Synthesis of Multiwalled Carbon Nanotube/Fluorine-Containing Poly(*p*-phenylene benzoxazole) Composites Exhibiting Greatly Enhanced Dielectric Constants

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ABSTRACT: A series of high-performance polymer/carbon nanotube (CNT) composites with different nanotube contents have been prepared via condensation of *N*-silylated diamino terminated precursor of the polymer with acid chloridefunctionalized CNTs and subsequent thermal cyclodehydration. The composites have been fully characterized by infrared and Raman spectroscopy, electron microscopy, and thermal analysis. Various interesting morphologic features including helical structures have been observed in the composites as a result of

INTRODUCTION Polybenzoxazoles (PBO), one of the strongest polymer fibers known to date, are candidate polymers for a variety of applications due to their high mechanical strength and outstanding thermal and oxidative stability.¹⁻⁴ Carbon nanotubes (CNTs), an excellent material choice for composites because of their unique mechanical, thermal, and electrical properties, have been introduced into PBO matrix to induce significant changes in the physical properties of materials.⁵⁻¹⁰ CNTs function as mechanical reinforcements and enhance electrical conductivity of the resulting composites. Additionally, the polymer composites endow processibility of CNTs, which are well-known to aggregate into dense networks of ropes and have limited solubility in either organic or nonfuming acidic media. To disperse CNTs in polymer matrix, both chemical bonding and physical blending approaches have been used. Although simple physical mixing of PBO and CNTs results in macro-phase separation and significant agglomeration of nanotube bundles, the PBO/ CNTs composites are typically prepared by in situ polymerization of PBO oligomers or monomers (e.g., o-aminophenol derivatives) with carboxylic acid functionalized CNTs in the presence of polyphosphoric acid (PPA) that acts as both reaction medium and condensation agent.⁵⁻⁹ However, it is

covalent attachment of the polymer. The composites exhibit excellent thermal stability and a significant improvement in the dielectric constant and mechanical strength with the inclusion of CNTs. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 000: 000–000, 2012

KEYWORDS: carbon nanotubes; composites; covalent attachment; dielectric constant; dielectric properties; high performance polymers; polymer composites

rather challenging to disperse CNTs homogeneously in highly viscous PPA, which would in turn affect the interfacial adhesion between CNT additives and PBO matrix. Furthermore, for the monomers containing hydrochloric acid, the concurrent dechlorination during the exchange reaction between PPA and ammonium hydrochloric acid salts could be deleterious to purification of CNTs.¹¹

We report herein a two-step synthetic route that involves the preparation of fluorine-containing PBO precursor with activated diamino endgroups¹²⁻¹⁶ followed by grafting to surface-functionalized multiwalled carbon nanotubes (MWNT) and thermal cyclodehydration to afford the polymer composites. Although fluorine-containing PBOs generally have reduced mechanical strength in comparison with rigid PBOs, the presence of soft segments in their main chain leads to better solubility and processability. Whereas most of the reported studies are focused on the enhancement of mechanical and/or electrical conductivity of composites,^{5,8,10} the influence of CNTs on the dielectric properties has been investigated in this article. Additionally, the prepared composites have been fully characterized by infrared and Raman spectroscopy, electron microscopy, and thermal analysis.

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SCHEME 1 Preparation of MWNT-COCI.

EXPERIMENTAL

Materials

Unless otherwise noted, all solvents and reagents were purchased from J&K and Aldrich and used as received. MWNTs (98+%) were obtained from the Nanotech Port Company, Shenzhen, China. 2,2-Bis(3-amino-4-hydroxyphenyl)-hexa-fluoropropane (**6FAP**, 99%) was dried in vacuum at 105°C for 24 h before use. *N*, *N*-dimethylacetamide (DMAc, 99.9%) was dried by distillation over barium oxide before use.

