Flexible /PET/BaTiO₃/ layer–layer composite film with enhanced dielectric properties fabricated by highly loaded /BaTiO₃/ coating with acrylic resin as binder

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ABSTRACT: Flexible layer–layer poly(ethylene phthalate) (PET)/BaTiO₃ composite films with enhanced dielectric permittivity were fabricated by spin coating method, consisting of PET substrate film layer and modified BaTiO₃/acrylic resin hybrid coating layer. The thickness of coating layer was less than 3 μm (about 2% of PET film thickness), and therefore, the PET/barium titanate (BT) composite films remained flexible even at high volume fraction of BaTiO₃ fillers. The volume contents of BaTiO₃ were varied from 0 to 80%, and the solid contents of BaTiO₃/acrylic resin were in the range of 51.8–72.9%. Scanning electron microscopy showed strong interaction of finely dispersed BaTiO₃ particles with acrylic resin. Morphological profile also displayed uniform coating layer of modified BaTiO₃/acrylic resin and its strong adhesion with PET film. The dielectric constant of the PET/BaTiO₃ composite films increased by about 26% at 60 vol % BaTiO₃ loading when compared with the pristine PET film, whereas the dielectric loss decreased slightly. In addition, PET-grafted poly(hydroxylethyl methacrylate) brushes were used as substrate to introduce covalent bonding with the coating layer. Further enhancement of dielectric constant and reduction of dielectric loss were realized when compared with the composite films with bare PET substrate. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42508.

INTRODUCTION

In the past decades, it has been envisaged fast growth of portable electronics with high speed and powerful capacity which require high energy storage and charge control devices.[1] Capacitor, as one of the key passive devices, is widely used in fields ranging from industrial applications to automobiles, aircrafts, spaces, medical apparatus, and power supply devices.[2,3] Its electrostatic capacitance can be controlled with high precision.[2,4] However, with the trend of the miniaturization and integrated circuits, it is required to develop dielectric materials with high dielectric constant, low dielectric loss, high breakdown voltage, and compatible with the existing integrated circuit process.

Dielectric materials used in capacitor industry could be divided into three types, namely, inorganic ceramic, organic polymer, and inorganic/polymer composites. Inorganic ferroelectric ceramic materials, including BaTiO₃, BaSrTiO₃, and BaxSr₁₋xTiO₃, which have permanent dipole moments offer very high k values in the order of 10^3.[5–7] However, their brittle behavior and high-processing temperature cannot meet the requirements of the current integrated circuit technology, for example, to fabricate embedded capacitors.[8] Polymers are flexible and easy to process; however, their dielectric constants are relatively low. Thus, preparation of ceramic/polymer hybrid composite materials provides a potential route for combining the merits of polymers and ceramics.[9] The idea underlying this composite approach is to integrate complementary elements: high dielectric permittivity from the inorganic fillers and desired flexibility from the polymer matrix.[10] Furthermore, the dielectric characters of ceramic/polymer composites are related to several factors, such as the size of ceramic particles, volume fraction of ceramic filler, dispersion of fillers in the polymer matrix, and the interfacial interaction between filler and matrix.[11,12] Therefore, the efforts to improve the properties of the dielectric performance of the composite materials are also focused on these issues.

Generally, ferroelectric ceramic fillers are in particulate form. Perovskite barium titanate (BT) powder is the one of the most
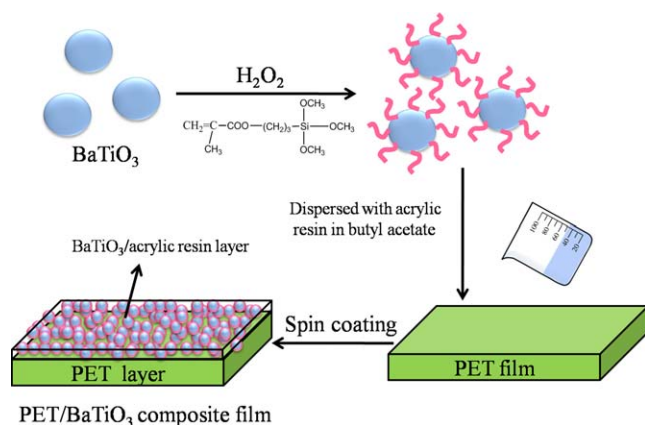
Scheme 1. Schematic illustration of preparing the PET/BT composite films with layer–layer structure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

often used ceramic fillers.[13] BT has two crystal structures, tetragonal and cubic phases, which depend on the sintering temperature and particle size. The former one has higher dielectric constant.[14] The another important factor on the dielectric constant of composites is the volume fraction of ceramic fillers loaded.[15] In general, high dielectric permittivity of the composite film requires high ceramic particles loading, which consequently results in the loss of flexibility and mechanical properties of the composite film. A successful solution to this issue is to use fibrous filler with large aspect ratio. Nan and coworkers[16] demonstrated that the dielectric constant of composites composed of dopamine-modified BT nanofiber and poly(vinylidene fluoride–trifluoroethylene) (PVDF-TrFE) was boosted significantly at much lower volume fraction of fillers when compared with particulate BT. However, the dielectric loss (tan δ) was not improved effectively because of the low surface energy of the fluoropolymers. The fillers modified by hydrocarbon chains cannot totally eliminate filler agglomerations and interfacial defects in nanocomposites.[12] Recently, we reported a facile method to improve the interfacial interaction and thus reduce the dielectric loss of the composite of BT nanofiber and PVDF.[17] BT nanofiber is usually prepared by electrospinning process, which is of cost inefficiency and low productivity. Similar to the other inorganic/organic composites, because of the low surface energy of polymer matrix, the agglomeration of the ceramic fillers in the composite is inevitable and gives rise to high dielectric loss and undesirable dielectric failure at much lower fields.[18] To improve the interfacial interaction, surface modification of the BT particles has been intensively investigated. For example, silane coupling agent–treated $BaTiO_3$/epoxy resin composites and dopamine-modified $BaTiO_3$/PVDF have been reported.[19,20] It was found that the nanocomposites prepared with silane-modified $BaTiO_3$ not only showed homogeneous nanoparticle dispersion but also had a higher dielectric constant when compared with the nanocomposites fabricated with the unmodified $BaTiO_3$.

