Available online at www.sciencedirect.com
ScienceDirect
Composites Science and Technology 67 (2007) 2528–2534
COMPOSITES SCIENCE AND TECHNOLOGY
www.elsevier.com/locate/compscitech

Preparation and properties of electrically conductive PPS/expanded graphite nanocomposites

Y.F. Zhao, M. Xiao, S.J. Wang, X.C. Ge, Y.Z. Meng *

State Key Laboratory of Optoelectronic Materials and Technologies/Institute of Optoelectronic and Functional Composite Materials, Sun Yat-Sen University, 135 Xingang West, Guangzhou 510275, PR China

Received 24 February 2006; received in revised form 16 November 2006; accepted 19 December 2006
Available online 11 January 2007

Abstract

Nanocomposites based on poly (phenylene sulfide) (PPS) and expanded graphite (EG) or ultrasonicated EG (S-EG) were prepared by melt blending. Morphologies of the nanocomposites were examined using both SEM and TEM. Electrical conductivity and thermal stability of PPS were notably enhanced by the introduction of EG. The percolation threshold values are 1 wt% (S-EG) and 2 wt% (EG) for PPS/S-EG and PPS/EG nanocomposites, respectively. The variation of mechanical strength with the weight fraction of EG and S-EG in the nanocomposites showed somewhat correlation with the threshold filler concentration. The crystallization behavior of PPS matrix in the nanocomposites was investigated using DSC, and the results indicated that the crystallization process was significantly accelerated, leading to an increase in crystallinity.

Keywords: A. PPS; A. Expanded graphite; A. Conducting polymer; A. Nanocomposite

1. Introduction

Polymer nanocomposites with conducting fillers have been the focus for many research groups in past few decades. The electrically conductive polymeric composites can be utilized in light emitting devices, batteries, electromagnetic shielding, anti-static, corrosion resistant coatings, and other functional applications [1,2]. The conducting fillers often used included natural graphite flake, carbon black and metal powders. Among the various conducting fillers, natural graphite, which possesses good electrical conductivity of about 10^4 S/cm at ambient temperature, has been widely used [3,4]. In most cases, relatively large quantities of graphite were needed to reach a critical percolation value. However, large quantity of graphite could lead to materials poor mechanical properties and high density of composite. In order to solve the problem of materials that have high conductivity and poor mechanical properties, nanoscale fillers have been extensively employed.

Graphite shows layered crystal structure. The carbon atoms are bonded covalently in a hexagonal arrangement within the layer and these layers are bonded to each other by weak van der Waals forces. The *d*-spacing between the carbon layers is 0.335 nm. Since the van der Waals forces are relatively weak, it is possible for a wide range of atoms, molecules and ions to intercalate between graphite layers to form the graphite intercalation compounds (GICs).

Expanded graphite (EG) is generally produced by subjecting H_2SO_4–GICs to rapid thermal treatment. EG maintains the layered structures similar to natural graphite flake but produces tremendous different size of pores and nanosheets with very high aspect ratio. Many polymeric nanocomposites using EG as conducting fillers, such as PMMA/EG [2,5], PA-6/EG [6], PE/EG [7], Nylon 6/EG [8,9], PS/EG [10,11], POBDS/EG [4,12–14], have been extensively reported recently.

Poly (phenylene sulfide) (PPS) is a typical engineering polymer that shows exceptional mechanical properties

* Corresponding author. Tel./fax: +86 20 84114113.
E-mail address: mengyzh@mail.sysu.edu.cn (Y.Z. Meng).

0266-3538/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.compscitech.2006.12.009

and good dimensional stability. Its high deflection temperature of about 500 K, flame retardancy and resistance to any solvents below 200 °C endow it many special applications, such as electronics, automotive industry [15] and heat detector. Although much effort has been devoted to improve the mechanic and thermal properties of PPS [16], little information is available for the PPS based conductive materials. In this regard, PPS/EG nanocomposites was prepared in this work by melt blending, the microstructure, electrical properties, mechanical and thermal properties were investigated and reported.

