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Surface Modification of Vapor-grown Carbon Nanofibers in Radio Frequency Plasma[†]

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Vapor-grown carbon nanofibers (VGCNFs) were treated in radio frequency (RF) plasma to activate their surface and thus to improve the compatibility with the matrix in polymer composites. The surface of VGCNFs was modified in atmospheres containing different ratios of O_2 and Ar. Fourier transform infrared spectroscopy and thermogravimetric measurement shows that when the O_2 content in mixture gases was 5%, C$-$O and O$-$H functional groups were produced abundantly in the surface of the VGCNFs. When O_2 content increased to 8%, most of the surface of carbon fibers was severely oxidized, resulting in defects in structures of the inner layers of VGCNFs.

Key words: Vapor-grown carbon nanofibers, Surface treatment, Functional group, Plasma

I. INTRODUCTION

Vapor-grown carbon nanofibers (VGCNFs), which are distinctively different from polymer (polyacrylonitrile and pitch) derived carbon fibers in preparation methods, physical properties and the prospect of low-cost fabrication, have many applications as fillers in composites, super-high hydrogen storage materials, and anode materials [1-6]. However, untreated fibers have non-polar nature and a low surface energy, and are unable to form strong bonds between their surfaces and the matrix in composite. Therefore, good adhesion between VGCNFs and polymer matrix is essential for the performance of polymer-based composite materials, and the mechanical properties of the composites are strongly influenced by the fibers' surface morphology and chemistry [7-12]. Recently, a lot of research has been devoted to the surface treatment of carbon fibers in order to improve their adhesion to the matrix, including gaseous or liquid-phase oxidation, electro-chemical methods, polymer coating, ultrasonic irradiation, and plasma [13-17]. Plasma is a region of space where high-energy species, such as electrons, ions, radicals, and excited molecules are present. Compared with other treatment methods, plasma treatments have been widely investigated due to their several advantages such as significant improvements of the interfacial adhesion, slight decrease of the

tensile properties of fiber, no waste of chemical solution, and environmentally friendly processing [18-22]. Aiming at the low interaction with polymer matrix, one way to increase the adhesion between these components is to increase the fibers' surface energy by a plasma chemical treatment [23].

In this work, we investigate the treatment of VGCNFs using O_2-containing gases in radio frequency (RF) plasma, which is expected to introduce oxygen-containing functional groups. The surface properties are characterised by FT-IR, TG, and Boehm's titration method [24,25].

II. EXPERIMENTS

A. Materials

The starting material VGCNFs were prepared from the cracking of deoiled asphalt with ferrocene as catalyst by chemical vapor deposition (CVD). Deoiled asphalt was supplied by China University of Petroleum-Beijing. According to the literature [2,6], in a cylindrical furnace in a horizontal quartz glass tube 32 mm in inner diameter and 1 m in length, 1.8 g mixture of deoiled asphalt and 0.2 g of ferrocene was placed in a small quartz boat, which was located at first in the cool zone of the quartz tube outside the furnace. After the reaction zone was heated to 1000 °C in Ar atmosphere with flow rate of 150 mL/min, the reaction was continued in such a way that the quartz boat was removed toward higher temperature zone for the complete pyrolysis of deoiled asphalt and ferrocene within 30 min. When cooled to room temperature in Ar flow, the prod-
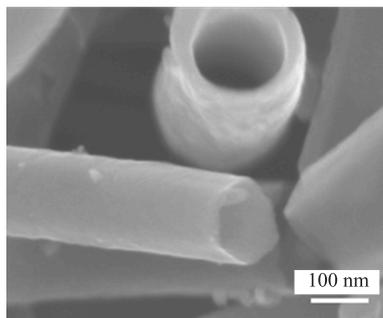
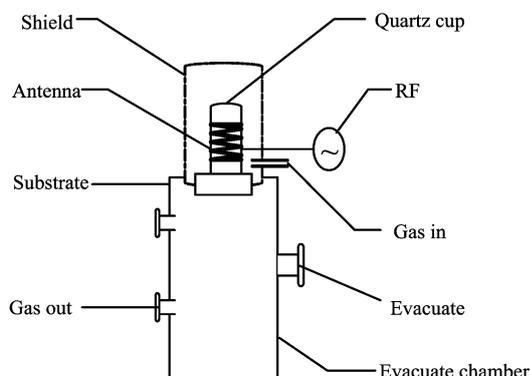FIG. 1 The FESEM images of as-synthesized VGCNFs.

FIG. 2 Device of radio frequency plasma.

ucts were collected from the inner wall near outlet of the quartz tube. The VGCNFs were characterized by field-emission scanning electron microscopy (FE-SEM). The outer diameters ranged from 100 nm to 200 nm, as shown in Fig.1.