Acyl Chlorination of MWNTs

As illustrated in Scheme 1, MWNTs were chemically oxidized and then treated with a HCl solution in the final step to fully recover the carboxyls (—COOH) on the nanotube surface from carboxylates (—COO—). In detail, the dispersion of 0.5 g MWNTs in 100-mL concentrated hydrochloric acid was subject to sonication and heated at 80°C for 24 h in a flask equipped with a condensing tube, followed by centrifugation and drying under vacuum at 60°C for 24 h. The MWNTs-COOH (100 mg) were then stirred in 20 mL of a 20:1 mixture of thionyl chloride (SOCl₂) and *N*, *N*-dimethyl formamide (DMF) at 70°C for 24 h under refluxing. After the acyl chlorination, the unreacted SOCl₂ was evaporated with a rotary evaporator, and the collected MWNT-COCl samples were dried *in vacuo* overnight.

Synthesis of Fluorine-Containing Poly(*o*-hydroxy amide) (6FPHA)

In a flame-dried flask, **6FAP** (2.5 mmol) was dissolved in DMAc (5 mL) while stirring under nitrogen. *N*, *O*-bis(trimethyl-siyl)acetamide (BSA) (10 mmol) was added to this solution and stirred at room temperature for 1 h to prepare the silylated monomers. The solution was solidified with liquid nitrogen, to which terephthaloyl chloride (TPC) (2.45 mmol) in one portion was added. The mixture was stirred at $0-5^{\circ}$ C with an ice-water bath for 10 h under nitrogen to obtain the resulting solution, which was subsequently poured into the water/methanol mixture (1:1 in volume). The precipitated **6FPHA** was collected, washed several times with the water/methanol mixture, and dried under vacuum at 60°C (Yield: 80%).

¹H NMR (500 MHz, DMSO- d_6 , δ): 10.4 (s, 2H, NH), 9.7 (s, 2H, OH), 8.07 (brs, 4H, benzene), 7.91 (s, 2H, benzene), 7.02 (brs, 4H, benzene). ¹³C NMR (500 MHz, DMSO- d_6 , δ): 63.16 (tertiary carbon), 122–150 (benzene ring), 115 (CF₃), 164 (C=O). Anal. calcd. for **6FPHA**: C 54.94, H 2.87, N 5.86; found: C 54.95, H 2.93, N 5.92.

Preparation of MWNT/Fluorine-Containing Poly(*o*-hydroxy amide) (6FPHA) Composites (MWNT/6FPHA) and MWNT/Fluorine-Containing Poly(phenylene benzoxazole) (6FPBO) (MWNT/6FPBO) Composites

The preparation of the composites is similar with that of **6FPHA** except for the addition of MWNT-COCl. Once the reaction between **6FAP** and TPC finished, the reaction solution was solidified again, to which this MWNT-COCl (100 mg, for **MWNT/6FPHA**, 8 wt %) in one portion was added. The mixture was stirred at $0-5^{\circ}$ C for 2 h and at room temperature 8 h under nitrogen. The **MWNT/6FPHA** composites were obtained after the post-treatment as described for **6FPHA**.

The **MWNT/6FPHA** sample was dispersed in DMF and sonicated for 30 min, which was then filtered through a 200-nm pore diameter Teflon membrane and washed repeatedly with DMF to remove the excess free polymers (as determined from the disappearance of **6FPHA** absorption peak in the filtrate). The collected **MWNT/6FPHA** was dried under vacuum at 60°C for 24 h.

The **MWNT/6FPBO** composites were prepared by thermal cyclodehydration of **MWNT/6FPHA** at 300°C for 10 h under N₂.

