



Enhanced dielectric properties of poly(vinylidene fluoride) composite filled with polyaniline-iron core-shell nanocomposites



Tian Chen*, Bo Liu

College of Materials Science and Technology, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, China

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ABSTRACT

Iron powder (IP) was modified by silane coupling agent to form coupling agent functionalized iron powder (CIP). Then surfactant polyvinylpyrrolidone was adsorbed onto the surface of CIP. Finally, the aniline was polymerized onto CIP surface. Polyaniline (PANI) shell was formed on metal iron surface and it was verified by transmission electron microscopy (TEM) characterization. The PANI-CIP core-shell nanoparticles were used as fillers within poly(vinylidene difluoride) (PVDF) to prepare the (PANI-CIP)-PVDF dielectric composites. The dielectric constant of (PANI-CIP)-PVDF was obviously larger than that of IP-PVDF composite. 20%-(PANI-CIP)-PVDF showed high dielectric constant of 72.35 at 0.1 Hz, which was almost 3.5 times larger than that of 20%-IP-PVDF.

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1. Introduction

Ever-increasing energy requirements and the exhaustion of fossil fuels demand the search for sustainable and renewable resources. Low-cost and environmentally friendly energy conversion and storage systems, such as batteries, fuel cells, electrochemical capacitors, and dielectric-based capacitors, are constantly being developed recently. Dielectric-based polymer capacitors, which store energy electrostatically and possess an intrinsic high power density due to their very fast energy uptake and delivery, have attracted much attention and thus hold great promise for the generation of high performance power electronics [1–4]. However, most pure polymers are still obviously unsuitable for dielectric capacitor applications because of their intrinsic low dielectric constant values [5,6]. To overcome these problems, significant efforts have been carried out to fabricate the polymer-based dielectric materials with high dielectric constant.

Proper selection of fillers of different types and shapes can help in greatly improving the dielectric performance of the polymer nanocomposites [3]. Generally non-conducting and conducting fillers have been employed to synthesize high dielectric constant polymer-based nanocomposites [4]. Non-conducting fillers include ceramics like barium titanate (BaTiO_3), lead zirconate titanate ($\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$), copper calcium titanate ($\text{CaCu}_3\text{Ti}_4\text{O}_{12}$), et al. [7,8].

Conducting fillers like nanometals and nanocarbons are also widely used [9–12]. By the use of conducting fillers, comparatively higher values of dielectric constant can be easily achieved at low concentrations in comparison to non-conducting fillers.

Recently, core-shell nanoparticles with dielectric shells are ideal candidates to be used as fillers in polymer nanocomposites [13–15]. They provide not only a barrier layer between the fillers and matrix but also the possibility of tuning the dielectric properties. Based on the above expounding, the core-shell PANI-CIP nanocomposites were prepared by in-situ polymerization with the intermediary of polyvinylpyrrolidone (PVP) upon the coupling agent functionalized iron powder in this paper. We expect this particular core-shell structure nanocomposites can endow flexible electroactive PVDF with fine dielectric performance. The effects of the core-shell structure of polyaniline coated Fe nanoparticles on the dielectric properties of the PVDF composites were discussed here briefly.

2. Experimental

2.1. Materials

Nano iron powder, coupling agent γ -(2,3-epoxypropoxy) propyltrimethoxysilane (KH560), PVP, aniline, and ammonium persulfate were supplied by Sinopharm Chemical Agent Co., Ltd. PVDF was supplied by Shanghai 3F new Materials Tech Co., Ltd.

* Corresponding author.

E-mail address: chentian@nuaa.edu.cn (T. Chen).

2.2. Preparation of PANI-CIP

The synthesis of polyaniline-coated coupling agent functionalized iron powder (PANI-CIP) core-shell nanocomposite divides into three main steps (shown in Fig. 1). Firstly, the surfaces of nano iron powders were functionalized by silane coupling agent KH560. The typical functionalization process is as follows: 5 g of nano iron powder were added to 50 mL deionized water. Then 0.2 g KH560 was added to the nano iron powder-water mixing solution with for the grafting reaction for 4 h under mechanical stirring at room temperature. Coupling agent functionalized iron powders (CIP) were prepared after drying the above mixing solution. Secondly, the surfaces of coupling agent functionalized iron powders were modified by PVP surfactant. The typical adsorption process is as follows: a certain proportion of CIP and PVP (5 g CIP and 0.15 g PVP) were mixed in water under mechanical stirring then the surface adsorption process was made. Finally, the PANI-CIP nanocomposites were synthesized by in-situ chemical oxidative polymerization of aniline with ammonium persulfate as oxidant and hydrochloric acid as dopant at low temperature. The typical polymerization process is as follows: 0.5 mL of aniline was dissolved in 30 ml of distilled water containing 0.5 mL hydrochloric acid (1 M) aqueous solution. The mixed solution was cooled to 0 °C in ice bath. Then the solution was added into the CIP-PVP mixture solution. After that 5 mL of ammonium persulfate (1 g) aqueous solution was slowly added into the mixed solution under mechanical stirring. The mixture was stirred for 24 h and the temperature was kept at 0 °C in ice bath. After magnetic separation the solids were washed with distilled water and anhydrous ethanol for several times. The final products were then dried at 60 °C under vacuum for 24 h.

