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Chemical Engineering of the Single-Walled Carbon Nanotube−Nylon 6 Interface

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Abstract: We report an approach to the chemical engineering of the single-walled carbon nanotube (SWNT)−polymer interfacial interaction in a nylon 6 graft copolymer composite which is based on the degree of SWNT functionality. Continuous fibers are drawn from composites fabricated from the in situ polymerization of caprolactam with SWNTs possessing a range of carboxylic acid (SWNT-COOH) and amide (SWNT-$CONH_2$) functionalities. Mechanical performance evaluation of the composite fibers shows that a high concentration of the carboxylic acid functional groups leads to a stronger SWNT−nylon interfacial interaction, as reflected in greater values of the Young's modulus and mechanical strength. Replacement of the COOH group by $CONH_2$ in the SWNT starting material changes the grafting polymerization chemistry, thereby leading to the covalent attachment of longer graft copolymer chains to the SWNTs, and alters the composite morphology while increasing the composite flexibility and toughness.

Introduction

Carbon nanotubes (CNTs) are considered to be the ideal reinforcing agent for high-strength polymer composites because of their tremendous mechanical strength, nanometer-scale diameter, and high aspect ratio.[1−4] However, to fully realize these exceptional properties in composite reinforcement, there are a number of issues that have to be resolved. Optimization of the polymer−CNT interfacial interaction so as to ensure efficient stress transfer from the polymer matrix to the nanotube lattice is one of the main concerns.[1,5−15] This can be realized by increasing the polymer−CNT physical contact or by constructing chemical bonds between nanotubes and the polymer matrix.[5,16,17]

Polymer−CNT physical contact in the composite can be enhanced by increasing the amount of polymer absorbed on CNTs,[5] selecting polymers that are compatible with or tend to crystallize on the nanotubes,[16−20] functionalizing CNTs to make them compatible with the polymeric matrix,[17,20−24] or using nanotubes of smaller diameter to increase the surface area.[5] These methods are applicable where it is possible to select a polymer that is compatible with the CNTs under the conditions of composite preparation.

The formation of a polymer−CNT covalent bond constitutes the strongest type of interfacial interaction and is superior to physical adsorption; when properly executed, the resulting material becomes a hybrid of the starting materials and can

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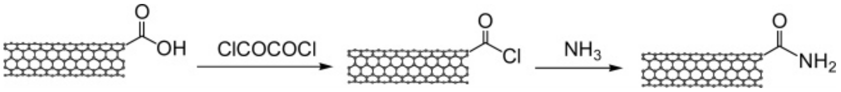
Scheme 1. Synthesis of Amide-Functionalized SWNTs



produce a homogeneously blended composite in which phase separation is precluded by chemistry. In the composite, the grafted polymer chains penetrate and become a part of the polymer matrix and bridge the connection of the CNTs to the matrix. In this way, the presence of the chemically bonded polymer chains transforms the smooth graphene-like, nonreactive surface of the CNTs into a hybrid material that has the characteristics of both CNTs and polymer. Polymeric resins stick strongly to the nanotubes and increase the polymer−CNT interfacial interaction. Grafting poly(methyl methacrylate) (PMMA) on multiwalled carbon nanotubes (MWNTs) by opening the MWNT π-bond has exhibited an improved interfacial strength in the composites.[21,25]

In our previous study, we reported a new route to synthesize single-walled carbon nanotube (SWNT)−nylon 6 (PA6) composites and demonstrated that the existence of grafted PA6 chains on SWNTs can improve the SWNT−nylon interfacial interaction.[26] In the present study, we investigate the nanoscale manipulation of the SWNT−nylon interfacial interaction by systematically engineering the functionality. We evaluate the effect of the concentration of grafted polymer chains and their chain length on the SWNT−nylon mechanical performance. This is accomplished by utilizing SWNTs with a range of carboxylic acid group concentrations (SWNT-COOH) to synthesize the SWNT−nylon composites; the variation in the COOH concentration results in different grafting yields of PA6 chains on SWNTs, and this affects the SWNT−polymer interfacial interaction, as manifested in the mechanical performance of the composites. We also synthesized composite from SWNTs bearing the amide functional group (SWNT-$CONH_2$), which was found to increase the length of the grafted PA6 chain. Comparison of the materials prepared from SWNT-COOH and SWNT-$CONH_2$ demonstrates the power of carbon nanotube chemistry in controlling the grafting polymerization reaction, the morphology, and the mechanical performance of the composite.