Surface-initiated controlled radical polymerization is an alternative pathway to fabricate the hybrid ceramic/organic polymer

composites as dielectric materials. Xie et al.[11] prepared a core–shell structured $BaTiO_3$@PMMA (PMMA grafted from the surface of BaTiO3 particles) nanocomposites, and the dielectric constant was increased significantly when compared with the pure PMMA. Maliakal et al.[21] reported the organic/inorganic hybrid material of polystyrene grafting from TiO_2. The results revealed that the dielectric losses of both $BaTiO_3$@PMMA and TiO_2@PS were much higher than those of PMMA and PS. Recently, we synthesized core–shell dielectric nanocomposite by grafting fluoromonomer 1H,1H,2H,2H-perfluorooctyl methacrylate onto the surface of BT nanoparticle (BT@PPFOMA). The dielectric constants of the nanocomposites were increased about three times when compared with the pure PPFOMA.[22] Almost at the same time, Jiang and coworkers[23] also reported that the nanocomposites by blending BT@fluoropolymer nanoparticles with P(VDF-HFP) achieved high energy density and low dielectric loss. These studies first revealed that the dielectric loss of the composite could be significantly reduced by simply grafting a thin layer of fluoropolymer chains onto the BT nanoparticles.

However, the above-mentioned technologies which focused on fabricating bulk composites could not solve the intrinsic problem of requiring high volume fraction of ceramic fillers, which will eventually result in the inferior flexibility of the composite. In this article, we present a new strategy to fabricate flexible composite film with layer–layer structure (as illustrated in Scheme 1). The bottom layer is poly(ethylene phthalate) (PET) film, which is widely used in film capacitor, as flexible supporting substrate.[24] Top layer is a thin composite layer coated with high BT volume fraction (up to 80%) and acrylic resin as binder to offer high dielectric constant. Because the thickness of the composite layer is less than 3 μm, it is expected to have no significant impact on the flexibility of the composite film. In addition, the overall dielectric constant is the sum of the two layers, and thus, this layer–layer composite film could have higher dielectric constant. The results demonstrated that the top surface of the composite film was uniform, crack-free and that the BT/acrylic resin coating layer cannot be peeled off with the 3M tape. The dielectric constant of the composite film was increased to about 26%, and the dielectric loss was slightly reduced when compared with the PET film.

EXPERIMENTAL

Materials
Commercially available PET film with thickness of about 135 μm was extracted with acetone by a Soxhlet extractor for 24 h and then dried at room temperature. BT (HBT-020), tetragonal phase with particle size about 200 nm, was purchased from Shandong Sinocera Functional Material. 3-(Methacryloyloxy)-propyltrimethoxysilane (97%, KH570) was purchased from Alfa Aesar China (Tianjin). Hydrogen peroxide, benzoyl peroxide (BPO), methylmethacrylate (MMA), butyl acrylate (BA), hydroxyethyl methylacrylate (HEMA), and butyl acetate were all analytical-grade reagents and bought from Sinopharm Chemical Reagent, China. Hexamethylene diisocyanate (HDI) was purchased from TCI China and used as received. Deionized water was supplied by a Direct-QTM water purification system of Millipore.

Synthesis of Acrylic Resin

Acrylic resin was synthesized by free radical polymerization with MMA, BA, and HEMA as comonomers and BPO as initiator. First, about 37.5 g butyl acetate solvent was added in a three-necked round flask equipped with a condenser. Then, 15 g MMA, 5.5 g BA, 4.5 g HEMA, and 0.5 g BPO were mixed. About one-third of the mixture was introduced into the flask at the beginning, and the rest part was dropped into the flask in 2 h at 110°C. After this process, the reaction was continued for another 2 h. The solid content of prepared acrylic resin was 56.3 wt %, M_n was 15,100, $M_w/M_n = 1.62$. The composition of the copolymer is 60.9% PMMA, 25.3% PBA, and 13.7% poly(-hydroxylethyl methacrylate) (PHEMA) determined by ^{1}H-NMR.

Surface Modification of BT Nanoparticles

The procedure details and setup of hydroxylating BT fillers have been described in the literature.[25] Briefly, about 10 g BaTiO$_3$ nanoparticles and 80 mL aqueous solution of H$_2$O$_2$ (30 wt %) were added into a round-bottomed flask. The mixture was sonicated for 10 min and refluxed at 105°C for 8 h. Then, the nanoparticles were recovered by centrifugation at 8000 rpm for 5 min and were washed with deionized water for three times. At last, the product (noted as BT-OH) was dried at 80°C in a vacuum oven until it reached a constant weight. Next, the BT-OH was modified with silane coupling agent KH570.[22] About 9 g BaTiO$_3$ and 50 mL ethanol were added into a round-bottomed flask and sonicated for 20 min. Then, 0.09 g KH570 (1% to BT-OH) was added into the mixture and heated at 70°C for 8 h. The nanoparticles were recovered by centrifugation at 8000 rpm for 5 min and washed with ethanol for three times. At last, the product, noted as BT-OH-KH570, was dried at 80°C in a vacuum oven to a constant weight.

