Co-continuous structural polystyrene/poly(vinylidene fluoride) nanocomposites with high dielectric constant and magnetic properties

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ABSTRACT

The effect of selective localization and surface modification of iron (Fe) nanoparticles on the dielectric and magnetic properties of polystyrene/poly(vinylidene fluoride) (PS/PVDF) composites with co-continuous structure was systematically studied. The carbon nanotubes (CNT) were used as co-filler with fixed content in PVDF phase to increase the dielectric properties. The modified Fe nanoparticles (*p*-Fe) were successfully prepared by coating the PS on the surface of Fe nanoparticles, which presented a good dispersion in the polymer matrix. The X-ray diffraction and fourier transform infrared spectroscopy results of composites show CNT and Fe/*p*-Fe nanoparticles have the nucleation effect on β phase of PVDF. Meanwhile, the selective localization of Fe nanoparticles in PS phase produce a high dielectric constant (ε) and the effect of selective localization of *p*-Fe nanoparticles in the ε is stronger than that of Fe nanoparticles and restrains the increase of dielectric loss. The composites with the selective dispersion of 4 vol% Fe nanoparticles filled in PS phase have the highest saturation magnetization than the other three. The difference of real part (μ′) of the complex magnetic permeability of the composites can be ignored and the value of μ' have low frequency dependence. This work could shed some light on the better optimization of such polymer composites.

1. Introduction

The composites including nanoparticles and polymer matrix have attracted increasing research focus on the development of dielectric and magnetic properties, which have potential applications use in microwave absorption devices, future communication system, electronic devices, high-density magnetic storage media, et al. [1–6]. Magnetic nanoparticles are used as filler in the composites to achieve dielectric and magnetic properties for the composites [7–10]. Among these fillers, iron (Fe) nanoparticles used as filler in polymer composites have attracted increasing attention in material fields due to their high saturation magnetization and magnetic permeability at room temperature [11]. However, the Fe nanoparticles used as filler in polymer composites have limitation for the improvement of the dielectric properties of the polymer composites. For example, in the oleylamine-coated Fe/epoxy resin (Fe/ER) system, the dielectric constant (ε) of the composites with 20 vol% fillers is ca. 9 at 100 Hz, and the biggest value of ε in Fe@Fe$_x$O$_y$/ER system is ca. 13 at 100 Hz [12,13]. On the other hand, the high density and large specific surface area of Fe nanoparticles cause serious aggregate phenomenon in polymer matrix,

which restricts the practical application of Fe/polymer composites. One effective method to solve this problem is to modify the surface of Fe nanoparticles [14–17].

The introduction of electrically conductive fillers is an effective method to improve the ε of polymer composites. For example, Y. Yang et al. studied the dielectric properties of polyimide (PI) embedded with CaCu$_3$Ti$_4$O$_{12}$ (CCTO)/Ag nanoparticles (CCTO@Ag), their results show the dielectric constant of PI/CCTO@Ag composites is significantly increased to 103 (100 Hz) at 3 vol% filler loading.[18] Q. G. Chi et al. studied the dielectric properties of ferroferric oxide (Fe$_3$O$_4$)-deposited nanosized CCTO/PI (nano CCTO-Fe$_3$O$_4$/PI) hybrid film, the result shows a high dielectric constant of 308 and relatively low dielectric loss of 0.60 at 100 Hz are simultaneously achieved when the content of nano Fe$_3$O$_4$ was only 12 vol% [19]. On the other hand, our previous works have reported the carbon tube (CNT) and Fe$_3$O$_4$ used as co-fillers can be adjusted the dielectric and magnetic properties of the poly(vinylidene fluoride) (PVDF) nanocomposite films with triple-layer structure [20]. Besides, Tsonos et al. reported the incorporation of Fe$_3$O$_4$ inclusions in the PVDF composites with CNT loading well above the percolation threshold gradually increase both electrical

conductivity and dielectric permittivity [21]. Therefore, the addition of CNT used as co-filler is a viable method for the improvement of dielectric properties of polymer composites.

In addition, the dispersion of co-fillers in the matrix is crucial for the properties of composites. Controlling the selective localization of fillers in different phases is beneficial to improve the dispersion of co-fillers in binary immiscible polymer blends with co-continuous morphology. Designing and preparing the polymer blends with co-continuous structure became an important method for the preparation of polymer composite with superior properties [22–24]. For example, Zhao et al. studied the dielectric, thermal and mechanical properties of the polymer composites with co-continuous structure by controlling the selective localization of CNT [22].

In this work, polystyrene (PS) and PVDF were used as polymer matrix and formed the co-continuous structure with the volume ration of 1:1 by mixing method. The CNT was used as conductive filler with the fixed content and Fe nanoparticles were used as magnetic filler. The effect of the selective localization and surface modification of Fe nanoparticles on the dielectric and magnetic properties of polymer composites have been investigated. This work could shed some light on the better optimization of such polymer composites.

2. Experimental

2.1. Materials

PVDF (Solef 6008) pallets with density of 1.78 g cm^{-1} were purchased from Shunjie plastic rubber Technology Co. Ltd. (China). PS (666D) pallets with density of 1.05 g cm^{-1} were purchased from Sinopec Beijing Yanshan Co. (China). CNT with density of 2.10 g cm^{-1} and inner diameter of 5–10 nm, outer diameter of 10–20 nm, and 10–30 μm in length were purchased from Chengdu Organic Chemicals Co. Ltd. (China). Fe nanoparticles with diameter of ca. 70 nm were purchased from Shanghai Chaowei Nanotechnology Co. Ltd. (China). Styrene (GR), chloroform (AR), methylbenzene (AR), potassium persulfate (AR) and cetylpyridinium chloride (AR) were purchased from Beijing Chemical Plant (China).

