

## Multiwalled Carbon Nanotubes with Chemically Grafted Polyetherimides

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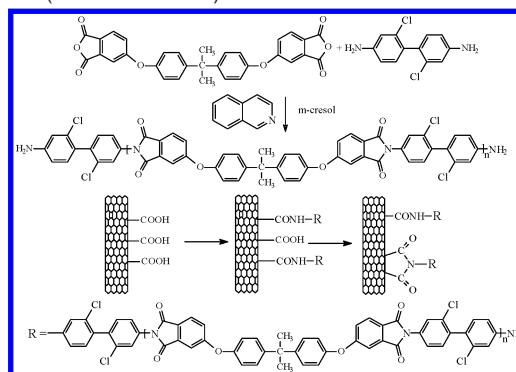
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Multiwalled and single-walled carbon nanotubes (MWNTs and SWNTs) are of scientific interest because of their outstanding structural, chemical, electrical, and thermal performance.<sup>1</sup> Noncovalent functionalization of the carbon nanotubes (CNTs) was studied in biomolecules, conducting polymers, and polyacrylonitrile<sup>2</sup> for potential applications in nanosensors and nanoelectrodes. In addition, the covalent attachment of aliphatic molecules<sup>3</sup> and acrylic/vinyl polymers<sup>4</sup> onto CNTs has been discussed using acyl chloride-functionalized SWNTs, alkylolithium, in situ anionic polymerization, organometallic coupling, and atom-transfer radical polymerization. To transfer the superior properties of the CNTs to the polymer matrix in lightweight and ultrastrong composites for use in the aerospace industry, critical challenges lie in achieving excellent interfacial adhesion between the CNTs and organic polymers.

Aromatic polyimides are one of the most important high-performance polymers due to their excellent thermal stability, dimensional stability, mechanical properties, and superior electrical insulating capabilities as well as their importance in microelectronic and electro-optical devices.<sup>5</sup> Recently, fluorinated polyimide/CNT composites with high thermal stability, excellent solubility, and optical clarity have been investigated via  $\pi$ - $\pi$  stacking,<sup>6</sup> silane modification,<sup>7a</sup> and acyl chloride functionalization.<sup>7b</sup> It was still difficult to detect the amide linkages formed between the polyimide and acyl chloride-functionalized SWNTs in <sup>1</sup>H and <sup>13</sup>C solution NMR due to broadening effects and/or unexpected signal shifts.<sup>7b</sup> Chemically attaching the polyimide onto CNTs to generate stronger ultra-lightweight composite materials remains a great challenge. This work presents a new strategy to chemically graft cost-effective, soluble, non-fluorinated polyetherimide onto CNTs using simple carboxylic acid-functionalized MWNTs.

Raw MWNTs were synthesized on quartz substrates by the pyrolysis of ferrocene and xylene at 600–900 °C in Ar/H<sub>2</sub>.<sup>8</sup> To uniformly disperse the MWNTs in the polyimide matrix, the MWNTs were first oxidized at elevated temperature and purified in a 6 M HNO<sub>3</sub> solution with sonication. They were then washed and filtrated with tetrahydrofuran (THF), acetone, and deionized water until the pH value was close to ~7, resulting in carboxylic acid-functionalized MWNTs. After the purification, neither detectable graphite nor amorphous carbon layers were found. A newly designed non-fluorinated polyetherimide (BisADA-DCB) was synthesized via the condensation polymerization of 4,4'-bis(4'-isopropylidene diphenoxy)-bis(phthalic anhydride) (BisADA) and 2,2'-dichloro-4,4'-biphenyldiamine (DCB) (see Scheme 1) in *m*-cresol with isoquinoline at elevated temperatures via one-step imidization. The resulting BisADA-DCB containing diamine end groups is colorless, and it is soluble in many solvents such as

**Scheme 1.** Schematic Presentation for Functionalized MWNTs Attached with the Aromatic Polyimide Synthesized from BisADA and DCB (Not on the Scale)



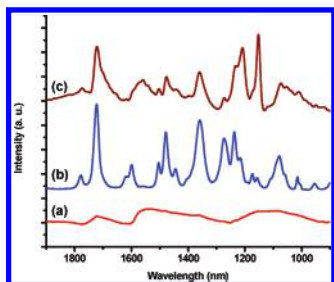
chloroform, methylene chloride, THF, and cyclopentanone, due to the twisted conformation of the 2,2'-substituted biphenylene unit.<sup>9</sup> The number-average molecular weight ( $M_n$ ) was 8390 g/mol, with a polydispersity (PDI) of 2.13, as measured in THF using gel permeation chromatography (GPC), with a glass transition temperature of 225 °C (S1, Supporting Information). The carboxylic acid-functionalized MWNTs were dispersed in the BisADA-DCB/anhydrous THF solution without any surfactants, to form a uniform black suspension with sonication. After THF removal, the interfacial grafting reactions between the MWNTs and the polyimide occurred in the solid state at 150–160 °C for 96 h under N<sub>2</sub> without the addition of catalysts or force fields.

