Covalent Functionalization of Multiwalled Carbon Nanotubes with Polybutadiene

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ABSTRACT: Covalent functionalization of multiwalled carbon nanotubes (MWNTs) with polybutadiene was accomplished by coupling of isocyanate-decorated MWNTs with hydroxyl-terminated polybutadiene (HTPB) in dry toluene. The MWNT precursor, isocyanate-functionalized MWNTs, was prepared by directly reacting commercial hydroxyl functionalized MWNTs with excess toluene 2,4-diisocyanate (TDI). HTPBs with different molecular weights ($M_n = 1900$, 2600, and 3600 g/mol) were subjected to this coupling reaction, resulting in the formation of polymer functionalized MWNTs. FTIR spectroscopy was utilized to follow the introduction and consumption of isocyanate groups on the MWNTs. Thermogravimetric analysis (TGA) indicated that HTPB was successfully grafted onto MWNT surface, with the final products having a polymer weight percentage of around 30 wt %. Transmission electron microscopy (TEM) was utilized to image the polymer functionalized MWNTs, showing relatively uniform polymer coatings presented on the surface of MWNTs. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 116: 1272–1277, 2010

Key words: multiwalled carbon nanotubes; functionalization; polybutadiene; grafting to

INTRODUCTION

Carbon nanotubes (CNTs) are unique nanostructured materials with remarkable physical, mechanical, and electronic properties.[1–4] These properties make them attractive for applications in many scientific and technological fields such as electronic structures,[5,6] polymer composites,[7] and biological systems.[8] Among these potential applications, the prospect of obtaining high performance CNT-based polymeric nanocomposites has attracted the efforts of researchers in both academia and industry.[9] The combination of organic polymer components with CNT fillers in a single material has extraordinary significance for the development of advanced materials with remarkable mechanical, electrical, thermal, and multifunctional properties.[10–12] However, these enhanced properties can only be achieved by homogeneously dispersing CNTs within the polymer matrix as well as effective load transfer from matrix to nanotubes.[13–15] So far, due to weak interaction between nanotubes and the polymer, the reinforcing role of nanotube in composites is still very limited. Additionally, CNTs tend to exist as bundles and are entangled as agglomerates due to strong intertubes van der Waals interactions, resulting in a poor dispersion within the polymer matrix.[16] Therefore, debundling or unroping the nanotubes for homogeneous dispersion remains a challenge for the preparation and application of CNT-based composites.

Recently, significant efforts have been made to address issues that directly affect the composite properties, such as deagglomeration of bundles and ropes, CNTs dispersion, as well as interfacial bonding. An effective approach for these requirements is to covalently functionalize CNTs with polymeric structures,[17–27] which not only serves to facilitate CNTs dispersion and prevents their agglomeration within a polymer matrix or in solution, but also can improve the load transfer from the matrix to the smaller bundles and, ideally, to the individual nanotubes within composite materials due to the enhanced polymer-nanotube interfacial interactions. Currently, both "grafting-to"[17–22] and "grafting-from"[23–27] functionalization strategies have been reported to bond polymeric chains to CNT surfaces.

Besides the modification methods, the types of polymers to be incorporated onto CNT surfaces are also of interest. Vinyl polymers have been widely utilized in CNT modifications.[23–27] In addition, other polymers like polyether,[28] polyamide,[25] polyurea,[29] and polyurethane[30] have also been covalently linked to CNTs. Considering the preparation of advanced CNT-based polymeric composites, the major purpose of CNT modification, as mentioned above, is to achieve a homogeneous dispersion of CNTs in polymer matrix as well as optimal load transfer from matrix to nanotube. It is noteworthy that functionalization of nanotubes with polymers that are identical or structurally similar to the matrix polymers is an ideal approach to result in high-quality composites. Although many kinds of polymers have been used as matrix in preparation of polymer-CNT composites, limited reports[31,32] involve with the composites of rubber, such as polybutadiene, and CNTs, even though the rubber could be the most attractive polymers for reinforcement and property enhancement.

