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Study on the preparation and characterization of ultra-high molecular weight polyethylene–carbon nanotubes composite fiber

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Abstract

The ultra-high molecular weight polyethylene (UHMWPE)–carbon nanotubes (CNTs) composite fibers were prepared by gel spinning. To realize the homogeneous dispersion and good load transfer between the CNTs and the polymer matrix, the purification and functionalization of CNTs were carried out. TEM, SEM, XRD, IR were used to characterize the CNTs, their dispersion in the matrix and the functional group changes on the surface of the CNTs. The results showed that there was no obvious agglomerating of CNTs in obtained composite fibers and consequently a good interaction between CNTs and UHMWPE matrix was also established. Furthermore, it was found that the adding of CNTs resulted into a peculiar structure, a more regular alignment of the UHMWPE morphology. The mechanical and thermal properties of UHMWPE–CNTs fibers prepared by gel spinning and ultra drawing were improved compared with that of pure UHMWPE fiber.

Keyword: Carbon nanotubes

1. Introduction

The discovery of carbon nanotubes (CNTs) has created enormous attraction in recent years due to their unique structure and properties [1]. They are quasi-one-dimensional cylindrical tubules formed from wrapped tubular graphite sheets and possess extremely high aspect ratio, high elastic modulus, low density and fierce resistance to failure, so CNT is one of ideal reinforcing materials for polymer composites, especially for the composite fibers. Polymer–CNTs composites have already been investigated into the functional application in display, conductive polymer, flame-retardant material, electromagnetic interference shielding, optical emitting devices, and lightweight, high strength composites.

The recent discovery of CNTs has stimulated much interest in preparation, characterization and application of it as a reinforce component for polymer materials [2,3]. Generally, there are two methods to fabricate the polymer–CNTs composites, i.e., direct mixing and in situ polymerization. But there are still many practical challenges in both preparation methods due to the agglomerate structures of CNTs. The reinforcing efficiency of CNTs in composite applications depends strongly on the uniform dispersion of CNTs throughout the polymer matrix without destroying the integrity of the nanotubes. Furthermore, good interfacial bonding between polymer and CNTs is also required to achieve load transfer across the polymer–CNTs interface to

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improve the mechanical properties of polymer–CNTs composites. In order to optimally utilize the CNTs as a reinforcing component in polymer matrix, some special treatments [4–6] of CNTs, such as physical or chemical functionalization, are performed to achieve a good interface between CNTs and polymer matrix and to obtain polymer–CNTs composites with good properties.

Ultra high molecular weight polyethylene (UHMWPE) has excellent properties, such as low density, high strength high modulus, good abrasion and chemicals resistance, high-energy absorption, impact strength, low frictional coefficient etc. The finding of gel spun and ultra drawn UHMWPE fiber with high strength and high modulus has expanded available for applying to some special applications to fit different requests. Unfortunately, the fiber has some weaknesses such as poor flow behavior and consequently difficult to process, low yield and high cost, poor thermal property (the highest serviceable temperature is only as low as about 70 °C), and the fiber is quite liable to creep under tension. These greatly limit its further applications in some special fields.

In this paper, the UHMWPE–CNTs composite fibers were prepared by gel spinning. In order to improve the compatibility between the matrix and the CNTs, the purification and functionalization of the CNTs were carried out. The study is focus on the preparation and characterization the UHMWPE–CNTs composite fibers.

2. Experimental

2.1. Purification of CNTs

The CNTs used in this experiment are multi-walled carbon nanotubes (MWNTs) produced by Shenzhen Nanotech Port Co., Ltd, China, with the mean internal, external diameters and length as 20, 40 nm and 0.5–50 μm, respectively. First, MWNTs are dispersed in an initial prepared solution of potassium permanganate and sulphuric acid in an ultrasonic bath at room temperature for about 2 h. The mixture is refluxed at 120 °C for about 4 h and then the CNTs are filtrated out and washed with deionized water until the pH of mixture reaches 7. At last, they are dried at 100 °C in the vacuum. Finally, the gained CNTs are furthermore ground for use.

2.2. Functionalization of the CNTs

The functionalization process is necessary in order to obtain a uniform UHMWPE–CNTs gel, otherwise the swelling process is difficult to carry out because of the severe agglomerating of CNTs. The purified CNTs and certain amount of titanate coupling agent are added into certain amount of ethanol, ultrasonicated for about 1 h to disperse the CNTs uniformly, and then refluxed at about 78 °C for about 2 h. The functionalized CNTs are gained when ethanol is evaporated.

