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In situ preparation and continuous fiber spinning of poly(*p*-phenylene benzobisoxazole) composites with oligo-hydroxyamide-functionalized multi-walled carbon nanotubes

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ABSTRACT

A graft-from approach has been performed to achieve covalent functionalization of multi-walled carbon nanotubes (MWNTs) with oligo-hydroxyamide (oHA). Pristine MWNT was first oxidized to MWNT-COOH and then functionalized to MWNT-COCl by acyl chloride. MWNT-COCl was copolymerized with oHA to produce oHA-grafted MWNTs (MWNT-oHA). The thickness of the oHA shell in MWNT-oHA is about 7.5 nm. MWNT-oHA has a remarkable solubility in polar solvents and a good thermal stability because characteristic dehydrative ring closure occurs upon heating and forms a thermally more stable benzoxazole component. MWNT-oHA has been further covalently incorporated with a rigid-rod polymer matrix, poly(*p*-phenylene benzobisoxazole) (PBO), through in situ polymerization. Continuous PBO–MWNT composite fibers with different MWNT compositions have been fabricated using dry-jet wet-spinning technique. The structure and morphology of PBO–MWNT composite fibers have been characterized and their mechanical, thermal, conducting properties have been investigated. The tensile modulus, tensile strength, and thermal stability of PBO–MWNT composite fibers have been improved because of a good dispersion and high alignment of MWNTs in PBO as well as enhanced interfacial interaction between these two components. Furthermore, increased conductivity has been discovered in the PBO–MWNT composite films and the inner core of the composite fibers; however, not on the outer surface. The phenomena can be interpreted using percolation model together with the heterogeneous fiber morphology and nanotube distribution over the cross-section of the fiber.

1. Introduction

Since carbon nanotubes (CNTs) were first reported by Iijima in 1991 [1], they have attracted tremendous attention because of their excellent electrical and superior mechanical properties [2,3]. Diverse applications based on this unique material have been proposed. Particularly, polymer–CNT composites have been pursued with the hope of delivering CNTs' properties to a processable and synergistic host material. To date, a variety of polymers have been used to prepare polymer–CNT composites for different targeting applications [4–22].

However, owing to their rigidity and chemical inertness, CNTs are difficult to dissolve or disperse in common organic solvents or polymeric matrices for making useful articles. Great efforts have been focused on applying the methods of covalent or non-covalent functionalization to improve the solubilization of CNTs [7–22]. Covalent functionalization also provides a means for engineering the CNT–polymer interface to achieve optimal composite properties [10–22]. With respect to mechanical properties, enhanced interfacial adhesion and maximized load transfer could be accomplished through covalent or non-covalent interactions between the functional groups on the nanotubes and polymer matrix [9].

In the present study, we report a covalent modification of multi-walled carbon nanotubes (MWNTs) using a low-molecular-weight polyhydroxyamide (PHA) or oligo-hydroxyamide (oHA) to improve the solubility, dispersivity, and interfacial adhesion of MWNTs in polymer matrix. More importantly, this method can be used to explore the potentials of MWNTs in fabricating macroscopic functional articles such as high-performance fibers or films. PHA can form a thermally more stable polymer, poly(*p*-phenylene benzobisoxazole) (PBO), through further ring closure in polycondensation at elevated temperature [23–29]. Although many polymer–CNT

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composites including a few PBO–CNT composites have been reported [30–34], the improvement in electrical conductivity has not yet been achieved. The earlier reported PBO–CNT composites were prepared using in situ polymerization of PBO with pristine CNTs or carboxylated CNTs [30–32,34], or solution blending of PBO and MWNTs [33].

Our approach in this report is to prepare a series of PBO–MWNT composites at different compositions of MWNT (ϕ_{MWNT}) using in situ polymerization of PBO in the presence of this novel oHA-functionalized MWNT (MWNT-oHA). Moreover, long, continuous composite fibers have been fabricated using dry-jet wet-spinning technique. The dispersion, orientation, and interfacial adhesion of CNTs in the PBO–MWNT composite fibers have been characterized for understanding the effects of oHA-grafted MWNTs on the morphological, thermal, mechanical, and electrical properties of PBO–MWNT composites.

2. Experimental

2.1. Materials

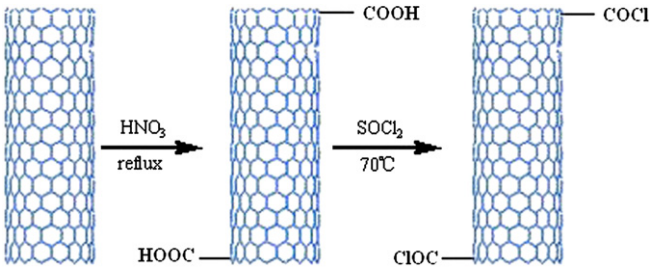
One monomer for polymerizing PBO, 4,6-diaminoresorcinol dihydrochloride (DAR·2HCl), was synthesized in our laboratory according to the previous reports [35–41]. Another monomer terephthalic acid (TPA) was purchased from Shanghai Reagents Co. and ground to powder in a glove box prior to use. Methanesulfonic acid (MSA) was purchased from Sigma–Aldrich Chemical Co. Terephthalic chloride (TPC), polyphosphoric acid (PPA), dimethyl acetamide (DMAc), *N*-methyl-2-pyrrolidone (NMP), thionyl chloride ($SOCl_2$), pyridine, acetone, tetrahydrofuran (THF), and other chemicals were also purchased from Shanghai Reagents Co. The low-boiling-point organic solvents were distilled and kept in the presence of 4 Å molecular sieves to eliminate water. MWNT was provided from Tsinghua-Nafine Nano-Powder commercialization engineering center in Beijing, China.

