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Surface modification of multi-wall carbon nanotube with ultraviolet-curable hyperbranched polymer

Wei Zhou, Jianwen Xu, Wenfang Shi *

Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, PR China

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Abstract

Surface modification is a general and efficient approach to improve the compatibility of carbon nanotube (CNT) with various matrixes. Here we report the modification of multi-wall carbon nanotube (MWCNT) with hyperbranched polymer which contains UV reactive functional groups. The modification promotes the incorporation of CNT into UV-curable resin, and when cured under UV irradiation to form a homogeneous film, the CNT will be chemically bonded with the matrix by crosslinking photopolymerization. For the unique mechanical properties of CNT, the mechanical properties of the cured MWCNT/UV-curable resin film were greatly improved compared with pure resin film as indicated by the increasing of Young's modulus, tensile strength, and toughness.

Keywords: MWCNT; UV-curable; Stress–strain; Scanning electron microscopy; Multiwall carbon nanotubes

1. Introduction

Carbon nanotubes (CNTs) exhibit exceptional mechanical, thermal, and electrical properties due to their unique one-dimensional all-carbon structure [1–4]. Therefore, CNTs have potential for a vast range of applications, especially much attention has been paid to explore CNT composite materials with the aim to improve mechanical and electronic properties [5–9]. The challenge to prepare CNT composites is to disperse exfoliated individual CNTs in matrix, since the as-produced CNTs are held together in bundles by very strong van der Waals interaction, and the bundling has been proved to result in diminished mechanical properties as compared to exfoliated individual CNTs [10]. Several approaches have been developed to efficiently disperse individual CNT in matrix, among them surface modification of CNT has been intensively studied as an efficient approach to increase the compatibility of CNTs with matrix [11], and accordingly promote the dispersion of the CNTs. Till now, most approaches lead to modified CNTs without functional groups, it means that the mixing of CNTs with matrix is only physical blending, which is not so stable as the change of external conditions. CNT with functional groups which can react with the matrix will be very promising since through chemical reaction CNT will be chemically bonded with the matrix which is more stable than just physical blending.

In this work, the modification of multi-wall carbon nanotube (MWCNT) with hyperbranched polymer containing functional UV-curable groups was reported. Hyperbranched polymer was applied to modify MWCNT for its unique feature of bearing large number of functional end-groups at the molecular surface [12,13], so the modification will introduce large amount of functional groups onto MWCNT, and at the same time the defects on MWCNT which comes from the modification will be low to maintain the original properties of MWCNT.

2. Experimental section

2.1. Materials

Boltorn™ H20 (H20) (structure shown in Fig. 1) was supplied by Perstorp AB, Sweden, which is an aliphatic hyperbranched

* Corresponding author. Tel.: +86 551 3606084; fax: +86 551 3606630.
E-mail address: wfshi@ustc.edu (W. Shi).

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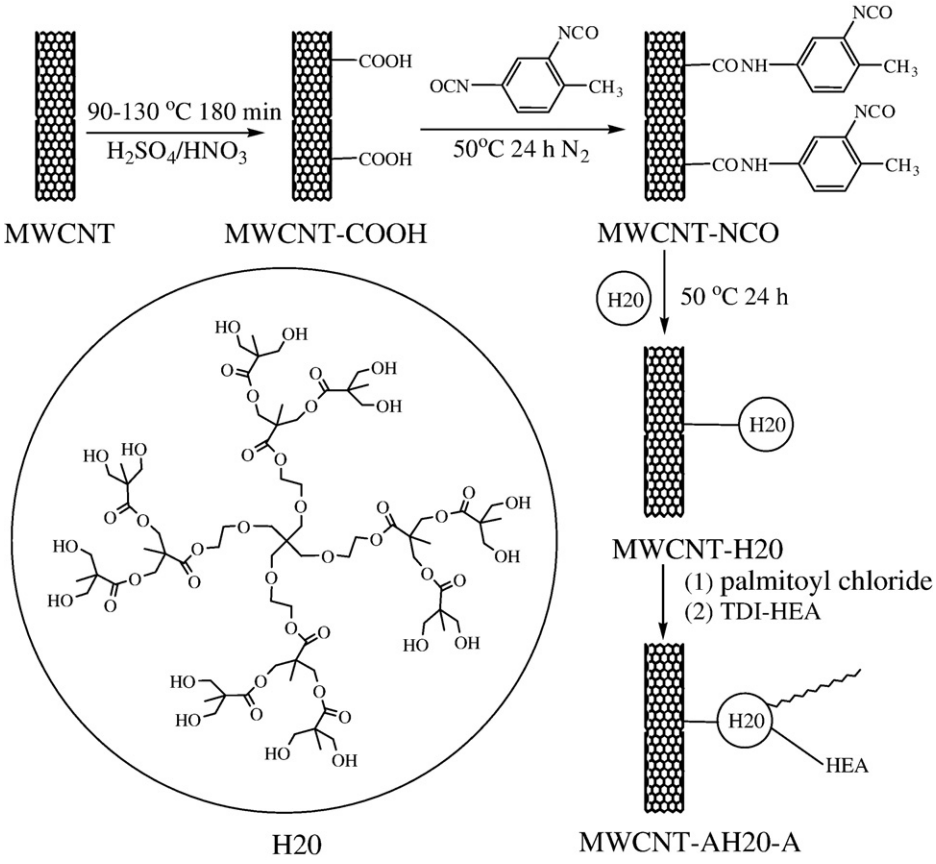

