



In situ grafting of polybutylene terephthalate onto multi-walled carbon nanotubes by melt extrusion, and characteristics of their composites with polybutylene terephthalate



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ABSTRACT

Multi-walled carbon nanotubes (MWCNTs) functionalized with hydroxyl groups were explored as effective fillers for polybutylene terephthalate (PBT) composites with expected in situ transesterification between hydroxyl groups in MWCNTs and ester groups in the PBT during melt extrusion. The interfacial adhesion energy between PBT and PBT-grafted MWCNTs (PBT-g-MWCNTs) calculated by using drop-on-fiber method was higher than that between PBT and pristine MWCNTs. As a result of higher interfacial adhesion energy, the dispersion of MWCNTs in the PBT matrix and interfacial adhesion between the MWCNTs and PBT matrix were better in the case of the PBT/PBT-g-MWCNT composite than in the case of the PBT composite with pristine MWCNTs. The former also exhibited better mechanical properties and electrical conductivity than the latter at the same MWCNT content.

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1. Introduction

Carbon nanotubes (CNT) have attracted considerable attention in the research and industrial fields due to the extraordinary mechanical, electrical, and thermal properties of individual tubes [1–4]. The excellent properties of CNTs make them promising candidates for use as reinforcing fillers in polymer composites. However, fabrication of composite having desired properties often limited owing to the inherent inert properties of CNTs. CNTs easily agglomerate and entangle due to their high aspect ratio and strong inter-tube van der Waals interactions [4–11]. Therefore, the major challenge in the fabrication of composite is how to achieve homogeneous dispersion of CNTs in the polymer matrix and good interfacial adhesion between the CNTs and polymer matrix.

Many techniques including solution casting and melt compounding have been developed to fabricate polymer/CNT composites [5–15]. Melt processing is the preferred method for the commercial fabrication of composites. Solution processing is not suitable for the large-scale production due to the post treatment of the solvent. To use CNTs as effective nanofillers for producing polymer composites, homogeneous dispersion of CNTs and strong

interfacial adhesion between the CNTs and polymer matrix must be achieved by melt processing. Simple routes to commercially produce polymer/CNT composites having excellent CNT dispersion and interfacial adhesion were recently reported [10,11]. Epoxy composites with liquid-like amine functionalized MWCNTs and nylon 6,6 composites with the acyl chloride functionalized MWCNTs produced by melt compounding were examined. These composites exhibited improved MWCNT dispersion, better interfacial adhesion and mechanical properties than the composites with pristine MWCNTs.

Polybutylene terephthalate (PBT) has attracted interest in many industrial fields because of its excellent solvent resistance and mechanical strength [16]. The range of applications of PBT further broadens with CNT-reinforcement-induced improvements in mechanical strength, thermal resistance, and electrical conductivity. PBT composites with CNTs have been investigated in previous studies [7–9,12,13]. The introduction of functional groups onto the CNT surface was commonly used to improve CNT dispersion and interfacial adhesion between CNTs and the polymer matrix. The MWCNTs functionalized with dibutyl tin(IV) oxide and those functionalized with carboxylic acid were examined as nanofillers for PBT composites [13,14]. These composites exhibited improved MWCNT dispersion and better thermal and mechanical properties than PBT composites with pristine MWCNTs.

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In this study, we developed a practical route to produce PBT composites with PBT-g-MWCNTs from PBT and MWCNTs functionalized with hydroxyl groups. The PBT-g-MWCNTs were formed when the reaction between the hydroxyl groups on MWCNTs and the ester groups in the PBT possibly occurred during melt extrusion. This was analyzed via various spectroscopic techniques. The interfacial adhesion energies between PBT and pristine MWCNTs or PBT-g-MWCNTs were quantified by using the drop-on-fiber method [17], and the mechanical and electrical properties of the composites were investigated.

2. Materials and procedure

2.1. Materials

Commercially available PBT (grade: GP-1000S, $\bar{M}_w = 39000$ g/mol and $\bar{M}_n = 14500$ g/mol) was supplied by LG Chemicals (Seoul, Korea). Pristine MWCNTs (grade: CM250) produced by chemical vapor deposition with diameter and the average length of 10–15 nm and 1.6 μm , respectively, were purchased from Hanwha Nanotech Co. (Seoul, Korea). Hydrogen peroxide (H_2O_2) and hexafluoro isopropanol (HFIP) used respectively as a reactant to form hydroxyl groups on pristine MWCNTs and as a PBT solvent were purchased from Aldrich Chemicals (Milwaukee, WI, USA).

2.2. Preparation of MWCNTs functionalized with hydroxyl groups

MWCNTs functionalized with hydroxyl groups were prepared via a previously reported method [14,15]: First, pristine MWCNTs (0.5 g) were dispersed in an aqueous solution of H_2O_2 (concentration: 30 vol%, 500 ml) under sonication at 30 °C for 1 h, and then reacted at 60 °C for 24 h. The resulting mixture was diluted with deionized water (1000 ml) and then filtered through a nylon membrane (pore size: 450 nm). The resulting MWCNTs were washed with deionized water (5×200 ml) and dried for 24 h in a vacuum oven at 100 °C (hereafter referred to as “MWCNT-OH”).