Preparation of PET/BT Composite Films

The BT-OH-KH570 and HDI were dispersed in the acrylic resin solution of butyl acetate and homogenized by an IKA T-25 homogenizer. The BT volume ratio in BT/acrylic resin mixture was 20, 40, 60, and 80%, respectively. Thereafter, the dispersion was spin coated onto PET films using a Chemat Technology Spin Coater (Model KW-4A). The parameter was as follows: Speed I and Speed II were 2000 and 4000 rpm, and Time I and Time II were 3 and 30 s, respectively. To ensure the accuracy of the data, an average of more than six pieces of films were taken. Then, the PET/BT composite films were dried at 80°C for 24 h in a vacuum oven. To prepare even and uniform PET/BT composite films, the solid contents (total of BT and acrylic resin) were 72.9%, 64.2%, 57.3%, and 51.8% diluted by butyl acetate solvent at fixed BT loading.

Preparation of PET-g-PHEMA/BT Composite Films

To compare with the pristine PET as substrate to spin coating the BT/acrylic resin, we also checked the PET films with grafted PHEMA (PET-g-PHEMA) brushes as substrate. The preparation of grafted PET film was according to the reported method.[26] First, about 100 μL mixture of monomer HEMA (75 wt %), solvent acetone (25 wt %), and photoinitiator benzophenone (BP, 0.2 wt %) was sandwiched between two PET films and exposed to UV irradiation (1000 W high-pressure mercury lamp, irradiation intensity 8 mW/cm^2 at wavelength 254 nm,

and irradiation time for 30 min). At the end of grafting polymerization, PET films were extracted with acetone by a Soxhlet extractor for 24 h and then dried at room temperature. The final film was noted as PET-g-PHEMA. With the grafted PET film as substrate, BT/acrylic resin with HDI as crosslinker in butyl acetate was spin coated. The coated films were dried at 80°C in air for 24 h. The final films were noted as PET-g-PHEMA/BT composite film.

Characterization

The scanning electron microscopic (SEM) images were recorded using an S-4700 (Hitachi). All samples were prepared by fracturing the composite films in liquid nitrogen and then sputter-coated a homogeneous gold layer. X-ray photoelectron spectra (XPS) were recorded with an ESCALAB250 (VG Scientific) photoelectron spectrometer by the use of monochromatic Al Kα. The molecular weight of acrylic resin was measured by size exclusion chromatography and calibrated with polystyrene standards. Tetrahydrofuran was used as the eluent at a flow rate of 1 mL/min at 30°C. ^{1}H-NMR spectra were recorded on a Bruker AV400 spectrometer, operating at 400 MHz with CDCl$_3$ as solvent. An Agilent 4294A precision impedance analyzer was used to measure the impedance of the PET/BT composite film samples in the frequency range from 40 Hz to 30 MHz with ±0.08% impedance accuracy.

