 32.4 %.

Key Words: Carbon fiber, Reversible addition-fragmentation chain transfer, Poly(methyl methacrylate), Surface modification.

INTRODUCTION

In the past decade, carbon fibers (CF) have attracted extensively attention because of their high specific strength, high stiffness and chemical stability, which have been used in many fields, such as aerospace industry, automotive industry, steamship industry, petroleum and chemical industry[1,2]. Unfortunately, they have difficulty in forming a strong adhesive bond with polymer matrix due to their smooth surface and chemical inert nature[3-5]. Nowadays, since carbon fibers reinforced polymer composites become more and more important, several surface treatments are developed to modify carbon fibers surface, including chemical oxidation, plasma activation, electrochemical treatments and surface functional groups grafting procedure[6-11]. Among these methods, grafting polymer on carbon fibers is an effective way to provide a strong interfacial bond between carbon fiber surface and polymer.

In this paper, we focused on the study about the modification of carbon fiber with poly(methyl methacrylate) (PMMA) *via* reversible addition-fragmentation chain transfer polymerization (RAFT) for the purpose of improving the fiber-matrix interfacial adhesion. The functionalized carbon fibers with PMMA were studied by means of FT-IR, ^{1}H NMR and TGA.

EXPERIMENTAL

Carbon fibers used in this study were obtained from Hexcel. Methyl methacrylate (MMA) was purchased from Shanghai Reagents Co., Ltd. and was distilled under reduced pressure to remove the inhibitor before polymerization. 2,2'-Azo*bis*isobutyronitrile (AIBN) obtained from Aldrich was recrystallized with ethanol before use. 3-(Chloropropyl) triethoxy silane and the sodium ethyl xanthate were purchased from Arcos and used to synthesis silane coupling agent containing dithioester groups.

Synthesis of carbon fibres-reversible addition-fragmentation chain transfer agent: For the chemical oxidation of carbon fiber, the purified carbon fiber was mixed with the solution of conc. nitric acid and sulphuric acid in 1:3 ratio and the mixture was ultra sonicated for 8 h. The resulted fiber was then diluted with a slow and continuous flow of distilled water for 10 h, centrifuged at 4000 rpm and washed with deionized water. The oxidized carbon fibers were then modified by silane coupling agent with RAFT agent. At the end of reaction, the product was vacuum filtered through a 0.22 μm poly(tetrafluoroethylene) (PTFE) membrane and the functionalized carbon fiber was washed with anhydrous ethanol for three times. The RAFT agent functionalized carbon fiber [$CF-SC(S)OC_2H_5$] obtained was dried under vacuum at 45 ºC for 36 h.

Surface modification of carbon fibers by poly(methyl methacrylate *via* reversible addition-fragmentation chain transfer: For a typical experiment, a mixture of $CF-SC(S)OC_2H_5$, MMA, AIBN and DMF was added into a dried flask. The content was purged with argon for 10 min to eliminate the oxygen and then the flask was sealed. The polymerization was performed under ultrasonic irradiation. After a prescribed reaction time, the flask was cooled with ice water and opened. The reaction mixture was diluted with tetrahydrofuran (THF) and vacuum filtered with 0.22 μm PTFE membrane. The resulting filtered product was redispersed in 10 mL of THF, precipitated by the addition of abundant methanol and dried under vacuum at room temperature for 24 h. The procedure of surface modification of carbon fibers by PMMA is presented in Fig. 1.

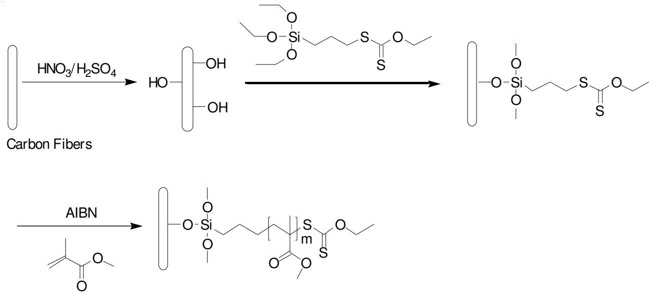

Fig. 1. Surface modification of carbon fibers

^{1}H Nuclear magnetic resonance (NMR) spectrum was recorded on a Bruker DMX 500 spectrometer in $CDCl_3$. Fourier transform infrared (FT-IR) spectra of the products were conducted on a Bruker 210 IR spectrometer at room temperature. Thermal gravimetric analysis (TGA) was recorded on a Shimadzu TG-50. The samples were heated from 25-700 ºC at a heating rate of 20 ºC/min under nitrogen atmosphere.

