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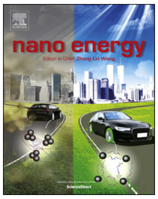

Full paper

Improved dielectric, tensile and energy storage properties of surface rubberized $BaTiO_3$/polypropylene nanocomposites

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ABSTRACT

The low permittivity of the polypropylene (PP) film has become a barrier for the further development of film capacitors with high energy storage density. An advanced strategy of the high-permittivity filler/polymer nanocomposite turns out to be a promising way of solving this problem. In this work, we coated ethylene propylene diene monomer (EPDM) as the shell on the surfaces of $BaTiO_3$ successfully to fabricate core-shell structural nanoparticles. The addition of surface rubberized $BaTiO_3$ into PP matrix promotes the permittivity to about 5.8, while the dielectric loss is barely changed as compared with PP itself. In addition, the elongation at break is as high as 364%, which is over 4 times higher than that of PP. The influences of shell thickness (3 nm, 5 nm and 7 nm) for the nanoparticles and hot-stretching process for the nanocomposite films were also carefully investigated, both of which greatly affected the properties of nanocomposites. Finally, the optimum breakdown strength as high as 370 MV/m is obtained, leading to a maximum energy density of 3.06 J/cm^3, which can be attributed to both high breakdown strength and high permittivity of the core-shell structural $BaTiO_3$/PP nanocomposites.

1. Introduction

Polypropylene (PP) has been applied as the dielectric film in commercial capacitors for dozens of years due to its low cost, ultralow dielectric loss, high breakdown strength as well as excellent mechanical properties [1,2]. As we have known, the permittivity of dielectric film is linearly related to the electric capacity of capacitor. However, because of its low relative permittivity, non-polar PP hinders the further development of film capacitors [3]. It has been well known that introducing high-permittivity (high-k) nanofillers into the polymer matrix to fabricate the nanocomposites shows a promising way of improving dielectric properties [4–6]. However, there are two typical challenges need to overcome for the realization of high-density energy storage nanocomposites. One is the severe aggregation of nanofillers due to their ultrahigh surface energy; the other is the poor compatibility between the polymer matrix and nanofillers. Both of them result in the decline of dielectric properties. To solve these problems, a strategy of preparing core-shell structure nanofillers was proposed for designing high-k nanocomposites, and significant progress has been made in developing nanocomposites with enhanced dielectric properties [7]. Huang and Jiang suggested that this strategy made it possible to prepare a polymer shell which possessed similar chemical structures with the polymer matrix [8].

For example, they functionalized poly(vinylidene fluoride-cohexafluoropropylene) [PVDF-HFP] with glycidyl methacrylate (GMA) through atom transfer radical polymerization (ATRP), and then grafted it onto the surfaces of the $BaTiO_3$ (BT) nanoparticles to fabricate core-shell structure BT nanoparticles [9]. The PVDF-HFP-GMA/BT nanocomposites exhibited an improved dispersion state as compared with the untreated BT/PVDF-HFP nanocomposites. And the results demonstrated that both the permittivity and energy density of the PVDF-HFP-GMA/BT nanocomposites increased greatly as a function of filler content. They also coated a shell of poly(pentafluorophenyl acrylate) (PPFPA) by in situ reversible addition–fragmentation chain transfer polymerization onto the $Ba_{0.7}Sr_{0.3}TiO_3$(BST) nanowire [10]. It was demonstrated that the addition of PPFPA@BST led to lower dielectric

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loss, higher breakdown strength and improved charge-discharge efficiency of the PPFPA@BST/PVDF-HFP nanocomposites. Thus choosing a proper shell turns out to be a key factor for the core-shell structure strategy [11–14].

When PP was applied as the polymer matrix, the introduction of core-shell structure BT nanoparticles also showed remarkable improvement of dielectric properties. Zhu et al. used polyhedral oligomeric silsesquioxane (POSS) as the shell of BT nanoparticles, and the results demonstrated that POSS@BT/PP nanocomposites not only decreased the dielectric loss but also enhanced the breakdown strength as compared with the BT/PP nanocomposites. As a result, the maximum energy density of POSS@BT/PP nanocomposites with 10 vol% filler was about 2.4 J/cm^3 at 360 MV/m [15]. They also fabricated high-k nanocomposites successfully through the in situ polymerization approach to the oxide-coated Al nanoparticles. The as-prepared nanocomposite with 10.4 vol% Al had a permittivity of about 10.5, while still retaining the breakdown strength of 119 MV/m. The resultant energy density reached 14.4 J/cm^3 [1].

In our previous work, we found that the addition of rubbers with proper concentration into the polymer matrix remarkably promoted the breakdown strength [16,17]. It is well known that the breakdown strength (E_b) is very important for the energy storage of dielectrics. For instance, the maximum energy density (W_{max}) of the linear dielectric can be defined as [18]

$$W_{max} = \frac{1}{2}\varepsilon\varepsilon_0 E_b^2 \tag{1}$$

where ε_0 is the vacuum permittivity (8.85×10^{-12} F/m), and ε represents the relative permittivity. The equation demonstrates that the promotion of breakdown strength can effectively improve the energy density. Methyl methacrylate-butadiene-styrene (MBS), a kind of commercial core-shell structure rubber nanoparticles, was introduced into poly(vinylidene fluoride) (PVDF), and an excellent compatibility between them as well as uniform dispersion state were observed [16]. The results showed that the breakdown strength of nanocomposite with 12 vol% MBS was as high as 535 MV/m, which was 1.7 times higher than that of pristine PVDF. Moreover, the polyurethane (PU) in PVDF exhibited the similar dielectric properties. The PU/PVDF composites with 3 vol% filler content had a breakdown strength of 537 MV/m and a maximum energy density as high as 10.36 J/cm^3 [17]. Nan and Shen also demonstrated that the addition of poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) (P(VDF-TrFE-CFE)) with lower modulus of elasticity can improve the breakdown strength of PVDF due to the reduced defects and decreased mobility of the polymer chains [19]. In these rubber/PVDF composites, the enhanced breakdown strength was attributed to the defect modification of rubber for the polymer matrix.

