A Simple Modification Method of Multiwalled Carbon Nanotube with Polyhydroxyamide

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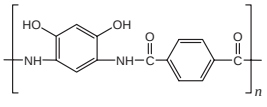
A simple coprecipitation method has been performed to achieve a noncovalent modification of multiwalled carbon nanotubes (MWNTs) with polyhydroxyamide (PHA). The PHA-wrapped MWNTs (PHA-MWNT) prepared was verified by FT-IR and SEM. The weight content of nanotubes in PHA-MWNT is determined and analyzed by TGA. There are the strong interaction between PHA and MWNTs including hydrogen bonds besides π–π stacking and van der Waals interactions. Moreover, PHA-MWNT has a remarkable solubility in polar solvents and a good thermal stability.

Carbon nanotubes (CNTs) have attracted tremendous attention because of their excellent electronic and superior mechanical properties. However, owing to their rigidity and chemical inertness, CNTs are difficult to dissolve or disperse in common organic solvents and polymeric matrixes and to process into useful articles, limiting their applications. Great efforts have been focused on this aspect. The noncovalent attachment is one main approach for the surface modification of CNTs to render them more dispersible in solution and to improve the interaction of nanotubes with polymer matrixes.[1] During the past decades, great researchs have been made on CNT/polymer composites[2] and there are indeed a few studies concerning CNT/poly(*p*-phenylene benzobisoxazole) (PBO) composites with a hope of attaining the tensile strength and modulus values of CNT/PBO fiber approaching and ultimately exceeding 10 and 400 GPa, respectively.[3,4] Recently, it has been found in our laboratory that a good interfacial compatibility between CNTs and polymer matrix is greatly important factor to realize the goal.[5] Polyhydroxyamide (PHA) (Scheme 1), one precursor of PBO, possesses not only better solubility than PBO but also can form PBO through further ring closure in condensation at an elevated temperature.

The covalent modification of multiwalled carbon nanotubes (MWNTs) with PHA in our earlier report is complex.[5b] In this paper, a simple noncovalent method was employed to achieve the PHA-wrapped MWNT (PHA-MWNT). MWNTs were first carboxylated to prepare carboxylic MWNTs (MWNT-COOH). Then MWNT-COOH was added to PHA/*N*-methyl-2-pyrrolidone (NMP) solution and the solution was slowly poured into water to result in PHA-MWNT, which was charactered by Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and thermal gravimetric analysis (TGA). Due to hydroxy and acylamide groups in PHA molecular chain, PHA was easy to form hydrogen bonds with MWNT-COOH, which can improve interfacial adhesion and maximize the load transfer between nanotubes and polymer matrix.



Scheme 1. Chemical structure of PHA.

NMP and *N*,*N*-dimethylacetamide (DMAc) were purchased from Shanghai Reagents Co. Methanesulfonic acid (MSA) was purchased from Sigma-Aldrich Chemical Co. MWNTs (ca. 30 nm in the width) was provided from Tsinghua-Nafine Nano-Power Commercialization Engineering Center in Beijing. A typical procedure of fabricating MWNT-COOH is described in our earlier research.[5] FTIR spectra was obtained on a Nicolet FTIR analyzer (Magna-IR550) with a KBr disc. MWNT-COOH and PHA-MWNT were examined with a JEOL JSM-6360LV SEM. TGA was carried out on a DuPont 1090B thermalgravimetric analyzer with a heating rate of 10 °C/min in a nitrogen flow.

PHA is synthesized according to previous report.[6] The intrinsic viscosity of prepared PHA was 0.8 dL/g measured in NMP at a concentration of 0.5 g/dL at 30 °C.

A typical procedure fabricating PHA-MWNT (Figure 1) was described as follows. To a 100-mL one-neck round-bottom flask equipped with a mechanical stirrer, 0.3 g of PHA and 20 mL of anhydrous NMP were added. The solution was stirred until it became homogeneous. A 10-mL portion of MWNT-COOH/NMP (0.01 g/mL), dispersed with ultrasonic bath (40 kHz) for 30 min, was injected dropwise into the flask using a syringe. Then, the solution was stirred at room temperature for 6 h. The PHA-MWNT product was precipitated by slowly pouring the reaction mixture into water, and the solid was collected by filtration onto a 0.45-μm PTFE filter. Then, the filter cake was washed with water and acetone and then dried under vacuum at 100 °C.

Figure 2 shows the ATR-IR spectra of MWNT-COOH, PHA, and PHA-MWNT. The C=O and –OH stretching modes of the carboxylic acid at 1712 cm^{-1} and ca. 3443 cm^{-1} in MWNT-COOH can be observed in Figure 2a. PHA exhibited –OH absorption at 3099 cm^{-1} and N–H group absorption at ca. 3406 cm^{-1} in Figure 2b. The strong peak at 1636 cm^{-1} in Figure 2b can be assigned to hydrogen-bonded carbonyl group formed with –OH or –NH.[7] In Figure 2c, it can be clearly seen

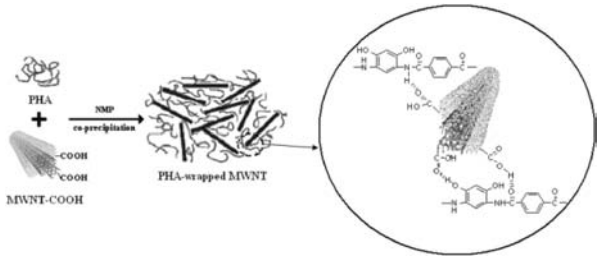


Figure 1. Synthesis of PHA-MWNT, and hydrogen bonds between MWNTs and PHA in PHA-MWNT.

