



Improvement of the mechanical and electrical properties of polyamide 6 nanocomposites by non-covalent functionalization of multi-walled carbon nanotubes



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ARTICLE INFO

Article history:

Received 7 March 2014

Received in revised form 23 June 2014

Accepted 17 July 2014

Available online 29 July 2014

Keywords:

A. Carbon nanotubes

A. Nano composites

B. Electrical properties

B. Mechanical properties

A. Polymer–matrix composites (PMCs)

ABSTRACT

Pyrene moieties containing amide functional groups with various alkyl chain lengths (butyl, octyl, and dodecyl) were synthesized and utilized in non-covalent functionalization of the surface of multi-walled carbon nanotubes (MWNTs). The *D/G* ratio of the MWNTs (derived from the Raman spectra) remained unchanged upon non-covalent functionalization of the surface of MWNTs, indicating that there were no increases in the number of defect sites on the surface of the MWNTs. PA 6 (polyamide 6)/MWNT nanocomposites were prepared by the melt-compounding method for evaluation of the mechanical and electrical properties. Flexural testing confirmed the much higher flexural modulus of the PA 6/non-covalently functionalized MWNTs relative to the PA 6/pristine MWNT nanocomposites. Furthermore, the PA 6/non-covalently functionalized MWNT nanocomposites exhibited better electrical properties due to preservation of the intrinsic structure of the MWNTs as well as the uniform dispersion of the MWNTs in the PA 6 matrix, which also played a role in the enhanced mechanical properties. It could be observed that the longer alkyl chain length of the pyrene moieties led to further improvement of the sheet resistance and mechanical properties, which is attributed to the enhanced compatibility with PA 6 derived from functionalization.

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1. Introduction

Numerous studies regarding carbon nanotubes (CNTs) have been conducted since their discovery, due to their attractive properties such as high aspect ratio, low density, and excellent mechanical, thermal, and electrical properties, which may be exploited in various applications [1–3]. In recent years, CNTs have been most widely utilized in polymeric nanocomposites [4,5]. The combination of polymers and CNTs can be expected to lead to enhanced mechanical strength and modulus as well as electrical properties. Such desirable properties have led to the recognition of CNTs as an ideal potential candidate for the reinforcement of polymeric materials. However, the strong self-interaction of CNTs due to van der Waals forces and the weak interfacial adhesions with the polymer matrix induce aggregation with consequently poor dispersion in the matrix [6–9]. A number of techniques have been developed in order to resolve these issues and obtain uniform or desired dispersion in the polymeric matrix. One of the most recognized approaches is covalent functionalization by introducing

functional groups on the surface of the CNTs. Although this method allows for strong interaction of the CNTs with the matrix [10–13], it simultaneously causes loss of the unique mechanical and electrical properties of the CNTs by disrupting the long-range π – π conjugation of the CNTs, and introducing defects into the structure of the CNTs, resulting in inferior mechanical and electrical properties [14,15]. In recent decades, non-covalent functionalization methods utilizing π – π interactions between the surface of the CNTs and organic compounds have been attempted [16–20]. Aromatic group-containing moieties [21] and polymeric surface modifiers [22] have been used to functionalize the surface of CNTs in anticipation of π – π interactions, as mentioned above, in order to maintain the intrinsic structure of the CNTs. These non-covalent interactions can effectively solubilize the CNTs in certain solvents and prevent their aggregation into bundles and ropes. Moreover, fewer defect sites such as pentagon–heptagon pairs called Stone–Wales, sp^3 -hybridized defects, and vacancies in the nanotube lattice may occur with this method than with covalent functionalization. The enhancement of the mechanical and electrical properties of polymer/CNT nanocomposites has been extensively studied. In preparing non-covalently functionalized CNTs, pyrene moieties have been representatively used to modify the CNTs *via* π – π

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interaction [23,24]. Organic molecules and polymers containing pyrene have been successfully used to incorporate pyrene moieties onto the surface of CNTs, and have been used in the preparation of polymeric nanocomposites, thereby conferring enhanced mechanical and electrical properties to the polymers. Polypropylene [25], polyethylene [26], and PA [27,28] have been evaluated as matrix materials with the expectation that the combination of the semi-crystalline material and CNTs should promote the formation of crystalline domains, thereby resulting in a higher electrical percolation threshold. Among the evaluated polymers, PA 6 has been frequently incorporated into nanocomposites with CNTs to achieve high performance such as good mechanical properties, and thermal and abrasion resistance with low density [29,30].

In the present study, the effects of non-covalent functionalization of MWNTs on the mechanical, electrical, and morphological properties of PA 6/MWNT nanocomposites are investigated to evaluate the surface-functionalization of MWNTs with pyrene-containing amide functional groups of various alkyl chain lengths (butyl, octyl, and dodecyl). The specimens for the measurements of mechanical and electrical properties of the PA 6/MWNT nanocomposites were prepared by melt-compounding.

2. Experimental

2.1. Materials

MWNT powder (S.A. NC 7000, purity 90%) was purchased from Nanocyl Co., Belgium. PA 6; Cheil Industries Inc., Korea was selected as a matrix. 1-Pyrenebutyric acid, oxalyl chloride, triethylamine (TEA), tetrahydrofuran (THF), and dichloromethane were purchased from Sigma-Aldrich and used as received. *n*-Butylamine, *n*-octylamine, and *n*-dodecylamine were obtained from Samchun Chemical Co., Ltd., Korea, and used without further purification.