RESULTS AND DISCUSSION

Morphology of Top-View and Cross Section of PET/BT Composite Films

As reported, the dielectric constant, loss tangent, and other properties of nanocomposites are greatly influenced by the compatibility between the organic phase and inorganic phases. To improve the interfacial interaction between ceramic BT fillers and polymer matrix, the coupling agents and dispersants are often used.[27,28] For example, Dang et al.[29] used silane coupling agent KH550 to modify BT particles in BT/PVDF composite. Iijima et al.[20] applied 3-glycidoxypropyltrimethoxysilane to attach epoxy groups on BaTiO$_3$ particles and to improve their compatibility with epoxy resin. In this work, BT particles modified by KH570, the volume fractions of which ranged from 20 to 80 vol %, were used to formulate coatings with acrylic resin for fabricating composite films. Figure 1 presents the surface morphology of the composite films, and Entry (d) was the control run, in which 60 vol % of unmodified BT was loaded. From these images, all the BT particles modified with KH570 except in Entry (e) were dispersed evenly and embedded entirely in acrylic resin. No obvious defects and aggregations were observed even when the volume fraction of BT particles was up to 60 vol % [Figure 1(c)]. From Figure 1(c; inserted), it could be observed that the particles were distributed in the acrylic resin matrix and covered with a uniform polymer coating layer. As a contrast, there were slight aggregations and poor distribution observed from the SEM image of the control sample [Figure 1(d)]. These results indicated that KH570-modified BT particles enhanced interaction between acrylic resin and BT particles, having apparently been improved the dispersibility of BT particles. However, as the BT loading was up to 80 vol %, the particles were crowded together obviously. There were more
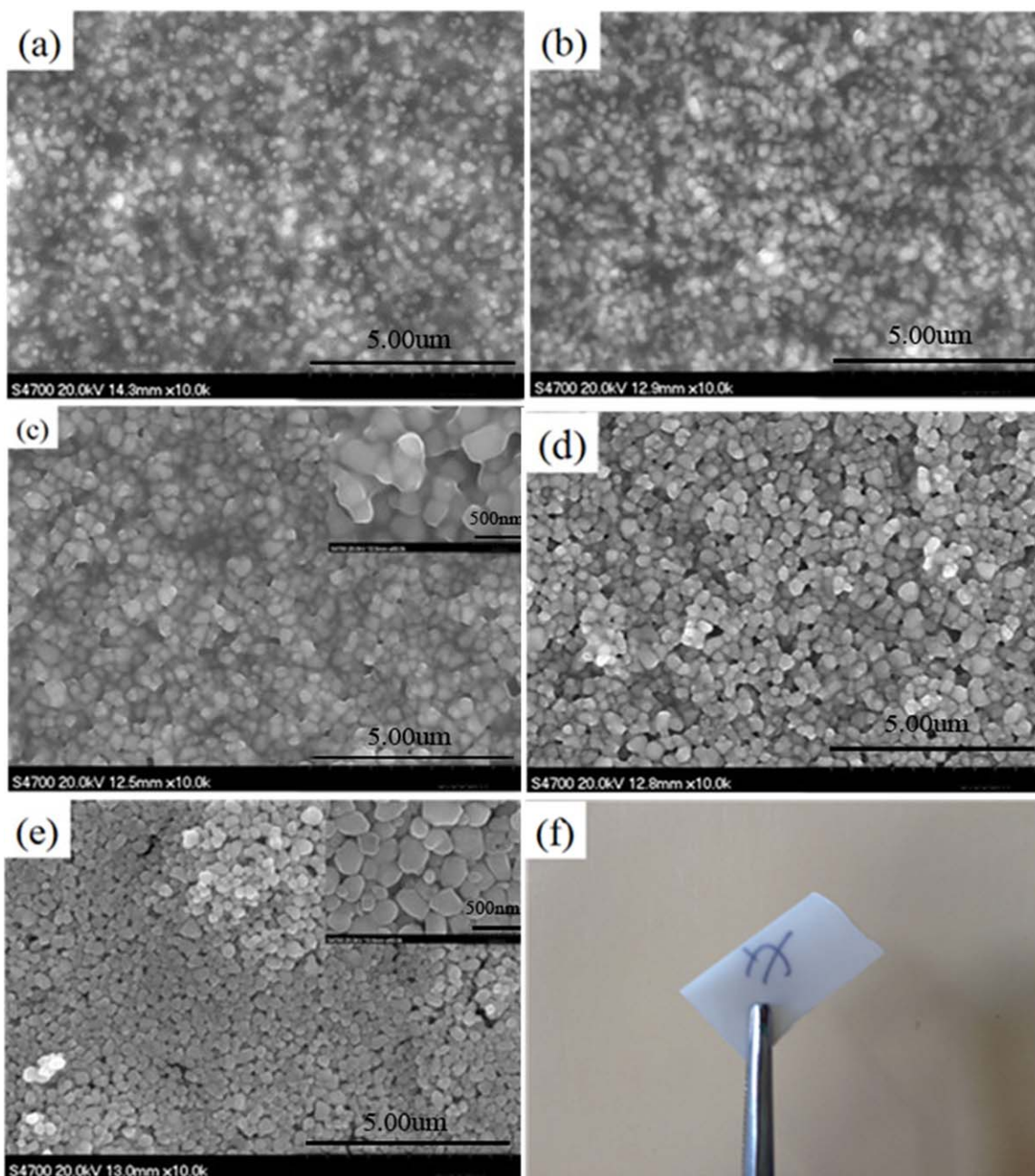
Figure 1. SEM images of the surface topography of PET/BT composite films with (a) 20, (b) 40, (c) 60, and (e) 80 vol % modified BT, (d) 60 vol % unmodified BT, and (e) digital image of the composite film of (c). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

voids and aggregations. In addition, the composite film coated with 60 vol % modified BT was flexible as shown in Figure 1(f).

Figure 2 exhibits the cross-sectional morphologies of PET/BT-coated composite films. Again, it could be observed that the distribution of modified BT nanoparticles in vertical direction was also very uniform. The coated layer was like cement that the BT particles were adhered together via the acrylic resin binder on PET substrates. Figure 2(b) was the coated composite film prepared with the addition of crosslinker HDI, and Figure 2(a) was the control run without it. As shown in Figure 2(b,c) [with

higher magnification of Figure 2(c)], there are some voids and vacancies which were due to the BT particles being pulled out of the BT/acrylic resin coating during the cyrofracturing process. The morphological profile also showed that the coating layer was adhered strongly to the PET film. The thickness of coating layer in Figure 2(a) was about 2.3 μm, less than 2% of the thickness of the PET film.