2.3. Preparation of the fibers

The UHMWPE powder sample is provided by Beijing No. 2 Chemical Company and the molecular weight is 3×10^6 g/mol. The mixture of olefin and functionalized CNTs with certain proportion is ultrasonicated for about 2–3 h until the CNTs uniformly dispersed, then certain amount of UHMWPE powder is added into the mixture. The mixture is then heated with appropriate heating rate and agitating speed until a homogeneous UHMWPE solution is obtained. The solution is subsequently spun into gel fibers by gel spinning. The obtained gel fiber is extracted by gasoline repeatedly until the gasoline does not show any muddiness. At last, a three stage drawing process is carried out on the as-spun fibers with high drawn down ratio to obtain UHMWPE–CNTs composite fibers.

2.4. Characterization

NEXUS-670 Infrared spectroscopy, Hitachi H800 transmission electron microscope (TEM) and SM-5600LV Scanning Electron Microscope (SEM) are used to characterize the modified CNTs and the obtained composite fibers.

3. Results and discussion

The crude CNTs always include some impurities such as raw nanotube material of soot and metal catalyst particles remained during the production process. Because the existence of the impurities has been known to have negative effects on the properties of the composite, it is therefore a request of removing these impurities from CNTs. The appropriate chemical oxidation can introduce oxygen-containing functional groups onto surface, which provides the possibility for the further functionalization of CNTs to prepare the composites with good properties. Several purification methods, such as oxidation, micro-filtration and chromatography methods, have been reported. These methods can be divided into two kinds, e.g., physical and chemical purification. In this paper, the chemical methods, oxidation method, was employed to purify the CNTs. Theoretically and experimentally, different oxidative speeds between CNTs and impurities could be used to achieve this target.

Fig. 1 shows the TEM images of both unpurified and purified CNTs, respectively. A comparison of these two figures indicated that most of the impurities have been removed. Obviously, this suggests that the oxidation

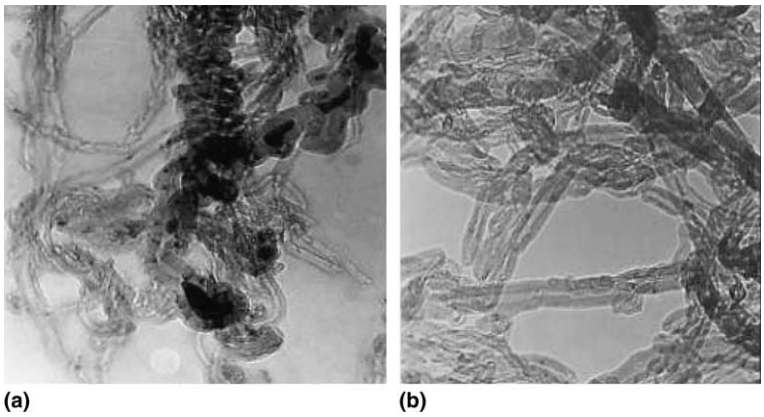

Fig. 1. TEM images of the unpurified and purified CNTs: (a) unpurified CNTs, (b) purified CNTs (50,000 magnitude).

treatment is an effective method for purification of CNTs.

The advantages of carbon nanotube fillers have not been fully realized because it is difficulty to obtain fully homogeneous and stable nanotubes. Also the lack of affinity of the nanotubes for polymer matrix inhibits load transfer from the matrix to nanotubes. To get a good dispersion for CNTs in matrix to receive a high interfacial adhesion between nanotubes and matrix, it is necessary to attach some organic functional groups on the surface of CNT. Principally, the presence of oxidizing groups is availably to help the attachment of molecules onto the surface of the CNTs to increase the compatibility and realize the load transfer between the matrix and the CNTs. For example, Chen et al. [7] and Zhao et al. [8] have demonstrated that the oxidation process can introduce carboxyl groups onto the surface of CNTs to benefit a further functionalization. In addition, octadecylamine [9], dichlorocarbene, alkanes [10] and fluorine [11] have been also observed successfully grafted onto the surface of the CNTs to arrive the same effect. In this paper, the titanate coupling agents was used.