2.2. Preparation of the modified fe nanoparticles

Styrene was used to coat Fe nanoparticles. The synthesis procedure was described as follows: 5 g Fe nanoparticles were added in 100 mL aqueous solution containing 0.35 g cetylpyridinium chloride under mechanical stirring for 1 h. Then 0.5 g styrene was added to the solution and the stirring was run at 35 °C for 24 h to make sure the adsorption of styrene onto the surface of Fe nanoparticles. Afterwards, 0.03 g potassium persulfate was added in the obtained solution and the temperature raised 70 °C, and kept 24 h to initiate the polymerization reaction. The obtained nanoparticles were washed several times with methylbenzene, ethanol and deionized water, respectively. Finally, the obtained nanoparticles were dried in an oven at 60 °C and denoted as *p*-Fe.

2.3. Preparation of the PS/PVDF@CNT, PS/PVDF/CNT/Fe and PS/PVDF/CNT/p-Fe composites

Prior to use, all polymers were dried at 80 °C for 24 h under vacuum. A Haake mixer was employed for the melt blending. The volume ration of PS and PVDF was 1:1 in all composites. The prepared process of PS/PVDF@CNT composites is presented as follows: Firstly, PVDF was mixed with different volume ratios CNT at 190 °C and 120 rmp for 20 min, the obtained composites were denoted as PVDF@CNT. Secondly, the PVDF@CNT composites were further mixed with PS pellets at 190 °C and 120 rmp for 2 min. The obtained composites were denoted as PS/PVDF@CNT, which represents the CNT in PVDF phase. The preparation process of PS@Fe/PVDF@CNT and PS/

PVDF@CNT@Fe composites is presented as follows. PS or the obtained PVDF@CNT were mixed with Fe nanoparticles with different contents at 190 °C and 120 rmp for 20 min, the prepared composites were denoted as PS@Fe and PVDF@CNT@Fe, respectively. Then the obtained PS@Fe composites were further mixed with PVDF@CNT and PVDF@CNT@Fe composites were further mixed with PS pellets at 190 °C and 120 rmp for 2 min, the prepared composites were denoted as PS@Fe/PVDF@CNT and PS/PVDF@CNT@Fe, which represent the CNT in PVDF phase, and the Fe nanoparticles in PS phase and PVDF phase, respectively. The PS/PVDF@CNT@*p*-Fe and PS@*p*-Fe/PVDF@CNT composites were prepared with a similar procedure to the PS/PVDF@CNT@Fe and PS@Fe/PVDF@CNT composites. In addition, the PS/PVDF blends without filler were prepared for comparison.

2.4. Extraction of PS phase in PS/PVDF blends

The PS phase was extracted in order to observe the co-continuous structure of PS/PVDF blends. Samples of 0.1–0.2 g were immersed in large volume of chloroform and magnetic stirred gently at room temperature for 12 h to selectively extract the PS phase, and then the samples were dried and weighted. The procedure carried out several times until the mass of the samples was constant and indicted the PS phase was extracted completely.

2.5. Characterization

Thermal gravimetric analysis (TGA) measurements was carried out on a SDT Q600 analyzer with the sample mass of 10 mg and a heating rate of 10 °C/min under nitrogen protection in temperature range from 30 to 800 °C. The Fourier transform infrared (FTIR) spectra were measured by KBr disc method with a Nicolet 6700 spectrometer over the range of 500 to 4000 cm^{-1} for the Fe and *p*-Fe nanoparticles. The FTIR spectra of the film samples were recorded in ATR mode over a range of 650–1500 cm^{-1}. X-ray diffraction (XRD) measurements were performed on a DMAXRB 12 Kw diffractometer (Rigaku, Japan) with the K ray of Cu (the wavelength is 0.15406 nm). The scanning voltage and current were 40 kV and 150 mA, respectively. The measured 2θ range was 10–40° with a scanning interval of 0.02° and scanning rate of 10° min^{-1}. Morphologies of the composites were characterized by scanning electron microscopy (SEM S4700, Hitachi, Japan) with an accelerating voltage of 20 kV. The samples were fractured in liquid nitrogen and then the fractured surface was sputtered with gold. Dielectric properties of the samples were performed by Agilent 4294 A impedance analyzer in the frequency ranges from 10^2 to 10^6 Hz at room temperature. Both sides of samples in disc shape with area of ca. 1 cm^2 and thickness of ca. 1 mm were coated with silver as electrodes before testing.

For the magnetic hysteresis loops measurement, the samples with mass of ca. 20–40 mg were measured on a Vibration Sample Magnetomerer (BKT-4500Z, Beijing Zetian Technology Co. Ltd., China) at room temperature. For the magnetic permeability measurement, the cylindrical samples with an outer diameter of ca. 20 mm, inner diameter of ca. 6 mm, and thickness of ca. 5 mm were measured on an Agilent 8361A Network Analyzer over the frequency range of 1 MHz to 1 GHz at room temperature.

3. Results and discussion

3.1. Characterization of Fe and p-Fe nanoparticles

Fe nanoparticles are coated by styrene in order to improve the dispersion of Fe nanoparticles in polymer matrix. Fig. 1(a) shows the FTIR spectra of Fe and *p*-Fe nanoparticles. The strong band at 500–600 cm^{-1} is corresponding to Fe-O stretching vibration. Compared to Fe nanoparticles, two peaks at ca. 1500 cm^{-1} in the spectrum of *p*-Fe can be clearly observed, which are associated with the aromatic C=C