Dielectric Permittivity of PET/BT Composite Films

The primary parameter of material dielectric properties is dielectric constant.[30] Figure 3(a) shows the dielectric constant
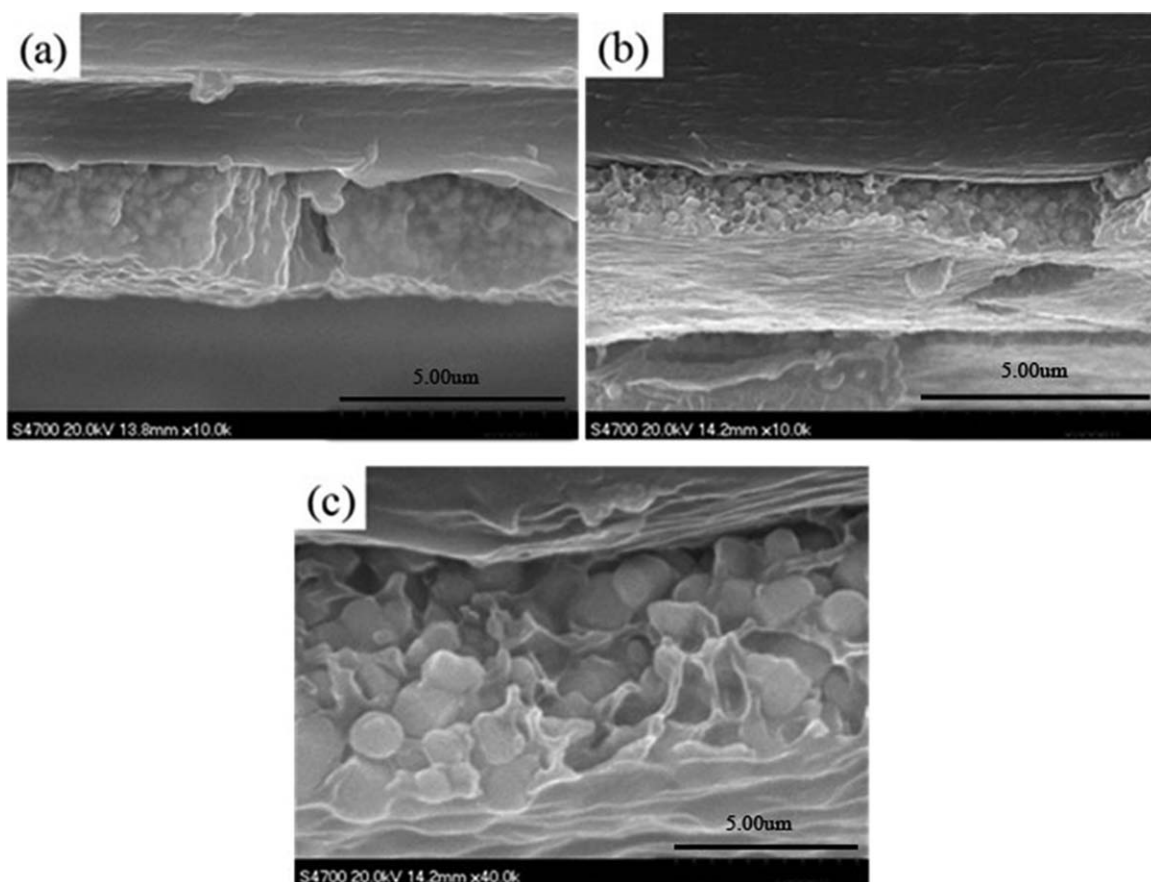
Figure 2. SEM images of the cross section of PET/BT composite films with 60 vol % BT without the addition of HDI (a) and with the addition of HDI at lower magnification (b) and higher magnification (c).

(k) of the PET/BT composite films as a function of frequency, which contained 0, 2, 40, 60, and 80% volume fraction of BT particles modified by KH570. Similar to common dielectric materials, the k values decreased steadily with the increasing of testing frequency.[31–33] The dielectric constant was up to 2.94 at 100 kHz as the BT loaded to 60 vol %, increased to about 26% when compared with the pristine PET film. Considering that the thickness of the coated layer is less than 3 μm, about 2% of that PET film, the significant increasing of the k is attributed to the coating layer in which was incorporated BT particles with higher polarization than that of polymer matrix.[32] As it was reported, the k value could reach maximum at 60 vol % BT modified by 2,3,4,5,6-pentafluorobenzyl phosphonic acid (PFBPA) in PFBPA-BT:P(VDF-HFP) nanocomposite film.[28] Figure 3(a) shows that k increased from about 2.34 to 2.94 as BT vol % increased from 0 to 60%, whereas the k value declined to 2.56 as BT up to 80 vol % at 100 kHz. The k value is related to the polarity of composite films, including dipole polarization and interfacial polarization.[11] When BaTiO$_3$ ceramics respond to the current in an alternating electric field, BaTiO$_3$ will produce induced electric moment and then become a dipole. Each dipole arrange along the direction of electric field, which causes the dielectric polarization.[22] The more BT particles were loaded in the composite, the stronger dipole polarization of the PET/

BT composite films possessed. Claudia et al.[34] used noctylphosphonic acid and PFBPA as surfactants, sodium dodecyl sulfate or BYK-W 9010 as dispersant to inhibit BT particles agglomeration and to improve the dielectric properties of BaTiO$_3$– P(VDF-HFP) nanocomposite films. These two components can increase the relative permittivity by factor 5 when compared with the pure polymer material. In the case of 60 vol % BT fillers, all the BaTiO$_3$ particles were capped by insulating polymer shells and showed homogeneous dispersion in the polymer matrix, which exerted preferable permittivity. What is more, the interfacial interaction between BT particles and acrylic resin was strong, resulting in superior interfacial polarization. These two factors made k value to be increased. However, as BT volume fraction increased from 60 to 80%, the interface and compatibility between inorganic BT fillers and acrylic resin polymer weakened distinctly, leading to the decline of k value.

