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Investigation of dielectric and thermal conductive properties of epoxy resins modified by core-shell structured PS@SiO_2

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ABSTRACT

In this study, the core-shell structured polystyrene@SiO_2 (PS@SiO_2) microspheres were successfully synthesized by tetraethylorthosilicate (TEOS) hydrolysis method. The synthesized PS@SiO_2 microspheres were subsequently characterized by FTIR spectroscopy, XRD, SEM, and TEM respectively. The results indicated that the particle size of PS@SiO_2 microspheres is about 2 μm, and the PS microsphere is uniformly coated by amorphous SiO_2 shell. PS@SiO_2/cyanate ester (CE)/epoxy resin (ER) composite films were prepared with PS@SiO_2 microspheres as fillers and morphology of the films was inspected by AFM. The images showed that the PS@SiO_2 microspheres were well-distributed in epoxy matrix. Thermal conductivity of PS@SiO_2/CE/ER composite increases 131% by adding 1.0 wt% of PS@SiO_2 microspheres. The volume resistivity of composites decreased with increasing of the loading of PS@SiO_2 fillers and still keeping an excellent insulating performance. In addition, the dielectric constant as well as the dielectric loss of composites increased with the increased the content of PS@SiO_2 microspheres.

1. Introduction

During the past decade, the polymer/inorganic composite microspheres have attracted considerable scientific and technical interest because such these hybrid particles can possess combined properties of both incorporated inorganic materials and base polymers [1–3]. The addition of inorganic spherical particles to polymers allows the modification of the polymers physical properties as well as the implementation of new features in the polymer matrix. The composites have many applications in many fields, for example, aerospace structures, dielectrics, aircraft, and others requiring special materials [4]. Surface modification of fillers with core-shell structures in polymer/inorganic composites can greatly enhance performance of composites, such as electrical, dielectric and thermal conductivity [5].

A lot of excellent research works were reported related with core-shell polymer/inorganic composites. For example, Li et al. synthesized high-quality and stable polystyrene (PS)/TiO_2 core-shell microsphere colloidal crystals and the results exhibited that these colloidal crystals were gifted with higher mechanical stability than TiO_2 microspheres [6]. Liang et al. prepared TiO_2-coated coarse nylon and polyethylene particles composite abrasives, which can help to improve the attenuation of the UV spectrum as compared with pure TiO_2 [7]. Fang et al. reported a novel-shell structured PS/Fe_3O_4 microbeads was prepared by a facile method to improve magnetorheological (MR) properties [8]. Their results showed that MR performance of the PS/Fe_3O_4 microbeads could improve greatly because of a smaller density presented. Mu et al. also reported a non-rigid core-shell structured PS/SiO_2 composite abrasives were synthesized successfully and the results showed that the composite abrasives exhibited lower surface roughness, lower topographical variations as well as less scratches and residual particles than that of pure SiO_2 abrasives [9].

Epoxy resin systems are used in high voltage transformers, cable terminations, bushings, power apparatus, or insulation for X-ray tubes. The interpenetrating networks of co-cured cyanate ester (CE) with epoxy resin (ER) have excellent dimensional stability, resistance to irradiation, low dielectric constant and low out gassing property due to its wide range of physic-chemical, electrical, and thermal properties [10,11]. Meanwhile, ER is one of the most kindly used thermosetting polymers applied in structural adhesives, surface coatings, engineering composites, and electrical laminates [12]. Several properties of ER could be improved by modifying with co-reactive the component CE, which possess excellent dielectric, thermal, and mechanical characteristics, low water absorption property, good heat and radiation resistance, and low volume shrinkage [13]. The thermal conductivity of

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polymer composites such as CE/ER is an important property for many applications, but still widely unexplored [14]. Due to the fact that CE/ER exhibits a rather low thermal conductivity, it is of certain interest to obtain an enhancement for some applications.

Herein, in this study, core-shell structured PS@SiO_2 particles were chosen as fillers in ER in order to enhance the thermal conductivity and improve the dielectric properties of polymer composites. The core-shell structured PS@SiO_2 microspheres were synthesized by TEOS hydrolysis method and were characterized by FTIR, SEM, XRD, and TEM. The morphology, dielectric and thermophysical properties of PS@SiO_2/CE/ER composites were investigated in detail.

2. Experimental

2.1. Synthesis of PS@SiO_2 core–shell microspheres

Firstly, 0.17 g polystyrene (PS) (Suzhou SmartyNano Technology Co., Ltd.) emulsion (36.3% solid content), 0.6 ml ammonia solution, 0.5 ml deionized water and 20 ml ethanol were added to a 100 mL flask equipped with a magnetic stirrer at room temperature. Then, TEOS (1.5 ml) was added dropwised to the above solution and stirred for 30 min. The reaction was performed with vigorously stirring at 35 °C for 6 h. The PS@SiO_2 composite microspheres were obtained by centrifuged and washed several times with water and ethanol, and then dried at 80 °C for 4 h.

2.2. Preparation of PS@SiO_2/CE/ER composite

The calculated PS@SiO_2 microspheres were separately dispersed into 15 g Bisphenol A based Epoxy Resins (ER, Laizhou Baichen Insulating Materials Co., Ltd.) and sonicated for 30 min. 15 g 2,2-Bis-(4-Cyanatophenyl) propane (CE, Zhejiang Shangyu Chemical Co., Ltd.) were heated at 160 °C for 15 min with vigorous stirring. Then, the temperature was decreased to 100 °C. Finally, PS@SiO_2/ER mixtures were mixed with CE until the mixture was stirred to form homogeneous liquid for 0.5 h.