Experimental Section

1. Materials and Instrumentation. SWNTs with 0.0% (P2-SWNT), 4.2% (P3-SWNT), 6.0%, and 6.8% concentration of carboxylic acid groups were obtained from Carbon Solutions, Inc. (www.carbonsolution.com); to denote the presence of the carboxylic acid functionality, SWNT material with different carboxylic acid groups is referred to as SWNT-COOH and is specifically tailored for functionalization chemistry.[27] The SWNT samples used in this study have a relative carbonaceous purity of 80−90%.[28]

The concentration of carboxylic acid groups in the SWNTs was estimated by acid−base titration.[29] Before the titration, the SWNTs were stirred in water for 2 days under argon and collected via filtration to remove acid residue. In a typical titration experiment, pretreated SWNTs (93.03 mg) were stirred in 50.00 mL of 0.05 M aqueous NaOH solution under argon for 48 h. The mixture was filtered through a 1.2 μm pore-size membrane and washed with deionized water until the filtrate was neutral. The combined filtrate and washings were titrated with 39.50 mL of 0.05 M aqueous HCl solution to reach the neutral point (pH = 7.00), as monitored by a pH meter (Corning pH meter 445), and thus the content of acidic sites in the SWNTs is calculated to be 0.53 mmol. The carbon content of the SWNTs is estimated to be 7.75 mmol by assuming that the SWNTs are solely composed of carbon, and thus the molar ratio of the acidic sites in the SWNT sample is 6.8%.

The other chemicals were purchased from Aldrich and used as received. Mid-IR spectra were measured on a Nicolet Nexus 670 FT-IR spectrometer. Scanning electron microscopy (SEM) images were taken on a Philips SEM XL-30 microscope. TGA data were recorded on a Perkin-Elmer Instruments, Pyris Diamond TG/DTA thermogravimetric/differential thermal analyzer, at a heating rate of 5 °C/min in air.

2. Synthesis of Nylon 6−SWNT Composites. The composites in this study were synthesized with the same SWNT loadings of 0.5 wt % following a procedure reported previously:[26] 44 mg of SWNT-COOH (with 0.0%, 4.2%, 6.0%, or 6.8% carboxylic acid group) or SWNT-$CONH_2$ (with 4.2% amide) and 8 g of caprolactam were loaded into a 50 mL three-neck round-bottom flask. The mixtures were sonicated at 80 °C for 2 h. The flask was then transferred to a preheated oil bath (100 °C), and 0.8 g of 6-aminocaproic acid was added to the suspension. The suspension was heated at 250 °C with mechanical stirring under an argon atmosphere. After 6 h, the product mixture was poured into water, and a very hard polymer precipitated. The precipitate was chopped into small pieces and washed with hot water at 80 °C for 1 h to remove unreacted monomer and low-molecular-weight oligomers.

3. Polymer Fiber Fabrication. Fibers of the composites were fabricated through melt extrusion using a custom-made spinneret assembly as described in our previous study,[26] and the SEM images of the fiber cross section are shown in the Supporting Information (Figure S1).

4. Synthesis of Amide-Functionalized SWNTs (SWNT-$CONH_2$). The synthetic procedure is shown in Scheme 1; SWNT-COCl was prepared using SWNTs with 4.2% carboxylic acid groups (P3-SWNT, Carbon Solutions, Inc.), following the process we reported previously:[30] SWNT-COOH (40 mg) was first sonicated in 60 mL of anhydrous DMF to give a homogeneous suspension. Oxalyl chloride (1.5 mL) was added dropwise to the SWNT suspension at 0 °C under N_2. The mixture was stirred at 0 °C for 2 h and then at room temperature for an additional 2 h. Finally, the temperature was raised to 70 °C, and the mixture was stirred overnight to remove excess oxalyl chloride. The SWNT-COCl was collected by filtration through a PTFE membrane (pore size 0.2 μm) and then re-dispersed in 60 mL of anhydrous DMF. The amide-functionalized SWNTs were synthesized by passing NH_3 into the dispersion of SWNT-COCl in DMF for about 4 h with magnetic stirring at 0 °C. The mixture was brought to room temperature, filtered through a PTFE membrane (0.2 μm pore size), and gave rise to 37 mg of product after washing with water.