2. Experimental

2.1. Materials

Expandable graphite with an expandable volume of 200 mL/g, was supplied from Shandong Pingdu Jiaodong Graphite Co. (China). PPS was commercial product (injection grade), supplied from Guangzhou Kingfa Sci. & Tech. Co. Ltd. (China). The melt flow index (MFI) of the PPS is 235 g/10 min measured according to Chinese GB/T 3682-2000 standard (316 °C, 5 kg, 1.18 mm).

2.2. Sample preparation

Expanded graphite (EG) was obtained by heating the expandable graphite in a muffle furnace at 950 °C for 30 s. The expanded graphite was immersed in a 95% of aqueous alcohol solution and subjected to powdering in an ultrasonic bath for 2 h. The resulting suspension was then filtered and dried in the vacuum oven at 50 °C for 12 h to obtain graphite nanosheets (S-EG). PPS was dried under vacuum at 150 °C for 24 h before compounding.

2.3. Nanocomposite preparation

PPS/EG, PPS/S-EG composites were prepared by melt blending in a twin rotary mixer (Haake Rheomix_600) at 290 °C. The rotor speed and mixing time was fixed at 40 rpm and 10 min, respectively. Pure polymer PPS were also processed under the same conditions. The composites were hot pressed at 300 °C under a pressure of 15 MPa into specimens for testing.

2.4. Characterization

2.4.1. Electrical conductivity

The conductivity (σ) of PPS and composites were measured by electrochemical workstation (Solartron 1255B) at room temperature when the σ was less than 10^{-3} S/cm. The circular specimens with a diameter of 10 mm and thickness of 2 mm were placed between two gold test electrodes, and then the resistance was measured. Removing the specimen, the resistance of test cell was measured again under the same condition to obtain the reference resistance. The resistance of the specimen was obtained by subtracting the reference resistance. The resistivity or conductivity of the specimen was determined by the following equation:

$$\rho = R_s \frac{A}{L} = \frac{(R_T - R_B)A}{L} \quad (1)$$

$$\sigma = \frac{1}{\rho} \quad (2)$$

where ρ, σ, A and L are the resistivity, the conductivity, the cross-sectional area and the thickness of the specimen, respectively. R_T, R_B and R_S are total resistance, reference resistance and specimen's resistance, respectively.

When σ of the specimen was greater than 10^{-3} S/cm, it was tested by SDY-4 four-probe instrument (Guangzhou, China).

2.4.2. Mechanical property

Three-point bending tests were performed on Sansi testing machine (CMT4104, China) at room temperature. The crosshead speed was 1 mm/min and the support span was 25 mm. The sample dimensions were $30 \times 3 \times 2$ mm^3, five specimens of each composition were tested and the average values were reported.

2.4.3. Morphology observation

Morphologies of EG and PPS/EG composites were examined on a scan electron microscope (JSM-6380LA, JEOL). Prior to the test, the specimens were cryo-fractured and the fracture surface was sputtered with gold. Transmission electron microscopy (100CX-II, JEOL) micrograph was obtained using an acceleration voltage of 100 KV. Ultrathin samples were obtained using an IB-Vmicrotome.

2.4.4. Thermal property

Thermogravimetric analysis (TGA) was performed on a Perkin–ElmerTG/DTA 6300 instrument at a heating rate of 20 °C/min under N_2 (300 ml/min) atmosphere. Differential scanning calorimetry (DSC) analysis was carried out on NETZSCH DSC-200PC under N_2 atmosphere. Samples were heated from room temperature to 320 °C at a rate of 20 °C/min and held at that temperature for 3 min to eliminate the heat history. The samples were then cooled to 50 °C at a rate of 20 °C/min. After keeping at 50 °C for 3 min, samples were heated to 320 °C at a rate of 20 °C/min again. The thermal parameters were obtained from the cooling and reheating scans for the crystallization and melting behavior of PPS composites. The degree of crystallinity was calculated from the following equation:

$$\%X_c = \frac{\Delta H_c}{\Delta H_f(1 - W_f)} \times 100\% \quad (3)$$

where X_c is the degree of crystallinity, ΔH_c is the heat of crystallization, ΔH_f is the heat of crystallization of a 100% crystalline PPS, W_f is the weight fraction of EG content in the composite.