2.3. Preparation of cured PS@SiO_2/CE/ER composite

Firstly, a preheated mold with silicon coating on the inner surface was heated at 120 °C for 1 h. The pre-polymer was poured into the preheated mold with silicon coating on the inner surface. Secondly, the prepolymer was degassed at 120 °C for 0.5 h in a vacuum oven. Finally, the pre-polymer was cured via the following procedure: 150 °C/1 h + 180 °C/1 h + 200 °C/2 h + 220 °C/2 h, and post-cured at 240 °C/4 h.

2.4. Measurements and characterization

The particle size and morphology were visualized by using a FEI Quanta 600 FEG scanning electronic microscope (SEM) and a FEI Tecnai G2 F20 S-TWIN transmission electron microscope (TEM). The morphologies of core-shell microspheres in composite films were examined by atomic force microscope (AFM, Bruker Dimension Icon; operated in the peakforce QNM mode at 0.8 Hz scanning rate). The broadband frequency dielectric properties of the composites were measured using a Concept 80 impedance analyzer (Novocontrol, Germany) over the frequency range of 10^{-1} to 10^6 Hz. All samples were prepared by fracturing the composites at liquid nitrogen temperature and then sputter-coated with a homogeneous gold layer to avoid accumulation of charges. The thermal diffusivity (δ) and specific heat (C) were measured on disk samples by using a LFA447 light flash system (NETZSCH, Selb, Germany) at 25 °C. The bulk density (ρ) of the specimen was measured by water displacement. The thermal conductivity (λ, $W{\cdot}m^{-1}{\cdot}K^{-1}$) was given by the product of the thermal diffusivity (δ, $mm^2{\cdot}s^{-1}$), specific heat (C, $J{\cdot}g^{-1}{\cdot}K^{-1}$), and bulk density ($\rho$, $g{\cdot}cm^{-3}$):

$$\lambda = \delta \cdot C \cdot \rho$$

The volume resistance (R_V) of the samples was measured by an Agilent 6517B high resistance meter after obtaining the thickness of these composites pellets. The voltage and current limits were set at 1.0 V and 5 mA for all samples. Broadband dielectric spectrum test system (concept 80, Novocontrol technologies, Germany) was used to collect the dielectric data at room temperature.

3. Results and discussions

Fig. 1a shows the FT-IR spectra for PS microspheres and as-prepared PS@SiO_2 particles. It is showed that benzene ring folding appeared at ca. 695 cm^{-1}, C—H bending of the benzene ring at ca. 757 cm^{-1}, C—C stretching of the benzene ring at ca. 1497 cm^{-1} and ca. 1599 cm^{-1} and C—H stretching of the benzene ring at

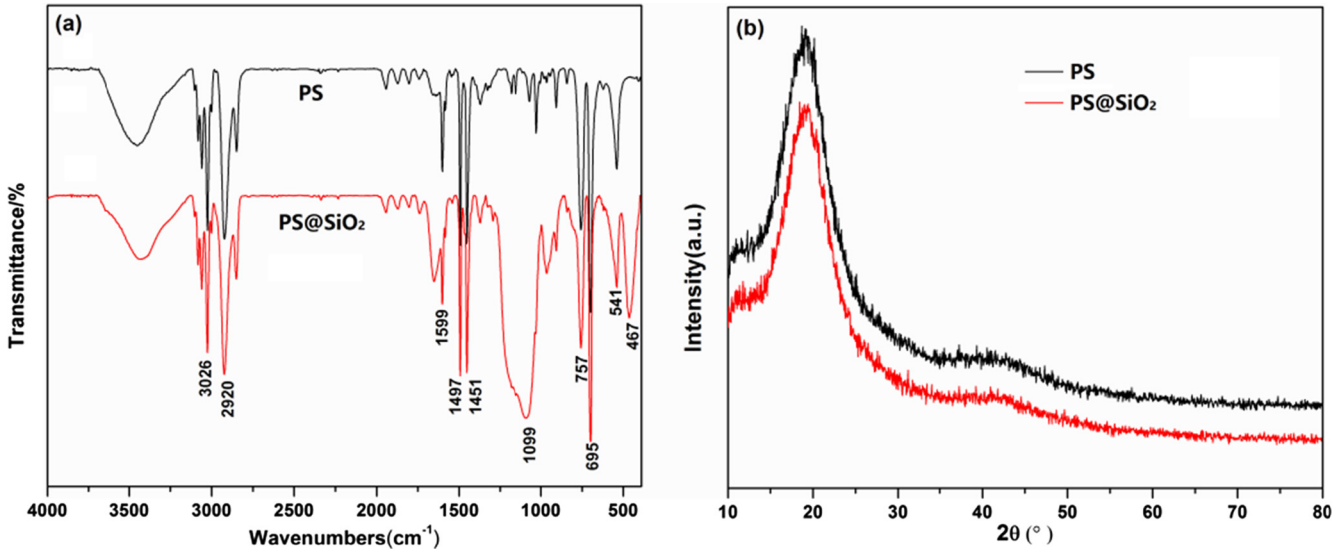

Fig. 1. FTIR spectrum (a) and XRD patterns of PS microspheres and core-shell PS@SiO_2 microsphere. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)