Materials Letters 120 (2014) 90–93

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Preparation of core – shell structured carbon nanotube-silsesquioxane hybrids by a direct free-radical reaction

Da Sun [a], Qifang Li [b,*], Guang-Xin Chen [a,b,**]

[a] Key Laboratory of Carbon Fiber and Functional Polymers, Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, PR China
[b] College of Material Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, PR China

ARTICLE INFO

Article history:
Received 18 November 2013
Accepted 10 January 2014
Available online 20 January 2014

Keywords:
Carbon nanotubes
Electrical properties
Microstructure
Particles
Nanosize

ABSTRACT

Traditional methods to functionalize carbon nanotubes (CNTs) for preparing composites involve complex acid-treatment processing. In this study, a synthetic strategy is reported to prepare crosslinked octa-methacrylate polyhedral oligomeric silsesquioxane (POSS) coated multi-walled CNTs (MWCNTs) by direct in situ free-radical polymerization in a controlled manner. A series of core – shell structured hybrids with MWCNT at the center were obtained. The thickness of the shell was adjusted from about 5, 15, 25, to 40 nm. The hybrids of coated MWCNTs were well dispersed in the organic solvent and showed a controlled electrical performance (from 0.75 Ω cm to 2505 Ω cm) with varied coating layer thicknesses. The process is well suited for industrial production on larger surfaces.

1. Introduction

The unique structure-dependent properties of carbon nanotube (CNT) make it a central element in the composite materials for many electronic applications [1]. Many efforts have been devoted to exploit the electrical properties of the polymer–CNT composites to allow the ultra-low electrical percolation threshold [2–5]. However, sometimes high performance polymer – CNT composites are demanded with controlled electrical properties; for example, the dielectric loss can be reduced in High-k polymer–CNT percolative composites by adjusting the conductivity of CNTs [6].

In our previous research, we reported a method to functionalize acid treated-CNT with a SiO_2 layer, which provided a flexible way to prepare hybrids with controlled electrical conductivity [7]. In that process, the carboxylic acid groups have to be introduced onto the surface of CNTs by nitric acid oxidation. Although acid-treatment is currently powerful, it still possesses several disadvantages: (i) strong corrosion and high pollution; (ii) low product weight (~60 wt% yield); and (iii) breaking of CNTs.

\Some researchers attempted to functionalize CNTs by using free radicals to avoid pollution. Ying et al. [8] first reported the method using benzoyl peroxide (BPO) to functionalize single-walled CNTs. Peng et al. [9] reported that CNTs and their fluorinated derivatives react with organic peroxides to produce phenyl and undecyl sidewall functionalized CNTs, respectively. Some researchers used the peroxy [10–13] and azo derivatives [14–16] successfully to modify CNTs. However, these studies mainly focused on the grafting of CNTs using small molecules, linear, or branched macromolecules instead of crosslinked materials, where the controlled electrical conductivity of CNTs was hardly achieved.

In this study, we report a synthetic strategy to prepare core – shell hybrids (POSS@CNTs) by encasing the CNTs to a crosslinked polyhedral oligomeric silsesquioxane (POSS) sheath by direct in situ free-radical polymerization in a homogeneous system. Unlike conventional functional techniques, our chemical route does not require any acid treatment of CNTs, which helps to maintain the original performance of CNTs. POSS@CNTs exhibit excellent dispersion and controlled electrical property, which provide good possibilities and directions for further preparation of devices and composites.

