



# Characterization of non-covalently, non-specifically functionalized multi-wall carbon nanotubes and their melt compounded composites with an ethylene–octene copolymer

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## ABSTRACT

Multi-wall carbon nanotubes (MWCNTs) were functionalized with a hyperbranched polyethylene (HBPE) using a non-covalent, non-specific functionalization approach. The adsorption behavior of HBPE on MWCNTs was characterized by means of an adsorption isotherm. HBPE adsorption reached a plateau value of 0.3:1.0 (w/w) HBPE:MWCNT, corresponding to a surface coverage of approximately 30%. The functionalized MWCNTs were better dispersed in tetrahydrofuran (THF), forming smaller aggregates compared to their unmodified counterparts. Pristine and HBPE-functionalized MWCNTs were melt compounded with a low-viscosity ethylene–octene copolymer (EOC) matrix. Electrical and rheological percolation thresholds were observed at nanotube loadings of less than 1 wt%. Functionalization did not affect significantly the electrical conductivity and rheological properties. The improved dispersion of the functionalized MWCNTs within the EOC matrix resulted in improved ductility over the non-functionalized counterpart. This study demonstrates that this method of functionalization results in partial surface coverage of the nanotubes, therefore providing an efficient means for achieving good nanotube dispersion, without compromising their surface properties.

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## 1. Introduction

Polymer/carbon nanotube (CNT) composites have been widely studied, because of their superior mechanical, thermal and electrical properties [1–7]. The preparation of polymer/carbon nanotube composites has been an area of active scientific research, since the exceptional properties of CNTs may extend the end-use applications of polymeric materials. Owing to their low density, improved mechanical properties and electrical conductivity, these composites can find applications in structural materials, antistatic films, electromagnetic interference (EMI) shielding, and coatings for electrostatic painting, hydrogen storage media and nanometer-sized semiconductor devices, probes and interconnects [8], automotive parts, reinforced aerospace materials, and sporting goods [9].

The use of CNTs in polymer composites has been greatly hindered due to their incompatibility with polymers and consequently, their poor dispersion in polymer matrices, especially in melt compounding operations. CNTs tend to exist as bundles of single wall carbon nanotubes (SWCNTs), or aggregates of multi-wall carbon nanotubes (MWCNTs) held together by van der Waals

forces and  $\pi$ – $\pi$  interactions, which make their separation and successful dispersion into polymers a very difficult task. Other factors influencing the dispersion of CNT include the viscosity of the polymer matrix, the melt compounding procedure, etc. [10,11].

Melt compounded thermoplastic composites containing MWCNTs have the potential of producing composite systems, with electrical conductivity higher than  $10^{-4}$  S/m [12], at relatively low nanotube loadings, suitable for applications such as electrostatic painting, electromagnetic interference (EMI) shielding, electrostatic discharge and conductive coatings, and other injection molded parts. However, in order to broaden the field of application of these composites to include large structural components, the mechanical properties must also remain at an acceptable level, and not be compromised by excessive aggregation.

A number of surface functionalization methods have been developed in order to either render MWCNTs dispersible in solvents, or improve their dispersibility in polymers. Local strain in carbon nanotubes, arising from pyramidalization and misalignment of the  $\pi$ -orbitals of the  $sp^2$ -hybridized carbon atoms, makes nanotubes more reactive than a flat graphene sheet, thus more amenable to chemical functionalization [13]. Covalent functionalization of nanotubes can improve the properties of the resulting composites through better nanotube dispersion in the matrix and enhanced nanotube/polymer interfacial binding [14]. Covalent

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functionalization can, however, disrupt the extended  $\pi$  conjugation in CNTs, which may introduce structural defects resulting in profound decline in the electrical properties of the nanotubes. An alternate way of tuning the surface properties of nanotubes without introducing irreversible changes is through non-covalent functionalization [15–17]. Recently non-covalent, non-specific functionalization using a hyperbranched polyethylene (HBPE) that establishes only CH– $\pi$  interactions with the nanotubes was employed successfully to improve the dispersion of MWCNTs in organic solvents [18] and in polyolefin-based composites prepared by solution blending [19].

While our previous work [19] has demonstrated the efficacy of this approach in composites prepared by solution blending, the focus of the present research is to develop melt compounded polyolefin/MWCNT composites with low electrical percolation thresholds while at the same time maintaining good mechanical properties by avoiding excessive aggregation through non-covalent, non-specific nanotube functionalization using HBPE. Composites of MWCNTs with an ethylene–octene copolymer were prepared by melt compounding. The morphology, surface properties, electrical conductivity, rheological and mechanical properties of the composites containing pristine nanotubes and HBPE-modified nanotubes are studied in order to understand the effects of non-covalent, non-specific functionalization of the MWCNTs with HBPE on the composite properties.

