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Functionalization of multi-walled carbon nanotubes grafted with self-generated functional groups and their polyamide 6 composites

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ABSTRACT

Fourier transform infrared spectroscopy, transmission electron microscopy, Raman spectroscopy, and X-ray photoelectron spectroscopy were applied in this study to demonstrate that multi-walled carbon nanotubes synthesized from ethanol flames (F-MWCNTs) inherently have functional groups on their surfaces. This finding clearly indicates that the covalent functionalization of carbon nanotubes can be achieved without oxidation as pretreatment. Thus, *n*-hexadecylamine functionalized F-MWCNTs (H-MWCNTs) can be synthesized simply, without disrupting the primary structures of the nanotubes. The melt-compounding method was used to fabricate polyamide 6/MWCNTs composites. Scanning electron microscope results confirmed that both F-MWCNTs and H-MWCNTs have much better nanoscopic dispersion in PA6 matrix than commercial MWCNTs, and the tensile strength, Young's modulus, dynamic mechanical properties, and thermal behavior of their PA6 composites are considerably improved.

1. Introduction

Carbon nanotubes (CNTs) are regarded as ideal reinforcing fillers for polymer composites because of their unique structures (large aspect ratios with low densities) and superior electrical and mechanical properties (moduli that can approach 200–4000 GPa) [1–6]. However, the difficulty in dispersing CNTs, especially those prepared by chemical vapor deposition (CVD), homogeneously in most organic and aqueous solvents becomes a stumbling block in developing CNTs/polymer composites. This poor chemical compatibility greatly limits the solution-phase manipulation and processability of CNTs [7–9]. Extensive research has thus focused on the surface modification of CVD-synthesized CNTs (C-CNTs) to provide enhanced compatibility and dissolution, mainly in terms of severe oxidation by acid [7,10–12] or $KMnO_4$ [13] that allows the introduction of carboxyl and hydroxyl groups to their surfaces. Long alkyl chains, polymer chains, and biomolecules can then be grafted onto C-CNTs by esterification or amidation reactions [7]. However, these methods have certain drawbacks. For example, C-CNTs are heavily wasted in the oxidization process, and chemical treatments using highly concentrated acid or other extreme oxidants can often disrupt their primary structures [14].

Flame synthesis is well known as a simple and cost-effective way of obtaining a potentially large mass of CNTs

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over a large area of production [15,16]. Not only multi-walled CNTs (MWCNTs), but also single-walled CNTs (SWCNTs) have already been achieved by flame synthesis in bulk [15–20]. In contrast to the CVD method, flame synthesis is very economic and energy efficient, where a portion of the fuel is combusted to provide hydrocarbon gaseous precursors and the remnant serves as the growth reagent [17,18]. Recent studies have found this method renders the as-synthesized CNTs with appealing characteristics, such as field emission performance [20], desirable capacitance [21], recoverable photoluminescence [22], and even well aligned CNTs can be produced in the synthesis process by electric field [15].

However, few published studies have detailedly analyzed the surface structures of flame-synthesized CNTs or their application in polymer composites. The study reported here investigated the chemical structures of MWCNTs synthesized in ethanol flame (F-MWCNTs) using a series of techniques, including Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermal gravimetric analysis (TGA), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). The results confirmed the previous point that F-MWCNTs possess unique microstructures with considerable defects [21,22], and further proved that abundant chemically active functional groups, such as carboxyl and hydroxyl groups, are inherently attached to the surfaces of pristine F-MWCNTs. This kind of MWCNTs can thus be further modified without oxidation, which makes it favorable for use as reinforcing fillers for polymer composites.

Long-chain molecules of *n*-hexadecylamine were subsequently grafted onto F-MWCNTs by a one-step reaction in this study. *n*-Hexadecylamine functionalized F-MWCNTs (H-MWCNTs) with polyamide 6 (PA6) composites were then fabricated via the melt-compounding method. Their morphological characteristics were examined by SEM, which revealed their good wettability and homogeneous dispersion in the PA6 matrix. Moreover, the mechanical properties of the PA6 composites exhibited desirable results after the incorporation of F-MWCNTs or H-MWCNTs, and favorable crystallization and melting behavior were observed from differential scanning calorimetry (DSC).

