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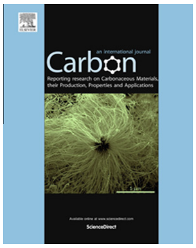

Noncovalent functionalization of multi-walled carbon nanotubes with pyrene-linked nylon66 for high performance nylon66/multi-walled carbon nanotube composites

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ABSTRACT

A new interfacial agent, 1-pyrenebutyric chloride (PBC), was synthesized for use in nylon 66 (PA66)/multi-walled carbon nanotube (MWCNT) composites. It has been shown that the pyrene units in PBC adsorb onto the MWCNT surface by physisorption, and the acyl chloride units in PBC react with amine end groups in PA66 during melt extrusion. As a result, PBC that was covalently bonded with PA66 formed at the interface between the MWCNT and PA66 matrix. The PA66/MWCNT composite containing PBC exhibited the best interfacial adhesion between MWCNT and PA66 and the highest level of MWCNT dispersion in the PA66 matrix among the composites examined. It was also found that the PA66/MWCNT composite with the higher interfacial adhesion energy between PA66 and MWCNT exhibited a higher level of reinforcement.

1. Introduction

Carbon nanotubes (CNTs), which have an ultrahigh length to diameter ratio in addition to excellent mechanical, electrical and thermal properties, have been regarded as the ultimate reinforcement materials [1–7]. CNT-filled composites are expected to make an enormous technological and commercial impact in applications where electrical conductivity, superior heat conduction and mechanical robustness are desired [7–20]. For many years, researchers have attempted to introduce CNTs into polymer composites, but most fell short of the desired results [6–9]. Several reasons could account for this dissatisfaction. CNTs are difficult to disperse in polymer matrixes, are an inherently inert material, and easily agglomerate and entangle due to their high aspect ratio and strong inter-tube van der Waals interactions. The weak interfacial adhesion between CNTs and polymers also restricts the application of CNTs as a reinforcement.

A homogeneous dispersion and good interfacial adhesion between CNTs and a polymer matrix must be achieved for CNTs to be effective nanofillers in polymer composites. Surface modifications of CNTs by acid treatment and covalent functionalization were developed to improve the dispersion and interfacial adhesion [10–20]. However, these modifications usually require sophisticated control of the reaction conditions and negatively impact many of the desirable properties of the CNTs due to the reduction of the aspect ratio and damage to the molecular structure of the CNTs. The techniques that best maintain the CNT structure and electric properties have been implemented with pyrene derivatives

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[21–25]. Pyrene derivatives attach to the CNT surface by physisorption, which is the result of π–π stacking interactions between the pyrene moiety and the CNT sidewall. The use of pyrene derivatives to introduce a variety of functional groups or polymers onto CNTs by π–π stacking has been investigated. Pyrene derivatives such as pyrene carboxylic acid and trimethyl-(2-oxo-2pyren-1-yl-ethyl) ammonium bromide; polymers containing pendent pyrene groups such as pyrene end-capped polystyrene, block copolymers of polymethylmethacrylate and 4-pyrene-1-yl-methyl methacrylamide (PMMA-b-pyrene); and random copolymers of PMMA and (1-pyrene)methyl-2-methyl-2-propenoate have been investigated [21–24]. The surface modification of CNTs by pyrene derivatives or pyrene-containing polymers is an efficient method for CNT dispersion in a variety of organic solvents and polymers.

Nylon 66 (PA66) is an important thermoplastic material with outstanding properties including high tensile strength, abrasion resistance and a low frictional coefficient and has widely been used for tire cords, ropes and airbags [26–28]. This wide range of applications of PA66 can be further extended by enhancing the stiffness and strength of PA66 with CNT reinforcement. The covalent introduction of functional groups on the CNT surface has been commonly used to enhance interfacial adhesion between CNTs and nylon matrices [15–17,20]. Noncovalent functionalization of CNT with naphthalene-containing copolymer was also examined to enhance the dispersion of CNT in PA66 matrix [28]. Nylon composites with functionalized CNTs exhibited better mechanical strength than those with pristine CNTs. Fabrication of PA66 composites containing CNT noncovalently functionalized with pyrene derivatives has not been published to date.