RESULTS AND DISCUSSION

Reversible addition-fragmentation chain transfer agents grafting on the carbon fiber: The covalent bond of RAFT agents on the surface was determined through FT-IR spectroscopy. Fig. 2 presents the FT-IR spectra of pristine carbon fiber and CF-SC(S)OC_2H_5. Compared with the pristine carbon fiber, CF-SC(S)OC_2H_5 spectrum shows a broad absorption peak at 3500-3100 cm^{-1} attributed to vibrations of the -OH groups on the carbon fiber surface. The broad absorption peaks at 2950 and 2865 cm^{-1} are due to the aliphatic hydrogen of the grafted RAFT agents. The two well resolved peaks which appeared at 1220 and 1050 cm^{-1} are assigned to the stretching vibrations of C-O and C=S, respectively. From the FT-IR results, it can be deduced that RAFT agents have been grafted on the carbon fiber surface through the formation of covalent bonds. The dithioester groups of the RAFT agents can further react with MMA *via* the RAFT process to form a polymer chemically bonded to the carbon fiber surface.

Grafting PMMA from the carbon fibers surface: The carbon fibers functionalized with PMMA (CF-PMMA) were prepared by RAFT process. For the FT-IR spectrum of CF-PMMA in the Fig. 3, peak at 1730 cm^{-1} which is attributable to C=O stretching vibrations of ester units appears. The peak at 2950 cm^{-1} is due to the C-H bending. In addition to, the peak at 1150 cm^{-1} can be assigned to the C-O stretching of the ester group. The FT-IR data confirm the presence of PMMA chains on the carbon fiber surface.

The covalent bonding of PMMA onto the carbon fiber surface is further supported by NMR. The ^{1}H NMR spectrum of PMMA cleaved from the carbon fiber surface is shown in the Fig. 4. The signals at 0.7-1 ppm are assigned to the protons of methyl groups adjacent to the backbone. The signal at 3.4 ppm is assigned to methyl protons of methyl ester group. The peaks at 1.8 ppm are also observed. We assign these peaks to the proton of the methylene groups in the backbone of the PMMA chains. In addition, the signal at 2.6 ppm is attributable to the methylene protons of the grafted RAFT agent.

