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Short communication

Fabrication and characterization of polycarbonate/carbon nanotubes composites

Li Chen [a,*], Xiu-Jiang Pang [b], Mei-Zhen Qu [c], Qing-tang Zhang [c], Bin Wang [c], Bai-Lan Zhang [c], Zuo-Long Yu [c,*]

[a] *Key Laboratory of Rubber-Plastics, Qingdao University of Science and Technology (QUST), Ministry of Education, Zhengzhou Road, Qingdao, Shandong 266042, China*
[b] *Department of Chemistry and Molecular Engineering, QUST, Qingdao 266042, China*
[c] *Chengdu Institute of Organic Chemistry, Graduate School of Chinese Academy of Sciences, National Center for Nanoscience and Nanotechnology, Chengdu 610041, China*

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Abstract

Polycarbonate composites containing carbon nanotubes can be prepared through a method combined solution mixing and precipitation together. The surface chemical state of the purified carbon nanotubes was studied through X-ray photoelectron spectroscopy, and the state of carbon nanotubes in the composites through transmission electron microscopy and scanning electron microscopy. Results showed that some polar functional groups such as C—O, C=O and O—C=O were present on the surface of the purified carbon nanotubes, and carbon nanotubes coated with polycarbonate layers were well dispersed through the polycarbonate matrix. Ultrasound is supposed to play an important role in the uniform dispersion of carbon nanotubes into the polycarbonate solution and the formation of the composites. The preparing method is regarded as an easy way of producing polymer based nanocomposites on a large scale.

Keywords: A: Carbon nanotubes; A: Polymer–matrix composites; B: Microstructures; D: Electron microscopy

1. Introduction

Since the discovery of carbon nanotubes (CNTs), polymer based composites including CNTs have attracted considerable attention in the research and industrial communities, due to their good electrical conductivity, high stiffness and high strength at relatively low CNTs content [1–8]. This can be attributed to the special electrical and mechanical properties of CNTs. For example, CNTs have diverse electrical properties, capable of acting as either conductors or semiconductors depending upon the chirialities of the CNTs [9,10]. What is more, various studies have demonstrated that CNTs have moduli and strength levels in the range 200–1000 GPa and 200–900 MPa, respectively [11,12]. So, CNTs have been regarded as good candidates for producing new functional composites.

A key issue in producing polymer/CNTs composites is how to achieve a homogeneous dispersion of CNTs in target polymer base. Currently, three methods are commonly used to introduce CNTs into polymers: (1) solution mixing or film casting of suspensions of CNTs in dissolved polymer [13], (2) in situ polymerization of CNTs-polymer monomer mixture [14], and (3) mechanically melt mixing of CNTs with polymer melts [15]. Studies using melt processed thermoplastic polymer/CNTs composites have been quite limited. The tendency of nanotubes to form aggregates may be minimized by appropriate application of shearing force during melt mixing. For example, Haggenmueller et al. [4] applied a method that combined solvent casting and melt processing together to produce

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[*] Corresponding authors. Tel./fax: +86 532 8402 3977 (L. Chen).
E-mail address: chenli720516@hotmail.com (L. Chen).

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films of poly(methyl methacrylate) (PMMA) containing single walled carbon nanotubes (SWNTs). The films obtained by this melt processing technique had a more uniform nanotube distribution than the cast film and led to much better mechanical properties. Ferguson et al. [7] reported on kilogram quantities of polycarbonate(PC)-based nanotube formulations produced in a Buss Kneader. The results showed a better dispersion of the fibrils in as produced composites. PÖtschke et al. [16] examined the rheological properties of multi-walled carbon nanotubes (MWNTs) filled PC nanocomposites formed by melt extrusion.

Ultrasonic irradiation, as a new technology, has been widely used not only in chemical synthesis, but also in dispersion, emulsifying, crushing, and activation of particles. By taking advantage of the multi-effects of ultrasound, the aggregates and entanglements of CNTs can be effectively broken down. Xia et al. [17,18] prepared polymer-encapsulated spherical inorganic nanoparticles through ultrasonic irradiation.

Here, we produced PC based composites incorporating MWNTs by a combination of solution mixing and precipitating, and examined the state of CNTs in the composites through transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Results showed that CNTs were disentangled and well dispersed through the PC matrix, from which a tight interface binding can also be deduced. X-ray photoelectron spectroscopy (XPS) was also used to study the surface chemical state of the purified MWNTs.

