Composites Science and Technology 71 (2011) 1706–1712

Contents lists available at SciVerse ScienceDirect

Composites Science and Technology

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

Electrical and dielectric properties of polypropylene nanocomposites based on carbon nanotubes and barium titanate nanoparticles

Chang-Rong Yu[a], Da-Ming Wu[a], Ying Liu[a], Hui Qiao[a], Zhong-Zhen Yu[a,*], Aravind Dasari[b,*], Xu-Sheng Du[c], Yiu-Wing Mai[c]

[a] State Key Laboratory of Organic–Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, China
[b] School of Materials Science & Engineering (Blk N4.1), Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore
[c] Centre for Advanced Materials Technology (CAMT), School of Aerospace, Mechanical and Mechatronic Engineering J07, The University of Sydney, Sydney, NSW 2006, Australia

ARTICLE INFO

Article history:
Received 29 November 2010
Received in revised form 11 April 2011
Accepted 30 July 2011
Available online 10 August 2011

Keywords:
A. Nanocomposites
A. Carbon nanotubes
B. Electrical properties
B. Surface treatments

ABSTRACT

Functional polypropylene (PP) nanocomposites were prepared by melt compounding with multiwalled carbon nanotubes (MWNT) as the electrically conductive component and barium titanate (BT) spherical nanoparticles as the ferroelectric component. To make PP electrically conductive, more than 3 wt.% MWNT is required. Surface modification of either MWNT or BT with titanate coupling agent further improves the electrical conductivity of the PP/MWNT/BT ternary nanocomposites. Interestingly, by modifying both MWNT and BT, 2 wt.% MWNT are sufficient to make the ternary nanocomposite electrically conductive. In addition, the incorporation of MWNT greatly increases the dielectric permittivity of PP/BT nanocomposites. However, to retain a low dielectric loss, the MWNT loading should be slightly less than the percolation threshold of the nanocomposites. The improved electrical conductivity and dielectric properties make the ternary nanocomposites attractive in practical applications.

1. Introduction

Since the discovery of carbon nanotubes (CNT), their superior electrical [1,2], thermal [3,4] and mechanical properties [5,6] made them very attractive for incorporation in polymer materials for a range of applications including electrostatic dissipation, electromagnetic interference shielding [7,8], electro-thermal nanoprobe [9], dielectric materials with high dielectric permittivity [10–12] and conductive adhesives. Although solution blending [13] and *in situ* polymerization techniques are widely used to prepare polymer/CNT nanocomposites, considering the economics and industrial needs, melt compounding is still the preferred route [14]. Generally, with the increase of CNT loading, a three-dimensional conducting network is expected to form in a polymer matrix whereby the resulting nanocomposites show a sharp transition from electrically insulating to conducting behavior. But to form an effective conducting network, uniform dispersion of CNT in the polymer matrix is required. Thus, for this purpose, surface modification/functionalization of the CNT is often conducted [15]. Kodgire et al. [16] used a sodium salt of 6-aminohexanoic acid to modify CNT in order to obtain a homogeneous dispersion in polyamide 6 (PA 6) matrix during melt compounding, hence leading to a large improvement in electrical conductivity of the nanocomposites.

Another method to improve the electrical conductivity of a polymer/conducting filler nanocomposite is to take advantage of the volume-exclusion concept [17–21]. Meincke et al. [18] blended acrylonitrile–butadiene–styrene with PA 6/CNT nanocomposites by melt compounding. Due to the selective localization of the CNT in PA 6 phase, the ternary nanocomposites showed a reduced percolation threshold. Recently, Dasari et al. [21] added maleated polyethylene–octene copolymer (POE-g-MA) to a PA 6/MWNT blend by melt compounding and obtained improvements in not only electrical conductivity but also toughness of the ternary nanocomposite. The presence of MWNT in PA 6 matrix and their absence in the POE-g-MA particles increased the electrical conductivity caused by the volume exclusion effect of POE-g-MA; meanwhile, the dispersed POE-g-MA particles participated in toughening processes similar to PA 6/POE-g-MA binary blend, yielding greatly improved toughness.

