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Material Properties

Lipophilic carbon nanotubes and their phase-separation in SBS

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Highly lipophilic multi-walled carbon nanotubes (MWNTs) were successfully prepared by grafting PAA onto the surface of MWNT, followed by replacing carboxyl groups of PAA with octadecylamine through amidation. The improved dispersion of functionalized MWNTs and enhanced mechanical properties of nanotube/SBS composites were observed. The composite thin films with different MWNT loading prepared via spin-coating were investigated by means of atomic force microscopy (AFM) in order to study the dispersion of MWNTs in the polymer matrix. The evolution of MWNT/SBS composite thin film surface morphology with the variation of MWNT concentration is presented. When the MWNT concentration is lower than 1 wt%, the composite thin film is homogeneous. With increase of MWNT concentration, phase separation can be clearly observed. It is found that the state of aggregation of MWNTs in the polymer matrix determine the mechanical properties of the composites.

1. Introduction

The unique mechanical, electrical, and thermal properties of carbon nanotubes [1,2] have greatly accelerated their applications in the development of high-strength composites [3–8], electrical materials [9,10] and optical limiting materials [11–13]. However, the expected enhancement in properties of the composites has not been fully achieved, which partly results from their insolubility in common solvents and poor dispersion in polymer matrices. Therefore, the properties of the nanotube-based composite are dominated by the collective behavior of the nanotube bundles rather than by the individual tubes. Improving the lipophilicity of CNTs provides an effective way to make homogeneous dispersion of CNTs in the polymer matrix and increase interfacial interaction. Since Haddon [14] first synthesized soluble CNTs by amidation reaction of an alkyl amine with nanotube-bound carboxylic acid groups, many approaches for synthesizing soluble CNTs have been developed [15–19]. However, most of these approaches are not powerful enough to exfoliate the agglomerates into individual nanotubes and, therefore, cannot completely meet the need of practical applications, for example, in preparing CNT/polymer composites.

Herein, we report the synthesis of lipophilic MWNTs with multiplex pendant octadecylamine groups (MWNT-ODA) and their reinforcement of SBS materials. The lipophilic MWNTs synthesis involves two steps. Water-soluble MWNTs with abundant carboxylic acid groups were first synthesized by grafting polyacrylic acid (PAA) onto the surface of MWNTs, and then the carboxylic groups on PAA moiety were used to react with octadecylamine (ODA) through amidation, resulting in the generation of multiplex pendant octadecylamine groups in the side chains of PAA at the surface of the MWNTs. With this synthesis route, the number of octadecylamine (ODA) groups at the MWNT surface should be more than without PAA. The high solubility and long alkyl chains which could form entanglement with the polymer chains provide interfacial interaction between CNTs and SBS, and good mechanical properties of the composites. We further investigated the dispersion and

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phase separation of such lipophilic MWNTs in SBS with different loading through MWNT/SBS blend thin film by atomic force microscopy (AFM). It was found that the composite thin films exhibited different evolution of surface morphology during the spin-coating process with variation of the MWNT concentration, and the mechanical properties of the composites is well correlated with the aggregation state of MWNTs in the polymer matrix.

2. Experimental

2.1. Materials

Multi-walled carbon nanotubes (MWNTs) were purchased from Shenzhen Nanotech port Co., Ltd (China). 1-Ethyl-3-(3-dimethyllaminopropyl) carbodiimide hydrochloride (EDC) was obtained from Shanghai Medep Co., Ltd (China). *N*-Hydroxysuccinimide(NHS)and 2,2′-(Ethylenedioxy)-diethylamine were obtained from Sigma–Aldrich Co., Ltd. Octadecylamine (ODA) and thionyl chloride ($SOCl_2$) were purchased from Sinopham Chemical Reagent Co., Ltd (China). Tetrahydrofuran was obtained from Nanjing Chemical Reagent Co; Ltd (China). The solvent was distilled and kept in the presence of 4 Ǻ molecular sieve to eliminate any traces of water before use. Poly(acrylic acid) (PAA, M_W: 2000) was purchased from Acros CO., Ltd. Liner SBS was obtained from China Petroleum & Chemical Corporation, with a molecular weight $M_W = 90$ kDa, and a polystyrene fraction of 0.4 (wt%).

