



Triggering compatibility and dispersion by selective plasma functionalized carbon nanotubes to fabricate tough and enhanced Nylon 12 composites



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ABSTRACT

Here, we described a simple approach for the development of advanced composites based on Nylon 12 by selectively modified multiwalled carbon nanotubes (MWCNTs). Prior mixing, MWCNTs were modified by a new combination of plasma treatment i.e. oxygen + nitrogen (PL-MWCNTs) in order to improve its dispersion in the nylon matrix and enhance the interfacial adhesion by increasing the compatibility. With incorporation of only 1.2 wt % PL-MWCNTs, the tensile strength, Young's modulus, elongation at break and storage modulus of Nylon 12 were dramatically improved by ~66%, 64%, 69% and 39%, respectively. These results were found to be higher than individual plasma treated CNTs. Such large increments were due to the effects of excellent homogeneous dispersion of PL-MWCNTs in the Nylon matrix and strong interfacial adhesion within themselves, which is believed to be effects of both oxygenated and nitrogenated functional groups generated on the surface of CNTs during plasma treatment.

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1. Introduction

Over past two decades since first reported by Ijima in 1991 [1], carbon nanotubes (CNTs) have received immense attention due to their high aspect ratio, high mechanical strength, excellent thermal and electrical properties, nanosize in diameter, low density and flexibility. All these features lead CNTs to be one of the most attractive and potential reinforcing fillers for high performance polymer composites [2–4] as well as for other advanced nanomaterial applications [5–10]. However, the major stumbling blocks hindering in development of high-performance polymer/CNT composites are revealed as (i) non-homogeneous dispersion of CNTs in the polymeric matrix and (ii) weak interfacial interactions. This is due to their large surface energy (~ 45.3 mJ/m²) [11], high aspect ratio and strong van der Waal's forces. Thus, uniformly-dispersed CNTs with high bonding affinity with the polymer matrix have become a most challenging part in case of composites. Several

articles have shown that uniform dispersion and enhanced interaction between polymer matrix and CNT can be achieved by surface modification of CNT which can simultaneously participate in efficient load transfer from the polymer matrix to the CNTs and also eventually improve the strength of the composites. There are several approaches engaged in functionalization of CNT surfaces to enhance their dispersion and interactions with the polymer matrices. These include surface functionalizations by acid oxidation [12–14], chemical functionalization [15,16], ozone oxidation [17] plasma oxidation [18–20], and polymer wrapping [21–23]. However, surface functionalization by means of fast, non hazardous and low cost process is still on high demand as well as of great interest.

In recent years, multiwalled carbon nanotubes (MWCNTs) reinforced Nylon (polyamide) composites have been explored intensively for various high-performance applications. However, compared with other grades of Nylon such as Nylon6, Nylon 66 or Nylon 11, Nylon 12 has not been focused much yet. Nylon 12 (PA12), a semi-crystalline engineering thermoplastic polymer belongs to the polyamide family with longer aliphatic ($-\text{CH}_2$) chains and lower melting point than Nylon 6 (PA6) and Nylon 66 (PA66). Though Nylon 12 is more expensive than Nylon 6 and Nylon 66, but due to its many superior properties such as low moisture absorption, high

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pressure resistance, very high impact and notched impact strengths, high mechanical performance at extreme temperatures, exceptional resistance to abrasion and stress cracking, better chemical resistance, high UV resistance and high processability it is currently taken into consideration. Recently, Sahoo et al. [24] reported the effects of various functionalized MWCNTs on mechanical and thermal properties of Nylon 6 based composites prepared by both melt mixing, and extrusion process followed by injection molding. Despite of moderate increments in above properties (tensile strength increased ~126%; from 16 to 36.2 MPa and TGA increased 21 °C at 10% decomposition) the amount of MWCNTs used was considerably high (10 wt %). Logakis et al. [25] prepared Nylon 6/MWCNT composites by melt mixing method and studied the morphological, thermal and dynamic mechanical properties. From their study it was found that addition of such a large amount of MWCNTs i.e. 20 wt % had made it able to increase the storage modulus only by 33% as compared to the pure Nylon sample. Xu et al. [26] demonstrated the fabrication of Nylon 6/CNT composites by in-situ polymerization process. Prior to mixing, the CNTs were ball milled for 20 min and acid treated for 2 h in boiling concentrated nitric acid to modify the sidewalls. The tensile strength values showed significant improvement from 54.7 MPa for pure Nylon to 130 MPa for the 15 wt % Nylon6/CNT composites, while the toughness and elongation at break were decreased largely from 12.4 kJ/m² to 4.03 kJ/m² and 320 %–31 %, respectively. Liu et al. [27] described the preparation of Nylon 6/MWCNT composites with different MWCNT loadings by melt mixing process. Before compounding, the MWCNTs were oxidized in acids to generate more carboxylic and hydroxyl groups on their surfaces. The results indicated that comparing with neat Nylon 6, the elastic modulus and the yield strength of the composite are greatly improved by about 214% (from 396 to 1241.8 MPa) and 162% (18–47.2 MPa), respectively on addition of only 2 wt % MWCNTs. Very recently, Roh et al. [28] described the fabrication of Nylon 6,6 composites containing Nylon 6,6 grafted MWCNTs by reactive extrusion process. Despite of good grafting, the composites didn't show much improvement in mechanical properties as compared to the un-grafted MWCNT/Nylon 6,6 composites. On the basis of above literature survey, it is clear that much research work have been focused on Nylon 6 or Nylon 6,6 based CNT-composites, while composites based on Nylon 12 has not been explored such yet.