The IR spectra of the functionalized SWNTs are shown in Figure 1; the broad band at 1630 cm^{-1} corresponds to the stretching vibration of the C=O group of the amide functionality in SWNT-$CONH_2$.[31−33]

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Table 1. Mechanical Properties of Composite Fibers Prepared Using SWNTs with Different Functional Groups at a SWNT Loading of 0.5 wt %

	pure nylon	0.0% –COOH	4.2% –COOH	6.0% –COOH	6.8% –COOH	4.2% –CONH$_2$
tensile strength (MPa)	40.9	69.1	83.4	88.6	98.5	108.8
break strain (%)	417	250	224	224	251	350
Young's modulus (MPa)	440	575	840	1470	1500	790

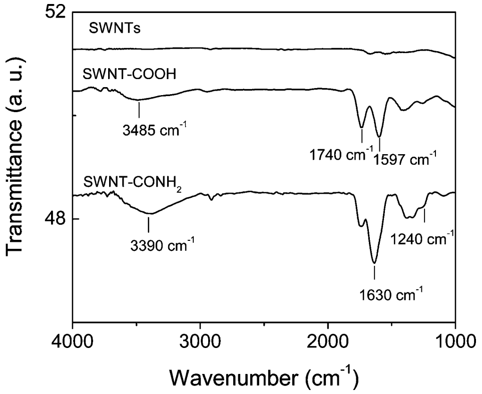

Figure 1. Mid-IR spectra of nonfunctionalized SWNTs, SWNT-COOH (P3-SWNT), and SWNT-CONH$_2$.

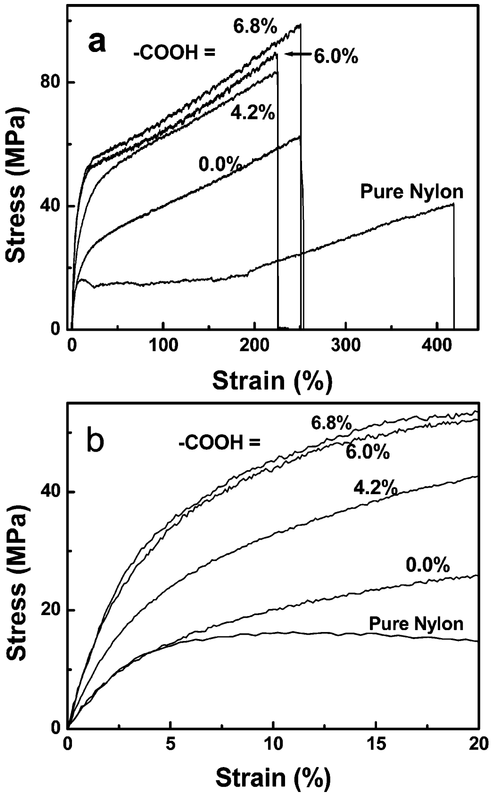

Figure 2. Stress–strain curves of composite fibers prepared using SWNTs bearing 0.0%, 4.2%, 6.0%, and 6.8% carboxylic acid groups at 0.5 wt % SWNT loading: (a) to strain failure point; (b) at low strain, showing the difference in Young's modulus.

The bands at 1240 and 3390 cm^{-1} are assigned to C–N and N–H bond stretching vibrations,[34] respectively. In the spectrum of SWNT-COOH, the broad peak at 1597 cm^{-1} is assigned to the C=C double bonds located near the functionalization sites[35] and the peak at 1740 cm^{-1} corresponds to the C=O stretch of the carboxylic acid groups.[31]

Results and Discussion

Nylon–SWNT Fibers Fabricated Using SWNTs of Different Carboxylic Acid Group Concentrations. The mechanical properties of the composite fibers fabricated using SWNTs with 0.0%, 4.2%, 6.0%, and 6.8% carboxylic acid groups at the same SWNT loading (0.5 wt %) were evaluated using an Instron 5543 instrument, in which a 3 cm length of fiber was stretched at a rate of 2 mm/min. Three tests were conducted for each type of fiber, and the deviation in the mechanical characteristics given in Table 1 was ~5%. The stress–strain curves in Figure 2a show that the tensile strength of the composite fibers increases with the concentration of carboxylic acid functional groups in the starting SWNTs. Composite fibers prepared using SWNTs with 0.0%, 4.2%, 6.0%, and 6.8% carboxylic acid groups show tensile strengths of 69.1, 83.4, 88.6, and 98.5 MPa, respectively (Table 1). All of the SWNT composite fibers are stronger than pure nylon fiber, which has a tensile strength of 40.9 MPa. Figure 2b indicates that the Young's modulus of the composite fiber also increases with the concentration of carboxylic acid groups on the SWNTs.

