Composites: Part A 91 (2016) 77–84

Contents lists available at ScienceDirect

Composites: Part A

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

Thermal and electrical properties of poly(phenylene sulfide)/carbon nanotube nanocomposite films with a segregated structure

Tae Jong Yoo, Eun-Byeol Hwang, Young Gyu Jeong *

Department of Advanced Organic Materials and Textile System Engineering, Chungnam National University, Daejeon 305-764, Republic of Korea

ARTICLE INFO

Article history:
Received 19 May 2016
Received in revised form 28 September 2016
Accepted 30 September 2016
Available online 30 September 2016

Keywords:
A. Carbon nanotubes
A. Nanocomposites
B. Electrical properties
B. Thermal properties

ABSTRACT

Structurally segregated poly(phenylene sulfide) (PPS)-based nanocomposite films containing multi-walled carbon nanotube (MWCNT) of 0.5–10.0 wt% were manufactured by solid-mixing and following melt-compression. The cross-sectional optical and electron microscopic images of the nanocomposite films revealed that MWCNTs form a segregated and percolated conductive network structure in the PPS matrix. DSC and TGA data demonstrated that melt-crystallization temperatures and thermal degradation temperatures of the nanocomposite films are slightly increased with the MWCNT content, which are owing to the nucleating agent and thermal protection effects of MWCNTs, respectively. The electrical conductivity of the nanocomposite films increased significantly from $\sim 10^{-10}$ to ~ 0.11 S/cm with the increment of the MWCNT content from 0.0 to 10.0 wt%, especially at a low percolation threshold of ~ 0.33 wt% MWCNT. Accordingly, PPS-based nanocomposite films with 1.0–10.0 wt% MWCNT exhibited high performance in electrical resistive heating behavior under applied voltages of 5–100 V by achieving steady-state maximum temperatures of 30–190 °C within a relatively short period of time of ~ 10 s.

1. Introduction

Poly(phenylene sulfide) (PPS) consisting of aromatic rings linked with sulfides is one of leading engineering thermoplastic polymers. Owing to its excellent heat resistance, chemical resistance, fatigue resistance, dimensional stability, thermal stability, flame retardancy, electrical insulation, wear resistance, and processability, PPS has been used in a variety of fibers, specialty membranes, electronic products and industries [1,2]. PPS, which is otherwise electrically insulting, is also considered as the precursor to a conducting polymer of the semi-flexible rod polymer family, because it can be converted to the semiconducting form by oxidation or use of dopants [3].

To expand the applications of PPS by improving the physical properties, carbon nanotube (CNT), graphene and their derivatives have been chosen as reinforcing nanofillers for PPS [4–6]. Especially, CNTs have been extensively selected as one-dimensional reinforcing nanofillers for advanced polymeric nanocomposites due to their excellent electrical conductivity of 10^4–10^5 S/cm, thermal conductivity of 3000–6600 W/m K, carrier mobility of 1000–4000 cm^2/V s, Young's modulus of 0.27–1.25 TPa, and thermal stability up to ~ 700 °C in air [7–9]. Diez-Pascual and Naffakh investigated that PPS-based nanocomposites incorporating a polymer derivative covalently grafted single-walled CNT (SWCNT) have highly improved thermal and thermomechanical properties in aspects of high thermal stability, flame retardancy, glass transition/heat deflection temperatures, tensile strength/modulus, and low thermal expansion coefficient, which are ascribed to strong matrix-filler interfacial interactions combined with a compatibilization effect [4]. Gao et al. reported that hot-stretched PPS composite fibers reinforced with multi-walled CNT (MWCNT) have remarkably enhanced tensile strength and modulus owing to the presence of the strong interfacial adhesion via π-π interaction between the benzene ring of PPS and the surface of MWCNTs [5].

In most of the cases of thermoplastic polymer nanocomposites including MWCNT, melt mixing is the preferred composite compounding method [10], since aggregate formation can be minimized by suitable application of shear during the melt mixing [11]. Melt mixing for PPS/MWCNT nanocomposites is more simple and handy than other processing techniques, and can achieve the production on a large scale in the PPS industries [12]. Many researchers also reported the degree of MWCNT dispersion in the PPS matrix below and above the electrical percolation threshold [13–16]. In general, polymer nanocomposites with random conductive networks require high conductive filler loadings at the insulator/conductor transition. To date, forming a controlled segregated structure in a conductive polymer composite has remained

---

* Corresponding author.
E-mail address: ygjeong@cnu.ac.kr (Y.G. Jeong).

http://dx.doi.org/10.1016/j.compositesa.2016.09.022
1359-835X/

the most promising strategy for attaining low electrical percolation threshold. Accordingly, the morphological control of conductive network in polymer composites and their use as electroactive multifunction materials have been also investigated [17,18]. In the polymer composite materials with a segregated structure, the conductive nanofillers are primarily located at the interfaces between the polymeric matrix particles instead of being randomly arranged throughout the entire polymer composite system [19–23].

In this study, we fabricated a series of PPS/MWCNT nanocomposite films with a segregated structure via an efficient solid-mixing and following melt-compression, and investigated their morphological features, thermal and electrical properties as a function of MWCNT content (0.5–10.0 wt%). The segregated but percolated structure of MWCNTs in the PPS matrix was identified by using optical and electronic microscopes. The electrical percolation threshold of the nanocomposite films was analyzed by using a power law relation. The electrical resistive heating performance of the PPS nanocomposite films with different MWCNT contents was characterized in terms of temperature responsiveness, steady-steady maximum temperature, and electric power efficiency under different applied voltages.

