



Hindered phenol grafted carbon nanotubes for enhanced thermal oxidative stability of polyethylene

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ABSTRACT

A hindered phenolic antioxidant has been covalently grafted onto the surface of multi-walled carbon nanotubes (MWCNTs) to improve their dispersion state and antioxidant ability in the polymer matrix. An aminosilane coupling agent was chosen as the surface modifier of the MWCNTs to create chemical bonding between the phenolic antioxidants and the MWCNTs. Two contrasting routes, two-step functionalization and one-step functionalization of MWCNTs, were developed. The corresponding MWCNT/polyethylene composites were prepared by melt blending. Fourier transform infrared spectroscopy, energy dispersive X-ray spectroscopy, thermal gravimetric analysis, transmission electron microscopy, and Raman spectroscopy confirmed the successful functionalization of MWCNTs. Electron spin resonance spectra revealed that the free radical scavenging activity of MWCNTs was greatly increased after functionalization. The resultant MWCNTs exhibited improved dispersion and antioxidant efficiency in the polyethylene matrix. Compared with the two-step functionalized MWCNTs, the one-step functionalized MWCNTs were more efficient in preventing polyethylene from thermal oxidative degradation.

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1. Introduction

During the past decade, the use of carbon nanotubes (CNTs) as fillers to enhance the physical properties of polymer matrices has received wide attention. Incorporation of small amounts of CNTs into a polymer matrix can greatly improve the mechanical, electrical, and flame retardant properties of the polymer material [1–6].

As their antioxidant property revealed recently, CNTs offer another candidate as an antioxidant additive to improve thermal oxidative stability of polymer. Watts et al. [7] were the first to report that multi-walled carbon nanotubes (MWCNTs) can act as weak antioxidants in polystyrene, polyethylene (PE), polypropylene, and poly(vinylidene fluoride), preventing the polymer from oxidation. Zeynalov and Friedrich [8] tested the anti-oxidative effect of MWCNTs using the oxidation of cumene as a model reaction. Their experimental measurements of the oxygen uptake clearly showed reduced values of oxidation rates in the presence of MWCNTs, which proved the antioxidant behavior of MWCNTs. Our previous study [9] verified the antioxidant property of both single-walled carbon nanotubes (SWCNTs) and MWCNTs, and revealed

that MWCNTs are more effective than SWCNTs in preventing PE from thermal oxidation. The antioxidant behavior of CNTs in polymer is considered to obey a free radical scavenging mechanism as illustrated by electron spin resonance (ESR) studies. It is observed that CNTs exhibit remarkable radical scavenging capacity when in contact with hydroxyl or superoxide radicals [9,10]. Recently, some theoretical studies have also addressed the free radical scavenging capacity of SWCNTs [11–13]. The theoretical calculation indicates that the scavenging ability of SWCNTs is mainly affected by the tube diameter, chirality, surface defects and functional groups. The thin and zigzag SWCNTs with hydroxyl groups on the tubes' walls are recommended as those with the best antiradical activity among the studied SWCNTs. Apparently, both the experimental and the theoretical studies have confirmed the free radical scavenging activity and the antioxidant ability of CNTs. However, it is worth noticing that the antioxidant capacity of common CNTs (pristine SWCNTs and MWCNTs) is limited. With the incorporation of 5 wt% CNTs in the PE matrix, the oxidation induction time (OIt) of the composite at 200 °C is less than 10 min [9]. On the other hand, CNTs are insoluble and easy to aggregate. The non-uniform dispersion and the poor chemical compatibility of CNTs in polymer matrices greatly affect the final properties of CNT/polymer composites and become stumbling blocks in developing CNT reinforced polymer composites. Numerous researches have thus devoted to improving the dispersion of CNTs by surface modification. Functionalization of

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CNTs with organic molecules has attracted intense attention because the dispersion state and compatibility of CNTs can be greatly improved with the help of the grafted organic molecular chains. A wide range of organic molecules, such as long chain polymer [14–18], silane coupling agents [19–22], hexadecylamine [23] etc., have been used to functionalize CNTs. In most cases, although the grafted organic molecules can improve the solubility and the dispersion of CNTs, the thermal and antioxidant ability of the materials are simultaneously deteriorate due to the inherent degradability of the grafted organic molecules [24].

With the above considerations in mind, this study aims to introduce antioxidant groups onto MWCNTs, anticipating that both the antioxidant ability and the dispersion state of MWCNTs in polymer matrices can be improved. A hindered phenolic antioxidant (3,5-di-*tert*-butyl-4-hydroxyphenylpropionic acid) was chosen for its high reactivity due to the terminal reactive carboxyl group and its linear molecular structure. A silane coupling agent was used as a linkage between the hindered phenol and the MWCNTs. In order to obtain a high grafting rate of the hindered phenol, two contrasting routes are proposed and the maximum grafting amount of hindered phenols was achieved. It is revealed that the thermal oxidation of the polymer matrix is significant inhibited with the incorporation of the hindered phenol-grafted MWCNTs. The antioxidant mechanism of the obtained MWCNTs during polymer oxidation was proposed, combined with the free radical scavenging mechanism and the chain-breaking hydrogen donor mechanism.

