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Novel exfoliated graphite nanoplates/syndiotactic polystyrene composites prepared by solution-blending

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ABSTRACT

Novel exfoliated graphite nanoplates (xGNPs)/syndiotactic polystyrene (sPS) composites were prepared by a simple and effective solution-blending method. The uniform dispersion of xGNPs in sPS matrix was confirmed by scanning electron microscopy. The effect of xGNPs on sPS crystallization behavior was investigated by wide angle X-ray diffraction and differential scanning calorimetry. It was found that the existence of xGNPs increased the crystallization ability of sPS and facilitated the formation of the β phase crystalline structure. By adding 10 wt.% of xGNPs, the increase in the onset degradation temperature of the xGNPs/sPS composite could reach 12°C. The AC electrical conductivity at 1000 Hz increased from 3.8×10^{-10} S/m for neat sPS to 2.25×10^{-4} S/m for xGNPs/sPS composite containing 2.93 vol.% of xGNPs. Moreover, the thermal conductivity of the xGNPs/sPS composite containing 8.26 vol.% has been significantly improved from 0.21 to 1.63 W/m·K when compared with that of pure sPS.

1. Introduction

Syndiotactic polystyrene (sPS) is an important plastic prepared by the polymerization of styrene monomer in a metallocene/MAO (catalyst/cocatalyst) catalytic system. sPS possesses many advantages such as high mechanical strength, good thermal stability, excellent chemical and moisture resistance, as well as high dimensional stability [1]. However, sPS is an insulator so that the very low electrical and thermal conductivities of sPS seriously limit its further application [2,3]. It has been reported that the incorporation of conductive fillers into polymer matrix can effectively improve the conductivity of resultant composites. Therefore, the fabrication of sPS-based composites with both high electrical and thermal conductivities is not only necessary but also should be possible. Meanwhile, sPS has very fast crystallization rate together with polymorphic crystalline structure (α, β and γ phase) strongly depending on thermal history and solvent-treatment [4–7], which will in turn affect its properties significantly. Hence, understanding of the crystallization behavior and the crystalline structure is very important for the utilization of sPS and its composites.

Recently, there has been an increasing interest in sPS-based composites containing nanoscale reinforcing agents, which mostly focused on the effect of nanofillers on their crystallization behavior and physical properties. Especially, various carbonaceous nanofillers have been used to enhance the properties of sPS. For example, Sun et al. found that multi-walled carbon nanotubes (MWCNTs)

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could simultaneously increase the crystallization temperature, the onset degradation temperature and the electrical conductivity of sPS [4]. Similarly, carbon nanofibers not only had a nucleating effect on the crystallization of sPS but also could improve the thermally and electrically conductive properties as compared with pure sPS [5]. Wang et al. prepared sPS-based composites filled with well-dispersed carbon nanocapsules (CNC) by solution-blending [6]. The morphology and properties, such as crystallization behavior and thermal degradation of the as-prepared CNC/sPS composites, were studied.

Exfoliated graphite nanoplates (xGNPs) are new carbon-based nanomaterials with layered structure and nanoscale thickness in which there are a few layers of graphene stacking tightly [8]. xGNPs possess good mechanical performance, excellent electrical and thermal conductivity, high aspect ratio, as well as cost-effectiveness, which makes them ideal nanoscale reinforced agents for polymers [8]. However, up to now, there is no research reporting on xGNPs/sPS composites.

Several processing methods, such as ball milling [9], melt blending [10], solution blending [2,3] and *in-situ* polymerization [11], have been adopted for preparing xGNPs/polymer composites. In the case of preparing xGNPs/sPS composites, ball milling is not easy to handle owing to the high stiffness of sPS; melt-bending is also difficult because of the high melting temperature of sPS which is very close to its degradation temperature [4]; while for *in-situ* polymerization the presence of xGNPs may adversely affect the polymerization procedure due to its adverse effect on the catalyst [4]; As far as the solution-blending method is concerned, Kim et al. have already reported that solution mixing showed better dispersion of xGNPs in linear low density polyethylene (LLDPE) matrix than melt mixing [10].