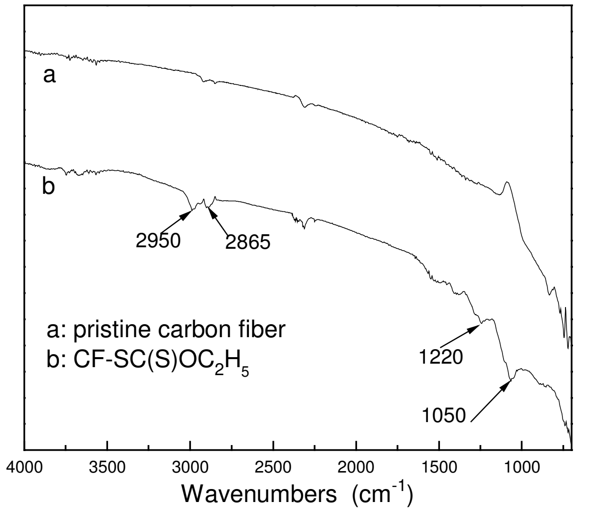

Fig. 2. FT-IR spectra of pristine carbon fiber and CF- SC(S)OC_2H_5

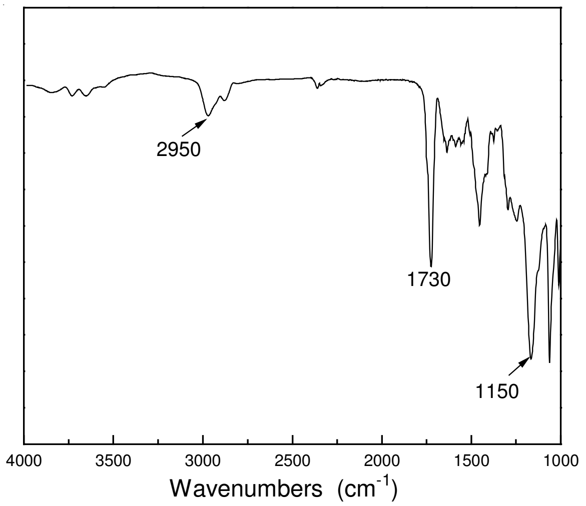

Fig. 3. FT-IR spectrum of CF-PMMA

The amount of grafted polymer on the carbon fiber surface was determined through the TGA analysis by comparing the TGA traces of pristine carbon fiber, CF-SC(S)OC_2H_5 and CF-PMMA and the results are showed in Fig. 5. The sample of pristine carbon fiber decomposes slowly with the increasing of temperature because of the losing of functional groups or absorbed water on the carbon fiber surface and the weight loss is about 5.4 % between 25 and 700 ºC. On the contrary, the sample of CF-SC(S)OC_2H_5 displays weight loss of about 13.2 %. This weight loss results from the losing of RAFT agent on the surface of carbon fiber and the weight loss is consistent with the content of RAFT agent grafted onto the carbon fiber. Compared with the pristine carbon fiber and CF-SC(S)OC_2H_5, the TGA curve of CF-PMMA showed three main weight loss

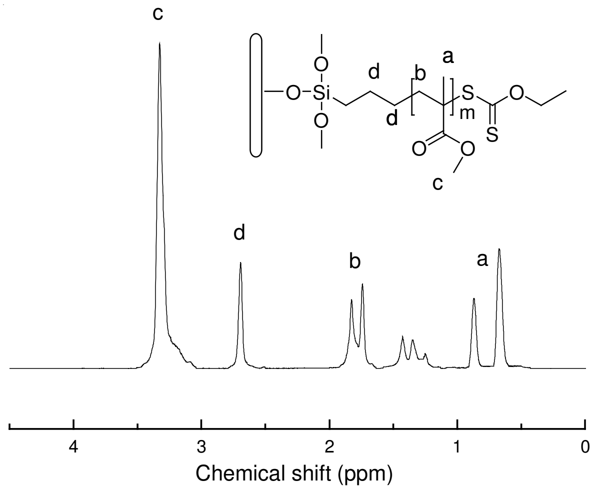

Fig. 4. ^{1}H NMR spectrum of PMMA cleaved from CF-PMMA

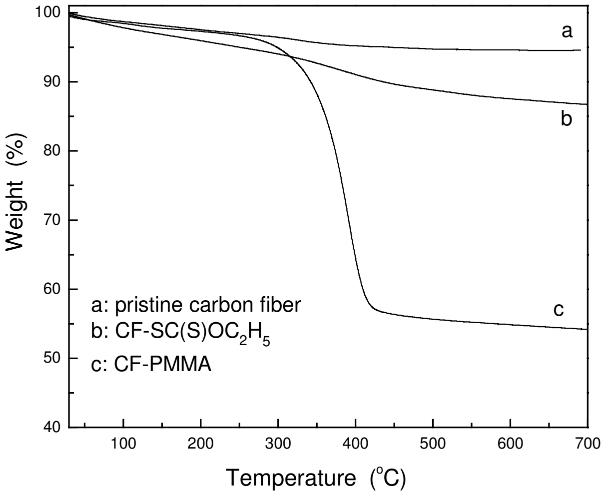

Fig. 5. TGA curves of different carbon fibers

regions. The first weight loss region below 250 ºC can be attributed to the decomposition of the functional groups on the carbon fiber surface. The second region (250-400 ºC) shows a rapid weight reduction which may come from the decomposition of PMMA and RAFT agent. A little loss in weight in the third region (400-700 ºC) can be assigned to the further decomposition of polymer segments. The amount of polymer calculated from TGA data is *ca.* 32.4 %.

Conclusion

In this study, the preparation of RAFT agent grafted onto the carbon fiber surface and the functionalization of carbon fiber with PMMA *via* RAFT polymerization were studied. After the RAFT agents were introduced onto the carbon fiber surface, the PMMA chains were successfully grafted from the carbon fiber surface *via* RAFT polymerization. The resulted products were characterized by means of FT-IR, ^{1}H NMR and TGA. The results demonstrated that the PMMA was successfully grafted from the carbon fiber surface and the amount of the polymer grafted on the carbon fiber is *ca.* 32.4 %. The realization of polymerization of MMA monomers on the carbon fiber surface by the convenient RAFT "grafting from" strategy would pave the way for the fabrication and application of more carbon fiber-polymer composites.

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