Herein, we report a facile strategy to covalently attach hydroxyl-terminated polybutadiene (HTPB) onto the multiwalled carbon nanotube (MWNT) surfaces using 2,4-toluene diisocyanate (TDI) as coupling agent. The HTPB was chosen because it is an important commodity polymer with a wide variety of applications in adhesives, sealants, electrical potting, and waterproof coatings. Moreover, the immobilized HTPB with an unsaturated hydrocarbon chain can be further modified with a vinyl-group containing monomer or mixture of monomers that are capable of forming grafts onto the HTPB backbone. Additionally, the unsaturated bonds in polymer chains can be easily epoxidized. These incorporated epoxy groups along with the terminated hydroxyl groups will make them compatible with other bisphenol A and cycloaliphatic epoxies. On the other hand, HTPB can be used as starting material to prepare urethanes with excellent water resistance due to good reactivity of the hydroxyl end-groups.[33–40] Therefore, it is reasonable to regard the HTPB-modified CNTs as a universal compatibilizer precursor in compatibilizing polymer and nanotubes in their composites, because the HTPB-modified CNTs can be subsequently transformed to polymeric structures that are similar to the matrix polymers, and thus, improvement of bonding to matrix as well as a better dispersion of the CNTs could be observed. Hence, the preparation of HTPB-functionalized CNTs is highly relevant and beneficial to the preparation of advanced CNT-polymer nanocomposites.

EXPERIMENTAL

General

MWNTs with 1.06 wt % concentration of hydroxyl groups (MWNT-OH) purchased from the Chengdu Organic Chemicals Co., Chinese Academy of Science (China), were dried in vacuum at 100°C for 12 h before use. The preparation details for the MWNT-OH have been protected by patent (CN1463919). HTPB with different molecular weights (M_n = 1900, 2600, and 3600 g/mol, alcohol functionality f_{OH} = 2.2), supplied by Liming Research Institute of Chemical Industry (China), was dehydrated at 80°C under vacuum for 5 h before use. TDI was freshly distilled prior to use. Toluene was reflux with sodium and then distilled. All other chemicals were used as received. FTIR spectra in KBr pellets were recorded on a Perkin-Elmer Spectrum One FTIR spectrophotometer. Thermogravimetric analysis (TGA) was carried out on a STA 449C instrument with a heating rate of 5°C/min in flowing N_2. Ultraviolet-visible (UV-vis) spectra were measured using a PE Lambda 20 spectrophotometer. Transmission electron microscopy (TEM) was conducted using a JEM 3010 electron microscope.

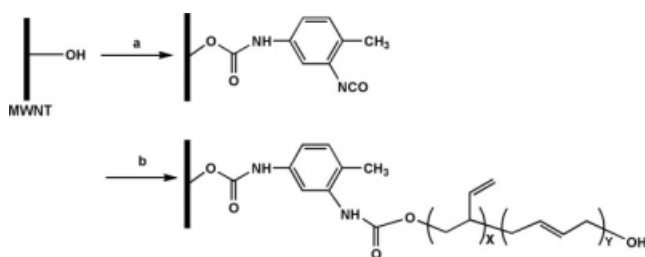### Preparation of isocyanate-functionalized MWNTs

One hundred milligram of MWNT-OH (0.0624 mmol of hydroxyl group) was dispersed in 50 mL of TDI (0.352 mol) under stirring, and the functionalization was endured in a dry nitrogen atmosphere at 80°C for 72 h. The functionalized MWNTs were then filtered through a PTFE (200 nm pore size) membrane to recycle TDI. The collected solid was washed with anhydrous toluene to completely remove the residual TDI. After being dried in vacuum at 40°C for 24 h, the functionalized MWNTs containing isocyanate groups were obtained.

Preparation of HTPB functionalized MWNTs

In a typical experiment, isocyanate-functionalized MWNTs (50 mg, 0.0244 mmol of isocyanate group) and HTPB (6 equiv/mol of isocyanate group) were sonicated in 100 mL of anhydrous toluene for 10 min to give a homogeneous suspension. Then, the mixture was stirred at 100°C in a nitrogen atmosphere for 36 h. After cooling to room temperature, the mixture was filtered through a PTFE (200 nm pore size) membrane and washed thoroughly with THF. The black solid was collected and dried in vacuum at 60°C for 24 h.

RESULTS AND DISCUSSION

In this study, MWNT-OH with 1.06% mass concentration of hydroxyl group, and a length of 10–20 μm, purchased from the Chengdu Organic Chemicals Co., Chinese Academy of Science, was dried before use. The preparation details for MWNT-OH have been protected by patent (CN1463919). The MWNT-

Scheme 1 Synthesis of HTPB functionalized MWNTs, (a) TDI, 80°C; (b) HTPB, toluene, 110°C.