2. Experimental

MWNTs used were synthesized from methane via catalytically chemical vapor deposition (CCVD). A horizontal quartz glass reactor, 30 mm in diameter and 1000 mm in length, was used for the growth of MWNTs. The heat source was a tubular electric furnace. Temperatures were monitored using thermocouples coated with thin quartz tubes inserted into the reactor. The gas flow into the reactor was controlled by mass flow controllers with an accuracy of 0.1 ml for all gases. In all experiments, the reaction pressure was maintained at the ambient level. First, the catalysts were reduced from their oxidized state in a flow of H_2 (20 ml/min) starting at room temperature and rising to 1073 K, then held at the latter temperature for 0.5 h. Then the reactor temperature was lowered to 973 K for the reaction. After sweeping with N_2 gas, methane was introduced into the reactor, passing over the catalyst at 30 ml/min for 60 min. After cooling to ambient temperature in a flow of N_2, the products were collected. The as produced MWNTs were treated with acid to remove the remained catalyst particles and the support of catalysts. The as purified MWNTs were dried in a oven at 150 °C for 24 h. The as produced MWNTs existed as agglomerates and curved intertwined entanglements [19] with an average diameter of 20 nm. The PC powder was obtained from Gang Yang-da Plastics Co. Ltd. Guang Zhou, China, and dried at 110 °C under vaccum prior to use.

The production of the PC-based composites containing MWNTs was as follows: Firstly, 10 g PC powder was solubilized in 60 ml chloroform ($HCCl_3$); Secondly, under a power output of 130 W, the as purified MWNTs were dispersed into the above solution of PC by sonicating at a frequency of 20 kHz for 10 min; Finally, precipitation was carried out to extract the PC/MWNTs composite particles which were then separated and fully dried in a vacuum oven. In this way, composites with different contents of MWNTs can be conveniently produced just by changing the amount of MWNTs incorporated.

The as purified MWNTs and PC/MWNTs nanocomposites were characterized by TEM using a JEM-100cx instrument with an accelerating voltage of 20 kV. The samples were ultrasonicated in ethanol suspensions with ultrasonic bath and then the dispersion was dropped on a copper grid to observe the morphology.

Thermo-gravimetric analysis (TGA) was used to determine the purity of purified CNTs, and a SEIKO EXSTAR6000 was used to characterize weight loss during the oxidation of the samples in air heating to 750 °C at a rate of 10 °C/min.

The surface state analysis of purified CNTs were performed by XPS employing a Kratos XSAM 800 spectrometer with Al Kα (1.48 keV) radiation. The system pressure was normally maintained at 6.7×10^{-7} Pa. The spectrometer was run in fixed retarding ratio (FAT) mode at a pass energy 12 kV and 15 mA. All binding energies were referred to the carbon 1s (BE = 284.6 eV) peak for sample charging.

SEM was also carried out on the fracture surface of the thin slice molded from the aforesaid PC/MWNT composites by using a JSM-5900LV instrument with an accelerating voltage of 20 kV.

3. Results and discussion

It is well-known that most as produced CNTs contain some impurities such as amorphous carbon, fullerenes,

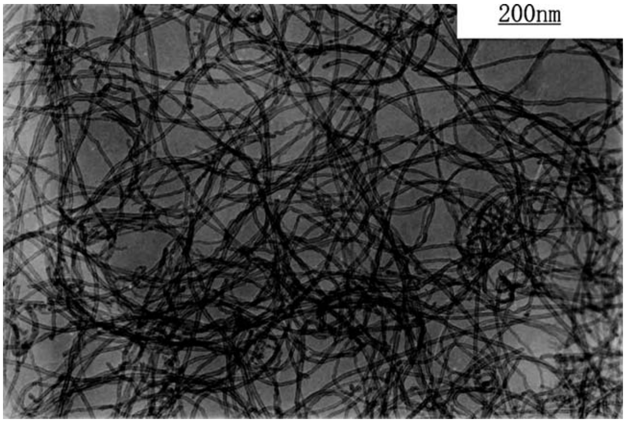

Fig. 1. TEM image of as purified MWNTs.

nanocrystalline graphite and catalyst particles, which were a serious impediment for CNTs to be directly used as functional filler in polymer based composites. Fig. 1 showed the TEM image of purified MWNTs in which the long intertwined CNTs with a diameter of about 20 nm were very clean and almost all impurities have been removed without destroying the basic structure of nanotubes. Thus, the purification for MWNTs was effective. TGA results in Fig. 2 further indicated that the residue weight of purified MWNTs was rather low and the purity was about 98.0%.

