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Preparation of exfoliated graphite/polystyrene composite by polymerization-filling technique

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Abstract

A composite based on exfoliated graphite (EG) and polystyrene was prepared by a polymerization-filling technique. With augmentation of filled EG, the molecular weight of polystyrene in the resulting composite increased and the molecular weight distribution decreased. The glass transition temperature of the polystyrene was determined by dynamic mechanical analysis (DMA) and showed that it increases to 123.74°C. The thermal degradation behavior of the composite was studied using thermogravimetry (TG) and showed a higher thermal stability than that of pure polystyrene and polystyrene/EG composite prepared by melt-blending. The DC conductivity of the composites prepared by the polymerzation-filling technique and melt-blending, respectively, were measured. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Exfoliated graphite; Polystyrene; Thermal and electrical properties

1. Introduction

Conducting polymer composites are of great interest from a practical point of view, because their electrical properties can be tailored by properly choosing the components and their relative concentration. Of the various methods, the formation of conducting polymer composites by melt-blending is the most straightforward. But due to the absence of specific interfacial interaction, the mechnical properties are often drastically reduced. Polymerization-filling technique is a new way to produce polyolefin-based composites with remarkbly improved perfomances [1]. By this method, composites are produced in a single step as the olefin is polymerized by a coordination catalyst anchored on the surface of filler. One of the main targets of the polymerization-filling method is homogeneity of the final composites and the combination of high impact strength, ductile fracture, and high modulus that can be achieved by this method. The mentioned properties have been sought in composites for a long time.

Exfoliated graphite (EG) has excellent conductivity which can be obtained by exfoliation of graphite intercalate [2]. EG flakes have an accordion-shaped appearance and the expansion along the *c*-direction can be as much as two orders of magnitude when the intercalate is heated over a critical temperature. As a conductive filler, EG has been incorporated successfully into polymer matrix by mechanically mixing [3], static melt dispersion mixing [4] or in situ exfoliation [5]. These composites have many important uses, such as electrode material [6], electrical and thermal conductors [7,8], sealing material [9]. More recently, Shiratori and his coworkers [10] prepared a poly(methyl methacrylate) (PMMA) encapsulated EG composite by polymerization of methyl methylacrylate in the presence of EG. The composite could be directly molded by hot press and the electrical conductivity and the shielding effect for electromagnitic interference of the molded product were superior to those of the EG–PMMA composite made by mechanical mixing. This paper is concerned with the preparation of EG/polystyrene composite by the polymerization-filling technique and the melt-blending method. The thermal and electrical properties of the composite were studied in detail.

2. Experimental

The expandable graphite (supplied by Bao Ding Lianxin Carbide Ltd.), which was prepared with H_2SO_4 as an intercalant and HNO_3 as an oxidant, with average particles 300 μm in size were dried at 60°C for 12 h to remove any moisture before heat treatment. Heat treatment was performed by inserting a steel crucible containing ca. 2 g

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of expandable graphite powders into the furnace held at a constant temperature of 800°C and being kept for 30 s in an air atmosphere. Expansion and exfoliation occurred during the heat treatment. Styrene was purified according to the usual method. Benzoyl peroxide (BPO) was purified by recrystallization before usage. General polystyrene, POLYREX, was purchased from Nanhai Polymer Co.

A procedure for the preparation of EG/polystyrene composite by polymerization-filling technique is described below. Styrene (50 ml) was put into a four-necked flask. To this, first, 0.6 wt% BPO was added as initiator and stirred until the BPO dissolved completely. Then a filler of EG (expansion volume is 210 cm^3/g) amounting to 1–50% of the calculated weight of the filled polymer composite was loaded into the reaction vessel. After stirring for 10 min in a nitrogen atmosphere at ambient temperature, the reaction mixture was kept stirring for 4 h at 85°C in a water bath. The temperature was then raised to 150°C in an oil bath and the mixture was stirred for 2 h. The floating system was then centrifuged and the solids were dried at 60°C in vaccum for 24 h and the EG/polystyrene complex was obtained. As a control, EG-filled polystyrene composite was prepared by blending EG and polystyrene at 170°C on a two-roll mill.

To isolate polystyrene from the composite prepared by polymerization-filling technique, the composite was dispersed in tetrahydrofuran and the dispersion was filtered. The molecule weight of polystyrene was measured by gel percolation chromatography. The precipitate was extracted with tetrahydrofuran by using a Soxhlet apparatus until no more polymer could be detected in the refluxing solvent. The percentage of grafting was determined by the following equation:

$$\text{Grafting (\%)} = \frac{\text{Polymer grafted (g)}}{\text{Graphite charged (g)}} \times 100\%$$

Dynamic mechanical analysis (DMA) was carried out on a TA Instruments DMA-2980 with a three-point bending geometry at a frequency of 1 Hz and at a heating rate of 4°C/min from 30°C to the temperature at which the sample loses its dimensional stability. Thermogravimetry (TG) was carried out on a TA Instruments TGA-2050 at a heating rate of 10°C/min in nitrogen atmosphere. When the volume resistivity of the samples was lower than $10^3\ \Omega$, it was measured using the four-probe instrument and when it was beyond this value, high resistivity meter was used.