OH was thus reacted with TDI to synthesize isocyanate-decorated MWNTs as depicted in Scheme 1. This chemistry allows for preferential reaction between the *para*-isocyanate group and the hydroxyl group on MWNT surfaces, leaving the *ortho*-isocyanate group intact due to steric hindrance within the TDI molecule.[41] In a typical experiment, 100 mg of MWNT-OH was reacted with 50 mL of TDI at 80°C. Excess TDI was used as a solvent to disperse nanotubes as well as a reactant to drive the reaction to completion, and this excess reactant was easily removed after each reaction by ultra-filtration and washing with anhydrous toluene.

The coupling reaction between MWNT surface hydroxyl group and excess TDI was confirmed by FTIR spectroscopic analysis. Figure 1 shows the FTIR spectra of MWNT-OH (spectrum A), and isocyanate-functionalized MWNTs (spectrum B). The very weak absorbance at around 3500 cm^{-1} in spectrum A is attributed to the surface OH groups of the starting nanotubes.[42] Addition of excess TDI to the MWNT-OH resulted in the incorporation of isocyanate functionalities onto the surface of MWNTs. This
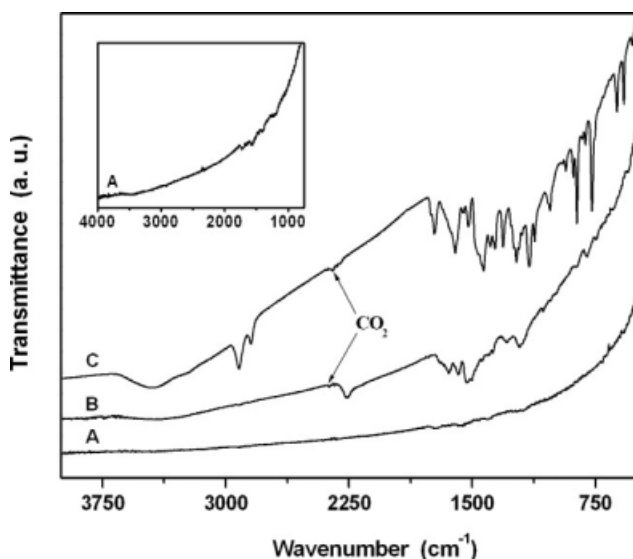

Figure 1 FTIR spectra of (A) MWNT-OH, (B) isocyanate-functionalized MWNTs, and (C) HTPB functionalized MWNTs.
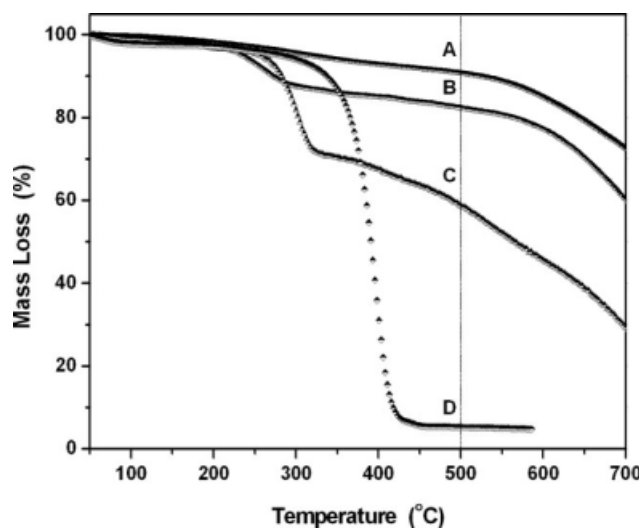
Figure 2 TGA data for (A) MWNT-OH, (B) isocyanate-functionalized MWNTs, (C) HTPB functionalized MWNTs with HTPB molecular weight of 2,600 g/mol, and (D) pure HTPB, acquired under nitrogen at a ramp of 5°C/min.

was evidenced by the appearance of a clearly discernable band at about 2265 cm^{-1} corresponding to asymmetric stretching of the appended terminal isocyanate groups, and the appearance of an aromatic C—C stretch at 1595 cm^{-1} in the FTIR spectrum B. Additionally, signals corresponding to the C=O and C—N stretches of the formed carbamate linkages between the nanotube and the isocyanate functionality in TDI-modified MWNTs can also be seen at 1645 cm^{-1} and 1223 cm^{-1}, respectively.[30]