The composite fiber synthesized using 6.8% carboxylic acid groups shows a Young's modulus of 1500 MPa, an increase of about 3.4 times in comparison to that the nylon fiber. By comparison, the composite fiber from nonfunctionalized SWNTs shows a Young's modulus (575 MPa) similar to that of pure nylon fiber (440 MPa). It is evident that the utilization of SWNTs with a high density of carboxylic acid functional groups can significantly improve the Young's modulus of the composite fiber.

The degree of SWNT dispersion within the composite fiber was examined with SEM. Cross sections of the composites were prepared by cutting the fibers in liquid nitrogen to give an intact surface fracture, and the resulting SEM images are shown in Figure 3.

The bright regions in these images are attributed to the SWNTs as a result of their high conductivity. It is apparent from Figure 3b–d that the SWNTs are homogeneously distributed in the nylon 6 matrix without aggregation for all the composites prepared using functionalized SWNTs. However, the morphology is quite different: in the composite prepared using SWNTs without functionality (0% –COOH group), micro-cracks are clearly observable in the fiber cross section (Figure 3a), indicating a limited reinforcement. The composite reinforced by SWNTs with 4.2% –COOH groups (Figure 3b) shows a very compact surface morphology without any micro-cracks. As the –COOH group density increases to 6.8%, the cross section of the composite fiber becomes noticeably rougher (Figure 3c), which may result from the stronger SWNT–polymer interaction.

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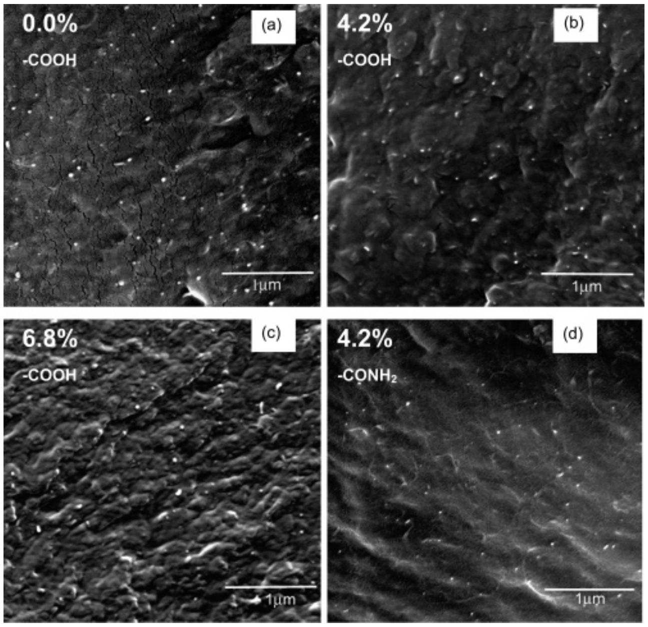
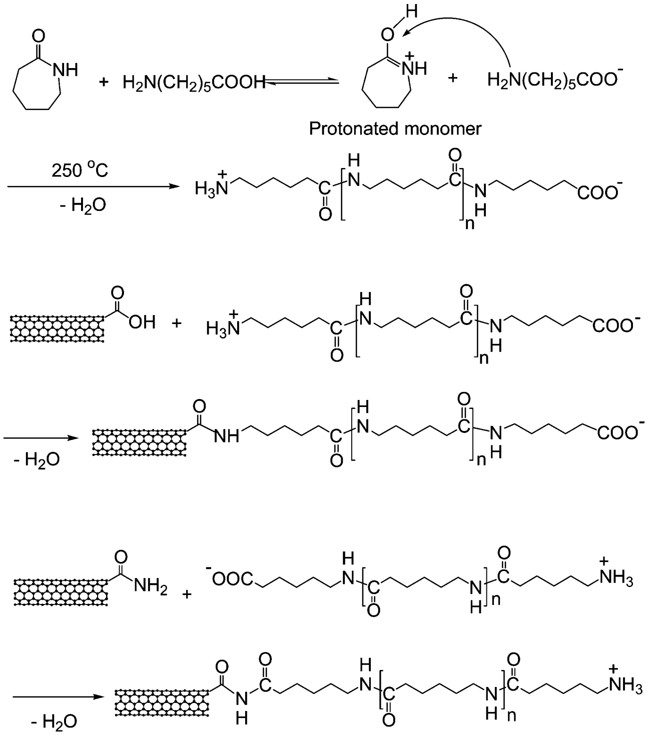


Figure 3. SEM images of cross-sectional structure of composite fibers fabricated with 0.5 wt % SWNT containing the following functionalities: (a) 0.0% −COOH, (b) 4.2% −COOH, (c) 6.8% −COOH, and (d) 4.2% $-CONH_2$.