Characterization

Fourier transform infrared spectroscopy (FTIR) spectra were conducted on a Nicolet FTIR analyzer (Magna-IR550) with KBr disks. Raman spectra were obtained using a Renishaw inVia Raman microscope (514 nm laser lines). Intrinsic viscosity of 6FPHA was measured in N-methyl-2-pyrrolidone (NMP) at 30°C using the Ubbelohde capillary viscometer. ¹H NMR spectra were recorded on Bruker AVANCE III NMR spectrometers operating at 500 MHz. Elemental analysis was carried out with an elementary analyzer (Elementar Vario EL-III). The morphology of MWNT-COOH and MWNT-6FPHA was characterized by a Hitachi S-4800 field-emission scanning electron microscope (FESEM) and JEOL JEM-2010 transmission electron microscope (TEM). Thermal gravimetric analysis (TGA) was carried out on a DuPont 1090B thermal gravimetric analyzer with a heating rate of 10°C/min in the nitrogen flow (20 mL/min). Differential scanning calorimetry (DSC) was performed with TA thermal analyzer (Q2000) in flowing nitrogen at a heating rate of 10°C/min. The mechanical properties were measured at $25^{\circ}C$ with a YG020C brute force machine (Shuang-gu Textile Instrument Co., Changzhou, China) at a displacement rate of 20 mm/min. For each



FIGURE 1 FTIR spectra of MWNT, 6FPHA, and the composites.

sample, at least 10 specimens ($50 \times 5 \times 0.03 \text{ mm}^3$, length \times width \times thickness) were measured and averaged. The dielectric properties of **MWNT/6FPBO** composites were measured on Agilent 4294A Impedance Analyzer at 1000 Hz as disk-shaped samples (20 mm in diameter, 1 mm in thickness). The disk-shaped samples were pressed at 5 MPa and room temperature for 3 min with a home-made mold.¹⁷ Gold electrodes were sputtered on the surfaces of the samples for dielectric testing.

RESULTS AND DISCUSSION

As shown in Scheme 2, the aromatic diamine monomer (**6FAP**) has low nucleophilicity due to the existence of the electron-withdrawing hexafluoroiso-propylidene group.¹⁸ The silylation reaction involving BSA was thus used to activate

the amino group of o-aminophenol and simultaneously protect the hydroxyl groups to furnish N, N', O,O'-terakis(trimethylsilyl) substituted bis(o-aminophenol)s (6FAP-SiMe₃). It has been demonstrated that N-silylated diamines can be selectively attacked by acid chloride to form exclusively the corresponding amide compounds.¹⁸ The slight off-stoichiometry condensation of 6FAP-SiMe3 with TPC gave a precursor of the polymer (6FPHA-SiMe₃) having N-silylated diamino terminal groups, which was then subject to the acid chloride-functionalized MWNTs prepared by oxidation and acyl chlorination.¹⁹ It is believed that acid chloride of MWNTs reacts predominately with activated amines to yield the MWNT/6FPHA composites with varied contents of grafted MWNTs. The intrinsic viscosity of 6FPHA is 0.65 dL/g measured in NMP at a concentration of 0.5 g/dL at 30°C. The elemental analysis result of 6FPHA is in good agreement with its theoretical compositions. Desilylation with methanol and thermal cyclodehydration were subsequently performed to generate the MWNT/6FPBO composites with benzoxazole rings in the polymer backbone.

FTIR was used to monitor the chemical transformations. As shown in Figure 1, MWNTs with carboxylic acid surface groups (**MWNT-COOH**) exhibit the prominent absorption bands around 3430 and 1710 cm⁻¹ ascribed to stretching modes of O–H and C=O of carboxyl groups, respectively. In the spectrum of **6FPHA**, the peaks at 1650 and 1540 cm⁻¹ are attributed to C=O stretching and N–H bending vibrations of the amide bonds, respectively. The broad absorption band at 3400 cm⁻¹ corresponds to N–H and O–H groups. The **MWNT/6FPHA** composite with 8 wt % MWNT shows a FTIR spectrum similar to **6FPHA**. When compared with the spectrum of **MWNT-COOH**, the absence of C=O stretching at 1710 cm⁻¹ in the spectrum of **MWNT/6FPHA** indicates that the acyl chloride groups originated from carboxylic acids on



SCHEME 2 Synthesis of high-performance 6FPBO and MWNT/6FPBO composites.