2.2. Syntheses of organic modifiers

2.2.1. Synthesis of amide like-1, 2, and 3

1-Pyrenebutyric acid (1 g, 3.4 mmol) was dissolved in dichloromethane (150 ml), and oxalyl chloride (0.66 g, 5.2 mmol) was added to the solution at 0 °C. The reaction mixture was stirred at room temperature (r.t.) for 3 h. After completion of the reaction, the solvent was evaporated and the product was dried under vacuum for 12 h to give 1-pyrenebutyric acid chloride (yield: 95%). To independent solution of 1-pyrenebutyric acid chloride (1 g, 3.2 mmol) in dichloromethane (200 ml) were added triethylamine (1.32 g, 13 mmol), followed by the addition of each 2 eq of the *n*-alkylamine (alkyl = butyl, octyl, and dodecyl) at 0 °C under nitrogen. The temperature was increased to r.t. and stirring was continued for 4 h. The crude product was extracted with dichloromethane and brine and subsequently purified by column chromatography (silica gel, *n*-hexane:ethyl acetate = 1:1). The target products amide like-1 (alkyl=butyl), amide like-2 (alkyl = octyl), and amide like-3 (alkyl = dodecyl) each as a white solid in yields as below) were obtained by evaporating the solvent and drying under vacuum.

Amide like-1 (79%)

¹H NMR (CDCl₃): 0.89 (t, 3H), 1.29–1.43 (m, 4H), 2.17–2.27 (m, 4H), 3.22 (q, 2H), 3.38 (t, 2H), 5.34 (brd s, 1H), 7.84 (d, 1H, *J* = 7.8 Hz), 7.96–8.17 (m, 7H), 8.29 (d, 1H, *J* = 9.3 Hz).

¹³C NMR (CDCl₃): δ (13.75, 20.07, 27.47, 31.72, 32.75, 36.10, 39.25, 123.40, 124.76, 124.90, 124.96, 125.85, 125.06, 126.70, 127.37, 127.46, 128.77, 129.91, 130.88, 131.39, 135.88, 172.46.

HRMS: calculated 343.1936 C₂₄H₂₅NO, observed 343.1939 C₂₄H₂₅NO.

Amide like-2 (83%)

¹H NMR (CDCl₃): 0.89 (t, 3H), 1.29–1.52 (m, 8H), 2.22–2.31 (m, 4H), 3.25 (q, 2H), 3.42 (t, 2H), 5.35 (brd s, 1H), 7.88 (d, 1H, *J* = 7.8 Hz), 7.99–8.20 (m, 7H), 8.33 (d, 1H, *J* = 9.3 Hz).

¹³C NMR (CDCl₃): δ (14.08, 22.61, 26.90, 27.43, 29.18, 29.23, 29.62, 31.76, 32.71, 36.04, 39.53, 123.37, 124.73, 124.87, 124.92, 125.02, 125.82, 126.67, 127.32, 127.43, 128.73, 129.87, 130.85, 131.35, 135.86, 172.44.

HRMS: calculated 399.2562 C₂₈H₃₃NO, observed 399.2556 C₂₈H₃₃NO.

Amide like-3 (78%)

¹H NMR (CDCl₃): 0.89 (t, 3H), 1.25–1.49 (m, 20H), 2.21–2.28 (m, 4H), 3.25 (q, 2H), 3.41 (t, 2H), 5.37 (brd s, 1H), 7.88 (d, 1H, *J* = 7.8 Hz), 7.98–8.19 (m, 7H), 8.32 (d, 1H, *J* = 9.3 Hz).

¹³C NMR (CDCl₃): δ (22.68, 26.91, 27.43, 29.28, 29.34, 29.53, 29.58, 29.63, 30.30, 30.34, 31.90, 32.72, 36.04, 39.53, 123.37, 124.73, 124.87, 124.93, 125.03, 125.82, 126.67, 127.33, 127.43, 128.74, 129.87, 130.38, 131.36, 135.87, 172.43.

HRMS: calculated 455.3188 C₃₂H₄₁NO, observed 455.3182 C₃₂H₄₁NO.

2.2.2. Non-covalent functionalization of MWNTs with amide like-1, 2, and 3

Respective 1 g samples of amide like-1, 2, and 3 were dissolved in 300 ml of THF, and the MWNTs (1 g) were dispersed in each solution. Sonication was carried out for 30 min using a typical bath-type sonicator. The solution was then filtered and washed with sufficient amount of THF (3 L) and dried under vacuum for 12 h.

2.3. Preparation of PA 6/MWNT nanocomposites by melt-compounding

Samples of the PA 6/MWNT nanocomposites with various MWNT loadings (1, 2, 3, and 5 phr) were prepared via the melt-compounding method by using a DSM Xplore micro-compounder (twin-screw mixer, X-polo, Netherlands) operated at 250 °C for 10 min with a screw speed of 100 rpm. The blended mixtures were injected into a test-specimen mold for flexural testing according to ASTM D 760. The injection molding temperature and pressure were set to 260 °C and 15 bar.

2.4. Characterization

¹H NMR (nuclear magnetic resonance, Bruker ARX-300 spectrometer) was used to confirm the chemical structures of the synthesized pyrene moieties. UV-Vis absorption spectroscopy (UV-2550 spectrophotometer SHIMADZU) was used to identify the presence of pyrene moieties on the surface of MWNTs after washing the functionalized MWNTs with excess THF. To quantify the surface modifiers non-covalently bonded the MWNTs, thermogravimetric analysis (TGA) measurements were performed under nitrogen atmosphere, from r.t. to 800 °C, at a heating rate of 10 °C/min, using a model TA3100 Instrument. Raman spectra (HORIBA Jobin Yvon) were acquired to confirm the *D/G* ratio in order to identify the formation of defect sites on the MWNTs from functionalization of the surface of MWNTs. Dynamic mechanical analysis (DMA, DMA 2980 TA instrument) was performed on a sample (50 mm length × 12.7 mm width × 1.6 mm thickness) using a DMA multi-frequency dual cantilever. The tests were

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