When the carboxylic acid-functionalized MWNTs reacted with the BisADA-DCB containing amine end groups, new characteristic bands were detected by attenuated total reflection (ATR) Fourier transform infrared (FT-IR, Nicolet Nexus 870) experiments using a Ge single-crystal detector with a resolution of 2.0 cm<sup>-1</sup>. As shown in Figure 1a, the carbonyl stretching for carboxylic acid groups is detected at 1725 cm<sup>-1</sup> as a broad and weak absorption on the surface of the oxidized MWNTs (MWNT-COOHs), while the 1570 cm<sup>-1</sup> band is assigned to phenylene stretching. In completely imidized pure BisADA-DCB, the bands at 1779 and 1723 cm<sup>-1</sup> are characteristic of the imide carbonyl stretching (Figure 1b). The C–N stretching for the imide linkage is observed at 1362 cm<sup>-1</sup>. When the BisADA-DCB reacts with the carboxylic acid-functionalized MWNTs at 150–160 °C for 96 h, BisADA-DCB-*g*-MWNTs form. Figure 1c is for the sample that was re-dispersed in THF to remove the free BisADA-DCB. In this figure, the amide linkages form via the reaction between MWNT-COOHs and amine-terminated-BisADA-DCB, causing new bands at 1559 cm<sup>-1</sup> (amide II), 1211 cm<sup>-1</sup> (amide III), and a shoulder at 1640–1680 cm<sup>-1</sup> (amide I). The imide carbonyl stretching absorptions broaden and shift to 1772 and 1722 cm<sup>-1</sup>, suggesting that the internal stress in the imide rings connected to the sidewall surfaces of the MWNTs could be different

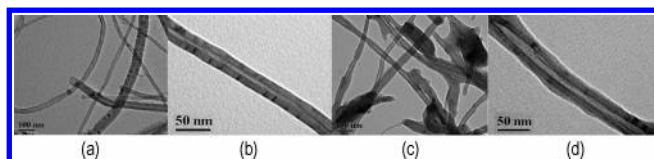
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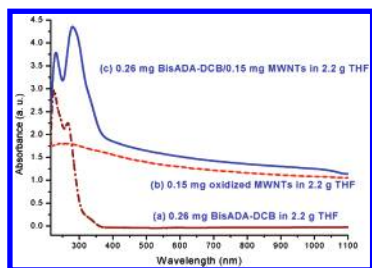
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**Figure 1.** Attenuated total reflection (ATR) FT-IR spectra of (a) MWNT-COOHs, (b) the neat polyetherimide, and (c) the carbon nanotubes chemically grafted with BisADA-DCB (BisADA-DCB-g-MWNT).



**Figure 2.** TEM images of (a) quite a few carboxylic acid-functionalized MWNTs, (b) an individual acid-functionalized MWNT, (c) a few BisADA-DCB-g-MWNTs, and (d) an individual BisADA-DCB-g-MWNT.



**Figure 3.** UV/vis absorption spectra for (a) the neat BisADA-DCB, (b) the carboxylic acid-functionalized MWNTs, and (c) the BisADA-DCB-g-MWNTs.

from those in the pure BisADA-DCB. It is speculated that the amide linkages form first, and then react with the residual neighboring carboxylic acids on the MWNTs to form more stable imide rings (Scheme 1). Therefore, BisADA-DCBs are grafted onto the MWNTs via not only the amide but also the imide linkages. Thermal gravimetric analysis (TGA TA-2050) results further confirm that this post-imidization reaction occurred between COOHs on MWNTs and amine-terminated BisADA-DCB (S2, Supporting Information).

Transmission electron microscopy (TEM) was used to investigate the size and distribution of the MWNTs before and after chemical grafting. Figure 2a shows quite a few acid-functionalized MWNTs with outer diameters of 10–50 nm. The wall surfaces of these MWNTs are smooth, without detectable amorphous layers. Figure 2b is an enlarged individual acid-functionalized MWNT with a tubular structure having an outer diameter of  $\sim 25$  nm. Figure 2c shows a large population of MWNTs coated by BisADA-DCB. A thin layer of BisADA-DCB with a thickness of 5–20 nm is observed on an enlarged individual MWNT (Figure 2d). The thin coating layers are the chemically grafted BisADA-DCB augmented with BisADA-DCB molecules physically absorbed to the MWNT surfaces. Interestingly, a red shift in the UV/vis absorption is detected in THF after this chemical attachment (Figure 3 and S3, Supporting Information). The conjugated length of the grafted BisADA-DCB molecules may thus increase when BisADA-DCB molecules are chemically grafted to the convex walls of the MWNTs.

The tensile strength and modulus of the BisADA-DCB films grafted with carboxylic acid-functionalized MWNTs increase with

the MWNTs' concentration (0.14–0.38 wt %). The tensile strength ranges between 131 and 194 MPa, the modulus between 3.7 and 4.4 GPa, and the elongation at break ( $\epsilon_b$ ) between 10% and 7%. These are compared to 121 MPa and 2.9 GPa with an  $\epsilon_b$  of 16% (S4, Supporting Information) without the MWNTs. The improvements in mechanical properties are therefore significant. The  $M_n$  in the soluble portion of the BisADA-DCB-g-MWNTs (0.14 wt %) films treated at 150 °C increased to 9900 g/mol, with a PDI of 2.09 (S1, Supporting Information). We also observed that a very small amount of coated MWNTs were difficult to re-disperse in organic solvents (such as THF), due presumably to partial chemical cross-linking. These enhancements may result from chemical and physical interface interactions among the carboxylic acid-functionalized MWNTs and the polymer matrix. Some of these observed mechanical properties are even higher than values predicted from physical random distribution theories. This may be an indication that interfacial interactions should not be negligible in these calculations.

**Acknowledgment.** This work was supported by the Collaborative Center in Polymer Photonics of Air Force Research Office, Air Force Laboratory Materials and Manufacturing Directorate, and NSF (DMR-0203994 and 0516602).

**Supporting Information Available:** Additional information on GPC (S1), TGA (S2), UV-vis (S3), and mechanical properties (S4). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA05024S