Figure 3(b) presents the dependence of the dielectric loss (tan δ) of the PET/BT composite films on the testing frequency. Generally, dielectric materials with a large loss tangent tend to dissipate a fraction of their stored energy in the form of heat, which are detrimental to the device performance as thermally facilitated breakdown.[28] So far, it has been reported that the dielectric loss of inorganic/organic polymer composites usually
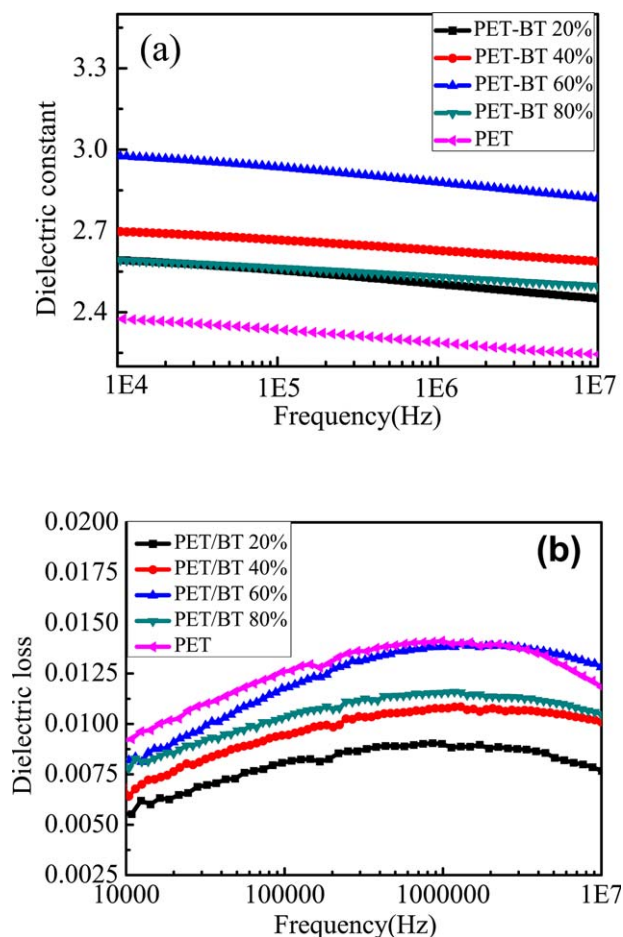
Figure 3. The k (a) and tan δ (b) of PET/BT films with different BT vol % in BT/acrylic resin. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. XPS Result of BT Modified by KH570 with and Without Hydroxylation

	Ba %	Ti %	C %	O %	Si %
BT-KH570	10.75	8.08	32.08	42.34	6.25
BT-OH-KH570	10.91	8.37	21.77	47.27	11.72

both k value and tan δ increased gradually with the increase of BaTiO$_3$ content from 0 to 50 vol % in polyimide/BaTiO$_3$ composites.[9] The reasons why tan δ decreased at 80 vol % are as follows: the addition of BT particles into acrylic resin matrix (1) reduces the contents of acrylic resin polymer in composites and (2) impedes the movement of molecular chains, which results in the decrease of dipole loss and β-relaxation. Furthermore, the formation of aggregates is also likely to generate the higher dielectric loss.[35] However, the dielectric loss of PET/BT composite films was still lower than pure PET film as the dielectric constant increased.

Effect of BaTiO$_3$ Modification with KH570 on the Dielectric Properties

Figure 4 shows the dielectric constant of PET/BT composite films at different volume fractions of KH570-modified BT and unmodified BT at 100 kHz. It is reported that the dielectric constant of the composite with BaTiO$_3$ modified by 1.0 wt %

increased with the increasing of dielectric constant.[35] As indicated in Figure 3(b), tan δ increased as the BT vol % increased from 20 to 60%, then declined at 80 vol % BT, which was associated with the variety of k value. Similar with other's results,
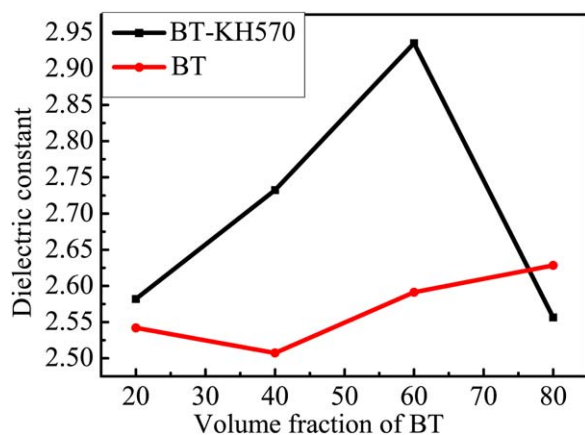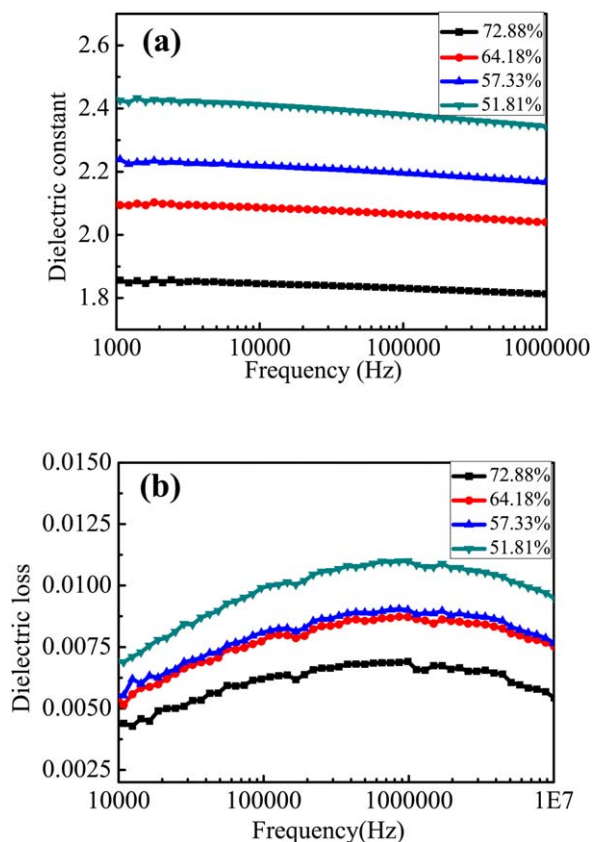