Materials



FIGURE 2 FESEM images of MWNT-COOH.

the surface of MWNTs have been fully converted to amides upon the reaction with **6FPHA-SiMe**₃. The cyclization of the hydroxyl and amide groups is confirmed by strong absorption bands at 1050–1100 and 1610 cm⁻¹ characteristic of the oxazole =C-O-C and C=N stretching, respectively, in the spectrum of **MWNT/6FPBO**.

The morphology of the MWNTs was investigated by FESEM and TEM. The FESEM image of **MWNT-COOH** demonstrates a smooth clean surface with an average diameter of \sim 50 nm and a loosely packed arrangement as shown in Figure 2.

On the other hand, it is evident from Figure 3 that the **MWNT/6FPHA** composite has a distinctly different surface morphology with irregular blobs of materials wrapped around the surface of the CNTs. Because the "free" polymers that are physically bound to the nanotube surface or have no interaction with MWNTs have been removed in the purification steps, the observed morphology can be correlated to the effect of the covalent bonding between MWNT and **6FPHA**. As examplied in Figure 3(a–c), the formation of T-shape junction is presumably a consequence of connection of two nanotubes in "end-to-side" configuration via **6FPHA**, whereas the

"end-to-end" interlinking of MWNT through the polymer is revealed in Figure 4(a–c). $^{20,21}\,$

Especially, it is interesting to note that an unusual helical structure, different from the rod-like **MWNT-COOH**, was observed as shown in Figure 5. It is reported that the helical CNTs are formed when paired pentagon–heptagon atomic rings arrange themselves periodically within the hexagonal carbon network.²² The helical CNTs are commonly produced by catalytic chemical vapor deposition and theoretically rationalized on the basis of the interactions between catalyst particles and growing nanostructures.²³ To the best of our knowledge, the existence of helical structure of CNTs in polymer composites has not been reported previously. It can be tentatively interpreted that the external stresses yielded from chemical grafting of the polymers alter the organization of the nanotubes and are responsible for the observed morphologic features.

Further evidence for covalent linkage between MWNTs and **6FPHA** was provided by Raman spectra as shown in Figure 6. The Raman spectrum of **MWNT-COOH** exhibits the characteristic peaks at 1340 cm⁻¹ (D-band) originating from the



FIGURE 3 FESEM images (a, b) of the end-to-side junctions formed by MWNT-6FPHA; (c) a schematic diagram of MWNT-6FPHA end-to-side configuration.



FIGURE 4 FESEM (a) and TEM (b) images of the end-to-end junctions formed by MWNT-6FPHA; (c) a schematic diagram of MWNT-6FPHA end-to-end configuration.

disordered graphite structure or sp³-hybridized carbons of the nanotubes.²⁴ The band at 1570 cm^{-1} (G-band) corresponds to a splitting of the E_{2g} stretching mode of graphite, which indicates the structural intensity of sp²-hybridized carbon atoms. The shoulder at 1604 cm⁻¹ (D'-band) is typical of defective graphite-like materials and also related to the extent of disorder in the nanotubes. Comparatively, the Raman spectrum of MWNT/6FPHA composite shows the similar peaks but at different frequencies, with the up shift of D-band to 1357 cm⁻¹, G-band to 1586 cm⁻¹, and D'-band to 1619 cm⁻¹. The shift of G- and D'-bands to higher frequencies in the MWNT/6FPHA composites is indicative of the increase in the elastic constant of the harmonic oscillator due to the strong attachment of the polymer to MWNT.²⁵ In agreement with earlier reports on the covalent modification of the graphene sheets that changes the position of the D-band,²⁶ the chemically grafted polymers cause field



FIGURE 5 TEM image of helical MWNT/6FPHA composites.

disturbance and physical strain in the graphite skeleton and makes excitation of D-vibrations of CNTs in the nonlinear Raman scattering process more efficient. Furthermore, the intensity ratio of the D- and G-bands (I_D/I_G) was measured to assess the relative degree of functionalization or defects in the nanotubes.²⁷ It is found that **MWNT/6FPHA** has a I_D/I_G ratio of 1.19, which remains almost the same with respect to that of **MWNT-COOH** (i.e., 1.18). This result indicates that the electronic structure of the MWNT is not perturbed by the covalent attachment of **6FPHA**.