In this work, PP was chosen as the polymer matrix because of its widespread and full-blown applications in the dielectric field. Ethylene propylene diene monomer (EPDM), a kind of rubber, was coated onto the surfaces of BT nanoparticles to fabricate core-shell structure EPDM@BT nanoparticles, which shows improved compatibility and uniform dispersion state in PP matrix. The introduction of EPDM@BT not only improves the permittivity with barely changed dielectric loss but also enhances the breakdown strength of nanocomposites. The hot-stretching experiment also proves the feasibility of preparing dielectric films for EPDM@BT/PP nanocomposites.

2. Experimental section

2.1. Materials

The BaTiO$_3$ (BT) nanoparticles (< 100 nm), 2-bromo-2-methylpropionic acid, CuprousBromide (CuBr) and N,N,N′,N,'N''–pentamethyldiethylenetriamine (PMDETA) were purchased from Shanghai Aladdin Bio-Chem Technology Co., LTD. γ-Aminopropyl triethoxysilane (APS) was obtained from Beijing Shenda Chemical Company. Polypropylene (B8101) was supplied by Sinopec Beijing Yanshan Company. Ethylene propylene diene monomer (EPDM) was obtained from Exxon Mobil Corporation. The solvents including hydrogen peroxide, ethanol, methylene dichloride, toluene and cyclohexane were purchased from Sinopharm Chemical Reagent Co., LTD. All the chemicals were used as-received unless otherwise specified.

2.2. Preparation of core–shell structure EPDM@BT nanoparticles

Hydroxylation for BT nanoparticles: BT nanoparticles (20 g) were putted into 100 mL of an aqueous solution with 30 wt% H_2O_2, and then the mixture was sonicated for 40 min (200 W) to disperse the nanoparticles. The dispersion liquid was refluxed for 9 h at 105 °C in a round-bottomed flask. The treated BT nanoparticles were recovered by centrifugation and washed with deionized water 3 times. Finally, the hydroxylated BT (HO-BT) nanoparticles were dried at 75 °C for 24 h.

Modification of HO-BT by APS: HO-BT nanoparticles (15 g) were putted into 100 mL of toluene and sonicated for 30 min (200 W). Acetic acid was used to adjust the pH value to 3–4, and then the mixture was refluxed at 80 °C for 24 h , while excess APS (10 g) was added slowly through a dropping funnel. The treated BT nanoparticles were recovered by centrifugation and washed with toluene for 3 times. Finally, the APS modified BT (APS-BT) nanoparticles were dried at 75 °C for 24 h.

Fabrication of core-shell structure EPDM@BT nanoparticles: APS-BT nanoparticles (5 g) were introduced into 50 mL of methylene dichloride sonicated for 30 min (200 W). 3 drops of triethylamine as stabilizer and then 1 mL 2-bromo-2-methylpropionic acid was added slowly into the dispersion liquid to react for 2.5 h in an ice-water bath. After that the mixture was putted at room temperature with moderate stirring for 12 h. The treated BT nanoparticles were recovered by centrifugation and washed with methylene dichloride for 3 times. Finally, the Br-APS-BT nanoparticles were dried at 75 °C for 24 h.

For the fabrication of the core-shell structure EPDM@BT nanoparticles, the Br-APS-BT nanoparticles and EPDM were respectively dispersed in cyclohexane by ultrasonication for 30 min, followed by mechanical stirring at 45 °C to dissolve EPDM absolutely. In addition, to prepare EPDM@BT nanoparticles with different shell thickness, the weight ratios of BT/EPDM were settled as 1/0.2, 1/0.5 and 1/0.75. Certain amounts of the two mixtures were poured together and stirred for 24 h at 60 °C with a little CuBr and PMDETA. To remove the unreacted EPDM and EPDM on the surfaces of BT nanoparticles through physical adsorption, the EPDM@BT nanoparticles were purified through the extraction filtration and washed with cyclohexane 5 times. Finally, the EPDM@BT nanoparticles were dried at 75 °C for 24 h.

Preparation of EPDM@BT/PP nanocomposites: Different amounts of EPDM@BT nanoparticles and PP were mixed at 190 °C for 10 min through a torque rheometer. And then the mixtures were hot-pressed to films (~60 μm-thick) at 190 °C with a pressure of 15 MPa using a platen press. In addition, BT/PP, EPDM/PP and BT/EPDM/PP (BT:EPDM = 6:1) nanocomposite films were prepared using the same method for comparison.

Hot-stretching experiment of EPDM@BT/PP nanocomposites: The films were cut into rectangular (4 cm × 2 cm), which were putted into the oven at 170 °C for 5 min. Then the preheated film was stretched slowly to the extension ratios of 1:1, 1:2, 1:3 and 1:4, respectively.

2.3. Characterization

Thermal Gravimetric Analyzer (TGA, SDT Q600) was applied to test thermostability of untreated and treated nanoparticles at a rate of 10 °C/min from 30 °C to 800 °C in the nitrogen atmosphere. The tensile tests were conducted using 3 samples for each composition with CMT4304 tensile testing machine (Zhuhai SUST Electrical Equipment Co., Ltd, China) at room temperature, maintaining a crosshead speed of