Improved rheological and electrical properties of graphene/polystyrene nanocomposites modified with styrene maleic anhydride copolymer

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ABSTRACT

Styrene–maleic anhydride copolymer (SMA) was used as a compatibilizer to improve the interfacial interaction between graphene sheets and polystyrene matrix. SMA mediated graphene sheets are closely encapsulated by a polymer layer and uniformly dispersed compared to the graphene sheets without SMA. The presence of SMA not only improves the melt modulus and its frequency-independence, but also results in an earlier transition from liquid-like to solid-like, indicating the formation of a percolated conducting network at a low content of graphene with the assistance of SMA. Accordingly, the different frequency dependences of electrical conductivity also lead to a much lower threshold of 0.17 vol.% for SMA modified nanocomposites compared to 0.52 vol.% for the unmodified counterparts, further confirming the earlier formation of a graphene network in the matrix. The improved rheological and electrical properties of the polystyrene nanocomposites are attributed to the homogeneous dispersion of the graphene sheets and the enhanced interfacial interaction between the graphene sheets and the polystyrene matrix.

1. Introduction

Graphene sheets have been widely used to improve electrical, thermal and mechanical properties of polymers [1–10]. The electrical properties of graphene are more valued and high electrical and electromagnetic interference shielding properties are achieved by the addition of graphene sheets in various polymer matrices including polystyrene (PS) [8,11], polyurethane [12], polyethylene terephthalate [9], polymethyl methacrylate [10], polycarbonate [13] and epoxy resin [14]. However, one of the challenges in maximizing these properties is to prevent the aggregation of the graphene sheets in these polymer matrices. Chemical modification has been applied to improve the dispersion of the graphene sheets in polymers [2,6,8]. However, the improved dispersion is achieved at the expense of the deterioration of the structural integrity and intrinsic electrical conductivity of graphene, and thus the electrical conductivity of its polymer nanocomposites may be inevitably affected [6,8,15].

Non-covalent modification is a promising approach to prepare electrically conductive polymer nanocomposites while maintaining the structure and property of nanofillers [16,17]. The interactions from π–π stacking between PS and graphene sheets can be used to improve the dispersion of graphene [17]. Based on the polar interaction, the residual oxygen functionalities on the thermally exfoliated and reduced graphene facilitate its dispersion in polar polymers [9,18,19]. However, the thermally exfoliated graphene does not have a satisfactory dispersion in non-polar polymers, such as polypropylene and PS [17,20]. The polarity mismatch can be alleviated by introducing polar groups onto polymers [20–22]. Kim et al. [20] endowed linear low density polyethylene with amino, cyano and isocyanate groups via ring-opening metathesis polymerization, which improved the dispersion of the graphene sheets. Maleic anhydride grafted polyolefin was also effective in enhancing the dispersion of organically modified layered silicates and expanded graphite nanoplatelets [23,24]. The interfacial interaction between carbon nanotubes and polymers was enhanced by the addition of styrene maleic anhydride copolymer (SMA) [21,22]. However, the influence of SMA on the graphene network and the properties of graphene/PS nanocomposites are rarely reported. In the present work, SMA is used as an interfacial compatibilizer to promote the dispersion of graphene sheets in PS matrix based on the interactions of the maleic anhydride groups of SMA

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with the residual oxygen-containing groups of the thermally exfoliated graphene sheets. The roles of SMA in influencing the microstructure, rheological and electrical properties of the PS nanocomposites are studied.

2. Experimental

2.1. Materials

Natural graphite flakes were supplied by Huadong Graphite Factory (Pingdu, China) with an average diameter of 13 μm. Potassium chlorate (98%), fuming nitric acid (65–68%), concentrated sulfuric acid (95–98%), hydrochloride acid (36–38%), tetrahydrofuran (THF, 99.7%), ethanol (99.7%) and methanol (99.5%) were purchased from Beijing Chemical Factory (China) and all used as received. PS and SMA were from BASF-Yangzi Co. Ltd (China) and their weight-average molecular weights are ~158,000 and ~128,000 g/mol, respectively.

2.2. Preparation of PS nanocomposites

Thermally exfoliated graphene was prepared by thermal exfoliation and reduction of graphite oxide powders at 1050 °C [9,25]. Graphene/PS (G–PS) and SMA-modified graphene/PS (SG–PS) nanocomposites were fabricated by solution blending followed by compression molding. In a typical procedure, the desired amount of graphene was dispersed in THF (1 mg/ml) via sonication for 30 min. The resultant suspension was then mixed with the THF solution of PS or PS/SMA (9/1, w/w) blend. After the mixure was homogenized with an IKA T18 homogenizer (Germany) for ~2 h in an ice-water bath, it was dropped into a large volume of vigorously stirred methanol to coagulate the PS nanocomposites, which were rinsed with methanol, filtered, dried and finally compression molded into 1 mm thick plates using a Beijing Kangsente KT-0906 vacuum hot-press (China) at 210 °C under ~10 MPa for 30 min. For comparison, graphene filled SMA (G–SMA) composite with 0.93 vol.% of graphene was also prepared using a similar procedure.