Figure 7 shows typical TGA thermograms of **6FPBO**, **MWNT/6FPHA** (8 wt %), and **MWNT/6FPBO** (8 wt %) under nitrogen. **MWNT/6FPHA** exhibits a different thermal behavior from those of **MWNT-COOH** and **MWNT/6FPBO**. The weight loss starts at around 250°C and comes to an end at about 400°C that is attributed to the thermal cyclodehydration of **6FPHA**. This observation is supported by the fact that both **MWNT/6FPHA** and **MWNT/6FPBO** composites show similar TGA curves in the range of 400–800°C, which suggests that our approach of conversion **MWNT/6FPHA** to **MWNT/6FPBO** through thermal cyclodehydration is feasible and effective. In addition, it is found the addition of MWNTs



FIGURE 6 Raman spectra of MNNT-COOH and MWNT/6FPHA.

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FIGURE 7 TGA thermograms of 6FPBO, MWNT/6FPHA (8 wt %), and MWNT/6FPBO (8 wt %).

greatly improves the thermal stability of **6FPBO** composites. The thermal decomposition temperature (T_d) of **MWNT**/ **6FPBO** increases with the addition of MWNTs up to 8 wt %. Because of the strong interaction between MWNTs and **6FPBO**, incorporation of MWNTs presumably provides thermo-oxidative stability to the polymers in the vicinity of the tube surfaces and enhances thermal conductivity of the composite and thus increases its thermal stability. The decrease of T_d for the composites with high contents (>8 wt %) of MWNTs suggests the formation of MWNT rich domains in the composites and poor interfacial interactions between matrix and fillers.

The glass transition temperature (T_g) of **MWNT/6FPBO** composites were investigated by DSC and summarized in Table 1. It can be seen that, consistent with the trend observed in T_d , T_g increases with increasing MWNT content up to 8 wt % and then decreases with the further increase of MWNT concentration. Regardless of the content of MWNTs, T_g of **MWNT/6FPBO** composites are higher than that of **6FPBO** (i.e., 315°C). This indicated that the mobility of polymer chains is reduced due to the constraint effect of MWNTs in the composites.

TABLE 1	Thermal	Resistance	of 6FPBO	and	MWNT/6FPB	0
Composi	tes					

Content of MWNT (wt %)	T _d ^a (°C)	Residual Weight (%, 750°C)	T _g (°C)
0	501	56.7	315
2	511	57.1	327
5	519	57.7	336
8	525	57.9	341
12	517	58.6	338

 $^{\rm a}$ The thermal decomposition temperature at which 5% weight loss occurred.

TABLE 2 Mechanical Properties of **6FPBO** and the **MWNT/6FPBO** Composites

Sample	Tensile Strength (MPa)	Tensile Modulus (GPa)	Elongation at Break (%)
6FPBO	64 ± 2	2.2 ± 0.3	2.3 ± 0.2
MWNT/6FPBO (2 wt %)	80 ± 3	2.6 ± 0.3	2.4 ± 0.2
MWNT/6FPBO (5 wt %)	94 ± 4	2.8 ± 0.3	2.7 ± 0.2
MWNT/6FPBO (8 wt %)	105 ± 5	2.9 ± 0.3	2.9 ± 0.2
MWNT/6FPBO (12 wt %)	83 ± 3	2.4 ± 0.3	2.4 ± 0.2

