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Influence of conductive network structure on the EMI shielding and electrical percolation of carbon nanotube/polymer nanocomposites

Mohammed H. Al-Saleh *

Department of Chemical Engineering, Jordan University of Science and Technology, Irbid, Jordan

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ABSTRACT

Conductive polymer nanocomposites (CPNC) are promising materials for electromagnetic interference shielding (EMI) applications. However, the relatively high cost of high aspect ratio nanofillers hinders the wide commercial use of these materials. Promoting the competitiveness of CPNCs requires formulation nanocomposites with the desired EMI capabilities at the lowest possible nanofiller loading. This requires better understanding for relation between the microstructure and EMI attenuation mechanisms, which is the objective of this work. Herein, CNPCs with segregated conductive network were prepared by placing carbon nanotube (CNT) particles at the external surface of ultrahigh molecular weight polyethylene (UHMWPE) powder by wet mixing. The microstructure, electrical and EMI shielding properties of the nanocomposites after compression molding were investigated. The EMI SE was found to increase with CNT content. An EMI SE of 50 dB was reported for a 1.0 mm thick plate made of 10 wt% CNT/UHMWPE nanocomposite. This nanostructured material is suitable for many applications in the computer and electronics industries. Compared to CNT/polymer nanocomposite of fine and well-dispersed CNT microstructure, the unique structure of the CNT/UHMWPE characterized by thick and segregated CNT network was found to enhance the EMI shielding by absorption and reduce the reflection of the EMI.

1. Introduction

Conductive polymer nanocomposites (CPNC) based on carbon nanotubes (CNT) have wide range of applications in the electronics, energy, aerospace and automotive sectors. For instance, CPNCs can be used as enclosures for protection from electrostatic discharge (ESD) and electromagnetic interference (EMI) [1–7]. Compared to metals, CPNCs possess cost, weight, design flexibility, corrosion resistivity and ease of processing advantages. The high aspect ratio and extraordinary electrical conductivity of CNTs were utilized to formulate nanocomposite materials with low electrical percolation threshold and electrical resistivity. The low percolation threshold is required to preserve the valuable properties of polymers and reduce the final nanocomposite cost, while the high intrinsic conductivity of the nanofiller is essential for applications requiring high levels of electrical conductivity such as the EMI attenuation.

The electrical and electromagnetic properties of polymeric materials filled with single-walled CNTs [8–12] and mutli-walled CNTs [13–21] have been investigated by many researchers. Based on the published results, it can be concluded that nanocomposites filled with high aspect ratio conductive nanofillers exhibit higher EMI shielding and lower electrical percolation threshold than the traditional composites based on microfillers such as carbon fiber. However, because CNTs are remarkably much more expensive than polymers, there is still a need for further reduction in the nanofiller loading to improve the competitiveness of CNT/polymer nanocomposite. Thus, it is crucial to understand the structure–property relationship in order to identify the structures that well serve the aforementioned objectives; and later on to determine the processing conditions/methods that can lead to such structures. The effects of different approaches/techniques on the electrical properties and to a lesser extent on the EMI shielding effectiveness (SE) of CPNCs have been studied [22,23]. For melt compounding, which is one of the most widely used techniques for composites preparation, factors such as operating conditions [23,24], selective localization of nanofiller in immiscible polymer blends [25–28] and mixing protocols [29,30] have been explored. The ultimate objective was identifying the conditions that lead to proper dispersion and distribution of nanotubes at the nanofiller scale without significant degradation of the aspect ratio.

There are minor and major objectives from this work. The minor objective is to report on the microstructure, electrical and EMI SE of CNT/UHMWPE nanocomposites as function of CNT concentration. The major objective is to answer the following question: does the

* Tel.: +962 2 7201000x22415; fax: +962 2 7201074.
E-mail address: mhsaleh@just.edu.jo (M.H. Al-Saleh).

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properties of nanocomposite materials such as the electrical and EMI shielding depends on the scale at which the nanofiller particles are distributed? Answering this question will help us in determining the type of structures that should be developed to serve better the electrical and EMI shielding properties. For this purpose, CNT/ultrahigh molecular weight polyethylene (UHMWPE) nanocomposite was prepared by wet mixing at room conditions. This simple compounding process allows the nanotubes to be selectively localized at the external surface of the UHMWPE powder particles that are on average ~50 μm in diameter. This structure creates a CNT-free zone that is 20–50 times larger than that created when nanotubes (assuming that the typical length of CNT is 1–2 μm) are dispersed in polymers by melt mixing or solution processing, where the average size of the CNT-free zone is around 1–2 μm. By analyzing the EMI shielding and shielding mechanism of CNT/UHMWPE and comparing them with reported profiles for nanocomposites prepared by melt mixing and solution processing, the effect of CNT distribution state, i.e., size of conductive mesh, on the EMI performance and mechanisms will be answered.