XPS analysis was applied to elucidate the surface state of the as purified MWNTs. Fig. 3 shows the XPS spectrum. According to the XPS studies about surface oxidized carbon fibers [20,21], activated carbons [22,23], carbon black [24], and carbon nanotubes [25], the broader C 1s peak region at 284.6 eV could be fitted to four line shapes with binding energies at 285.024, 286.620, 288.950, 291.070 eV. These different binding energy peaks were assigned to C—C at 285.024 eV, C—O at 286.620 eV, C=O at 288.950 eV and O—C=O at 291.070 eV [26]. So, in addition to the C—C groups, the surface of as purified MWNTs still contained other carbon-based surface polar oxygenated groups which were beneficial to the combination with PC matrix. These surface polar functional groups mainly come from the oxidation in its purification process. From the above results, the total area of the C 1s peak region of the MWNTs sample consists of 69.79% C—C, 18.55% C—O, 6.352% C=O and 5.299% O—C=O. These data are summarized in Table 1.

Table 1
Relative concentrations of functional components obtained from curve fitting the C1s peak of the as purified MWNTs sample

Surface functional group	Binding energy (eV)	Relative concentration (%)
C—C	285.024	69.79
C—O	286.620	18.55
C=O	288.950	6.352
O—C=O	291.07	5.299

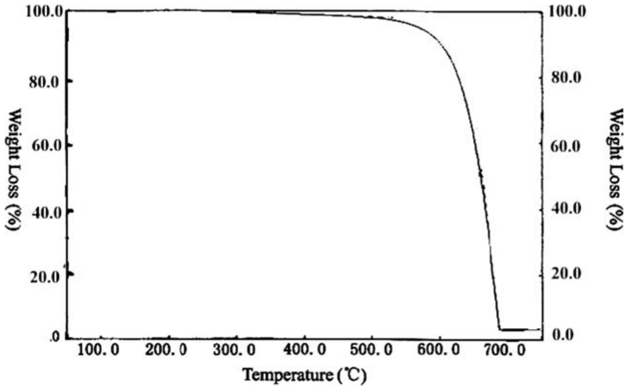

Fig. 2. TGA curve of as purified MWNTs.

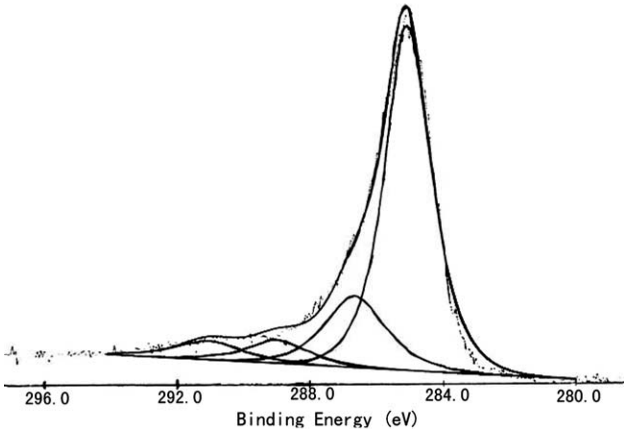

Fig. 3. XPS spectrum of purified MWNTs.

Fig. 4 shows the TEM images of PC/MWNTs composites with different contents of CNTs. It is not difficult to find that the diameters of MWNTs coated by PC matrix in the composites are larger and untangled, and the two different components combined with each other due to the strong attraction between their molecules. The PC molecules could be absorbed onto the surface of the as purified MWNTs with many polar functional groups. Because of the similar polar oxygen containing groups in these two molecules, they combined with each other through either Van derWaals force, H bond or other forms of covalent bond. Thus, the PC/MWNTs composites with a solid interface could be naturally formed in the process of mixing and precipitating. However, ultrasonic wave as well as mechanically stirring played important roles in the formation of the composites with a uniform particle size, for when the ultrasonic wave passes through a liquid medium, the chemical effects of ultrasound are due to high pressure produced during violent collapse of cavitation bubbles [27] in about a few microseconds. Sonochemical theory calculation and the corresponding studies suggested that ultrasonic cavitation can generate a high local temperature of 5000 K and a local pressure of 500 atm [28], which is a very rigorous environment. So, the ultrasound here was supposed to play a key role in the untangling, emulsifying and activation of the initial intertwined CNTs, in the uniform dispersion of nanotubes into PC solution, and even in the formation of the composites. It can also be found that the amount of PC layer on CNTs reduced with the increase of CNTs' weight percentage in the composites, for an example, the area of naked parts of CNTs in the composites with 17 wt% of CNTs was larger than that in the composites with 5.6 wt% of CNTs.