2.2. Oxidation of MWNTs (MWNT-COOH)

A 250 mL flask containing 2 g of pristine MWNTs and 100 mL mixture of concentrated sulfuric/nitric acid (3/1, v/v) was sonicated in a water bath for 35 h at room temperature. After that, the mixture was diluted with 5 times volume of deionized water. The black solid was recovered by vacuum filtration through a 0.45 μm polycarbonate membrane, and thoroughly washed with deionzed water until the pH value was 5–6. The acid-treated MWNTs (denoted as MWNT-COOH) were obtained as a black solid after being dried at 50 °C in a vacuum oven overnight.

2.3. Amination of MWNTs (MWNT-NH$_2$)

1 g of dried MWNT-COOH was suspended in 40 mL of $SOCl_2$ and stirred at 65 °C for 24 h to convert the surface-bound carboxylic acid groups into acyl chloride groups. After centrifugation, the remaining solid was washed with anhydrous tetrahydrofuran (THF). Subsequently, it was dried under vacuum at room temperature for 2 h. Thereafter, the resulting solid were added to the mixture of 400 uL of 2, 2′-(ethylenedioxy)-diethylamine and 40 mL anhydrous tetrahydrofuran. After few minutes of ultrasonication, the suspension was stirred under N_2 atmosphere at 80 °C for 72 h. Subsequently, the resulting mixture was vacuum-filtered through a 0.22 μm polycarbonate membrane, and washed with methanol to remove excess diamine compound. The black solid was dried at 40 °C in a vacuum oven for 12 h, to obtain MWNT-NH$_2$.

2.4. Attachment of poly(acrylic acid) (PAA) molecules to MWNTs (MWNT-PAA)

0.40 g of PAA, 0.448 g of EDC, 0.28 g of NHS and 200 μL of triethylamine (Et_3N) were added to a suspension of 0.8 g MWNT-NH$_2$ in 50 mL of deionized water. After being sonicated for 30 min, the mixture was stirred at room temperature for 72 h. The resultant suspension was then dialyzed against deionized water for 72 h using a dialysis bag (MWCO, 12000) to remove excessive PAA and small molecules. After removal of the water by a rotary evaporator and drying under vacuum at 50 °C overnight, the PAA functionalized MWNTs (MWNT-PAA) were obtained as a black solid.

2.5. Synthesis of lipophilic MWNTs with multiplex pendant octadecylamine groups (MWNT-ODA)

To make the MWNT-ODA, 0.5 g MWNT-PAA was stirred in 20 mL $SOCl_2$ at 65 °C for 24 h. After the reaction, the excess $SOCl_2$ was removed by distillation under reduced pressure, the resulting solid and 20 g octadecylamine (ODA) were evacuated and blown with N_2, and then stirred at 80 °C for 72 h. After cooling to room temperature, the resulting solid mixture was placed in a porous paper thimble of a Soxhlet extractor. A 300 mL portion of ethanol was used as extraction solvent to eliminate the excess amine. After 24 h, the ethanol solution was replaced by 300 mL of chloroform to obtain the soluble MWNTs. After another 24 h, a black chloroform solution with soluble MWNTs was obtained. The solvent was removed by rotary evaporator, the residual black solid (denoted as MWNT-ODA) was dried at room temperature under vacuum.

2.6. Preparation of MWNT-ODA/SBS composite

MWNT-ODA was dispersed in 5 mL of chloroform by ultrasonication for 10 min. Afterwards, a predetermined amount SBS was added. The solution was sonicated for 10 min and then the resultant mixture was poured into a Teflon pan and placed in an oven at room temperature to remove the solvent. The obtained composite were subsequently processed into test specimens for mechanical characterization. The proportion of MWNT-ODA in SBS covered 0.25 wt %, 0.5 wt %, 0.75 wt %, 1 wt %, 3 wt %, 5 wt %, 7 wt% and 10 wt %.

2.7. Preparation of MWNT-ODA/SBS composite thin film

Prior to spin-coating, the silicon substrates were cleaned and hydroxylated by immersing in a solution of sulfuric acid (98%) and hydrogen peroxide (30%) (7:3 v/v) at 90 °C for 2 h, and then the silicon substrates were rinsed in deionized water, and dried with compressed N_2. 70 mg of SBS was dispersed in 700 μL chloroform. Afterwards, a predetermined amount of MWNT-ODA was added. After sonication for 10 min the solution was spin-coated (1000 rpm for 60 s) on top of treated silicon substrates surfaces to prepare the composite thin films. The samples were placed at room temperature to eliminate the residual