The FTIR spectra for unpurified, purified and functionalized CNTs are shown in Fig. 1. Observe, the purification is well due to the carbonyl (C═O) stretched at about 1600 cm^{-1} presented comparing to the native sample. Moreover, the peak presented at about 3500 cm^{-1} assigned to hydroxy (O–H) stretching has also been found much stronger to support the purification occurrence for CNTs. Obviously, these evidences indicate that the carboxyl groups are introduced on the surface of CNTs by the oxidation (see Fig. 2).

In general, the use of the titanate-coupling agent in this case is able to let its long alkyl chain react with the carboxyl groups of CNT to introduce a steric hindrance effect and meanwhile to avoid the agglomeration for CNTs. This reaction was also proved by comparison of the FTIR spectra of functionalized CNTs and the original sample (Fig. 1). For example, the peak presented

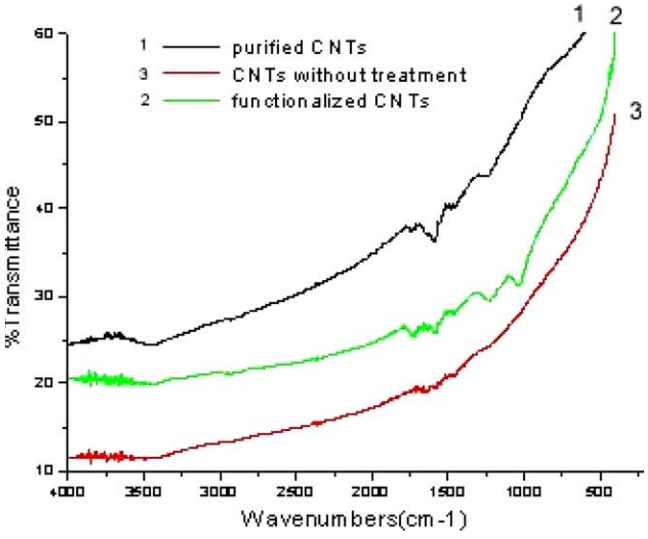

Fig. 2. FTIR spectra of the CNTs.

at 3500 and 1600 cm^{-1} for functionalized CNTs have been found weaker and less sharp than that of the original sample, respectively. These demonstrate that the reaction between CNTs and titanate coupling agent taken place.

Images of the fracture surface for pure and CNTs modified UHMWPE fibers were showed in Fig. 3. A comparison of two samples, e.g., pure UHMWPE fiber (a) and UHMWPE–CNTs composite fiber (b) showed there has a big difference between them. Fig. 3(b) shows that the unexpected agglomeration is not appeared in the UHMWPE–CNTs composite. The fracture morphology for (a) is a typical called ''towel gourd rib structure'', [12] while the (b) morphology is to be regularly. This is of interest and suggests that the addition of CNTs can cause the fibrillation effect as a uniformly regular structure for UHMWPE macromolecules. Assuming this phenomenon is caused by the small size effect in CNTs, further studies are thus necessary for understanding and explanation.

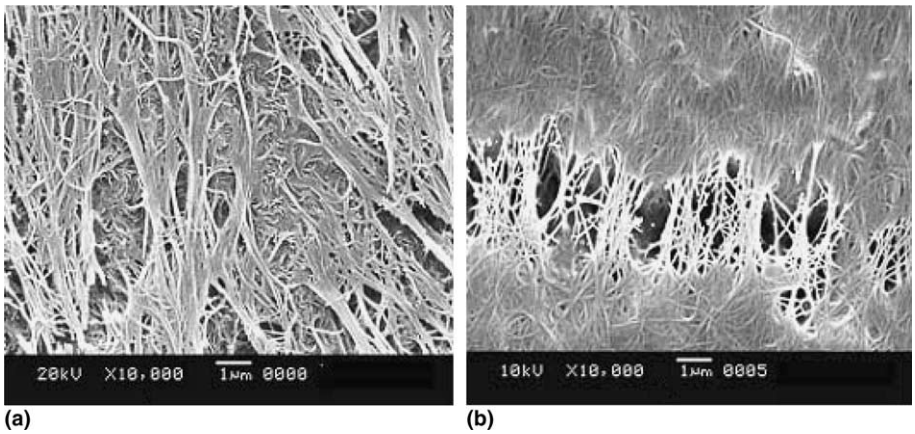

Fig. 3. SEM images of neat UHMWPE and UHMWPE–CNTs composite fiber: (a) neat UHMWPE as-spun fiber, (b) UHMWPE–CNTs composite fiber.