Therefore, in the present article, we have focused on the fabrication of advanced Nylon 12/MWCNT composites by a novel and facile surface modification of MWCNTs. The MWCNTs were modified by radiofrequency oxygen + nitrogen plasma treatment (PL-MWCNTs). The effects of oxidation on the structural integrity of MWCNTs were confirmed by X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy. The prepared Nylon 12/MWCNT composites were studied in terms of their mechanical, thermal, dynamic mechanical and morphological point of views. The composites were prepared by melt mixing process, as it is a simple, eco-friendly, industrially compatible process and readily produces high performance polymer composites in commercial scale at low cost.

2. Experimental section

2.1. Materials

The MWCNTs were bought from Cheap Tubes, USA. The outer diameter was <8 nm and length was in the range of 10–30 μm and purity is >95%. Nylon 12 pellets used in this study were purchased from Sigma Aldrich, Singapore. The pellet size was 5 mm and density was 1.01 g/mL at 25 °C. Prior to mixing, the Nylon pellets were dried in a vacuum oven for 8 h at 60 °C to remove residual

moisture. All solvents such as DMF, methanol and acetone were ACS grade and purchased from Sigma Aldrich, Singapore.

2.2. Plasma treatment and composite preparation

It is well known that the pristine or raw MWCNTs exist in form of big clumps where numerous nanotubes are aggregated with each other by strong van der Waals forces. Therefore, direct plasma treatment on pristine CNTs may not offer uniform oxidation throughout the CNT surfaces. As a result, while using them as fillers to fabricate polymer composites; not much change in the physical, thermal, mechanical and electrical properties were noticed. Hence, in this study, before conducting the plasma treatment, the raw MWCNTs were well dispersed in DMF solution and treated by a 20 kHz ultrasonic processor for 30 min (1 gm/200 ml in DMF) in order to make it free from agglomeration. The MWCNTs were immediately filtered and then vacuum dried for 24 h. After that, the CNTs were further separated by a mortar and pestle followed by strong mechanical shaking (using a vortex) and then subjected to further plasma treatment through the mixture of oxygen and nitrogen gases. These steps are useful in order to disentangle the nanotubes by destroying their inherent strong van der Waals forces, as a result facilitates greater numbers of CNTs to be functionalized in more uniform ways. The plasma treatment of MWCNTs was conducted using a radio frequency plasma machine (March PX500 series, USA) of 13.56 MHz. The plasma power and exposure time was set to 300 W and 6 min respectively, in order to ensure good treatment. The plasma chamber was attached with two mass flow controllers to control the flow of gases. The gas flow rate was set at 75 sccm (50 sccm O₂ + 25 sccm N₂) while the base pressure was 165 mTorr. Mixture of oxygen and nitrogen plasma was utilized for plasma oxidation as this was found to be the best in the surface oxidation of CNTs than that of individual oxygen or nitrogen plasma treatment [29]. Moreover, this oxidation process creates similar functional groups (amide) on the CNTs surfaces together with many others oxygenated and nitrogenated groups that could enhance better interaction during mixing with matrices having similar functional groups like Nylon. Finally, after the plasma treatment, the MWCNTs were exposed to air for ~30 min in order to stabilize the surface via peroxide and hydroperoxide groups formation [29].

Nylon 12 composites containing 0.4, 0.8 and 1.2 wt% of functionalized MWCNTs were fabricated by melt mixing using a micromixer (HAAKE MiniLab), equipped with two counter rotating screws at temperature of 183 °C with a screw speed of 70 rpm for 7 min under N₂ gas flow to avoid the degradation of Nylon. Film samples (~0.25 mm) were prepared by compression molding in a hot press at a temperature of 183 °C with a holding pressure of ~10 MPa. All samples were taken out at 35 °C by slowly cooling down the hot press at a cooling rate of 5 °C/min.

2.3. Characterizations

A Perkin–Elmer GX Fourier transform infrared spectroscope (FTIR) was used to identify the surface chemical compositions of the raw and plasma oxidized MWCNTs. KBr Pellets were prepared by mixing a small amount of MWCNTs with potassium Bromide (KBr) powders.

X-ray photoelectron spectroscopy (XPS) measurements were taken using Kratos Axis Ultra XPS spectrometer equipped with a monochromatic Al K α X-ray excitation source. The applied voltage was 15 kV and current was 10 mA. Detail of this test can be found from earlier publications [29].

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