2. Experimental

2.1. Materials

PPS chips (Fortron 0309, Ticona, Celanese) with a density of 1.350 g/cm^3 was selected as the polymeric matrix to fabricate the nanocomposites films. Pristine MWCNT (CM-95, Hanwha Chemical) with 10–15 nm diameter and 10–20 μm length, which was manufactured by thermal chemical vapor deposition (CVD), was used as a reinforcing nanofiller for PPS-based nanocomposite films.

2.2. Preparation of PPS/MWCNT nanocomposite films

A series of PPS/MWCNT nanocomposite films were fabricated by a solid-mixing and following melt-compression process. First, PPS chips were pulverized into powders with a particle size of 259.6 ± 96.7 μm. Second, predetermined amounts of PPS powders were mixed mechanically with pristine MWCNT for 3 min. In the solid mixtures, the pristine MWCNT content was controlled to be 0.5, 1.0, 3.0, 5.0, 7.0, and 10.0 wt%. Third, each solid mixture was melt-compressed in a hot press at 300 °C and 20 MPa for 10 min and then cooled to room temperature. The thickness of the nanocomposite films during the melt-compression was adjusted to be ~200 μm. Finally, the nanocomposite films were dried in a vacuum oven at 80 °C. The final nanocomposite films were named as PPS/MWCNT-x, where x denotes the content of pristine MWCNT by weight percent (wt%).

2.3. Characterization

The particle size and its distribution of PPS powders was analyzed by using a laser scattering particle size analyzer (HELOS/KR, Sympatec GmbH). The dispersion state of the pristine MWCNT in the PPS matrix was identified by examining the cross-section morphology of the nanocomposite films with aids of a scanning electron microscope (SEM, S-4800, HITACHI), a transmission electron microscope (TEM, Tecnai G2 F30, FEI) and an optical microscope (OM, S38, Bimience). For the TEM and OM experiments, thin specimens with 50–500 nm thickness were prepared by using a ultramicrotome (Leica EM UC6). The thermal transition properties of the nanocomposite films were investigated by using a differential scanning calorimeter (DSC, Mettler-Toledo). About 5 mg samples were heated from 0 to 300 °C at a heating rate of 10 °C/min under nitrogen atmosphere. The thermal stability of neat PPS and its nanocomposite films was investigated by using a thermogravimetric analyzer (TGA, Mettler-Toledo). About 4–5 mg samples were heated from 25 to 900 °C at a heating rate of 20 °C/min under nitrogen atmosphere. The electrical properties of the nanocomposite films with a variety of MWCNT contents were characterized by obtaining voltage-dependent current density and electric power density curves with an electrometer (2400, Keithley). The electrical resistive heating performance of the nanocomposite films at different applied voltages of 1–100 V was characterized with an infrared camera (SE/A325, FLIR system Inc.) and an electrometer (2400, Keithley). For the electrical property measurement and the electrical resistive heating experiment, the sample distance between electrical test probes was fixed to be 10.0 mm for all the nanocomposite films with 10.0 mm width and 30.0 mm length.

3. Results and discussion

3.1. Structural characterization

To identify the morphological features of neat PPS and associated nanocomposite films with different MWCNT contents, cross-sectional SEM images of the film specimens were obtained, as can be seen in Fig. 1. The SEM images of neat PPS film show relatively smooth and compact cross-sectional morphology without any micropores, which indicates that the solid-mixing and melt-compression processing was well controlled. In cases of the nanocomposite films, the SEM images exhibit regularly segregated and percolated morphology of MWCNTs in the PPS matrix, which was also confirmed by typical OM and TEM images of PPS/MWCNT-3.0, as shown in Fig. 2. As represented schematically in Fig. 3, it is highly conjectured that the irregularly segregated structure of MWCNTs can be driven by the manufacturing processes. At the melt-compression condition (300 °C, 20 MPa, 10 min), PPS chains above the melting point can diffuse into neighboring PPS powder domains surrounded by MWCNTs, which eventually leads to rather unclear PPS domain size in the nanocomposite films but contribute to good welding among PPS powders by minimizing micropores for the final nanocomposite films and by remaining interconnected MWCNTs around PPS domains.

3.2. Thermal transition and thermal stability

The influence of the pristine MWCNT on the melting and crystallization transition behavior of PPS-based nanocomposite films was investigated by obtaining DSC heating and cooling thermograms, as shown in Fig. 4. In the DSC heating thermograms, the melting transition temperatures (T_m) of neat PPS and nanocomposite films were found to be ~285 °C, irrespective of the MWCNT content, within the experimental error. It means that the melting transition is not affected by the presence of the pristine MWCNT in the manufactured nanocomposite films. However, it is noticeable that the melt-crystallization exothermic peaks are shifted to higher temperatures from ~238 °C for the neat PPS film to ~247 °C for the PPS/MWCNT-10 with the increase of the MWCNT content, which reveals that MWCNTs segregated regularly in the nanocomposite films can serve as nucleating agents for the melt-crystallization of PPS.

Fig. 5 shows TGA and DTG curves of neat PPS and nanocomposite films with different MWCNT content. It is found that neat PPS and its nanocomposite films maintain mainly their thermal stability up to ~450 °C and are rapidly pyrolyzed in the temperature range of 500–650 °C. In addition, the residues above ~650 °C are largely higher for the nanocomposite films with higher MWCNT loading, as can be seen in Fig. 5A. On the other hand, the thermal decomposition of the nanocomposite films is slightly delayed,