Materials and Design 85 (2015) 76–81

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/jmad

Electrically conductive carbon nanotube/polypropylene nanocomposite with improved mechanical properties

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ARTICLE INFO

Article history:
Received 13 June 2015
Received in revised form 18 June 2015
Accepted 28 June 2015
Available online 4 July 2015

Keywords:
Carbon nanotube
Polypropylene
Melt mixing
Electrical properties
Mechanical properties
Microstructure

ABSTRACT

Conductive polymer nanocomposites based on carbon nanotubes (CNTs) have wide range of applications in the electronics and energy sectors. For many of these applications, such as the electromagnetic interference (EMI) shielding, high nanofiller loading is typically needed to achieve the desired properties. The high nanofiller concentration deteriorates the composite's tensile strength due to the increase in nanofiller aggregation. In this work, highly conductive CNT/polypropylene (PP) nanocomposite with improved tensile strength was prepared by melt mixing. The effects of CNT content on the processing behavior, microstructure, mechanical and electrical properties of the nanocomposite were investigated. Scanning electron microscopy was used to investigate the composite microstructure. Good level of CNT dispersion with remarkable adhesion at the CNT/PP interface was observed. Based on a theoretical model, the interfacial strength was estimated to be in the range of 36–58 MPa. As a result of this microstructure, significant enhancement in ultimate tensile strength was reported with the increase of CNT content. The tensile strength of the 20 wt.% CNT/PP nanocomposite was 80% higher than that of the unfilled PP. Moreover, and due to the good dispersion of CNT particles, an electrical percolation threshold concentration of 0.93 wt.% (0.5 vol.%) was obtained.

1. Introduction

Polymer nanocomposites based on carbon nanotubes (CNTs) have been one of the major research disciplines since the introduction of these amazing nanofillers in 1991. CNTs possess superlative mechanical, electrical and thermal characteristics owing to their unique structures [1,2]. These combined characteristics, in addition to the high aspect ratio and high surface area to volume ratio, are essential prerequisites to formulate polymer nanocomposites with multifunctional properties [3–5]. For example, the high aspect ratio and conductivity of CNTs have enabled the researchers to formulate conductive nanocomposites at extremely very low nanofiller content [6]. Electrical percolation threshold concentrations lower than 0.1 vol.% CNT have been reported by many research groups [7]. Conductive nanocomposites have wide range of applications including static charge dissipation, electromagnetic interference (EMI) and structure damage monitoring [8,9].

In the field of conductive nanocomposites, CNT loading should be kept at its lowest possible level to reduce the final product cost and to avoid the degradation in the nanocomposite mechanical properties due to the agglomeration of CNT particles at high CNT concentrations. Theoretically and experimentally it is possible to induce conductivity in polymer nanocomposites at CNT concentration levels that do not alter the valuable properties of some polymer such as ductility, toughness and tensile strength. However, for applications requiring high levels of electrical conductivity the use of moderate to high levels of nanofillers is not avoidable yet. For example, to achieve an EMI shielding effectiveness of 30 dB in the X-band frequency range a 1.0 mm plate made of nanocomposite with an electrical resistivity of ~1.0 Ω·cm is required [10]. This level of conductivity requires, based on the currently available types of CNT, a nanocomposite filled with at least 5 wt.% CNT [10]. Thus, it is necessary to formulate nanocomposites with high level of CNT concentration and enhanced mechanical properties.

Many researches have been devoted for the investigation of the mechanical properties of polymers reinforced with unmodified-CNT and functionalized-CNT [2,4,11]. Most of the studies, especially with the unmodified-CNT, ended up with different levels of enhancement in the Young's Modulus and degradation in the tensile strength. For CNT/polypropylene (PP) nanocomposite, which is the nanocomposite of interest in this study, Andrews et al. [12] reported that compared with the unfilled PP, a 12.5 vol.% CNT/PP nanocomposite has a 100% higher Young's modulus and 60% lower tensile strength. Liu and Gao [13] reported that a 3 wt.% CNT/PP nanocomposite has improved tensile strength, compact strength and Young's modulus compared to that of the unfilled PP. Dondero and Gorga [14] found that the profiles of tensile strength and tensile modulus of CNT/PP filled with up to 3 wt.% CNT exhibited maximum peak at 0.25 wt.%. Identical behavior was reported by Zhou et al. [15] with a tensile strength peak at 1.0 wt.% CNT. At the peak, the tensile strength was 16% higher than that of the unfilled polymer.

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http://dx.doi.org/10.1016/j.matdes.2015.06.162
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Micusik et al. [16] reported an increase in Young's modulus and independence of yield strength on CNT content for nanocomposites filled with up to 8% CNT. Similarly, an independence of tensile strength on the CNT content was also reported for PP filled with up to 12.5 wt.% CNT [17]. On the other hand, a significant improvement in tensile strength was reported by Zhou et al. [3] for CNT/PP nanocomposites filled with up to 5 wt.%.

It is widely accepted that poor interfacial adhesion and bad dispersion of the nanofiller are responsible for the degradation of composite materials' mechanical properties. Interfacial adhesion is responsible for load transfer, which can be accomplished by mechanical interlocking, chemical bonding and physical intermolecular forces [18]. While chemical modification of nanotubes is expected to enhance the dispersion and load transfer at the polymer–nanofiller interface [11,19], it is known to degrade the electrical properties of the nanotube by creating insulating layer at the surface of nanotube [20]. Thus, for nanocomposite with multifunctional characteristics, chemical modifications of nanofillers should be avoided. This means that proper dispersion and good adhesion between the polymer matrix and nanofiller should be achieved by physical means.

