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Synthesis and properties of polystyrene/graphite nanocomposites

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Abstract

In this paper, graphite/polystyrene nanocomposite is synthesized by in situ polymerization of styrene in a tetrahydrofuran (THF) solution system of potassium (K)–THF–graphite intercalation compound (GIC). K–THF–GIC has proved to initiate polymerization of styrene by the anionic mechanism. Due to the interfacial interaction between the graphite nanolayers and the polymer, the composites exhibit higher glass transition temperature and higher thermal stability when compared to polystyrene. The percolation threshold in the conductivity of the composites is lesser than 8.2 wt% and the dielectric constant can reach as high as 136.

Keywords: Graphite intercalation compounds; Polystyrene; Nanocomposite

1. Introduction

During the past few years, much attention has been paid to polymer/layered silicate nanocomposites [1–5]. Layered silicates usually have very high aspect ratios (width-to-thickness). Once some layered silicates are uniformly dispersed in a polymer matrix, the properties of the polymer matrix can be largely improved.

Like layered silicates, the natural flake graphite (NFG) is also composed of layered nanosheets. Moreover, it is a good electrical conductor with an electrical conductivity of 10^4 S/cm at room temperature. Carbon atoms in a graphite layer are tightened by covalent bonds, while those positioned at adjacent planes are bound by much weaker van der Waals force. This weak interplanar force allows certain atoms, molecules and ions to intercalate into the interplanar spaces of the graphite. Although more than 100 kinds of graphite intercalation compounds (GICs) have been synthesized, only a few polymer/graphite nanocomposites have been reported because organic molecules are hard to be directly intercalated into the graphite. However, organic monomers can be cointercalated into some kinds of GICs or absorbed by some related graphite materials, thus the polymer/graphite nanocomposites can be synthesized by subsequent polymerization of the monomers. In our previous work, polymer/graphite oxide intercalation compounds were synthesized, and then the polymer/graphite nanocomposite was obtained by the reduction of graphite oxide [6–8]. Exfoliated graphite (EG), which can be obtained by the rapid heating of H_2SO_4–GIC, contains a large number of pores with their sizes ranging from 10 nm to 10 μm and the wall thickness between the pores is also in the nanoscale. Monomers can be absorbed into the pores of EG and be subsequently polymerized to form polymer/graphite nanocomposites. Composites thus formed exhibit good electrical conductivity [9,10]. Recently, Shioyama et al. [11] reported the preparation of delaminated polymer/graphite nanocomposite by the reaction of alkali metal–GICs with the vapor of unsaturated hydrocarbon. Their interest focused on the reaction site and reaction activity, with less attention being paid to the properties of the polymer/graphite nanocomposite.

In this work, polystyrene/graphite nanocomposite was synthesized by in situ polymerization of styrene in a ternary K–THF–GIC solution system. Thermal and electrical properties of the composite were studied in detail.

2. Experimental

2.1. Materials

NFG (grain size 120 mesh, purity 99%) was supplied by Bao Ding Lianxin Carbide. Potassium metal (chemical grade) was used as purchased. THF was dried over potassium hydroxide, refluxed over sodium and naphthalene until the solution turned dark green, and then distilled under

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nitrogen before use. Styrene was dehydrated with molecular sieve 4 and was purified by vacuum distillation.

2.2. Preparation of K–THF–GIC

Stage-1 K–THF–GIC was prepared as follows [12]. NFG and potassium metal in large stoichiometrically excessive amount were added to THF solution containing naphthalene, the concentration of which was 0.2 mol/l, and stirred in a sealed flask at room temperature for 3 days. The reaction products were filtered and washed by THF.

2.3. Synthesis of polystyrene/graphite composite

The prepared K–THF–GIC was quickly added to a round-bottom Pyrex flask containing freshly distilled THF. The flask was evacuated and sealed to maintain vacuum. Purified styrene monomer was then injected into the flask while stirring. Polymerization was carried out at room temperature for 3 h. The reaction product was precipitated in alcohol and dried.