B. Plasma treatment

O_2 plasma treatment conditions for as-synthesized VGCNFs by RF plasma were as follows: operating pressure of 4.5 Pa, working voltage of 380 V, reaction time of 10 min, Ar flow rate of 20 mL/min, process O_2 flow rate of 0, 0.6, 0.8, 1.0, or 1.6 mL/min. The experimental setup is shown in Fig.2.

About 0.1 g of as-synthesized VGCNFs was placed on a ceramic plate inside the plasma chamber. Firstly, a vacuum was established in the reaction chamber. Secondly, the mixture of O_2 and Ar at given ratio was allowed to flow into the chamber, the sample was treated in plasma for 10 min, and cooled to room temperature in Ar atmosphere. Finally the products were collected.

C. Characterizations of treated-VGCNFs

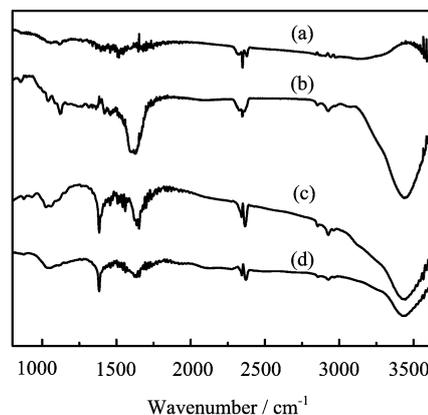In order to determine the reactive changes during the treatments, FI-IR spectra of the samples were obtained

FIG. 3 FT-IR spectra of VGCNFs plasma-treated in Ar with different content of O_2. (a)3%, (b) 4%, (c) 5%, (d) 8%.

with a Perkin-Elmer FT-IR spectrum 1730 spectrometer. The VGCNFs-KBr mixture was ground, then desorbed at room temperature and pressed to obtain IR-transparent pellets [26]. Thermoanalysis was conducted with a Netzsch TG 209F3 operating in air atmosphere from 35 °C to 950 °C at a heating rate of 10 °C/min.

The functional groups of plasma-treated VGCNFs were quantitatively measured by Boehm's titration method. About 0.1 g of modified VGCNFs was dried at 105 °C for 12 h. The sample was then dispersed in 50 mL of 135.5 mmol/L NaOH solution and supersonicated for 8 h. The suspension was filtrated and the filtrates were titrated with 547.7 mmol/L HCl to adjust the pH value of the filtrates to 7.0.

III. RESULTS AND DISCUSSION

Figure 3 shows typical FT-IR spectra of the VGCNFs samples for different content of O_2 in plasma. When the content of O_2 was lower, activated oxygen free radicals produced in RF plasma were not sufficient enough to induce the reaction, so no absorption peak occurred for VGCNFs sample treated in 3% O_2 plasma. The others had absorption bands at around 3440, 1645, 1380, and 1050 cm^{-1}. Bands at around 3440 cm^{-1} can be assigned to the $-$OH functional group, showing that the content of $-$OH in VGCNFs sample treated in 4% O_2 plasma was the highest, and further increase in O_2 content resulted in reduced $-$OH content. VGCNFs samples treated in 4%, 5%, and 8% O_2 plasma showed absorption bands in the range of 1635-1650 cm^{-1} which are attributed to C=C stretching vibration. Their intensity was reduced when the O_2 content was increased, indicating that the surface microcrystallite structure of VGCNFs were made defective. Moreover, VGCNFs sample treated in 5% O_2 plasma had the strongest absorption at 1380 cm^{-1} for CH$_3$ group. The band at 1050 cm^{-1} can be attributed to the C$-$O group, which was the strongest for sample treated in 4% O_2 plasma.
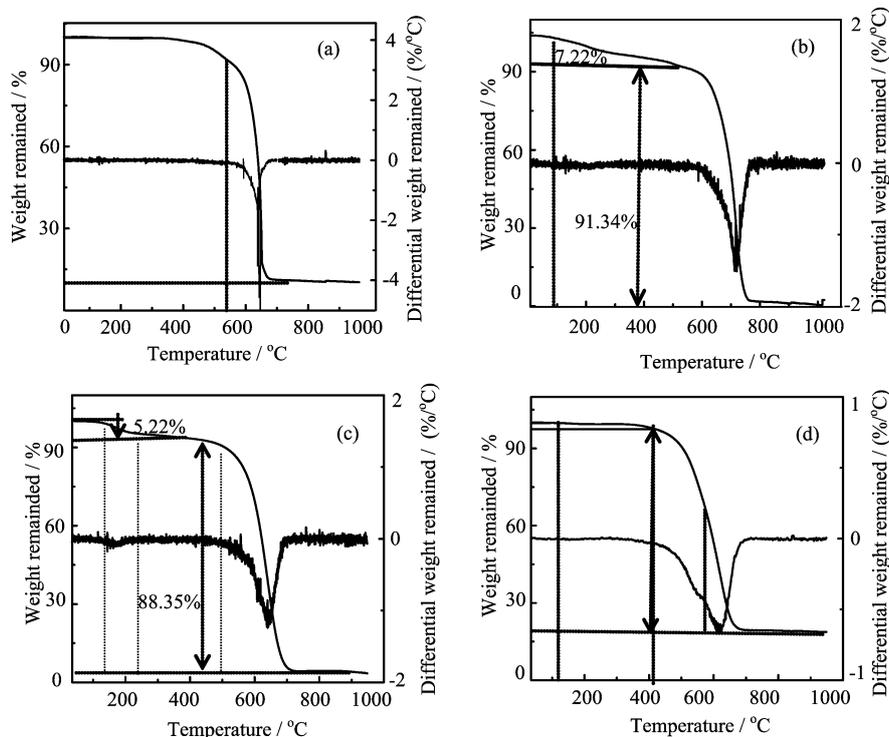
FIG. 4 TG curves of the samples treated in plasma containing different content of O_2. (a) 3%, (b) 4%, (c) 5%, (d) 8%.