In this study, CNT/PP nanocomposites filled with up to 20 wt.% CNT were prepared by melt compounding followed by compression molding. PP is a high-volume commodity polymer that has a wide-range of applications [21]. PP has low density, good resistance for many solvents and can be easily processed by melt compounding machines [22]. This study investigates the influence of a wide-range of CNT concentration on the microstructure, electrical and mechanical properties of the nanocomposite.

2. Experimental details

2.1. Materials

The PP (PP 504P, Sabic, Saudi Arabia) has a density of 905 kg/m^3 and a melt flow index of 3.2 kg/10 min (measured at 230 °C under 2.16 kg load). The nanotubes were multi-walled CNT (NC7000, Nanocyl, Belgium) produced by catalytic chemical vapor deposition. According to the manufacturer, NC7000 nanotubes have an average diameter of 9.5 nm, length of 1.5 μm, surface area of 250–300 m^2/g and carbon purity of 90%.

2.2. Nanocomposite compounding

The CNT/PP nanocomposites were prepared by melt compounding in a batch mixer (Type W 50 EHT, Brabender, Germany) connected to torque rheometer (Plastograph EC, Brabender, Germany). Before mixing, the PP pellets and CNT powder were dried overnight in vacuum oven at 80 °C and 130 °C, respectively. In a typical experiment, 28.3 g of PP was fed into a preheated (to 180 °C) mixing chamber and mixed for 3.0 min to melt down the polymer. After that, a predetermined amount of CNT powder was fed to the mixing chamber and the whole mixture was compounded for 10 min at 100 rpm. At the end of the compounding process, the nanocomposite was collected from the mixing chamber and left to cool at room temperature. A compression molding machine (Carver Inc., Wabash-IN, USA) was used to prepare 1.0 mm thick plates. The compression molding was conducted at 200 °C for 10 min under 27.5 MPa pressure. For the electrical resistivity characterization, the molded plates were ($40 \times 20 \times 1$ mm^3) rectangles. For the tensile properties characterization, initially ($65 \times 65 \times 1$ mm^3) plates were produced; then an ASTM D628-5-IMP die was used to cut dog-bone-shaped specimens.

2.3. Characterization tools

The nanocomposite microstructure was characterized using Quanta 450 FEG Environmental Scanning Electron Microscope (ESEM). Prior to imaging the samples were fractured in liquid nitrogen and coated with a thin layer of gold using sputtering machine (Q150R ES, Quorum Technologies Ltd., UK). The electrical properties were characterized using two different setups depending on the nanocomposite resistivity. For samples with electrical resistivity greater than 10^6 $\Omega \cdot$cm, the characterization was conducted using Keithley 6517B electrometer (Keithley, Ohio, USA) connected to Keithley 8009 test fixture. For more conductive materials, a set-up consisting of Keithley 2010 digital multimeter (DMM) connected to a 4-wire probe test fixture was used. The reported results represent an average of at least six specimens. Tensile testing was conducted according to the ASTM standard D638-03 using a tensile testing machine (WDW-20, Jinan Testing Equipment IE Corporation, China). For each formulation, at least six dog-bone-shaped specimens (Type V ASTM D638-03) were tested at a crosshead speed of 1 mm/min.

3. Results and discussion

3.1. Microstructure

The properties of a nanocomposite depend on its microstructure. SEM analysis was conducted to investigate the CNT particles dispersion state and the adhesion between the CNT particles and PP matrix. Figs. 1 and 2 show, respectively, representative SEM micrographs for 1 wt.% CNT/PP and 20 wt.% CNT/PP nanocomposites. At low CNT content (Fig. 1), it is apparent that there is a good level of CNT dispersion; however perfect dispersion cannot be claimed since aggregates of few microns in size can be observed. At high CNT content (Fig. 2), almost no CNT-aggregates can be seen. This apparent enchantment in CNT dispersion can be ascribed to the increase in the shear stress with the increase of CNT content, as shown in Fig. 4. The shear stress applies hydrodynamic forces on the nanofiller and enhances its dispersion. In addition, it is also possible that at high CNT concentration, the well-dispersed nanotubes and CNT-aggregates are undistinguishable because they are close to each other.

Regarding the adhesion between CNT and PP, Fig. 3 depicts high magnification SEM micrograph for one micron CNT aggregate. The micrograph clearly shows that the nanotubes at the external surface of the aggregate have good level of adhesion with the PP matrix. The average diameter of nanotubes is much larger than the average diameter of the CNT particles before mixing, which is 9.5 nm. This means that there is good adhesion between the CNT and the PP and/or it means that the CNT particles have acted as a nucleation agent and this layer is

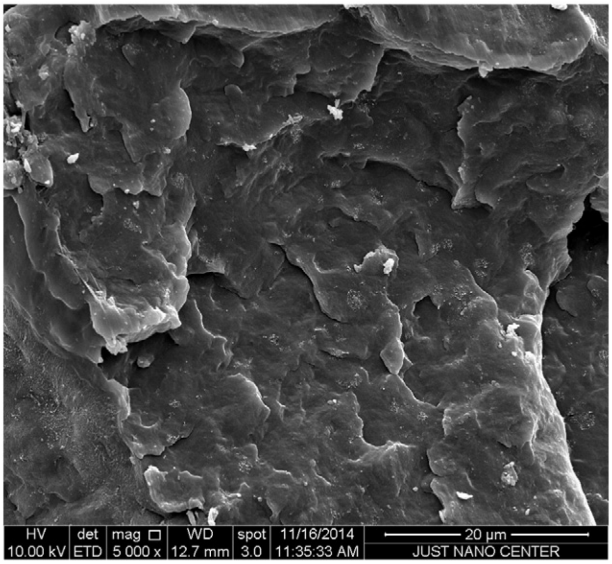

Fig. 1. SEM micrograph of CNT dispersion in melt mixed 1 wt.% CNT/PP nanocomposite.