Supporting evidence for the covalent attachment of TDI onto the MWNT surfaces comes from the TGA analysis. Figure 2 shows the TGA curves of MWNT-OH (curve A) and isocyanate-functionalized MWNTs (curve B). The TGA plot of MWNT-OH indicates a gradual mass loss of around 9% as the temperature reaches 500°C. However, there is a distinct mass loss region between 200 and 400°C for isocyanate-functionalized MWNTs. If the mass loss of the MWNT-OH at 500°C is used as the reference, the mass loss of isocyanate-functionalized MWNTs at 500°C is about 8.5%. This result indicates that the isocyanate graft density is about 0.59 mmol per gram of neat MWNTs. Considering that the starting nanotubes have a hydroxyl group concentration of 1.06 wt %, the TGA results indicate that above 90% of the available hydroxyl groups reacted with TDI despite the poor solubility of MWNTs.

The isocyanate-functionalized MWNTs were then used as a precursor to couple HTPB in toluene, yielding polymer functionalized MWNTs (Scheme 1). First, we choose HTPB with molecular weight of 2,600 g/mol to conduct this coupling reaction. Considering that the isocyanate functionalities are attached to the surface of rigid MWNTs, isocyanate
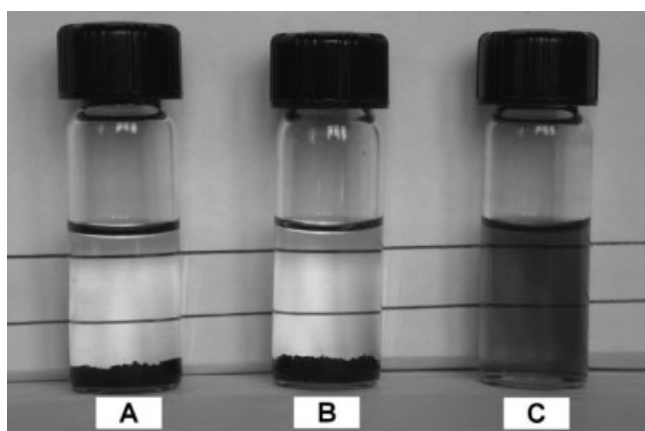
Figure 3 Photograph of three separate MWNT samples in toluene, (A) MWNT-OH, (B) isocyanate- functionalized MWNTs, and (C) HTPB-functionalized MWNTs.

dimerization or trimerization reactions were not observed,[43] allowing the coupling reaction to proceed smoothly. In this study, any ungrafted HTPB during the coupling was easily removed after each reaction by ultra-filtration and prolonged washing with toluene. In order to confirm this, a control experiment was performed in which MWNT-OH and free HTPB were blended in toluene solvent followed by efficient ultra-filtration and washing. TGA result indicated that the amount of adsorbed HTPB was less than 3 wt %, as opposed to values of ca. 30 wt % for the grafted materials (vide infra).

The first and simplest qualitative test to determine whether the "grafting to" functionalization procedure was successfully involved checking the solubility of the product in toluene (a good solvent for HTPB). Figure 3 shows three vials containing equal volumes of solvent and equal masses of MWNT-OH (vial A), isocyanate-functionalized MWNTs (vial B), and HTPB functionalized MWNTs (vial C), in which the molecular weight of HTPB is 2,600 g/mol and the degree of MWNT functionalization is ca. 30 wt %. Clearly, the MWNT-OH and isocyanate-functionalized MWNTs are all completely insoluble in toluene. Conversely, the polymer-functionalized MWNTs contained in vial C form a clear, dark-brown solution that contains no discernable particulate materials, and remains stable for a period of at least 3 months. This solubility is remarkable considering that the dissolved MWNTs are, on average, 10–20 μm in length.

FTIR spectroscopic analysis again provided additional evidences that the MWNT surface coupling reaction proceeded as illustrated in Scheme 1. The FTIR spectrum of HTPB-functionalized MWNTs is also shown in Figure 1. As expected, the broad but slightly less intense band at 3440 cm^{-1} is assigned to the stretching of the HTPB-terminated hydroxyl groups. The C–H stretching vibrations occur at 2853

and 2923 cm^{-1}. Additionally, distinct absorption bands of alkenes at around 1420, 930, and 890 cm^{-1}, originating from the out-of-plane bending vibrations as well as characteristic alkenes stretching band at 1605 cm^{-1} are appeared.[44] Although the isocyanate signal at 2265 cm^{-1} is weak, the spectra clearly indicate that the isocyanate signal is not present prior to reaction with TDI or after the coupling with HTPB. Compared with the FTIR spectrum of isocyanate-functionalized MWNTs, the disappearance of the isocyanate stretch after the addition to HTPB indicates that HTPB is, indeed, covalently attached to the MWNT surface, though the low intensity of this FTIR absorption leaves some uncertainty.