The mechanical properties of 6FPBO and MWNT/6PFPBO composite films are summarized in Table 2. It is found that the tensile strength, tensile modulus, and elongation at break of the MWNT/6FPBO composite with 8 wt % MWNT are 64%, 32%, and 26%, respectively, greater than those of 6FPBO. The greatly improved mechanical properties of the MWNT based composites is apparently due to the higher tensile strength of MWNT fillers compared with 6FPBO matrix. Similar to the trend observed in thermal stability, a further increase of MWNT content beyond 8 wt % leads to deteriorated mechanical properties. The dependence of the mechanical and thermal behaviors of composites on the MWNT content is consistent to the previous work.^{3,4} In general, if there are no chemical bonding or weak interactions between the organic polymer phase and the inorganic particles phase, the mechanical strength of the composites would be reduced even with higher tensile strength of CNT fillers. The reinforcement of thermal stability and mechanical properties evidently results from the existence of covalent bonding between the polymer chains and MWNT fillers.

The dielectric properties of the **MWNT/6FPBO** composites were evaluated using a LCR meter at room temperature and 1 kHz.^{28,29} The dependence of dielectric constant of the composites on the weight fraction of s is described in Figure 8. The dielectric constant increases from 2.78 to 118 with increasing the MWNT content to 12 wt %. The large



FIGURE 8 Dielectric constant and loss of the composites with varied MWNT contents.





dielectric constant in the composites can be explained in terms of Maxwell-Wagner polarization originating from the interfaces.^{30–32} MWNT insulating polymer-conductive MWNTs enable long-range migration of electronic carriers and thus give rise to the composites with large polarization. Moreover, the electron-withdrawing CF₃ groups of the polymer matrix may strengthen the interfacial polarization effect.³³ A further increase in the content of MWNTs leads to a reduction of the dielectric constant, suggesting that the conductive MWNT fillers reaches to the point of percolation for electron conduction. This is verified by a similar trend observed in the dielectric loss spectra, in which the dielectric loss undergoes a sharp increase when the content of MWNT approaches to 10 wt %. The resulting percolative composites show a further increase of the dielectric loss and decrease of the dielectric constant with increasing MWNT content beyond 12 wt %. The postulated percolation threshold at around 10-12 wt % for the composites is close to the value (~14 wt %) predicted for a perfectly random three-dimensional percolative system, implying a homogeneous distribution of MWNT in 6FPBO matrix.³⁴ Figure 9 presents the frequency dependence of dielectric constant of MWNT/6FPBO composite with different mass fractions of MWNTs. It is found that the dielectric constant of the composite is almost frequency independent as the MWNT concentration is less than 8 wt %. As the MWNT concentration is higher than 8 wt %, the dielectric constant decreases rapidly from 65 to 10 with the increasing of frequency from 10 to 107 Hz. The strong dispersion of the dielectric constant in the neighborhood of percolation threshold is a consequence of the presence of space charge polarization in the composite which contributes to the improved dielectric constant at low frequencies. When the concentration of MWNT in the composites is much lower than percolation threshold, the composites act as insulators, but when the concentration is higher than percolation threshold, the composites are electrically conductive.

CONCLUSIONS

In summary, high-performance polymer composites have been prepared through condensation reaction between N-silylated diamine-terminated polymers and acid chloridefunctionalized MWNTs and subsequent thermal cyclodehydration. The covalent attachment of the polymers to the nanotubes results in a variety of interesting morphologies including helical structures in addition to the improved thermal and mechanical properties. The composites are stable up to 520°C and exhibit a significant enhancement in the mechanical strength and dielectric constant with the inclusion of MWNTs. The 12 wt % MWNT composite has a dielectric constant of 118, which is over 40 times higher than that of the pristine polymer. This synergistic combination of excellent thermal stability and dielectric constant makes this class of polymer composites very attractive as dielectric materials for elevated temperature applications such as electric vehicles, aerospace, and microelectronics.^{35,36}

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