Fig. 1. Synthetic route for MWCNT-AH20-A.

polyester with the molecular weight of 1735 g mol^{-1} and average 15.6 end hydroxyl groups per molecule. MWCNTs (>90%) were purchased from Sun Nanotech Co. Ltd., Nanchang, China with the diameter of 10–30 nm and length of 5–15 μm. Toluene 2, 4-diisocyanate (TDI) and all solvents were purchased from Shanghai First Reagent Co., China and were used as received.

Aliphatic urethane acrylate, EB270, with an unsaturation concentration of 1.33 mmol g^{-1} and a molar mass of 1500 g mol^{-1}, was supplied by UCB Co. (Belgium). Hydroxylethyl acrylate (HEA) and ethylene glycol diacrylate (HDDA) were purchased from Eternal Chemical Co., LTD. (Taiwan). 1-hydroxy-cyclohexyl phenyl ketone (Runtecure 1104), 2-Hydroxy-2-methyl-1-phenyl-1-propanone (Runtecure 1103), 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino-propanone-1 (Runtecure 1107) and isopropyl thioxanthone (Runtecure 1105), supplied by Runtec. Co., Changzhou, China, were blended in a ratio of 8:8:3:1, and used as a multi-photoinitiator system.

2.2. Synthesis

The schematic outline to modify MWCNT with hyperbranched polymer was depicted in Fig. 1. The pristine MWCNTs were purified, shortened and carboxyl-functionalized according to the reported procedure [14, 15]. Briefly, 1 g MWCNTs was added to 40 mL mixed acid (nitric and sulfuric acid, 1:3 by volume), and then sonicated for 30 min, followed by stirring at 100 °C for 3 h. After cooling to room temperature, the reaction mixture was diluted by deionized water and vacuum-filtered through a 0.22 μm filter with polyvinylidene fluoride membrane. The solid was washed with deionized water until neutral, and then dried under vacuum at 40 °C for 24 h to obtain the carboxyl-functionalized multi-walled carbon nanotubes (MWCNT-COOH). The carboxyl group density of MWCNT-COOH was characterized by titration with 0.001 M NaOH solution to be 1.48 mmol g^{-1}.

The carefully dried MWCNT-COOH (0.1 g) together with TDI (0.25 g) was then dispersed in anhydrous acetone (20 mL) and stirred in a dry nitrogen atmosphere at 50 °C for 24 h. Then, the reactant was filtered and washed with anhydrous acetone to get rid of unreacted TDI. After being dried in vacuum at 40 °C for 24 h, MWCNT with isocyanate groups on the surface was obtained.

MWCNT-NCO (0.1 g) and H20 (1 g, 5.76×10^{-4} mol) were dissolved in 80 mL of anhydrous dioxane reacted at 50 °C in a dry nitrogen atmosphere for 24 h, after reaction the product was monitored by Fourier transform infrared spectroscopy (FTIR) that vibration of isocyanate groups at 2275 cm^{-1} totally disappeared.

Then palmitoyl chloride (1.58 g, 5.76×B10^{-3} mol) was added to the above reactant, and stirred for 16 h at 50 °C to obtain alkyl chain grafted MWCNT-H20 (MWCNT-H20-A).

1 g (3.45×10^{-3} mol) difunctional molecules (structure shown in Fig. 1) synthesized from TDI and HEA by our previously reported approach [16] were mixed with 0.1 g MWCNT-H20-A in anhydrous acetone and reacted at 70 °C for 24 h under a dried