Figure 4. The dielectric constant of PET/BT films with and without KH570 BT at 100 kHz. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 5. The k (a) and tan δ (b) of PET/BT films prepared with coatings of different solid contents of BT/acrylic resin. The content of BT in BT/acrylic resin was maintained at 20 vol %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
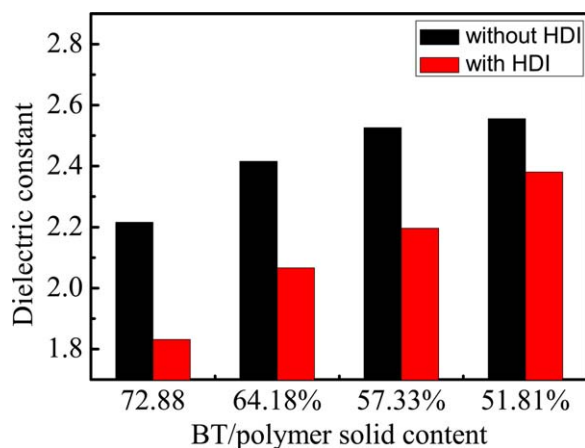
Figure 6. The dielectric constant of the composite films coated with BT/ acrylic resin without and with the addition of crosslinking agent HDI. The content of BT in BT/acrylic resin was maintained at 20 vol %. [Color figure can be viewed in the online issue, which is available at wileyonline-library.com.]

KH550 is always higher than that of the composite with raw BaTiO$_3$ over a broad frequency range.[29] Table I lists the elemental survey of BT modified with KH570 directly (BT-OH) and BT hydroxylated first and then modified with KH570 (BT-OH-KH570). It was obvious that element Ba, O, and Ti atom percents were nearly equal; however, Si atom % remarkably increased and C atom % reduced in BT-OH-KH570. It can be explained that the more hydroxyl on BT surface, the easier hydrolyzation with KH570 and the more Si—O—CH$_3$ groups introduced. As shown in Figure 4, the k values of PET/BT composite films modified with KH570 increased significantly when compared with that of the films made with unmodified BT particles especially at higher volume fraction of BT. This proved that the effect of KH570 was indispensible, consistent with the SEM image in Figure 1(c,d). In addition, it was also similar to our previous result.[22]

Solid Content of the Coating on the Dielectric Properties of Composite Films

Figure 5(a,b) shows the k and tan δ of PET/BT composite films with BT/acrylic resin coatings of different solid contents in butyl acetate at 20 vol % BT loading. The viscosity of BT/acrylic resin turned lower as more butyl acetate added, consequently generating more smooth and uniform composite films. It was shown in Figure 5(a) that the k value of PET/BT films increased when the solid contents of BT/acrylic resin decreased from 72.8% to 51.8%. The thickness of these coating layers measured through SEM image was 2.7, 1.9, 1.6, and 0.9 μm. The more uniform and thinner BT/acrylic resin coating was desired as the
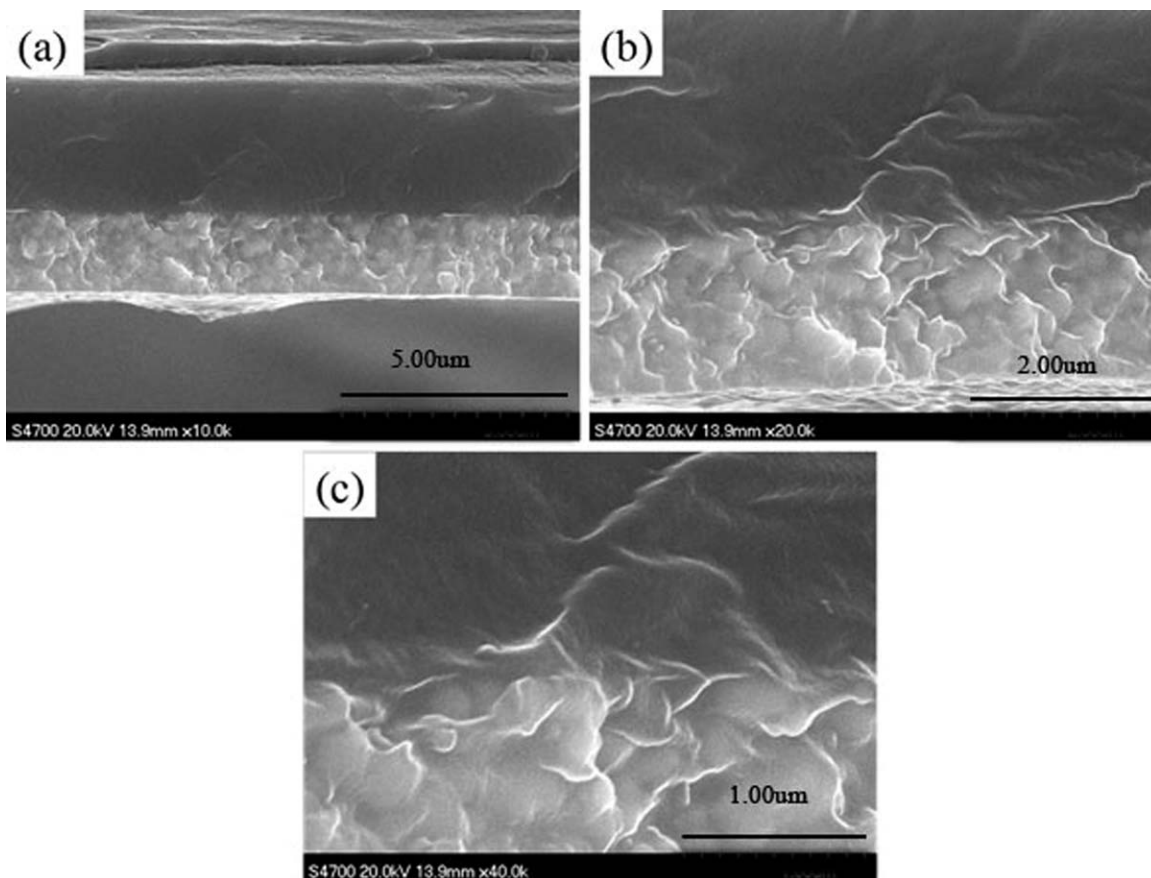