In order to further observe the dispersion state of MWNTs in the PC matrix, SEM characterization was performed on the PC/MWNTs composite. Fig. 5 shows SEM images of PC/MWNTs composites with 16.9wt.% of CNTs obtained at two different magnifications. The CNTs were uniformly distributed through the matrix, and even single nanotubes could be distinguished from each other. From

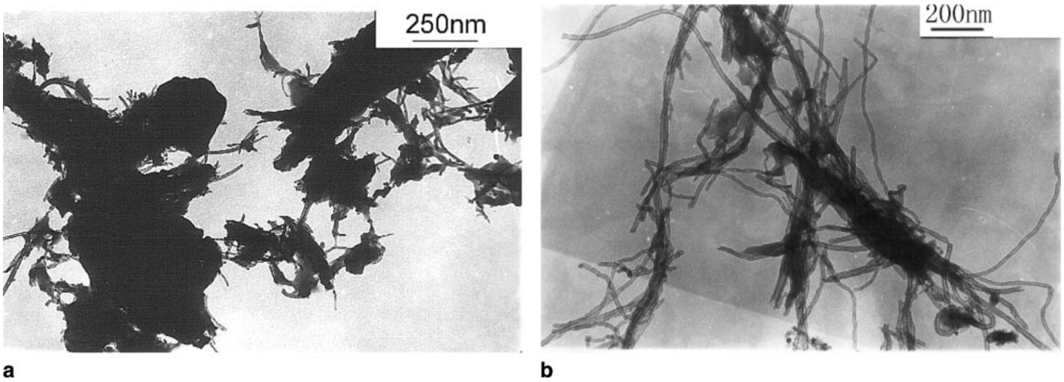

Fig. 4. TEM images of PC MWNTs composites with different contents of CNTs (a) 5.6% and (b) 17%.

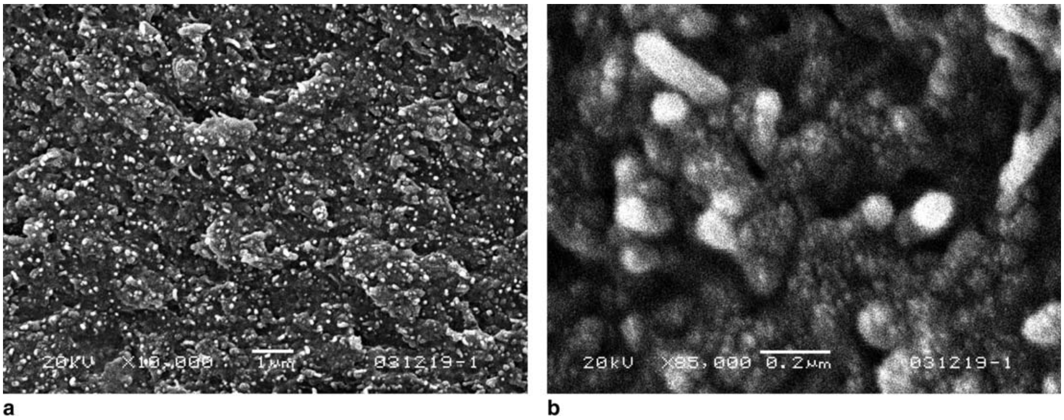

Fig. 5. SEM images of PC/MWNTs composites with 16.9wt.% of CNTs at two different magnifications.

the two images, it can be concluded that the CNTs were well dispersed into the matrix.

4. Conclusion

Generally speaking, the PC/CNTs composites could be produced through solution mixing and precipitation. The purified CNTs were untangled and well dispersed into the polymer matrix due to both ultrasonics and stiring. Furthermore, the polar functional groups on the purified CNTs' surface played an important role in accelerating both the dispersion of CNTs and the interfacial adhesion in the composites. The method of fabricating the composites is a convenient route to produce polymer-based nanocomposites on a large scale.

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