2. Experimental

Octa-methacrylate POSS (Hybrid Plastics America) (250 mg) was dissolved in 100 ml solvent and the solution was poured into a three-neck round-bottom flask which contained 50 mg multi-wall CNT (MWCNT, Chengdu Organic Chemicals Co., Ltd.). After an ultrasonic dispersion for 30 min, the initiator (benzoyl peroxide (BPO) or $FeSO_4/K_2S_2O_8$) was added into the mixed dispersion. Afterwards, the temperature of the mixture was kept at 80 °C for 6 h under a nitrogen atmosphere. Finally, the mixture was cooled to room temperature, filtered through a 0.22 μm PTFE membrane, and washed to remove the impurities. The purified product was

---

* Corresponding author. Fax: +86 10 64433585.
** Corresponding author at: Beijing University of Chemical Technology, College of Material Science and Engineering, Beisanhuan East Road 15, Beijing 100029, China. Fax: +86 10 64421693.
E-mail addresses: qflee@mail.buct.edu.cn (Q. Li), gxchen@mail.buct.edu.cn (G.-X. Chen).

0167-577X/$ - see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.matlet.2014.01.046

dried in a vacuum oven at 45 °C overnight as black powder. The samples were named and are shown in Table 1. Fourier transform infrared (FT-IR) (Bruker Tensor 27) and Raman (RenishawinVia) spectra were used to characterize the structure of hybrids. The morphology was measured by transmission electron microscopy (TEM, Tecnai $G^2$20). The electrical resistivity was tested by a four-probe tester SZT-2 (Suzhou Tongchuang Electronics Co., Ltd.). UV–vis was carried out on a Shimadzu 1800 UV–vis spectrophotometer.

3. Results and discussion

The hybrid of POSS@CNTs was characterized by FT-IR and Raman spectra, respectively (Fig. 1). Whatever the initiator was, BPO or $FeSO_4/K_2S_2O_8$ (Fig. 1A), the Si–O–Si stretching vibration from the POSS cage appeared at 1120 cm^{-1}. The C=O vibration peak at 1730 cm^{-1} fits the structure of POSS, which contains eight ester groups.The peaks from 2835 cm^{-1} to 3010 cm^{-1} are characteristic of C–H stretching. Their intensities were greatly enhanced after functionalization as compared with that of pristine MWCNT, which is explained by the attachment of alkyl groups onto the surface of MWCNTs.

Raman spectra were used to characterize CNTs before and after radical functionalization to verify the modification (Fig. 1B). With respect to the Raman spectra of MWCNTs, two intense features were assigned to the D band at 1345 cm^{-1} and to the G band at 1570 cm^{-1}. The intensity ratios of the D – G bands (I_D/I_G) can be used as a proof of disruption in the aromatic π-electrons of CNTs [17]. I_D/I_Gs of the hybrids shown in Fig. 1B are 0.896 in POSS@CNT-1, 0.897 in POSS@CNT-2, 0.859 in POSS@CNT-3, and 0.947 in POSS@CNT-4, which were larger than that of the pristine MWCNT (0.715). This result indicates that numerous sp^2 hybridized carbons were converted to sp^3 hybridized carbons because of the covalent attachment of POSS onto the sidewall of MWCNTs. All these results prove that the POSS and the MWCNT are connected by a covalent bond.

Table 1
Composition of POSS–MWCNT hybrids.

Samples	MWCNT/POSS (mg/mg)	BPO (mg)	$FeSO_4/K_2S_2O_8$ (mg/mg)
POSS@CNT-1	1/5	12.5	0
POSS@CNT-2	1/10	25	0
POSS@CNT-3	1/2	0	10/15
POSS@CNT-4	1/5	0	25/37.5