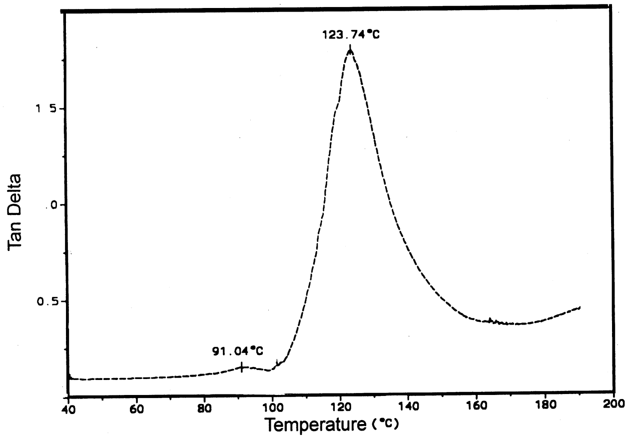

Fig. 1. The temperature dependence of the loss factor tan δ of the polymerization-filled EG/polystyrene composite.

Table 1
The effect of the amount of filled EG on the molecular weight and molecular weight distribution of polystyrene

	Amount of EG (%)		
	2.78	5.56	11.11
M_n	53 092	57 346	56 621
M_w	123 441	184 617	260 446
Polydispersity index	2.33	3.23	4.60

3. Results and discussion

For the radical polymerization of styrene, the molecular weight and molecular weight distribution of polystyrene synthesized in the presence of 2.78, 5.56 and 11.11% EG are shown in Table 1. It is clear that with increment of the amount of filled EG the M_w of polystyrene increases and the distribution of molecular weight widens. Similar results were also reported by Ignatov et al. [11].

The effect observed is caused by reduced contributions of the side process, which resulted in the termination of polymer chain growth. As EG has a good affinity for styrene, monomers absorbed by EG polymerize on the surface of EG and the process of the growth of the macromolecular chain occurs on the EG surface or in its vicinity. The interfacial interaction between EG and styrene limits the diffusion of styrene, which leads to a reduction in the termination of polymer chain growth. With increase in the amount of EG, the total surface of EG increases and the termination of polymer chain growth reduces substantially.

In the composite prepared by polymerization-filling technique, the grafting percentage of polystyrene on EG is 61.5%. Due to the relative high percentage of grafting, interfacial interaction between EG and polystyrene is strong, which brings about some changes in the thermal behavior of polystyrene. Fig. 1 shows the temperature dependence of loss factor tan δ of the polymerization-filled composite. Peaks appear at 91.04 and 123.74°C corresponding to two glass transition temperatures of the polystyrene chain. Moreover, the intensity of the peak at 123.74°C is much stronger than that at 91.04°C.

TGA curves of general polystyrene and EG/polystyrene composites prepared by the polymerization-filling and melt-blending method, respectively, are shown in Fig. 2. The

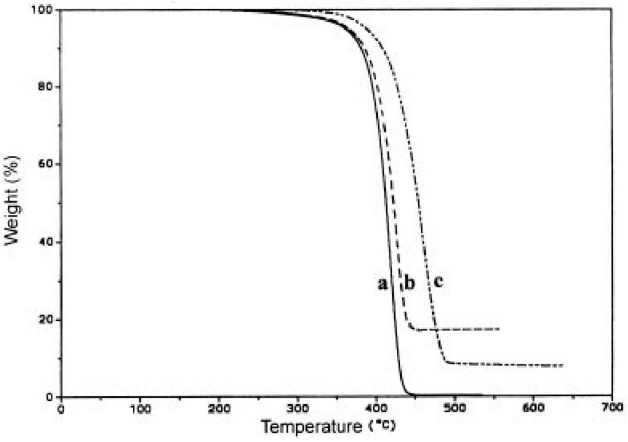

Fig. 2. TGA curves for: (a) polystyrene; and EG/polystyrene composites prepared by (b) melt-blending; and (c) polymerization-filling.

onset of degradation temperature for polystyrene and melt-blended composite is similar and the thermal stability of the melt-blended composite is only slightly improved when EG was incorporated. For comparison, the decomposition temperature of the polymerization-filled composite is 28.66°C higher than that of polystyrene. This improvement in the thermal stability of the composite should be ascribed to the heat shielding effectiveness derived from EG.