Table 1
Mechanical properties of UHMWPE fiber and UHMWPE–MWCNTs composite fibers

Sample	Tensile strength (cN/dtex)	Elongation at break (%)	Yang's modulus (cN/dtex)
UHMWPE	27.36	4.48	847.32
UHMWPE–MWNTs (0.25 wt%)	28.44	4.55	897.23
UHMWPE–MWNTs (1 wt%)	29.79	4.42	966.96
UHMWPE–MWNTs (2 wt%)	29.64	4.24	959.51
UHMWPE–MWNTs (3 wt%)	29.18	4.19	894.48

Table 1 shows the mechanical properties of UHMWPE fibers and UHMWPE–MWNTs composite fibers. The strength and modulus increases and elongation at break decreases with the addition of MWCNTs to 1%. However, when the adding amount of carbon nanotubes exceeds of 2%, the mechanical properties of UHMWPE–MWNTs have been found greatly reduced suggesting that the agglomeration might be occurred.

The thermal properties of UHMWPE fibers and UHMWPE–MWCNTs composite fibers are characterized by TGA in Fig. 4. The thermal decomposition temperature has been found goes up with the addition of carbon nanotubes.

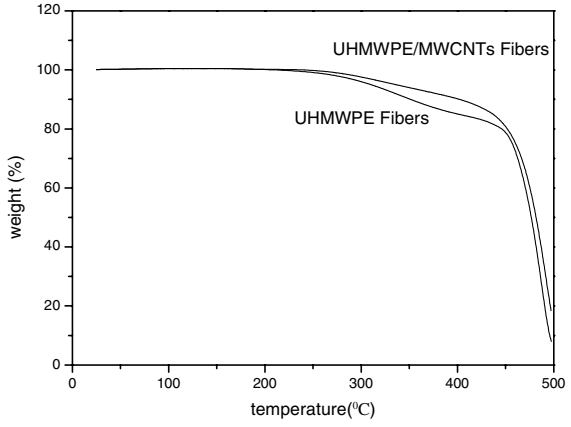

Fig. 4. TG curves of UHMWPE fibers and UHMWPE–MWNTs composite fibers.

4. Conclusions

1. Oxidation is an effective method for the CNTs purification, which can not only remove most impurities existed in the CNTs but also provide reactive groups suitable for further functionalization on the surface of CNTs.
2. The functionalized CNTs by the selective coupling agent can well be dispersed in the UHMWPE matrix and a good interface is formed between the CNTs and the matrix.
3. The mechanical and thermal properties of CNTs modified UHMWPE fibers are all improved compared with that of pure UHMWPE fibers.

References

[1] Sánchez-Portal D, Artacho E, Soler JM, Rubio A, Ordejón P. Phys Rev B 1999;59:12678.
[2] Shaffer MSP, Windle AH. Adv Mater 1999;11:937.
[3] Safadi B, Andrews R, Grulke EA. J Appl Polym Sci 2002;84:2660.

[4] Gong X, Liu J, Baskaran S, Voise RD, Young JS. Chem Mater 2000;12:1049.
[5] Andreas H. Angew Chem, Int Ed 2002;41:1853.
[6] Lin Yi, Apparao MR, Sadanadan Bindu, Kenik Edward A, Sun Ya-Ping. J Phys Chem B 2002;106:1294.
[7] Chen J, Hamon A, Hu H, Chen Y, Rao AM, Eklund PC, et al. Science 1998;282:95.
[8] Zhao W, Song C, Pehrsson PE. J Am Chem Soc 2002;124:12418.
[9] Grady BP, Pompeo F, Shambaugh RL, Resasco DE. J Phys Chem B 2002;106:5852.
[10] Boul PJ, Liu J, Mickelson ET, Huffman CB, Ericson LM, Chiang IW, et al. Chem Phys Lett 1999;310:367.
[11] Mickelson ET, Chiang IW, Zimmerman JL, Boul PJ, Lozano J, Smalley RE, et al. J Phys Chem B 1999;103:4318.
[12] Ruiling Cheng. Master Degree Thesis of DongHua University; 2003.