Fig. 2 shows the TEM images of the POSS@CNT hybrids. Fig. 2a shows a typical TEM image of the pristine MWCNT, which has a clean surface. The image of POSS@CNT-1 reveals the attachment of POSS onto MWCNT with layer thickness of about 5 nm. When the usage of POSS was increased, the coating layer thickness increased to about 15 nm (POSS@CNT-2). Fig. 2d and e shows the TEM images of POSS@CNTs with the radical initiators of $FeSO_4/K_2S_2O_8$, where the thickness of crosslinked POSS coated on MWCNT was higher than that of products initiated with BPO with the same ratio of POSS to MWCNT. As shown in Fig. 2d, the layer thickness of POSS@CNT-3 was about 25 nm, which is larger than that of POSS@CNT-1 and POSS@CNT-2. When the usage of POSS was five times of MWCNT, the coating thickness reached about 40 nm (Fig. 2e), and the core – shell hybrid with similar layer thickness was not obtained in the BPO system because of crosslinking. The TEM images of the POSS@CNT reveal that the attachment of POSS produces a “bumpy” sidewall morphology of MWCNT with different layer thickness, which is related to the surface regularity of the MWCNT, the stochastic reaction of radical initiator, and the difference between the initiator centers. By adjusting the ratio of the reactants and initiators, the novel hybrids with controllable coating of POSS on the surface of MWCNT, namely, about 5, 15, 25, and 40 nm in thickness, were successfully obtained.

Fig. 3A shows the electrical performance of POSS@CNT hybrids. The test samples are directly put into the mold and pressed at room temperature by a manual bench press machine under pressure 20 MPa for 10 min. The electrical resistivity of pristine MWCNT (0.75 Ω cm) is smaller than that of POSS@CNT hybrids (3.69 Ω cm in POSS@CNT-1, 347.6 Ω cm in POSS@CNT-2, and 2505 Ω cm in POSS@CNT-3). This result suggested that the controlled decrease of conductivity was related to the thickness of the POSS layer. Fig. 3B displays the UV–vis absorption spectroscopy of POSS@CNT-1 in DMF placed after a month. As can be clearly seen, the hybrid exhibits a typical electronic absorption spectrum of solubilized CNT [18] and induces a significant increase in light absorption intensity in the visible light region. The continuous absorption band in the range of 250–500 nm is caused by the addition of POSS@CNT-1. The light absorption intensity in the visible light region increases, accompanied by the augmented additional amount of POSS@CNT-1. The relationship of absorbance versus solution concentration is linear, which corroborates the uniformity of the POSS@CNT-1 dispersion in organic solvent.

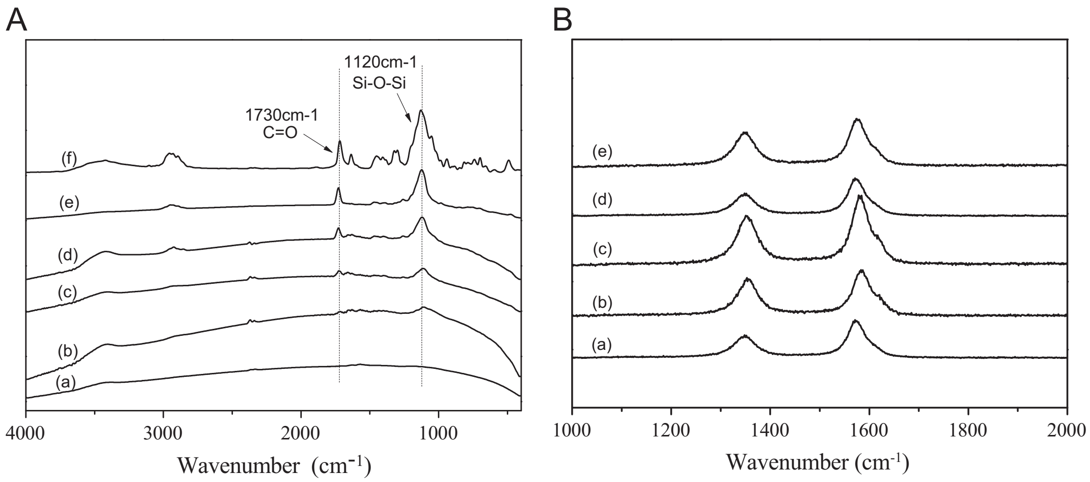

Fig. 1. FT-IR (A) and Raman (B) spectra of the POSS@CNTs (a) MWCNT, (b) POSS@CNT-1, (c) POSS@CNT-2, (d) POSS@CNT-3, (e) POSS@CNT-4, and (f) POSS.