2.4. Characterization of polystyrene/graphite composite

The molecular weight distribution of polystyrene in the composite was determined by gel permeation chromatograph (Waters 991). The microstructure of polystyrene/graphite composite was examined by TEM. Samples were microtomed with a diamond knife to obtain ultrathin (about 60 nm) sections for TEM. Thermogravimetric analysis was performed on a NETZSCH-Gerätebau thermogravimetric analyzer (TG209). Samples of about 5 mg were heated to 600 °C with a heating rate of 10 °C/min under nitrogen atmosphere. DSC curves were obtained using a TA Instruments Ltd product (DSC-2910). Samples of about 10 mg were initially heated to 200 °C and cooled to room temperature to eliminate thermal history, and then heated to 180 °C with a heating rate of 20 °C/min. The whole thermal scanning was conducted under nitrogen atmosphere. As for the electrical conductivity measurement is concerned, when the volume resistivity of the sample was lesser than $10^3\ \Omega$, it was measured by a four-probe instrument and when it was beyond this value, high resistivity meter was used. Dielectric constant of the composites was measured through an S914 Dielectric Test Fixture combined with an AS2851 Q meter over a frequency of 50 kHz and a capacitance of 25 mH.

3. Results and discussion

3.1. The mechanism for the polymerization of styrene initiated by K–THF–GIC

The polystyrene/graphite composite here was prepared by in situ polymerization of styrene initiated by K–THF–GIC. When styrene monomer was injected into the flask containing THF solution of K–THF–GIC, the evolution of heat and increase of viscosity was immediately observed. The known reaction scheme for the polymerization of styrene initiated by aromatic radical-anions such as potassium naphthalene is as follows: the naphthalene anion-radical transfers an electron to styrene to form the styryl radical-anion, which dimerizes to form the dicarbanion. Then anionic propagation occurs at both carbanion ends of the styryl dianion [13]. Polystyrene is obtained with a narrow molecular weight distribution, which is characteristic of momentary initiation and formation of 'living' polymer (living polymerization). As K–THF–GIC is somewhat similar in structure to potassium naphthalene, we assume that the polymerization of styrene initiated by K–THF–GIC proceeds through an anionic mechanism similar to that initiated by potassium naphthalene. The increase in the molecular weight of the polymer on introducing additional amounts of styrene proved our assumption (Fig. 1).

However, Fig. 1 showed that the molecular weight distribution of the polystyrene initiated by K–THF–GIC is not as narrow as that of polystyrene initiated by aromatic radical-anions. In curve I, there is a small tail in the low molecular weight range, and in curve II, there appear two peaks. This can be explained by the heterogeneous characteristic of the catalyst in the reaction system. The anions on the surface of the graphite layers can initiate styrene, once the styrene monomer is injected into the flask. Due to spatial hindrance, it takes some time for the styrene to intercalate into the interlayer space of the graphite and to be initiated by the anions in the interlayer spaces. This delay resulted in a small tail in the low molecular weight range in curve I. As for the double peaks in curve II, it is obvious that the left peak is

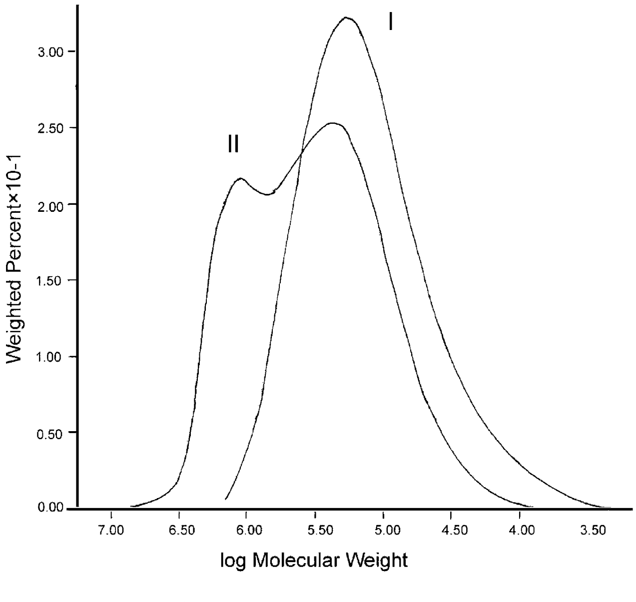

Fig. 1. GPC curves of polystyrenes initiated by K–THF–GIC. (I) 0.06 mol styrene was added to 40 ml THF containing 0.04 mol/l K–THF–GIC and the reaction lasted for 2 h and (II) 0.06 mol styrene was added to 40 ml THF containing 0.04 mol/l K–THF–GIC. After the reaction system was stirred for 2 h, an additional 0.06 mol styrene was added and stirred for another 2 h.