Instead of an organic third component, inorganic fillers were also utilized [22–25]. For example, Ma et al. [24] used a combination of CNT/carbon black (CB) nanoparticles in epoxy and found a synergistic effect on electrical conductivity resulting in a lower percolation threshold. Liu and Grunlan. [25] introduced electrically insulating clay layers into epoxy/CNT nanocomposites and showed that even with 2 wt.% clay, the percolation threshold could be reduced from 0.05 wt.% to 0.01 wt.% of CNT.

The combination of CNT with other inorganic fillers [26] was also used to improve the dielectric properties. Barium titanate (BT) is a ferroelectric crystal with high dielectric permittivity and

---

* Corresponding authors. Fax: +86 10 6442 8582 (Z.-Z. Yu), +65 6790 9081 (A. Dasari).

E-mail addresses: yuzz@mail.buct.edu.cn (Z.-Z. Yu), aravind@ntu.edu.sg (A. Dasari).

0266-3538/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.compscitech.2011.07.022

has been widely used to enhance the dielectric permittivity of polymers [27,28]. However, due to the low dielectric permittivity of most polymers, high loading of BT is required, which often impairs the mechanical properties and processability of the polymers. It is currently a challenge to decrease BT loading in a polymer matrix but retain a satisfactory dielectric permittivity. Surface modification of BT was found to be an effective way of improving its dispersion along with dielectric permittivity of the polymer composites [29–34]. Kim et al. [31] reported that phosphonic acids formed organic shells on the BT surface, leading to well dispersed BT in polymeric films with high dielectric permittivity and high dielectric strength. In addition, an abrupt increase in the dielectric permittivity was observed around the percolation threshold of polymer nanocomposites with conducting fillers [35–37]. Nanocomposites in the neighborhood of percolation threshold could become capacitors with good characteristics of charge storage. Dang et al. [38] reported PVDF/MWNT/BT nanocomposite with high dielectric permittivity based on hybrid fillers and percolation theory.

In the present work, functional PP nanocomposites were prepared by melt compounding using MWNT as the electrically conductive component and BT nanoparticles as the ferroelectric component. BT is also expected to have an effect on the electrical conductivity of PP/MWNT nanocomposites via the volume-exclusion mechanism. Similarly, the presence of conducting MWNT is believed to improve the dielectric permittivity of the PP/BT nanocomposites. Further, the effects of surface modification of MWNT and BT on microstructures, electrical and dielectric properties of the PP nanocomposites are studied.

2. Experimental work

2.1. Materials

Polypropylene (S1003) with a melt flow index of 3 g/10 min was purchased from Yanshan Petroleum Chemical Co. Ltd. (China). Vapor-grown MWNTs with a purity of 95% were supplied by Chengdu Organic Chemicals (China). The MWNT has an outer diameter of 20–30 nm and a length of 10–30 μm and it has 1.23 wt.% of the carboxyl group. BT ceramic powders with an average diameter of 100 nm were bought from Shandong Guoci Functional Materials (China). Titanate coupling agent (TTS) with a chemical formula of $(CH_3)_2CHO\text{-}Ti\text{-}(COO\text{-}C_{17}H_{35}R)_3$ was purchased from Anhui Hongsheng Fine Chemical Co. Ltd. (China). Silver paste (CD-2004) with a silver content of 55 wt.% was provided by the Great Wall Gold–Silver Refinery (China).

2.2. Surface modification of BT and MWNT

Prior to modification, BT and MWNT were dried in an air-circulating oven at 80 °C for 16 h. The dried BT or MWNT powders were suspended in ethanol under mechanical stirring. Subsequently, 4 wt.% titanate coupling agent (based on BT or MWNT) dissolved in ethanol was added. The resulting suspension was heated at 90 °C until the solvent was evaporated while stirring continuously. The modified powders were dried in the oven at 100 °C for 16 h and are designated hereafter as m-BT and m-MWNT.