2.2. Preparation of acyl chloride MWNT (MWNT-COCl)

A typical procedure (Scheme 1) of preparing MWNT-COCl is described as follows. The first step was to attach carboxyl groups onto the surface of nanotubes. In this carboxylation procedure, 1.5 g of pristine MWNT was added to 30.0 mL of 65% HNO_3 aqueous solution. The mixture was treated with ultrasonic bath (40 kHz) for 30 min, and then stirred for 20 h in reflux at 90 °C. After that, the mixture was filtered through a 0.2 μm millipore polycarbonate membrane, and washed with excess distilled water until no residual acid was present. The filtered solid was dried under vacuum for 12 h at 60 °C. Three hundred milligrams of the obtained MWNT-COOH was suspended in 20 mL of $SOCl_2$. The suspension was stirred at 70 °C for 24 h to convert the surface-bound carboxyl groups into acyl chloride groups. The solid was then filtered and washed with anhydrous THF. Subsequently it was dried under vacuum at room temperature for 2 h.

2.3. Synthesis of oligo-hydroxyamide (oHA)

A typical procedure for synthesizing oHA is illustrated in Scheme 2 and it proceeded as follows [23–27]. To a 100 mL three-neck round-bottom flask equipped with a nitrogen inlet, a mechanical stirrer and a condenser, 0.36 g (1.7 mmol) of DAR·2HCl, 0.54 g (6.8 mmol) of pyridine and 20 g of anhydrous NMP were added. The solution was stirred until it became homogeneous and then cooled to 5 °C in ice water. Then 0.34 g (1.68 mmol) of TPC was added dropwise to the solution and reacted at room temperature for 16 h. The resulted viscous solution was precipitated in 300 mL of deionized water. Precipitated oHA was collected by filtration and washed with methanol before it was dried under vacuum at 60 °C for 24 h. The intrinsic viscosity of oHA was 0.2 dL g^{-1} measured in NMP at a concentration of 0.5 g dL^{-1} at 30 °C. Anal. Calcd for oHA $(C_{14}O_4H_{10}N_2)_n$: C, 62.22; H, 3.70; N, 10.37. Found: C, 61.23; H, 3.86; N, 10.98.



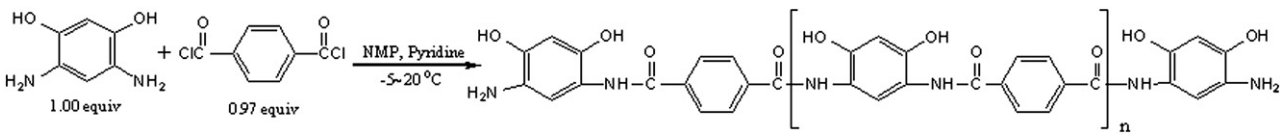
Scheme 1. Synthesis of MWNT-COCl.

2.4. Synthesis of oligo-HA-grafted MWNT (MWNT-oHA)

A typical procedure for synthesizing MWNT-oHA from MWNT-COCl and oHA is depicted in Scheme 3. Similar to the synthesis of oHA, 0.3 g of newly prepared oHA, 0.2 g of pyridine and 20 g of anhydrous NMP were added to a 100 mL three-neck round-bottom flask equipped with a nitrogen inlet, a mechanical stirrer, and a condenser. The solution was stirred until it became homogeneous and then cooled to 5 °C in ice water. Ten milliliters of MWNT-COCl/NMP solution with a concentration of 0.01 g/ml, dispersed with ultrasonic bath (40 kHz) for 30 min, was injected using a syringe dropwise into the flask. Then the reacting solution was stirred at room temperature for 16 h. MWNT-oHA was precipitated in water and filtered using a 0.45 μm PTFE filter. After being washed with excess water and acetone, MWNT-oHA was dried under vacuum at 100 °C.

2.5. In situ polymerization of PBO–MWNT composites

Viscous solutions of PBO or its composites with MWNT in PPA were prepared using the polycondensation [28,35–41] of DAR·2HCl and TPA without or with MWNTs-oHA. A typical procedure for preparing PBO–MWNT composite shown in Scheme 4, is as follows: 10 g of DAR·2HCl, 7.797 g of TPA, and 40.3 g of PPA were loaded into a 250 mL glass vessel equipped with a mechanical stirrer and nitrogen inlet/outlet. The mixture was stirred at 90 °C under a nitrogen atmosphere until complete removal of hydrochloride. Another 29.9 g of P_2O_5 and MWNT-oHA were then added to the mixture to bring the P_2O_5 concentration up to 85 wt% and result in a final polymer concentration of 14 wt%. The polymerizing mixture was first stirred under vacuum at 120 °C for 8 h. It was then heated to 180 °C stepwise at 5–10 °C h^{-1}, and kept at this temperature for



Scheme 2. Synthesis of oHA.