Figure 7. SEM images of the cross section of PET-PHEMA/BT composite at different magnifications: (a) ×10,000; (b) ×20,000; and (c) ×40,000.
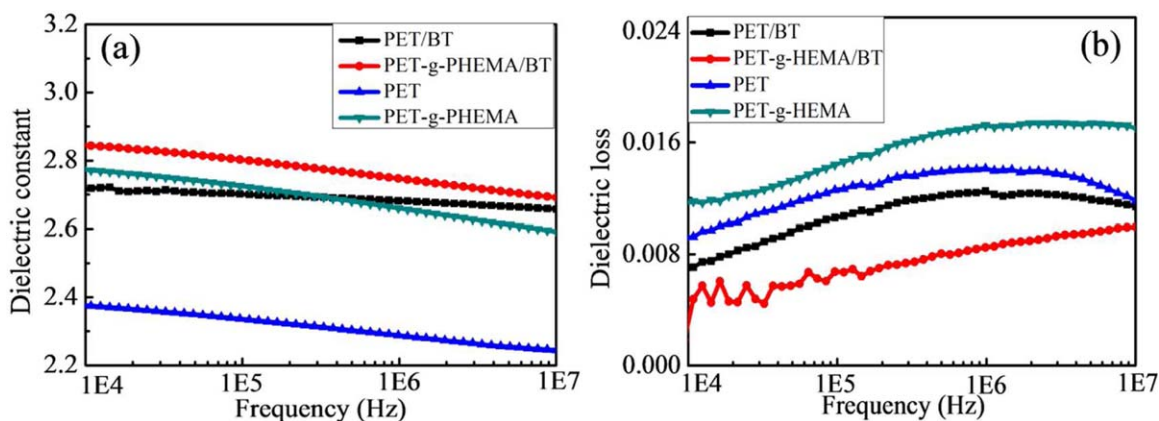
Figure 8. The k (a) and tan δ (b) of PET/BT, PET-PHEMA/BT, and PET films at the loading of 40 vol % BT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

solid content became lower. It was the reason that all the composite samples with low BT/acrylic resin solid content showed uniform particles dispersion, which resulted in similar enhancement of average electric field in the composites.[36] Figure 5(b) demonstrates that the variation trend of tan δ increased as the mass of butyl acetate increased, according to the theory that tan δ rises along with the k value.

Figure 6(a,b) shows the k tendency of PET/BT composite films with and without HDI at 20 vol % BT loading, respectively. As shown in Figure 6(a), the composite film prepared with no addition of HDI had higher dielectric constant at different BT/acrylic resin solid content at 20 vol % BT loading. This was because the crosslink between HDI and acrylic resin restrained the polarization of BT. Furthermore, the mobility of the polymer chain segments and the side groups in the BT/acrylic resin composite was significantly restricted because of the high crosslinker.[37] Consequently, smaller electrical displacements were achieved under the similar electrical field.

PET-*g*-PHEMA/BT Multilayer Composite Films
Figure 7(a) shows the cross-sectional morphology of PET-*g*-PHEMA/BT composite film. It was noted that there was one layer above PET-*g*-PHEMA film, namely, BT/acrylic resin layer solidified through OH (in PHEMA) and C≡N≡O bond (in HDI). Comparing Figures 2(a,b) and 7(a–c), it can be seen that the interfacial adhesion between BT/acrylic resin layer and PET film layer was so tight that the boundary was not clearly observable. Besides, the BT/acrylic resin layer did not simply adhere to the PET film but connected with covalent chemical bonds. Thus, this method can reinforce the interfacial action between PET film and BT/acrylic resin coating layer.

The dielectric performance of PET-*g*-PHEMA/BT films is shown in Figure 8. The k value of PET-*g*-PHEMA/BT composite film was higher when compared with PET/BT, PET, and PET-*g*-PHEMA film, whereas the tan δ was significantly declined at 40 vol % BT loading in the similar conditions. However, the k value of PET-*g*-PHEMA was 2.72 at 10 kHz, increasing obviously relative to the original PET film, whereas tan δ was quite higher than the other ones. There were two reasons accounted

for the better dielectric performance of PET-*g*-PHEMA/BT composite films. (1) The PHEMA grafted onto PET contributed to permittivity. It was reported that the dielectric constant of PHEMA-*g*-PVDF via free radical graft copolymerization technique is about 4.5 times higher when compared with pure PVDF at room temperature.[23] (2) The interfacial interaction between the PET film and BT/acrylic resin composite layer via covalent chemical bonding was beneficial for decreasing dielectric loss. In conclusion, the PET-*g*-PHEMA/BT composite film can improve the dielectric character.

CONCLUSIONS

We successfully fabricated flexible layer–layer structural PET/BT composite films with enhanced dielectric permittivity via spin coating method, with acrylic resin binding–modified particles and PET films. BT-OH-KH570 particles were well distributed when the volume content did not exceed 60%, and their dispersibility was better than the unmodified BT particles. The dielectric constant of PET/BT composite films reached 2.94 at 60 vol % BT (100 kHz), demonstrating an improvement of 26% when compared with the original PET film. Besides, higher k value and lower tan δ can be achieved when PET-*g*-PHEMA was used as the substrate, which introduced covalent bonding between PET and acrylic resin. Especially, the tan δ was much lower than that of original PET, which reduced to more than 39%.

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