To gain a more quantitative picture of the extent of nanotube functionalization, TGA analysis was performed on the reaction product (Table I, Run f) and the result was also shown in Figure 2. Because the pure HTPB can be completely decomposed at a temperature of 500°C as indicated in Figure 2 (curve D), therefore, the mass loss of polymer functionalized MWNT samples at 500°C is used to estimate the amount of polymer that covalently attached to the MWNT surfaces. As shown in Figure 2, the mass loss of HTPB-functionalized MWNTs at 500°C is about 42 wt %, indicating that the HTPB grafting conversion is 29.6 wt%^{a}. It is noteworthy that the estimation has not neglected the amount of organic functionalities that covalently attached to the MWNTs. Considering that the isocyanate graft density is about 0.59 mmol per gram of neat MWNTs, the TGA result indicates that only 33% of the available isocyanate groups have reacted with HTPB. The relatively low reaction efficiency can be attributed to the steric hindrance from attached polymer chains and relatively low reactivity of functional groups on the surface of MWNTs. In addition, trace moisture in HTPB can also lower the grafting efficiency.

The successful implementation of the coupling reaction on the MWNTs surface prompted us to investigate the effect of HTPB molecular weight, reaction temperature, as well as reaction time on the grafted polymer weight proportion (f_{wt}%) of the resulting polymer-functionalized MWNT samples. All experiments were carried out using a fixed

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^{a}The polymer grafting conversion (Y) can be expressed by the following equation:

$$[0.175w(1-Y) + wY]/w = 42\%$$

where w is the total mass of HTPB-functionalized MWNTs (HTPB-MWNTs), wY is the mass of HTPB in the HTPB-MWNTs sample, $w(1-Y)$ is the mass of isocyanate-functionalized MWNTs in the sample, respectively. A total of 17.5% is MWNTs, which can be estimated from the TGA curve of isocyanate-functionalized MWNTs, and 42% is the total mass loss of HTPB-MWNTs. From the equation, the HTPB grafting conversion (Y) is 29.6 wt %.

TABLE I
Results of the Coupling Reactions in Toluene

Run	$M_{n,\text{HTPB}}$/ kg/mol	Temp/°C	Time/h	$f_w\%$/wt %
a	1,900	100	36	25.8
b	2,600	100	36	28.0
c	3,600	100	36	29.4
d	2,600	80	36	14.2
e	2,600	90	36	20.8
f	2,600	110	36	29.7
g	2,600	110	12	13.8
h	2,600	110	24	19.8
i	2,600	110	48	31.8
j	2,600	110	60	32.3

molar ratio of 6/1 for HTPB hydroxyl end-group to MWNT-bound isocyanate group, and other conditions were systematically varied and their effects were evaluated by analyzing the value of $f_{\text{wt}}\%$, which was determined by TGA measurement. The mass loss of MWNT-polymer conjugates at 500°C is used to estimate the value of $f_{\text{wt}}\%$.

We first investigated the effect of the molecular weight of HTPB on the $f_{\text{wt}}\%$ for the polymer-functionalized MWNTs. The values of $f_{\text{wt}}\%$ analysis were conducted on the nanotube bound polymers produced in a series of reactions that the molecular weight of HTPB ranged from 1,900 to 3,600 g/mol. Table I lists the results of coupling reactions between isocyanate-functionalized MWNTs and HTPB. Comparing entries a, b, and c of Table I, provides an indication that polymer molecular weight has an impact on the $f_{\text{wt}}\%$ of the conjugate materials. To a certain extent, increasing the molecular weight of HTPB will result in slight increase in $f_{\text{wt}}\%$. In this study, HTPB with high molecular weight was not used for the coupling reaction due to the decreased reactivity of chain-end hydroxyl groups. Because polymer with high molecular weight usually adopts a more random coil structure in solution, which makes the chain-end functionality less accessible.

Additionally, comparing entries d-f, and b (Table I) provides information on the effect of reaction temperature on $f_{\text{wt}}\%$ of the final product. Under this reaction conditions, it appears that higher temperatures improve the efficiency of the coupling reaction. On the other hand, the effect of time can also be gleaned from entries g-j, and f (Table I) indicating that longer reaction times improve the value of $f_{\text{wt}}\%$, but this improvement almost diminishes beyond reaction times of 48 h.