2.3. Characterization

The freeze-fractured surfaces of the PS nanocomposites, after coating with gold, were observed with a Hitachi S4700 field-emission scanning electron microscope (SEM) at an accelerating voltage of 20 kV. G–PS, SG–PS and G–SMA nanocomposites were analyzed with a Nicolet Nexus 670 Fourier-transform infrared spectroscopy (FT-IR). Rheological properties of neat PS and its nanocomposites were measured with a TA Instruments ARES-G2 strain-controlled parallel-plate rheometer (USA) at 190 °C in nitrogen atmosphere. Firstly, a dynamic time-sweep was conducted at 10 rad/s to monitor the change of rheological properties versus time for each specimen. The dynamic strain was set at 1% for PS and PS/SMA blend, and 0.1% for their graphene nanocomposites to make sure that every specimen was in its linear viscoelastic region during the measurement. Then, a dynamic strain sweep at a frequency of 10 rad/s was carried out to find the critical strain γ_{crit} as the strain where storage modulus (G') falls to 90% of its limiting low strain value. After this was done, a new specimen was loaded and subjected to the same waiting time at 190 °C. Finally, a dynamic frequency sweep was performed in the range of 100–0.01 rad/s at $\gamma < \gamma_{crit}$ to obtain the linear viscoelastic response for the specimens. The alternative current (AC) electrical properties of neat PS and its nanocomposites were measured as a function of the frequency between 10^2 and 10^6 Hz using an Agilent E4980A impedance analyzer (USA).

3. Results and discussion

3.1. The effect of SMA on the microstructures of graphene/PS nanocomposites

Interfacial properies of polymer nanocomposites are crucial for their microstructure and properties [6,26]. The good compatibility of SMA with PS and graphene sheets makes it suitable for enhancing the interfacial interaction and improving the dispersion of the sheets. Fig. 1 shows the microstructures of G–PS and SG–PS nanocomposites. Slight graphene aggregates with protruded clean surfaces are observed in the G–PS nanocomposite (Fig. 1a); while well exfoliated and homogeneously dispersed graphene sheets are closely covered with a thin polymer layer and an interconnected graphene network is formed in the presence of SMA (Fig. 1b). The dispersion of graphene in different systems is further confirmed with TEM images (Fig. 1c and d). Compared to the aggregated graphene sheets in G–PS nanocomposite, graphene sheets are uniformly dispersed in the matrix as almost individual sheet, suggesting the formation of interconnected network for electron transportation. The distinct microstructures indicate that the interfacial interaction between graphene and PS matrix is obviously improved by SMA. The π–π stacking between PS and the graphitic surface of graphene and the polar interaction of the residual oxygen functionalities on graphene with the polar anhydride groups of SMA are responsible for the differences. The enhanced interfacial interactions between graphene and PS with SMA are confirmed by FT-IR spectra (Fig. 2e). The peak assigned to the C=O stretching vibration shifts from 1735.5 cm^{-1} for G–PS to 1737.0 cm^{-1} for SG–PS, and further to 1744.3 cm^{-1} for G–SMA [27], which may result from the polar interaction of the residual oxygen functionalities on graphene with the polar anhydride groups of SMA. Similar encapsulated microstructure was obtained in carbon nanotube/polyamide 12 nanocomposites with SMA as the compatibilizer [21,22].

3.2. Rheological properties of graphene/PS nanocomposites

As rheological properties of polymer composites are closely related to the dispersion quality, aspect ratio of fillers and their interactions with polymer chains [28,29], it is imperative to explore the effect of the interfacial compatibility on the rheological response of polymer composites. Fig. 2a and b shows the evolution of G' with time during the dynamic time sweeps of G–PS and SG–PS nanocomposites at a fixed frequency of 10 rad/s. Both PS and PS/SMA blend exhibit good thermal stabilities during the rheological measurements, evidenced by the small changes of G' less than 2% even after a waiting time over 7200 s. Note that the melt of PS/SMA blend shows similar G' in value to the neat PS melt. This result is different from the SMA-modified carbon nanotube/polyamide 12 nanocomposites, where G' is significantly increased due to the reactive coupling between the amine end groups of polyamide 12 and the maleic anhydride groups of SMA [21,22]. Therefore, the effect of interactions between PS and SMA on the rheological variations of SG–PS nanocomposites could be ignored.

The presence of SMA clearly improves the G' of the PS nanocomposites. With 0.46 vol.% of graphene, the G' of G–PS nanocomposite is very close to that of neat PS while that of the SG–PS nanocomposite is much higher due to the effective role of SMA in improving the dispersion of graphene sheets and their interfacial interaction with PS. In addition, the variation trend of G' with annealing time is also affected by SMA. The value of G' rises with the time at the later stage of the annealing for a given specimen, which follows a power law scaling ($G' \propto t^\beta$), where β is the logarithmic time-dependent exponent [30–34]. Compared to the β value of the G–PS nanocomposite with 0.46 vol.% of graphene, that of the SG–PS nanocomposite with