2. Experimental

2.1. *Materials*

The F-MWCNTs used in this study were prepared with the following procedure [15,16]. A nanocrystalline Ni layer was electrodeposited on the sampling surface of a copper substrate (20 × 20 × 5 mm). The modified surface was then placed face down into the central core of the flame from a common laboratory ethanol burner at a temperature ranging from 610 to 780 °C to synthesize F-MWCNTs. MWCNTs produced by CVD methods (C-MWCNTs) were commercially bought from Shenzhen Nanotech Port Co. Ltd. F-MWCNTs and C-MWCNTs were purified by hydrochloric acid in order to remove any undesirable impurities, such as metal particles, oxide particles and amorphous carbon materials before used [23], and no significant further oxidation or "aging" was observed after measurement and storage for more than 1 year [21] .Carboxylic acid modified C-MWCNTs (A-MWCNTs) were obtained by oxidization using a mixture of concentrated sulfuric and nitric acids (3:1 by volume). *n*-Hexadecylamine was purchased from Merck-Schuchardt, Hohenbrunn, Germany. PA6 resin was purchased Baling Petroleum and Chemical Company.

2.2. *Synthesis of H-MWCNTs*

A 250 mL flask was charged with 1.6 g F-MWCNTs, 75 mL thionyl chloride, 25 mL anhydrous toluene, and 1 mL dimethylformamide. The mixture was then stirred at 70 °C for 24 h. Thereafter, the solvent was removed under vacuum, and the remaining solid was washed three times with anhydrous tetrahydrofuran (THF), followed by drying at 40 °C for 10 h.

The resultant powders, along with 5.0 g *n*-hexadecylamine, were added into 100 mL of anhydrous toluene solvent. After being kept refluxed at 90 °C for 60 h, the suspension was vacuum-filtered through 0.22 μm Millipore polytetrafluoroethylene (PTFE) membranes. The filter cake was washed with anhydrous THF at least 5 times and dried under vacuum at room temperature for 24 h, yielding H-MWCNTs. The schematic reaction procedure is shown in Fig. 1.

2.3. *Fabrication of PA6/MWCNTs composites*

PA6/MWCNTs composites with 1.0 wt.% C-MWCNTs were fabricated by the melt-compounding method using a HAAKE Mini-Lab twin-screw extruder (Thermo Electron Corporation) at 230 °C for 25 min with a screw speed of 50 rpm, and the process was protected by nitrogen atmosphere. The extruded bar was cooled at room temperature and then pelletized. Finally, the pelletized extrudate was injection-molded to form test bars using a micro-injection molding machine (Thermo Electron Corporation). The injection temperature and mold temperature were 245 and 75 °C respectively. The PA6/MWCNTs composites containing 1.0 wt.% F-MWCNTs or H-MWCNTs were prepared using the same procedure.

2.4. *Measurements*

FT-IR was carried out at room temperature by a Nicolet 170 SX IR spectrometer using KBr pellets in the range of 4000 to 600 cm^{-1}. Surface state analysis of the MWCNTs was conducted by XPS using Kratos XSAM-80 instrument with AlKα irradiation. TGA analysis was recorded on NETZSCH STA449 from 50 to 600 °C at a heating rate of 10 °C/min under nitrogen. Raman spectra were recorded on a Thermo Fisher DXR Raman microscope with 532 nm laser excitation. The morphology of MWCNTs, and the PA6/MWCNTs composites with cryogenically fractured surfaces under liquid nitrogen were examined by FEI Sirion FEG-SEM. The morphology and microstructure of MWCNTs were also characterized by high-resolution transmission electron microscope (HRTEM, JEOL JEM 2010 FEF, Japan). The tensile properties of the composites were measured using Instron 8871 (UK) with a crosshead speed of 2 mm/min, according to ASTM D638 M. The length of each cylindrical dumbbell sample was 25 mm, and the data reported here represent the average of three successful tests. Dynamic mechanical analysis (DMA) of the PA6/MWCNTs