In this study, a new pyrene derivative, 1-pyrenebutyric chloride (PBC), was synthesized, and then attached to the surface of multi-walled carbon nanotubes (MWCNTs) by physisorption. The resulting MWCNTs were melt-mixed with commercially available PA66 using a twin extruder with the expectation of a condensation reaction between the amine end groups of PA66 and acyl chloride groups in PBC during melt extrusion. The formation of PA66 covalently bonded with PBC (PBC-PA66) by a condensation reaction during melt extrusion and its existence at the interface between the MWCNT and PA66 matrix were explored. The effectiveness of MWCNT treatment with PBC for PA66/MWCNT composites was examined in terms of the interfacial adhesion energy between PA66 and MWNCT, the dispersion of MWCNTs in PA66 matrix and the mechanical properties of PA66/MWCNT composites.

2. Materials and procedure

2.1. Materials

Commercially available PA66 was supplied by LG Chemicals (Seoul, Korea). According to the supplier, the molecular weight, as determined by gel permeation chromatography using polystyrene standards, was $\overline{M}_w = 43,000$ and $\overline{M}_n = 22,000$ g/mol. MWCNTs (grade: CM250) grown by chemical vapor deposition process were purchased from Hanwha Nanotech Co. (Seoul, Korea). The diameter of the MWCNTs was 10–15 nm, and the average length was 100 μm. Pyrene and 1-pyrenebutyric acid (PBA) used for noncovalent functionalization on MWCNTs were purchased from Aldrich Chemicals (Milwaukee, WI, USA). Methanol, N,N-dimethylformamide (DMF) and formic acid were used as solvents, and thionyl chloride ($SOCl_2$) was used as a reactant to replace the carboxylic acid group in PBA with an acyl chloride group; these were also purchased from Aldrich Chemicals. PA66 was dehydrated under vacuum at 100 °C for 24 h before use.

2.2. Preparation of 1-pyrenebutyric chloride

PBC was prepared by reacting PBA with thionyl chloride at 70 °C for 24 h as shown in Fig. 1a. PBA (1 g) was dissolved in DMF (10 ml) and mixed with thionyl chloride (50 ml) at 30 °C under nitrogen ambient conditions. After reacting at 70 °C for 24 h, deionized water (1000 ml) was added to the resulting solution in order to extract the PBC. The collected PBC was washed with deionized water (3 × 500 ml) and dried at 70 °C for 24 h in a vacuum oven to remove the remaining water.

2.3. Preparation of noncovalently functionalized MWCNT with pyrene derivatives

MWCNTs noncovalently functionalized with pyrene derivatives were prepared for this work. As shown in Fig. 1b, pristine MWCNTs (1.0 g) were dispersed in a methanol (1000 ml) solution containing PBC (0.5 g) in a sonicator for 2 h and then stirred for 3 h at 50 °C. Next, the suspension was vacuum-filtered through a 450-nm nylon membrane. The resulting MWCNTs were dried at 100 °C to remove residual solvent (hereafter referred to as "MWCNT-PBC"). The MWCNTs noncovalently functionalized with pyrene (hereafter referred to as "MWCNT-pyrene") and PBA (hereafter referred to as "MWCNT-PBA") were prepared using the same procedure as for the MWCNT-PBC preparation. The formation of MWCNTs noncovalently functionalized with pyrene derivatives was confirmed by X-ray photoelectron spectroscopy (XPS, ESCA2000, VG Microtech, UK) using a spectrometer with an Mg Kα X-ray source (1253.6 eV) and a hemispherical analyzer.

To compare the effects of noncovalently functionalization with those of covalently functionalization on the structure of MWCNTs and the mechanical properties of the composite, carboxylic-acid-terminated MWCNTs were also prepared. The pristine MWCNTs (1.0 g) were functionalized by heating (60 °C) in a mixture of concentrated H_2SO_4 (concentration: 98 vol.%) and HNO_3 (concentration: 70 vol.%) (2000 ml, mixing ratio of $H_2SO_4/HNO_3 = 3/2$ by vol) at reflux. After stirring at 60 °C for 24 h, the resulting mixture was diluted with deionized water (1000 ml) and then filtered through a 450 nm nylon membrane (hereafter referred to as "MWCNT–COOH"). Raman spectroscopy (LabRAM HR800, Horiba Ltd., Japan) with a He—Ne laser (633 nm) was employed to study changes in the structures of the MWCNTs.

2.4. Preparation and characterization of composites

PA66 composites containing noncovalently functionalized MWCNTs with pyrene derivatives were prepared by melt mixing in a twin extruder (BA-11, L/D ratio = 40, Bau Technology,