2. Experimental details

2.1. Materials

UHMWPE powder (GUR® 4120, Ticone, USA) with a density of 0.93 g/ml, mass melt-flow rate of <0.1 g/10 min at 190 °C/21.6 kg and molecular weight of about 5×10^6 g/mol was used as a polymer matrix. The nanotubes were NC7000 multi-walled nanotubes (Nanocyl S.A., Sambreville, Belgium). According to a manufacturer, NC7000 nanotubes have an average diameter of 9.5 nm and a length of 1.5 μm. HPLC grade chloroform was used to disperse the nanofiller and prepare UHMWPE suspension.

2.2. Nanocomposite preparation

CNT/UHMWPE nanocomposites filled with up to 10 wt% CNT were prepared by wet-mixing. In a typical experiment, X g CNT particles were dispersed in 20 ml chloroform using an ultrasonic bath (UC-02 Ultrasonic Cleaner, Lab Companion, Seoul, Korea) operated at a frequency of 40 kHz and output power of 70 W for 10 min. Meanwhile, $(1 - X)$ g UHMWPE powder was suspended in 20 ml chloroform by stirring. The CNT/chloroform suspension was added to the UHMWPE/chloroform suspension and the resultant mixture was mixed by sonication for another 10 min. After that, the mixture was cast at room temperature on glass dish and left overnight to allow the chloroform solvent to evaporate. Next day, the cast nanocomposite was placed in a vacuum oven for three hours at 70 °C to remove the remaining traces of the chloroform. For the optical microscopy, electrical conductivity and EMI SE characterization, rectangular (4×2 cm^2) specimens 1.0 mm in thickness were prepared by compression molding using Carver hot press (Carver Inc., Wabash-IN, USA). The molding was conducted for 10 min at a temperature and a pressure of 200 °C and 22 MPa, respectively. For each CNT concentration, at least three specimens were prepared and tested.

2.3. Characterization

2.3.1. Structure

Differential interface contrast microscope (Nikon, ECLIPSE, Japan) was used to characterize the structure of the nanocomposite. The optical microscopy sections (1 μm in thickness) were cut from molded rectangular plates using Reichert-Jung Ultracut E Ultramicrotome.

2.3.2. Electrical conductivity

The electrical resistivity characterization was done using two different setups. The first set-up is for composites with electrical resistivity $>10^6\,\Omega$ cm, this setup consists of Keithley 6517B electrometer connected to Keithley 8009 two-probe test fixture. For composite with electrical resistivity $<10^6\,\Omega$ cm, a set-up consisting of Keithley 2010 digital multimeter connected to a Keithley 5806 kelvin 4-wire probe was used. The reported results are the average of at least three different specimens.

2.3.3. EMI SE characterization

EMI SE characterization in the X-band (8.0–12.4 GHz) frequency range was conducted using N5242A microwave network analyzer connected with a WR-90 rectangular waveguide. The rectangular specimens were inserted between the two sections of the WR-90 waveguide and the S-parameters (S_{11},S_{12}, S_{22}, S_{21}) of each sample were recorded. Then the total EMI SE, shielding by reflection and shielding by absorption were calculated. The equations used in the calculations can be found in Section 3.3.

3. Results and discussion

3.1. Structure

The structure of the CNT/UHMWPE nanocomposites was characterized by optical microscopy to show the distribution state and location of CNT particles within the nanocomposite. Fig. 1 depicts the microstructure of the nanocomposites as function of CNT content. It is clear that the nanotubes are coating the external surface of the UHMWPE powder and forming continuous networks. UHMWPE is very viscous meaning that it is very difficult for the CNT particles to penetrate it in absence of shear mixing. Thus, CNT particles are exclusively located at the external surface of the polymer powder. In addition, as expected the thickness of the CNT layer that coats the polymer powder increase with the increase in the CNT weight fraction. For example, for the 0.1 wt% CNT nanocomposite a very thin layer of CNT particles coating the polymer powder can be observed. This observation reveals good distribution of the CNT particles within the polymer matrix. However, for the 10 wt% nanocomposite, CNT layers tens of microns in thickness can be observed.

3.2. Electrical properties

Polymer nanocomposites filled with conductive nanofillers are known to flow a typical electrical percolation behavior. This behavior is characterized by sudden and remarkable decrease in the nanocomposite's electrical resistivity at a critical filler concentration known as the electrical percolation threshold. The CNT/UHMWPE nanocomposite is not an exception from this typical behavior, as shown in Fig. 2. The nanocomposite exhibited a significant decrease in electrical resistivity at CNT concentration in the range of 0.05–0.1 wt%. Below 0.05 wt% CNT, the nanocomposite is insulator with electrical resistivity similar to that of the unfilled polymer. Above the percolation threshold, a reduction in electrical resistivity was associated with the increase in CNT content due to the increase in conductive pathways.

In order to estimate the electrical percolation threshold for the CNT/UHMWPE system, the power law (Eq. (1)) was used to fit the electrical resistivity data:

$$\rho = \rho_o(\upsilon - \upsilon_c)^{-t} \quad (1)$$

In the above equation, ρ is the nanocomposite electrical resistivity, ρ_o is a scaling factor, ν is the nanofiller volume fraction, ν_c is the