High-resolution TEM analysis of the HTPB-functionalized MWNTs was performed by placing a single drop of the methanol solution onto a holey carbon-coated copper grid. Figure 4 shows the representative TEM images of the starting MWNT-

OH (A) and polymer functionalized MWNTs (B-F), in which the degree of functionalization is about 40 wt % (Table I, Run b). As shown in Figure 4, the average diameter of MWNT-OH is around 40 nm, and the structure of its surface is featureless. Additionally, the image clearly shows the absence of a polymer layer on the tube surface [Fig. 4(A)]. Conversely, a core-shell structure with MWNTs at the center can be observed for polymer-functionalized MWNTs. The products resemble polymer-encapsulated nanotubes, with the polymer casing being relatively uniform along the entire nanotube length, suggesting a relatively high grafting density [Fig. 4(B,C,E,and F)]. Under higher magnification, the boundary between the tube and the polymer layer becomes distinct due to the differing electron contrast of the MWNTs and the polymer [Fig. 4(D)]. Clearly, the tube is enwrapped by an even polymer layer that is several nanometers thick, again suggesting relatively high grafting density. Moreover, TEM examination clearly shows that the bamboo-like structure of MWNTs is maintained after the modification process [Fig. 4(D)].
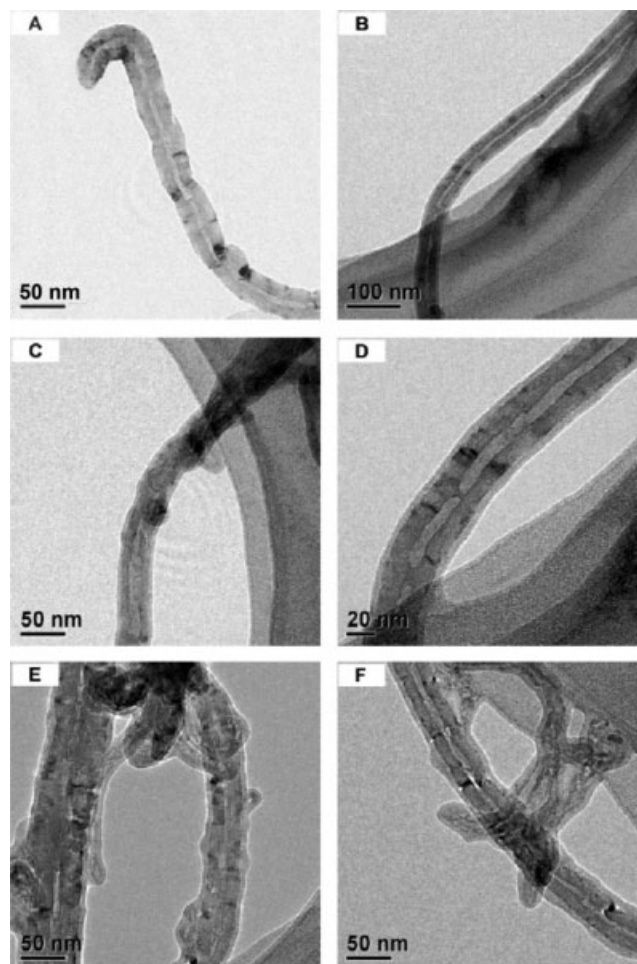

Figure 4 Representative TEM images of MWNT-OH (A) and HTPB-functionalized MWNTs (B-F).

CONCLUSIONS

We have demonstrated an efficient approach to the functionalization of MWNTs with HTPB using the grafting-to strategy in a two-step process. The formation of the isocyanate-functionalized MWNTs by the addition of toluene 2,4-diisocyanate to MWNTs surface hydroxyl groups was the first step. The second step was the coupling reaction between nanotube-bound isocyanate functionalities and hydroxyl end-groups of HTPB, allowing for the formation of polymer covalently functionalized MWNTs. FTIR and TGA analysis indicated that both nanotubes and polymers were present within the material isolated from the coupling reaction. Unlike simple blends of polymers and nanotubes, the two components of our composites could not be separated from one another by extensive filtration and washing, indicating that they are covalently bound. Analysis of these structures by TEM provided further evidence for the formation of polymerized nanotubes. The polymer-functionalized tubes exhibited high solubility in organic solvents, such as toluene and THF, and the solutions remained stable for at least 3 months.

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