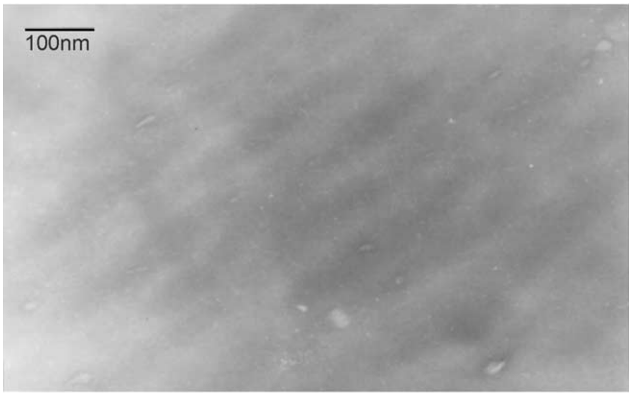

Fig. 2. TEM of polystyrene/graphite nanocomposite.

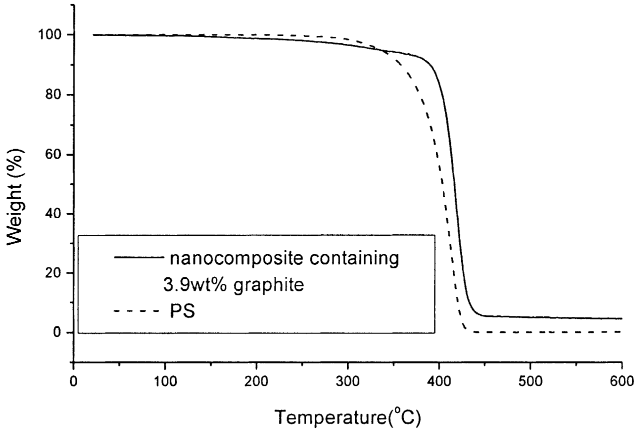

Fig. 3. TGA curves of polystyrene/graphite nanocomposite and polystyrene.

due to the resumed propagation of the polymer chain induced by the secondly introduced styrene at the end of the original polystyrene living chains, while the right peak is due to the initiation of the secondly introduced styrene by the unreacted anions deep inside the interlayer of the graphite.

3.2. Structure of polystyrene/graphite composite

Fig. 2 shows the TEM micrograph of polystyrene/graphite composite. The dark bands shown in the figure correspond to graphite layers. The graphite layers dispersed in the polystyrene matrix with thickness less than 100 nm, the orientation of the graphite nanolayers reflects the initial stacking arrangement of the layers of pristine NFG. It is shown that in this K–THF–GIC initiated styrene polymerization system, styrene can intercalate into the interlayer space of the graphite and be initiated by the anions in the interlayer space. However, due to the high activity of the anions on the surface of graphite layers, most styrene was polymerized on the surface of graphite. Some styrene polymerized in some of the interlayer space of the graphite, caused the graphite to exfoliate into lamellae with thickness less than 100 nm.

3.3. Thermal performance of the polystyrene/graphite composite

The thermal decomposition behavior of both polystyrene and polystyrene/graphite nanocomposite is shown in Fig. 3. The onset degradation temperature of the nanocomposite is 20 °C higher than that of polystyrene. The nanocomposite has higher thermal stability compared to polystyrene. This might result from the interaction between polystyrene and graphite lamellae. The graphite layers enhance the thermal stability of polystyrene.

Fig. 4 shows the DSC results of both polystyrene and polystyrene/graphite nanocomposite. The glass transition temperature of the nanocomposite is 5 °C higher than that of polystyrene. This indicates that there is a strong interaction between the polymer matrix and graphite layers at the interface, and due to this, mobility of the polymer segments near the interface become suppressed.

3.4. Electrical properties of the polystyrene/graphite nanocomposite

The volume resistivity of the polystyrene/graphite nanocomposites as a function of the mass percentage of the graphite is shown in Fig. 5.The volume resistivity decreases with increase in the amount of graphite in the composite. When the amount of graphite reaches 8.2 wt%, the volume resistivity of the nanocomposite is lower than that of polystyrene by 16 orders of magnitude. As the amount of graphite increases, the volume resistivity of the composite decreases slowly. This phenomenon demonstrates that the percolation threshold in the conductivity of the polystyrene/graphite nanocomposite is lesser than 8.2 wt%.