2.3. Preparation of PP nanocomposites

PP nanocomposites were prepared by melt compounding using a two-roll mill at 170 °C for 20 min. To minimize the thermal degradation of PP, 0.1 wt.% of antioxidant (1010) based on PP component was added. For the ternary nanocomposites, PP was first melt compounded with BT at 170 °C for 10 min, followed by blending with MWNT at the same temperature for another 10 min. Finally, 3 mm-thick plates of PP nanocomposites were made by compression molding at 200 °C with a pressure of 10 MPa.

2.4. Characterization

The surface chemistry of BT and MWNT before and after modification with the titanate coupling agent was characterized by Nicolet 6700 Fourier transform infrared spectroscopy (FT-IR). The melt viscosities of PP nanocomposites were measured on a TA ARES rheometer with 25 mm diameter parallel plates at 190 °C with frequencies varying from 0.1 to 40 rad/s. To evaluate the dispersion quality of BT and MWNT in PP matrix, freeze-fractured surfaces of

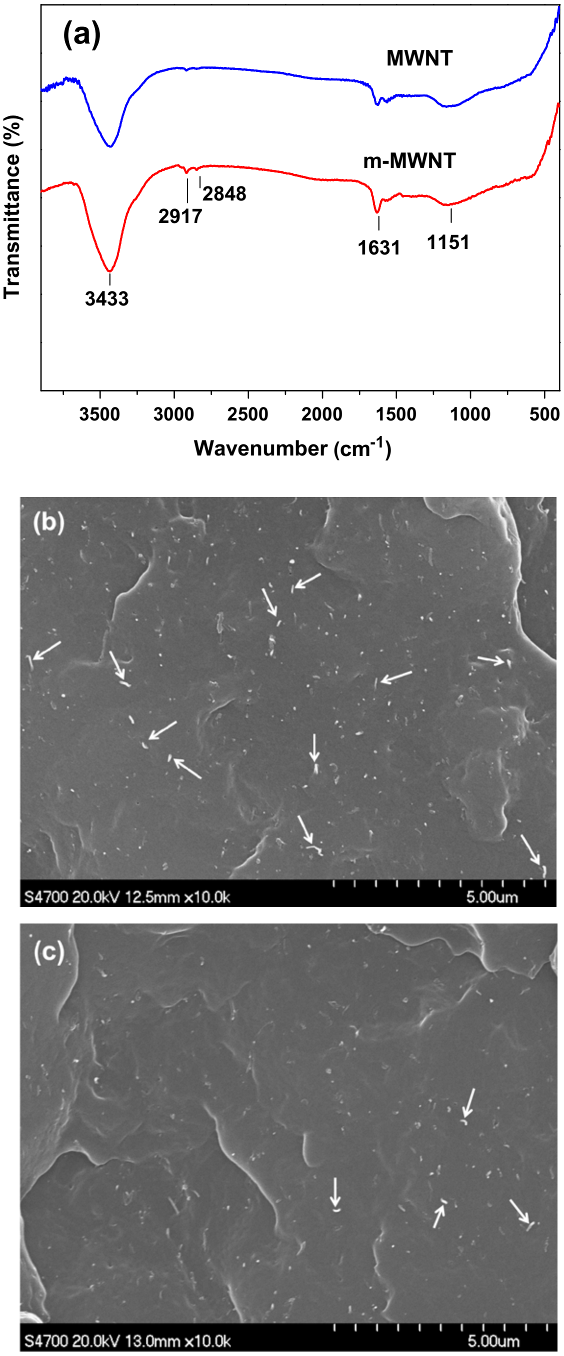

Fig. 1. (a) FT-IR spectra of MWNT before and after surface modification with the titanate coupling agent. (b) and (c) SEM micrographs of the PP nanocomposites with 2 wt.% of unmodified and modified MWNT, respectively. White arrows indicate pulled out nanotubes.