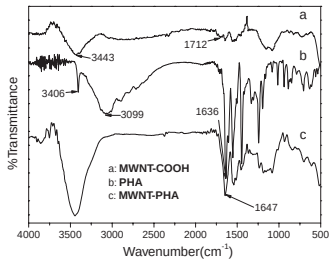


Figure 2. ATR-IR of MWNT-COOH (a), PHA (b), and PHA-MWNT (c).

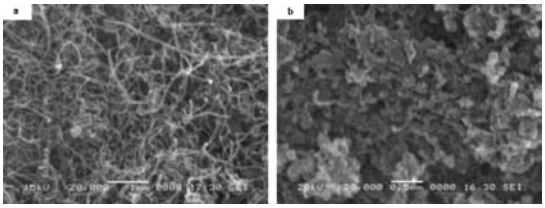


Figure 3. SEM images of MWNT-COOH (a) and PHA-MWNT (b).

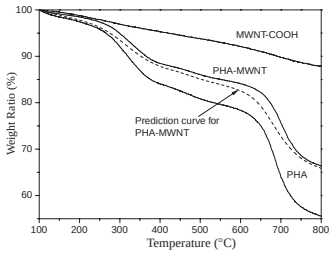


Figure 4. TGA thermograms of MWNT-COOH, PHA, and PHA-MWNT.

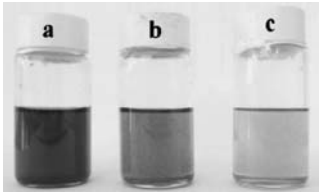


Figure 5. Photo of PHA-MWNT(1.25 mg/mL) placed in solvents after one week (a: MSA, b: NMP, c: DMAc).

that the peaks for C=O group was shifted from 1636 cm^{-1} in pure PHA to 1647 cm^{-1}, suggesting that PHA-MWNT is not simple noncovalent aggregate (π–π stacking and van der Waals interactions) but that it is under a strong interaction between PHA and MWNTs. Owing to the presence of –COOH on MWNTs surface, O–H, N–H, and C=O groups of PHA can form the hydrogen bonds with –COOH of MWNTs, as shown in Figure 1.

The structure of PHA-MWNT was studied by SEM and the micrographs are shown in Figure 3. Figure 3a shows the image of a part of MWNT-COOH entangled together with a diameter of ca. 30 nm. Figure 3b displays the images of modified MWNT with PHA layers, whose thickness is in the range of 20–30 nm. These observations indicate that PHA has thickly wrapped MWNT. Evidently, PHA wrapping can make MWNT more dispersible in solution and improve the interaction of nanotubes with polymer matrices.

Figure 4 shows the TGA curve of MWNT-COOH, PHA, and PHA-MWNT. MWNT-COOH decomposes slowly with increasing temperature by of losing carboxyl groups on the surface of MWNTs below 800 °C.[8] PHA showed two thermal degradation steps. The first degradation step occurs in the temperature range of 200–400 °C owing to the heterocyclization of PHA, forming PBO. The weight drop in this step is ca. 13.3 wt %. The second degradation step for PHA at ca. 600 °C can be attributed to the decomposition of formed PBO. In the TGA curve of PHA-MWNT, there also are two inflections similar to that of PHA. However, because of less acylamide group, the weight drop in the first degradation step for MWNT-PHA is ca. 9.0 wt %, lower than that for PHA. From the weight drop, the weight content of PHA and nanotubes in PHA-MWNT can be estimated to be ca. 68% and ca. 32%. Based on the compositions and also the weight drops for both components at different temperatures, a predicted curve shown as the dotted curve in Figure 4 can be made for PHA-MWNT, which is consistent with the experimental curve.

PHA-MWNT shows a different behavior in organic solvents. Figure 5 shows the dispersion of PHA-MWNT samples placed in various solvents for one week. PHA-MWNT demonstrates some extent of solubility in polar solvents such as DMAc and NMP, which is also a supportive evidence of strong interaction between PHA and the nanotubes. Furthermore, the solubility of PHA-MWNT in MSA is much better than that of MWNT-COOH,[5a] which indicated that PHA layer can enhance the solubility of MWNT.

In conclusion, noncovalent aggregation of carboxylic MWNTs with PHA has been achieved by a simple coprecipitation method based on π–π stacking, van der Waals interactions, and hydrogen bonds. PHA-modified MWNTs prepared in this work contain ca. 32 wt % of MWNTs. Moreover, the functionalized MWNTs could have a remarkable solubility in polar solvents and a unique thermally degradation characteristic. PHA-wrapped MWNT can become to a desirable filler to reinforce polymer matrix such as poly(*p*-phenylene benzobisoxazole) (PBO) fiber.

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