## 2. Materials and methods

### 2.1. Materials and characterization

MWCNTs (purity > 95%, diameter  $30 \pm 15$  nm and length 1–5  $\mu\text{m}$ ) from Nanolab Inc. (Massachusetts, USA) and (purity > 90%, diameter 10–15 nm and length 0.1–10  $\mu\text{m}$ ) from Sigma Aldrich (Missouri, USA) were used as received. The specific surface area (SSA) of the nanotubes was 300  $\text{m}^2/\text{g}$  and 224  $\text{m}^2/\text{g}$ , respectively, determined by Brunauer–Emmett–Teller (BET) characterization. MWCNT samples weighing 0.5–1.0 g were first degassed at 110 °C for 24 h and then subjected to a multipoint BET physisorption analysis (Autosorb-1 Quantachrome, USA) for nitrogen relative vapor pressures in the range 0.1–0.3 at 77 K. Based on the shape of the  $\text{N}_2$  adsorption–desorption isotherms (*type II* according to IUPAC classification [20,21]) in the whole relative pressure range, the estimated SSA corresponds to external surface area. The average pore size distribution of the MWCNTs as determined by the  $\text{N}_2$  sorption experiments was 1.48 nm, whereas the average pore size determined through the BJH method was 2.3 nm.

HBPE was synthesized from ethylene using a chain walking Pd–diimine catalyst, as described in detail by Ye and Li [22]. HBPE has a complex and irregular dendritic structure, containing a large number of branches of various lengths (from methyl to hexyl and higher) and, more importantly, abundant branch-on-branch structures [19]. The polyolefin matrix was a poly(ethylene-co-octene) (EOC), trade name Engage 8130, density 0.864  $\text{g}/\text{cm}^3$ , MFI 13 g/10 min at 190 °C, with copolymer content of 42 wt%, obtained from Dow Chemical (Michigan, USA). The melting and crystallization temperatures of this polymer, as determined by differential scanning calorimetry (DSC) are 56 °C and 38 °C, respectively and the degree of crystallinity is 13%.

### 2.2. Functionalization of MWCNTs

Mixtures of HBPE and MWCNTs in tetrahydrofuran (THF) with mass ratio between 0.0 and 3.0 were prepared by adding HBPE into dispersions containing 2.0 mg MWCNT/mL of THF. The resulting mixtures were sonicated for 1 h, and then stirred overnight. The

supernatant solutions were vacuum filtered drop-wise through Teflon membrane with pore size of 0.22  $\mu\text{m}$ . After being washed twice with equal volumes of THF (6 mL) the filters were dried in a vacuum oven overnight at room temperature [19]. Thermo gravimetric analyses were then carried out on dried samples using a Q500 TGA by TA Instruments (Delaware, USA). Data from TGA analysis was used to construct an adsorption isotherm [19].

### 2.3. Melt compounding

EOC composites containing pristine and HBPE-functionalized MWCNTs at contents ranging from 0.1 wt% to 5.0 wt% were compounded using a DSM Research 5 mL Micro-Compounder (DSM Resolve, Geleen, Netherlands) at a temperature of 150 °C, screw speed of 90 rpm and mixing time of 10 min.

### 2.4. Morphological characterization

HBPE/MWCNT suspensions in THF (2 mg/mL) were deposited onto carbon and Cu-Formvar/Carbon film and washed with THF to ensure monolayer coating. Following solvent evaporation, the samples were placed into a Hitachi-7000 Transmission Electron Microscope (TEM) (Hitachi HTA, Schaumburg, Illinois, USA) and images were captured at a magnification of 40,000 $\times$ . TEM images were also obtained for ultra-thin films of the polymer composites prepared using a Leica ultra-microtome. Images of the composites were obtained using a FEI Tecnai 20 instrument (FEI Co., Eindhoven, Netherlands). Composite melts were observed using an Olympus BX 51 optical microscope (Tokyo, Japan). Composite films were loaded on a Linkam SCC 450 Hot Stage (Surrey, UK) at 150 °C and pressed to a thickness of 20  $\mu\text{m}$  at 150 °C. Images were recorded using transmitted light.

### 2.5. Dynamic light scattering (DLS)

The size distribution of MWCNTs (pristine and functionalized) suspended in THF was analyzed by means of dynamic light scattering (DLS) (Zetasizer Nano ZS, Malvern Instruments Ltd., Worcestershire, UK) equipped with a monochromatic coherent 4 mW Helium Neon laser ( $k = 633$  nm) as the light source and Non-Invasive Back-Scattering (NIBS) technology (ALV GmbH, Germany). Very dilute suspensions containing  $5.0 \times 10^{-5}$  wt% MWCNT in THF were prepared by sonicating the suspension for 2 min and were allowed to settle overnight. The supernatant solution was used for the size distribution analysis at 25 °C. All measurements were performed in a glass cuvette with square aperture. Data analysis was done using the DTS (Dispersion Technology Software) 5.10, which includes cumulant analysis (in accordance to ISO 13321) and the multimodal size distribution, non-negative least square (NNLS) algorithm [21] to obtain the mean particle diameter and polydispersity of MWCNT in THF.

### 2.6. Electrical conductivity

Volume resistivity was measured under DC current at room temperature. Samples were prepared by compression molding the melt-compounded composites in a Carver press at 140 °C and a force of 1400 N to get a thin film of 0.6 mm. The thin composite film with a diameter of 6 cm was put into the measuring chamber (Keithley 8009 Resistivity Test Fixture) of the Keithley 6517B Electrometer/High Resistance Meter (Keithley Instruments, Inc., Cleveland, Ohio, USA) for an electrification time of 1 min.

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