The volume resistivity of the polymerization-filled composites as a function of the amount of filled EG is shown in Fig. 3. For comparison, the data of the corresponding melt-blended composites are shown as a reference. When 2.5 wt% of EG was incoporated into polystyrene, the volume resistivity of the polymerization-filled composite is 14 magnitudes lower than pure polystyrene, then with the increase in the amount of EG; the volume resistivity of the composite decreases slowly. This phenomenon demonstrates that the percolation threshold in conductivity of the polymerization-filled composite is lower than 2.5 wt%. However, the volume resistivity of the melt-blended composites decreases with the increase in the amount of EG, but no sharp decrease appears until the amount of EG reaches 20 wt% (see Fig. 4). The difference in conductive behavior of the composite prepared by polymerization-filling and melt-blending methods should be ascribed to the structural difference between the two kinds of composites. In the polymerization-filled composites, EG layers are interconnected to form conductive nets, polystyrene chain lies in the interspace of the nets (see Fig. 5a). However, in the melt-blended composites, during the process of mixing, the action of scissoring force derived from the mill destroys the EG nets and then EG layers disperse in the polystyrene matrix (see Fig. 5b),which leads to a relatively higher percolation threshold of conductivity.

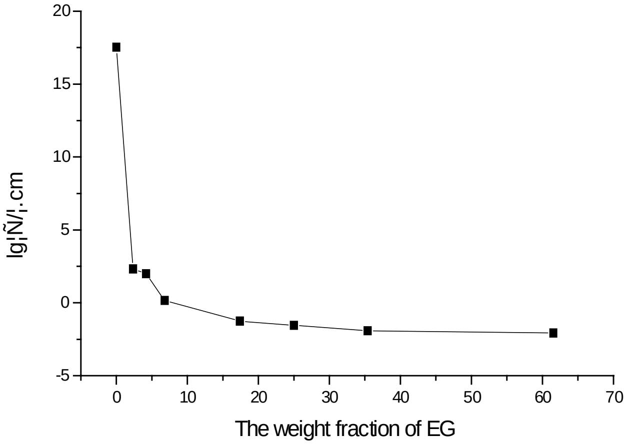

Fig. 3. Relationship between volume resistivity of polymerization-filled EG/polystyrene composite and the weight fraction of EG.

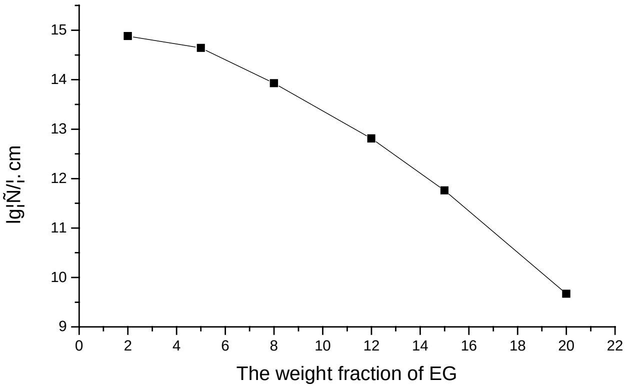

Fig. 4. Relationship between volume resistivity of the melt-blended EG/polystyrene composites and the weight fraction of EG.

4. Conclusions

EG/polystyrene composite has been prepared by the polymerization-filling technique. With increase in the amount of EG, the molecular weight of polystyrene increases and the molecular weight distribution widens. DMA demonstrates that two glass transition temperatures of polystyrene chain block appear at 91.04 and 123.74°C, respectively. The decomposition temperature of the polymerization-filled composite is 28.66°C higher than that of polystyrene, but the thermal stability of the melt-blended composite is only slightly improved when EG was incorporated. Composite prepared by the polymerization-filling technique has a conductive percolation threshold lower than 2.5 wt%.

Acknowledgements

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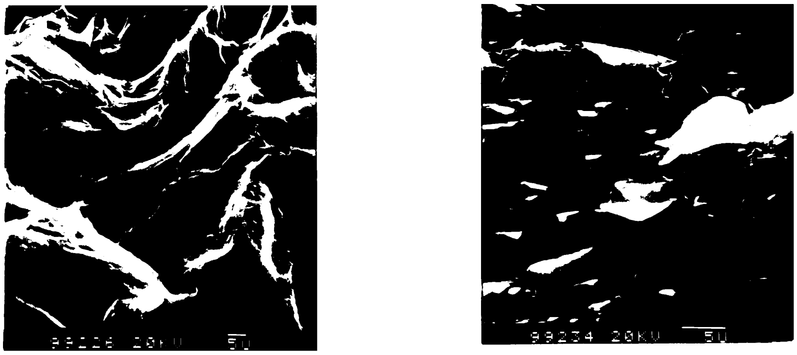

（a） (b)

Fig. 5. SEM micrographs of the EG/polystyrene composites prepared by: (a) polymerization-filling; and (b) melt-blending method.

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