The variation of dielectric constants of the polystyrene/graphite nanocomposite with the mass percentage of the graphite is shown in Fig. 6. The dielectric constants of the composites increase sharply with increase in the mass

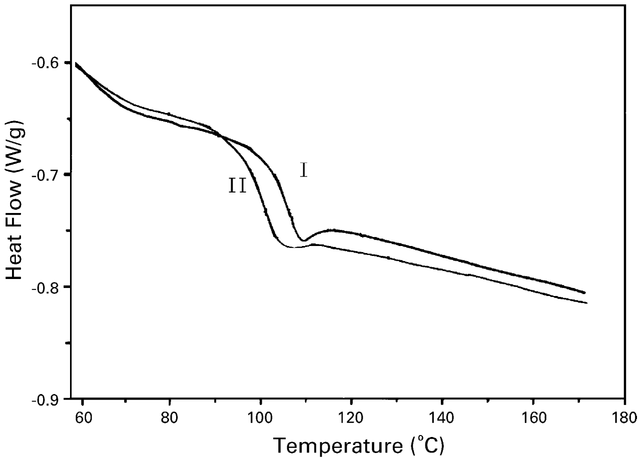

Fig. 4. DSC curves of: (I) polystyrene/graphite nanocomposite and (II) polystyrene.

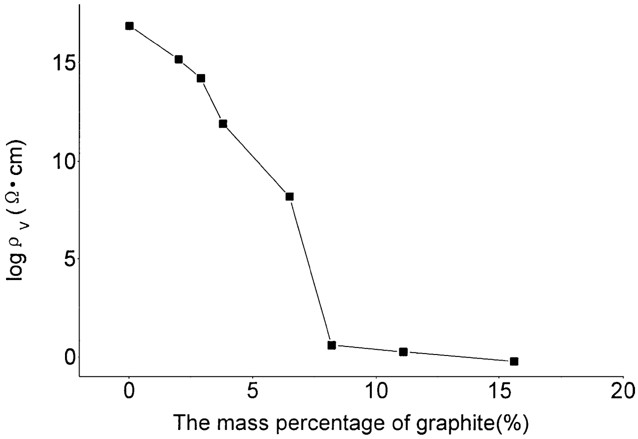

Fig. 5. Variation of volume resistivity ratio of the polystyrene/graphite composites with the mass percentage of graphite.

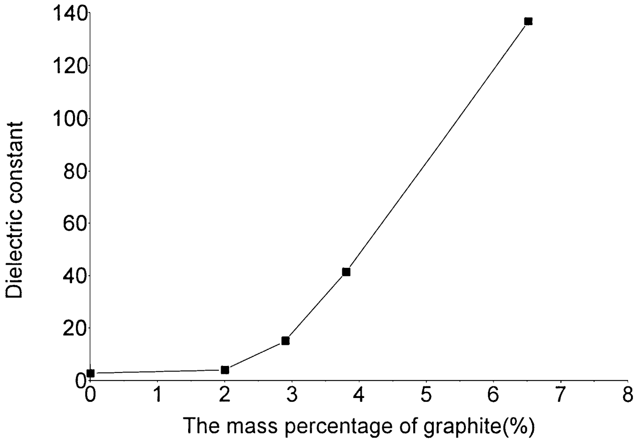

Fig. 6. Variation of dielectric constants of the polystyrene/graphite composites with the mass percentage of graphite.

percentage of the graphite in the composites. It reaches 136 when the mass percentage of the graphite is 6.5 wt%, which is 48 times that of polystyrene. It is obvious that well dispersed graphite nanolayers in the polystyrene matrix contribute to the good electrical conductivity and high dielectric constant of the composites, which cannot be obtained by simply mixing graphite with polystyrene.

4. Conclusions

Graphite/polystyrene nanocomposite is made by in situ polymerization of styrene in a THF solution of K–THF–GIC. K–THF–GIC has proved to initiate polymerization of styrene by the anionic mechanism. TEM micrograph shows that the graphite layers are dispersed in the polystyrene matrix of thickness lesser than 100 nm. Due to the interfacial interaction between the graphite nanolayers and the polymer, the composites exhibit higher glass transition temperature and higher thermal stability when compared to simple polymer. The T_g and the onset thermal degradation temperature of the composite are 5 and 20 °C higher than that of polystyrene, respectively. The percolation threshold in the conductivity of the composites is lesser than 8.2 wt%. The dielectric constant of the composites increases sharply with increase in the mass percentage of the graphite in the composites. It reaches 136 when the mass percentage of the graphite is 6.5 wt%.

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