2.3. Preparation of PBT composites with MWCNTs

The PBT composites with MWCNT-OH and that with pristine MWCNTs were prepared by melt extrusion with a twin extruder (BA-11, L/D ratio = 40, Bau, Seoul, Korea). The temperatures of the feeding zone, melting zone, mixing zone, and exit die of the twin extruder were 240, 260, 270, and 280 °C, respectively. The resulting melt-mixed composites were immediately quenched in a water bath and then chipped with a pelletizer. Composite films were also prepared by solvent casting from HFIP. PBT (2 g) was dissolved in HFIP (50 ml), and MWCNTs were dispersed in the PBT solution under sonication at 30 °C for 1 h. The resulting solutions were cast onto a glass plate and dried in an oven at 30 °C for 6 h until most of the solvent evaporated. The resulting films were then dried in a vacuum oven at 80 °C for 24 h.

2.4. Characterization of PBT-grafted MWCNTs

PBT and MWCNT-OH were melt extruded with the expectation that PBT-g-MWCNTs might be formed by the in situ transesterification between hydroxyl groups in MWCNTs and ester groups in the PBT (Scheme 1). Then, the PBT/PBT-g-MWCNT composite (2 g) was dissolved in HFIP (100 ml) at 30 °C for 24 h, and then, PBT-g-MWCNTs were collected using a centrifuge. The collected PBT-g-MWCNTs were again dissolved in HFIP (100 ml), and PBT-g-MWCNTs were again collected via centrifugation. This procedure was repeated five times to remove unreacted PBT completely. The resulting product was finally dried in a vacuum

oven at 100 °C for 12 h.

The formation of PBT-g-MWCNTs was confirmed by Fourier transform infrared spectroscopy (FT-IR, Magna 750, Nicolet, WI, USA), X-ray photoelectron spectroscopy (XPS, VG Microtech, ESCA2000, UK), field-emission scanning electron microscopy (FE-SEM, model: Sigma, Carl Zeiss, Germany), and high-resolution transmission electron microscopy (HR-TEM, model: JEM 2000EXII, JEOL, Japan). IR spectra were collected in the 4000–500 cm^{-1} region using the attenuated total reflection (ATR) mode. All binding energies in the XPS spectra were calibrated to carbon (C1s) at 284.5 eV and the widths of the Gaussian peaks were kept constant in each spectrum for curve fitting. The morphologies of the pristine MWCNTs, MWCNT-OH, and PBT-g-MWCNTs were investigated with FE-SEM and HR-TEM. Thermogravimetric analysis (TGA, model: TGA-2050, TA Instruments, USA) was carried out to determine the amount of PBT grafted on the MWCNTs. TGA analyses were performed under nitrogen at a heating rate of 20 °C/min.

2.5. Characterization of composites

Specimens for tensile testing were prepared in accordance with American Standards Testing Method (ASTM) specification D 638 by using a compression molding machine (model 25-12; Carver, Inc. USA). The PBT/MWCNT composites were dried in an air-circulating oven at 100 °C for 24 h before use. The mixture placed in the machine was compressed at a plate temperature of 270 °C and a holding pressure of 12 MPa. Then, the mixture was kept at 270 °C for 5 min before being cooled to room temperature by natural convection in 2 h. Next, the prepared specimens were placed in a vacuum oven at 30 °C before mechanical testing. Tensile tests were performed using a universal testing machine (UTM, UTM-301, R&B Corp, Daejeon, Korea) at a cross-head speed of 5 mm/min. The reported tensile property values represent the averages of five specimens. The electric conductivities of the composites were measured using an AC impedance analyzer (model: 1260A, Solartron, UK). A four-point probe method was employed to measure the electric conductivities of the composites using a cell (Kistech, Seoul, Korea) consisting of two platinum plates and two platinum wires.

The interfacial adhesion energy between the MWCNTs and PBT was characterized by analyzing symmetric barrel-type PBT droplets formed on the MWCNT. To form these PBT droplets, a dilute PBT (20 mg) solution containing MWCNTs (20 mg) and HFIP (50 ml) was prepared. PBT agglomerates were precipitated onto the MWCNTs from the PBT solution by using hexane as the nonsolvent. The resulting MWCNTs were annealed at 270 °C for 1 h to produce equilibrium droplets on MWCNTs and then quenched to 30 °C. The morphologies of the formed droplets were observed using FE-SEM. The contact angle between PBT and MWCNTs was estimated from the droplet geometry by using the generalized drop shape analysis method [17–21].

3. Results and discussion

3.1. Characterization of MWCNT-OH and PBT-g-MWCNTs

The molecular structures of pristine MWCNTs and functionalized MWCNTs were analyzed with FT-IR and XPS. As shown in Fig. 1, the FT-IR spectrum of MWCNT-OH is similar to that of pristine MWCNT, but a strong absorption peak appears at 1100 cm^{-1} due to hydroxyl groups covalently bonded with carbon, which does not appear clearly in the FT-IR spectrum for pristine MWCNTs [22]. The absorption peaks in the range of 2850–3000 cm^{-1} originating from butylene groups and the peak at 1710 cm^{-1} due to the ester groups in the PBT are observed in the FT-IR spectrum of PBT-g-MWCNT.

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