2.3. Preparation of (PANI-CIP)-PVDF and IP-PVDF

Polyaniline-coated iron powder/poly(vinylidene fluoride) and iron powder/poly(vinylidene fluoride) composites were prepared using solution cast method as described in our previous reference [16].

2.4. Characterizations

Fourier transform infrared (FT-IR) spectra were measured on Nicolet NEXUS 470FT-IR spectrometer. TEM images were taken by a FEI Tecnai G2 transmission electron microscope. The dielectric properties were obtained by a Novocontrol broadband dielectric/impedance spectrometer.

3. Results and discussion

We measured the FT-IR spectra of bare iron nanoparticles and core-shell structure nanoparticles. For the sample of bare iron nanoparticles (IP), the curve exhibited a ferrihydrite-like spectral feature with bands from surface hydroxyl groups (at 3400–3550 cm^{-1}), indicating surface hydroxylation of these iron nanoparticles. After coating, all the iron-induced signals were hidden by the bands from KH560, PVP and PANI. The spectrum of PANI-CIP nanoparticles showed absorption bands at 3430 cm^{-1} (the N–H bond stretching), 1577 cm^{-1} and 1491 cm^{-1} approximately (the C=C stretching deformations of quinoid and benzenoid stretching rings), the C–N stretching of secondary aromatic amine (1296 and 1252 cm^{-1}), 1097 cm^{-1} (–C≡N stretching of quinoid ring), and 820 cm^{-1} (C–H bending vibration) [17]. From the IR spectra of PANI-CIP we could also see that the absorption peaks at 2943 cm^{-1} and 2841 cm^{-1} ascribed to asymmetry stretching vibration, symmetry stretching vibration of C–H (KH560, PVP).

The TEM images of PANI-CIP were shown in Fig. 2. Due to PANI coating on the iron nanoparticles, the core-shell surface morphologies were obvious and clear. From Fig. 2b–d we could see that the PANI-CIP nanocomposites had typical sphere-like structures with rough surfaces, and the nano spheres were separated well from each other. The excellent core-shell structure nanoparticles were successfully prepared due to several reasons. Firstly, we used the KH560 coupling agent and PVP surfactant. The organic molecular could sterically hinder the aggregation of magnetic iron nanoparticles. Secondly, the interactions between PANI and KH560 coupling agent and PVP surfactant could avoid the aggregation of PANI, which was advantageous to the formation of PANI shell onto nano iron particles, and could enhance the physical stability of core-shell structure nanocomposites. The aniline monomers showed uniform growth upon the surface of functionalized iron nanoparticles. The reaction mechanism of core-shell structure of PANI-CIP composite was the typical “grafting from” mechanism [14].

It is well-known that the high surface energy of nanoparticles restricts the uniform dispersion of the fillers within the polymer. Surface modification of nanofillers can greatly reduce the surface energy of nanofillers while improving their dispersion to achieve required high dielectric performance [3]. Thus we measured the frequency-dependent dielectric properties of both IP-PVDF and (PANI-CIP)-PVDF composites at room temperature and at the frequency of 10^{-1} – 10^7 Hz. Fig. 3 showed the dielectric properties of the IP-PVDF and (PANI-CIP)-PVDF films with the filler contents of 5, 10, and 20 wt%, respectively. Increase in content of the fillers all led to the increase of dielectric constant. The dielectric

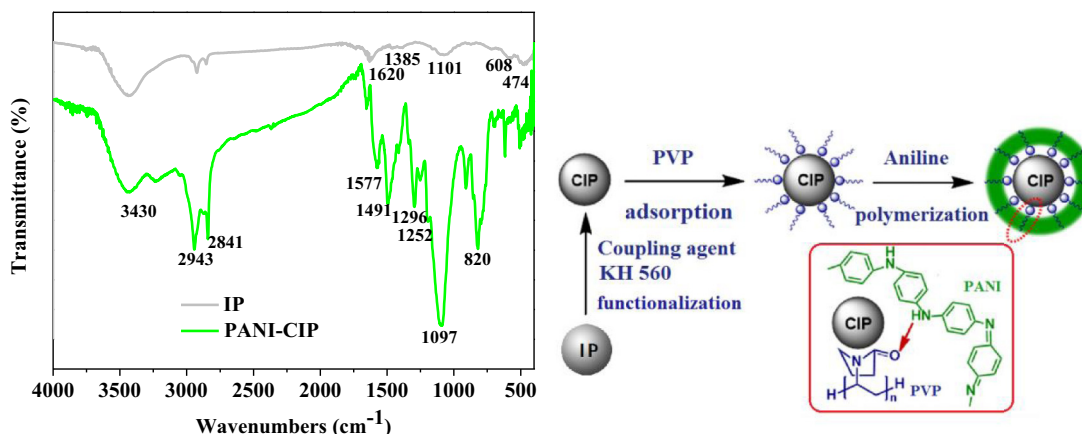


Fig. 1. FT-IR of PANI-CIP and IP (left); Schematic representation of the synthetic process of polyaniline-coated coupling agent functionalized iron powder (PANI-CIP) core-shell composite (right).

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