Given the facts that the concentration of carboxylic acid groups in the SWNTs does not significantly affect their dispersion in the composite, and that all the composites were synthesized at the same SWNT loading, we speculate that the mechanical performance differences are induced by the variations in the strength of interfacial interaction between the SWNTs and the nylon matrix. As reported in our previous study,[26] the condensation reaction between the carboxylic groups on the SWNTs and the amine-terminal groups of PA6 leads to a grafting copolymerization between the SWNTs and PA6 (Scheme 2). In this study, we have used SWNTs with a range of carboxylic acid group concentrations to refine our understanding of the effect of covalent bond formation on the interfacial interaction between the SWNTs and the nylon 6 matrix, with the expectation that the grafting yield of the copolymer will be higher in the presence of increased COOH group functionality in the SWNT starting material.

The effect of the concentration of COOH in the SWNTs on the grafting yields of PA6 was investigated using SWNTs bearing 0.0%, 4.2%, 6.0%, and 6.8% carboxylic acid functional groups. To facilitate the separation of PA6-grafted SWNTs from physically absorbed PA6 chains, we applied a very small amount of 6-aminocaproic acid (0.4 wt %) as an initiator, while 10 wt % initiator was applied in the composite synthesis. To remove the caprolactam and nongrafted nylon after completion of the grafting reaction, the product was first washed with copious amounts of methanol to remove the caprolactam and subsequently with formic acid to remove the physically absorbed PA6 chains from the SWNTs. PA6-grafted SWNTs synthesized using SWNT-COOH are soluble in formic acid (Supporting Information, Figure S2), a good solvent for nylon 6, and this allowed the separation of the PA6-grafted SWNTs from unreacted SWNTs.

Scheme 2. Synthesis of SWNT−Nylon Composite Using SWNT-COOH and $SWNT-CONH_2$



The TGA measurements show that the fraction of components which decompose below 400 °C (primarily nylon 6) increases with the concentration of carboxylic acid groups on the SWNTs (Supporting Information, Figure S3). This is presumably due to the fact that, at higher concentrations of carboxylic acid groups, there is an increased probability for condensation reactions between SWNT-COOH and the amine-terminal groups on the PA6 chain. The grafting reaction of the PA6 chains leads to the formation of chemical bonds between the SWNTs and the nylon matrix, and in the process the SWNTs begin to acquire the characteristics of nylon 6, which increases the absorption of PA6 chains on the SWNT surface and enhances the SWNT−nylon physical contact.

Nylon−SWNT Composite Fiber Fabricated Using $SWNT-CONH_2$. We utilized amide-functionalized SWNTs ($SWNT-CONH_2$) to prepare a SWNT−nylon composite, and the mechanical properties of the composite fibers reinforced with 0.5 wt % $SWNT-CONH_2$ and SWNT-COOH are compared in Figure 4. It may be seen that the composite fiber prepared using $SWNT-CONH_2$ has higher tensile strength and break strain while exhibiting a lower Young's modulus compared with the fiber synthesized using SWNT-COOH (Table 1). This implies that the composite fiber reinforced by $SWNT-CONH_2$ is tougher, while the fiber from SWNT-COOH is stronger.

Graft polymerization of the SWNT-COOH and $SWNT-CONH_2$ materials was carried out in order to examine the mechanistic effects on the morphology of the composite fibers. TGA studies (Figure 5) show that the grafting yield of PA6 on the SWNTs follows the order $SWNT-CONH_2 > SWNT-COOH$.