2. Experimental

2.1. Materials

Hydroxylated multi-walled carbon nanotubes (HO-MWCNTs) were purchased from Chengdu Organic Chemical Co. Ltd., Chinese Academy of Sciences. The purity, outer diameter, and length are 95%, 5–25 nm, and 10–30 μm , respectively. The content of hydroxyl group is 5.58 wt%. The hindered phenolic antioxidant 3,5-di-*tert*-butyl-4-hydroxyphenylpropionic acid (AO, purity 98%) and 3-(2-amino ethyl amino) propyl trimethoxysilane (APS, purity 96%) were purchased from Alfa Aesar and used as received. Toluene, thionyl chloride, dichloromethane and triethylamine were of analytical grade and distilled before use. Commercial PE (density = 0.949 g/cm³, melt flow index = 0.40 g/10 min) without additives was kindly supplied by SINOPEC Shanghai Petrochemical Co. Ltd. 5,5-Dimethyl-1-pyrroline-N-oxide (DMPO), a type of free-radical trapping agent, was purchased from Sigma–Aldrich. Sodium dodecyl sulfate (SDS) which was applied as a surfactant was purchased from Acros. All other chemicals were of analytical grade and used as received.

2.2. Functionalization of MWCNTs

Two different synthetic routes to functionalize MWCNTs are shown in Fig. 1.

2.2.1. Route A: two-step functionalization of MWCNTs

HO-MWCNTs (400 mg) were added into a three-neck flask with anhydrous toluene (200 mL) and dispersed through ultrasonication for 30 min. APS (1.5 g, 6.76 mmol) was added and the mixture was stirred at 65 °C for 24 h. The product was filtered and then washed by Soxhlet extraction for 24 h with absolute ethanol. The silane-treated MWCNTs (APS-MWCNTs) were dried in a vacuum oven overnight at 80 °C.

AO (0.35 g, 1.26 mmol) was dissolved in dichloromethane (50 mL). Thionyl chloride (1 mL) was then added into the solution.

The reaction mixture was refluxed under nitrogen for about 4 h until no AO was detected by thin layer chromatography. After that, thionyl chloride and dichloromethane were removed under reduced pressure. The obtained acyl chloride (AO–Cl) was firstly dissolved in anhydrous toluene (20 mL) and then added to the suspension of APS-MWCNTs (200 mg) in anhydrous toluene (200 mL) under stirring. Anhydrous triethylamine (1 mL) was subsequently added dropwise and the mixture was stirred for 40 h at 80 °C under nitrogen. The products, two-step functionalized MWCNTs (AO-MWCNTs-A), were filtered and washed with plenty of toluene and absolute ethanol sequentially for several times before dried in a vacuum oven overnight at 60 °C.

2.2.2. Route B: one-step functionalization of MWCNTs

AO–Cl (1.07 g, 3.6 mmol) was obtained following the procedure described above and dissolved in anhydrous toluene (50 mL). APS (0.354 g, 1.59 mmol) and triethylamine (1 mL) were added to the solution and the mixture was stirred for 40 h at 50 °C under nitrogen. Then the reaction mixture was filtered to remove triethylamine hydrochloride. The filtrate was concentrated under vacuum and the crude product was further purified by column chromatography (silica gel, CH₂Cl₂/CH₃OH, 20:1). The resulting solution was concentrated again under vacuum to give yellow viscous liquid (AO–APS, 0.480 g, 0.646 mmol, 40% yield). ESI–MS: $m/z = 741.8$ [M – H][–], 778.5 [M + Cl][–]; ¹H NMR (CDCl₃) δ (ppm): 6.979 (m, 4H), 5.278 (s, 2H), 5.038 (d, 2H), 3.545–3.466 (m, 9H), 3.398 (d, 2H), 3.192 (t, 2H), 2.842 (t, 4H), 2.584 (t, 2H), 2.411 (t, 2H), 1.615 (m, 2H), 1.405 (s, 36H), 0.528 (t, 2H).

HO-MWCNTs (200 mg) were added into a three-neck flask with anhydrous toluene (80 mL) and dispersed through ultrasonication for 30 min. The solution of AO–APS (0.45 g, 0.605 mmol) in toluene (20 mL) was added and the mixture was stirred at 80 °C for 24 h. The products, one-step functionalized MWCNTs (AO-MWCNTs-B), were filtered and washed with plenty of toluene and absolute ethanol sequentially for several times before dried in a vacuum oven overnight at 60 °C.

2.3. Preparation of MWCNT/PE composites

MWCNT/PE composites were prepared by melt blending of PE and MWCNTs using a HAAKE Rheomix CTW5 internal mixer (Thermo scientific, USA) at 180 °C with a screw speed of 60 rpm for 5 min. The content of MWCNTs was fixed at 5.0 wt% for each composite. Blank sample was also obtained following the same procedure as a base of comparison.

2.4. Characterization

The electro spray ionization–mass spectrometry (ESI–MS) was carried out on a Bruker Esquire-LC-0075 spectrometer. Proton nuclear magnetic resonance (¹H NMR) spectrum was recorded on a Bruker DRX-400 (400 MHz) instrument using CDCl₃ as the solvent and tetramethylsilane as an internal standard. Fourier transform infrared (FTIR) spectra were recorded using a Nicolet 5700 spectrophotometer (KBr disk). Energy dispersive X-ray (EDX) analysis was carried out by Oxford EDS Inca Energy Coater. Thermal gravimetric analysis (TGA) of MWCNTs was performed using a Mettler Toledo TGA/SDTA851^e thermo-balance. The samples were heated under nitrogen from 50 °C to 800 °C at a heating rate of 20 °C/min. The Raman spectra of CNTs were measured at room temperature using a Raman spectrometer (LabRAM HR800, Jobin-Yvon, France) with argon ion laser excitation 514.5 nm (4 mW power). The surface morphology of the MWCNTs was studied using a high resolution transmission electron microscopy (TEM, FEI Tecnai G2 F20 S-Twin working at 200 kV).

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