It should be noted that the selection of appropriate solvent will play an important role in the homogeneous dispersion of xGNPs in sPS matrix, and thus the potential of resultant xGNPs/sPS composites can be fully utilized. It is well known that N-Methyl-2-pyrrolidinone (NMP), as a highly polar organic solvent, is one of the best solvents to disperse carbonaceous nanofillers [4]. Also, it is a good solvent for sPS [2,3]. Therefore, in this work, NMP was chosen as the dispersing medium for xGNPs and the solvent for sPS to prepare xGNPs/sPS composites by solution-blending. Furthermore, the crystallization behavior, the thermal stability, the electrical conductivity and the thermal conductivity of the resultant xGNPs/sPS composites were investigated.

2. Experimental

2.1. Materials

Natural graphite (NG) flakes obtained from Qingdao graphite factory were used as the starting materials to prepare xGNPs. sPS was provided by Dow Chemical Company with M_w of 226,000 and M_w/M_n of 2.8. N-methyl-2-pyrrolidinone (NMP) and other chemicals were purchased from Guangzhou Chemical Reagent Company and directly used without any further treatment.

2.2. Preparation of xGNPs/sPS composites

Expanded graphites (EG) was prepared by acid intercalation of the NG flakes followed by rapid thermal expansion of the resultant intercalated NG flakes [12]. For the preparation of xGNPs/sPS composite, a desired amount of EG flakes was first ultrasonicated in 100mL of NMP for 6 hours to prepare xGNPs. Next, sPS was added to the xGNPs-NMP suspension. After vigorous mechanical stirring for 1 hour at 160 °C, the mixture was poured into cold water at 20 °C, filtered, and then dried to obtain the xGNPs/sPS composite. For comparison, pure sPS sample was obtained using the same procedure in the absence of xGNPs.

2.3. Characterization

The morphologies of NG flakes, EGs, xGNPs, and xGNPs/sPS composites were observed by scanning electron microscope (SEM, JEOL Model, JSM-6490). The morphology of xGNPs was also studied by transmission electron microscope (TEM, JEOL Model, JEM-2010), Wide angle X-ray diffraction (WAXD) measurements were carried out on a high solution X-ray diffractometer system (Bruker D8 Discover). Differential scanning calorimetry (DSC) characterizations were conducted a Perkin Elmer DSC-7 differential scanning calorimeter. Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere from 30 to 800 °C at a heating rate of 10 °C/min using a thermogravimetric analyzer (Netzch STA 449C, Jupiter). The electrical conductivity was tested as a function of frequency from 10^3 to 10^7 Hz at room temperature using an Agilent 4294A impedance analyzer. The thermal conductivity was measured by a TPS2500 thermal conductivity apparatus (Hot Disk, Germany) using a transient plane heat source method. The testing parameters on the thermal conductivity apparatus were p = 10 mW, t = 20 s.

3. Results and discussion

3.1. Morphology of xGNPs and xGNPs/sPS composite

xGNPs was prepared by subjecting NG flakes sequentially to acid intercalation, rapid thermal expansion and ultrasonication in NMP solvent. As shown in Fig. 1a, NG flakes have a flat-plate structure with micro-thickness, and the graphite sheets stack layer by layer in a highly ordered manner. EGs were obtained from acid intercalation of NG flakes followed by rapid thermal expansion, leading to a porous worm-like structure (see Fig. 1b). At higher magnification as shown in Fig. 1c, a significant increase in distance between stacked graphite sheets can be observed for EGs due to the large expansion along the perpendicular direction of NG-flake surfaces after the thermal treatment. The fabrication of xGNPs can be very easily realized by the ultrasonication of EGs in NMP. It is worth noting that the selection of appropriate solvent as an ultrasonic medium is very important to transfer ultrasonic energy. NMP is one of the best solvents to disperse carbon nanotubes and graphene because of its good affinity to carbon-based materials [4]. Hence, we used NMP as the solvent to prepare a suspension of xGNPs. Fig. 1d presents the layer structure of