As we reported in our previous paper,[26] once the amine-terminal groups of PA6 condense with the carboxylic acid groups of SWNT-COOH, the grafted PA6 chain will only be able to propagate via the COOH terminal groups. This will result in the early termination of PA6 chain propagation because the

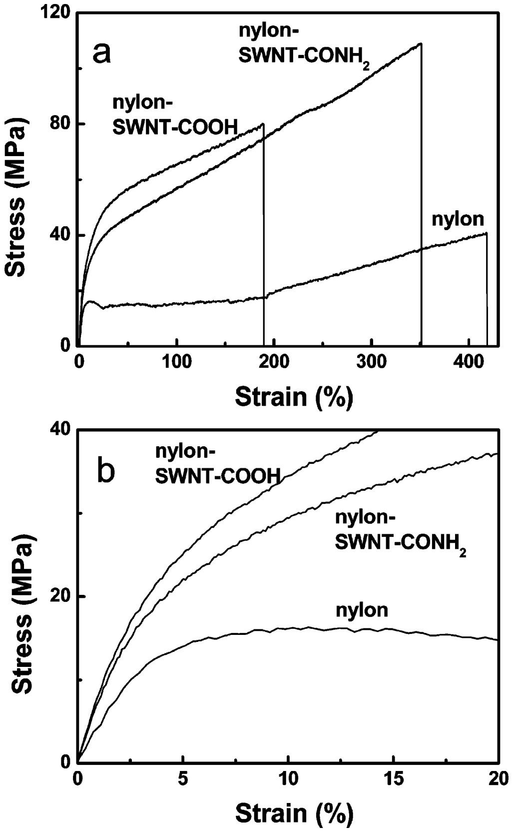


Figure 4. Stress−strain profile of composite fibers prepared using SWNT-COOH and SWNT-CONH$_2$ at a nanotube loading of 0.5 wt %: (a) to strain failure point; (b) at low strain, showing the difference in Young's modulus.

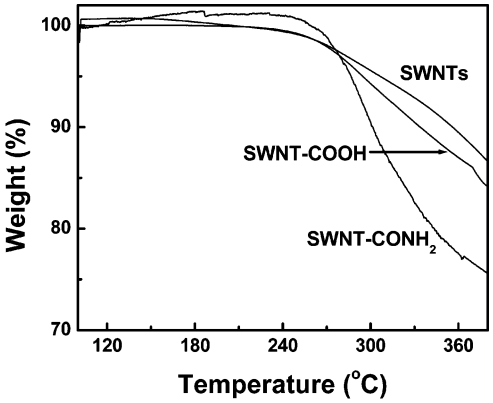


Figure 5. TGA profiles of nylon-grafted SWNTs synthesized using SWNT-COOH, SWNT-CONH$_2$, and nonfunctionalized SWNTs.

ring-opening polymerization of caprolactam can only propagate through the amine-terminal group of PA6.[36−42]

For SWNT-CONH$_2$, the PA6 chain will be grafted onto SWNTs by the reaction between the carboxylic acid groups of PA6 and the amide group of SWNT-CONH$_2$; the grafted PA6 chains will therefore have amine-terminal groups through which the grafted PA6 chains can continue to propagate (Scheme 1). Hence, the grafted PA6 chain on SWNT-CONH$_2$ is expected to be of higher molecular weight than the polymer chain on SWNT-COOH, because both SWNT-COOH and SWNT-CONH$_2$ contain the same functional group concentration (4.2%). We therefore conclude that the number of grafted polymer chain will be about the same, but the longer chain length of grafted PA6 explains the higher grafting yield for SWNT-CONH$_2$. The long chemically bonded PA6 chains on SWNT-CONH$_2$ are expected to increase the plasticity of the composite and is probably responsible for the higher break strain and toughness of the composite.

Conclusions

We have synthesized SWNT−nylon composites using SWNTs bearing a range of functionalities from precursors allowing the fabrication of continuous fibers from these composites. Mechanical performance evaluations show that SWNTs with a higher concentration of carboxylic acid groups can form a stronger SWNT−nylon interfacial interaction, which consequently improves the mechanical properties. Comparison of the composites prepared using SWNT-COOH and SWNT-CONH$_2$ indicates that the nature of the functional groups affects the grafting chemistry of the SWNTs and thereby the SWNT−nylon interfacial interaction, composite morphology, and mechanical properties. This paper demonstrates a process to engineer the SWNT−polymer interface by using SWNT chemistry.

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Supporting Information Available: SEM images of the cross-sectional structure of SWNT−nylon 6 composite fibers, optical micrographs of dispersions of carbon nanotube materials in formic acid, and TGA measurements of nylon graft copolymer fibers. This material is available free of charge via the Internet at http://pubs.acs.org.

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