TG curves for the samples treated in plasma containing different amount of O_2 are shown in Fig.4. The initial temperature of VGCNFs sample treated in 3%O_2 plasma was 522.3 °C and no O−H functional groups were introduced on their surface for O_2 content of 3%. The weight loss of VGCNFs sample treated in 4%O_2 plasma can be divided into two parts. First, between 110 and 500 °C, the sample lost 7.22% of total weight, which was mostly hydroxy-water. Next, 91.34% of the sample's weight was lost from 538.6 °C to 720 °C, mainly through the combustion of carbon fibers. The temperature of initial weight loss during the first step for VGCNFs sample treated in 5%O_2 plasma is the lowest, indicating the surface hexagonal carbon network was correspondingly made defective, and C−O and O−H functional groups were produced in the surface of VGCNFs. By comparison to Fig.4(b), Fig.4(d) indicates lower temperature of initial and final weight loss in second part and higher rate of weight loss. The surface of VGCNFs sample treated in 8%O_2 plasma was oxidized severely.

It is well known that surface modification on VGC-NFs can offer not only a more hydrophilic surface structure, but also a larger number of oxygen-containing functional groups, which would increase the ion-exchange capability of carbon fibers [24]. The functional groups on the surface can be quantitatively measured by Boehm's method. According to this method, sodium hydroxide can neutralize acidic functional groups, including carboxyl groups, lactones and phenols, so the different quantities of functional groups in different samples can be calculated through the known volume of used base and acid [25,26]. Total amount of the NaOH-titrated oxygen containing functional groups of the VGCNFs samples treated in plasma containing O_2 with different content of 3%, 4%, 5%, and 8% was 0.22, 0.31, 0.52, and 0.48 mmol/g, respectively. It can be seen that the VGCNFs treated in 5%O_2 plasma contained the most oxygen-containing functional groups, and the acidity of these fibers was notable. The results confirmed the TG and FT-IR analysis.

During plasma treatment, the surface of the VGCNFs reacted with activated oxygen atoms and sub-stable state molecules, defects were introduced on the surface microcrystallite structure, C=C bonds were fractured and hydrocarbon (CH_x) was generated. At the same time, hydroxyl groups were formed. It is supposed that the main hydrogen source was the fibers themselves which contained residual hydrogen from the preparation process. Previous characterization has shown that [2,6] two types of carbon layers exist in VGCNFs: the inner walls are highly ordered graphitic carbon layers precipitated from the carbon solid solution, and are stable structures which are difficult for oxidation at low concentration of oxygen atoms; the outer walls are composed of amorphous carbon with a loose surface structure, so even with only a small amount of oxygen in the reaction chamber, VGCNFs could be modified to some content. When the oxygen content in plasma gradually

built up to 5%, the outer layers of VGCNFs reacted, and the single bonded carbon atoms were oxidized partly to $C{-}O$ groups. As the content of O_2 was increased to 8%, the reaction occurred in the inner layers of VGCNFs.

IV. CONCLUSION

VGCNFs were plasma-treated in O_2 and Ar atmosphere. This type of treatment was proved to be a feasible way to modify the fibers surface in order to improve the matrix-fiber stress transfer for enhanced mechanical properties of fiber-polymer composite. The surface of VGCNFs was modified in atmospheres containing different ratios of O_2 and Ar by RF plasma. FT-IR and TG measurement shows that when O_2 content in mixture gases was 5%, many $C{-}O$ and $O{-}H$ functional groups were produced in the surface of the VGCNFs. Moreover, with O_2 content increased to 8%, most of the surface of carbon fibers was oxidized severely, which resulted in defects in the structures of the inner layers of VGCNFs.

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