Enhancing the dielectric properties of poly (arylene ether nitrile) by introducing co-modified BaTiO$_3$

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Abstract. In this study, a facile co-modification of dopamine (DA) and methylphenyldimethoxysilane (MPDS) was utilized to functionalize barium titanate (BaTiO$_3$) nanoparticles with organic functional film. With the organic film coated on surface of BaTiO$_3$, the compatibility between BaTiO$_3$ and PEN matrix was greatly enhanced, which led to the promotion in thermal and dielectric properties. Results indicated that the glass transition temperature ($T_g$) of BaTiO$_3$@(MPDS+PDA)/PEN composite showed increment from 171.9$^\circ$C to 181.2$^\circ$C. Besides, the dielectric constant of PEN composite containing 20 wt.% of BaTiO$_3$@(MPDS+PDA) improved to 9.32 with a relative low dielectric loss compared to BaTiO$_3$/PEN under the same additive ratio.

1. Introduction

Nowadays, the utilization of polymer-based dielectric materials has sparked research upsurge in the field of energy storage [1, 2]. By contrast to the available dielectric ceramics, polymer-based dielectric materials owned superior merits such as facile processing ability, fair cost, desirable flexibility as well as relatively light weight [3]. Among various polymeric dielectric materials, a special engineering plastic called poly(arylene ether nitrile) (PEN) accumulated surge of interest, ascribing to its remarkable thermostability and excellent mechanical properties which enabled its application in extreme environments [4]. To the regret, the PEN possessed dielectric constant with low extent which limits the further application of PEN in energy storage field. This was blamed for the case that ionic component showed little effect on dielectric constant of polymers. Thus, it’s of great necessity to search efficient approach to overcome this inherent disadvantage of PEN.

Recently, incorporating nanofillers with high dielectric permittivity into PEN becomes a facile and effective way to enhance the dielectric constant to a satisfying degree [5, 6]. With various high dielectric nanofillers investigated, a typical dielectric ceramic called barium titanate (BaTiO$_3$) was regarded as the promising candidate to reinforce the dielectric properties of PEN, contributing to its excellent dielectric permittivity and dielectric loss angle with high temperature endurance [7]. However, the inorganic BaTiO$_3$ possesses undesirable compatibility with the organic PEN matrix. This is ascribed to the high surface energy of BaTiO$_3$ nanoparticles that would form serve aggregation in PEN matrix, which further lead to the negative decline on the dielectric performance of PEN composites [8]. To settle this problem, a variety of research works spares no efforts on various surface modification techniques, which not only
provides feasible and ebullient approach to strengthen the compatibility between inorganic BaTiO₃ and organic PEN but also improve the homogeneous dispersity of BaTiO₃ nanoparticles in PEN.

In this work, BaTiO₃ was functionalized via methylphenyldimethoxysilane (MPDS) and dopamine (DA) through a co-modification method to synthesized BaTiO₃@(MPDS+PDA). Then the prepared BaTiO₃@(MPDS+PDA) were introduced into the PEN to fabricate BaTiO₃@(MPDS+PDA)/PEN composite film through solution casting method. The thermal and dielectric performance of the BaTiO₃@(MPDS+PDA)/PEN composite film was investigated particularly.

2. Experimental section

2.1 Modification of BaTiO₃

The synthetic process of BaTiO₃@(MPDS+PDA) was as following: 0.52 g tris (hydroxymethyl) aminomethane buffer was dispersed in 200 mL deionized water followed with the addition of 2 g BaTiO₃ and 0.8 g DA within ultrasonic under agitation of 600 rpm. Next, 0.1 mL MPDS was added to the mixture dropwise, reacting with continuous mechanical stir at ambient condition for 5 h. Then, the acquired product was filtered with deionized water several time via centrifuge and dried with freeze drying. The detailed synthesize process was illustrated in Fig.1 to provide more information.

2.2 Fabrication of BaTiO₃@(MPDS+PDA)/PEN composite films

BaTiO₃@(MPDS+PDA)/PEN composite films were fabricated via solution casting method reported previously. Typically, 1 g PEN was transferred to 10 mL NMP solvent with vigorous agitation. After the mixture was stirred to a transparent homogenous phase, BaTiO₃@(MPDS+PDA) nanoparticles with mass percent of 10 wt.% and 20 wt.% were introduced into the PEN mixture with stir and ultrasonic for 2 h. Finally, the PEN solution containing BaTiO₃@(MPDS+PDA) were poured to a horizontal glass plate, following with a heating process: 80, 100, 120, 160°C for 1h, 200, 230°C for 2h orderly. To set contrast samples, BaTiO₃/PEN composite films were also fabricated through the same method.

2.3. Characterization

BaTiO₃@(MPDS+PDA) was characterized by Fourier transform infrared spectroscopy (FT-IR, IS5,
Nicolet, America). Differential scanning calorimetric analysis (DSC, Q100, TA Instruments, America) was employed to verified the change on T_g of PEN composites. Thermal gravimetric analysis (TGA, Q50, TA Instruments, America) was employed in N_2 atmosphere to investigate the thermostability of the PEN composites. Dielectric properties of the samples were studied by a precision LCR meter (TH 2819A, Tong hue Electronic, China).

3. Results and Discussion

To verify the change on the chemical structure of functionalized BaTiO_3 nanoparticles, FT-IR analysis was employed and the results were plotted as spectra in Fig.2. By contrast with the pure BaTiO_3, a series of peaks were emerged from the range of 1000 cm\(^{-1}\) to 1500 cm\(^{-1}\) on BaTiO_3@(MPDS+PDA) spectrum, ascribing to the stretching vibration of Si-O bond. The new peak locating at 1634 cm\(^{-1}\) could be aligned as the stretching vibration mode of C=\(\text{N}\) bond. Besides, the two peaks detected at 2849 cm\(^{-1}\) and 2928 cm\(^{-1}\) were originated from the nonsymmetric and symmetric stretching mode of C-H group in methyl group on (MPDS+PDA) composite film \[9\]. Additionally, BaTiO_3@(MPDS+PDA) possessed the stronger intensity of the peak settled in 3441 cm\(^{-1}\) compared to pristine BaTiO_3. These could be explained by the extra -OH and -\(\text{N}\)H groups on (MPDS+PDA) composite film that strengthened the typical peak signal. Based on the results, it could be concluded that (MPDS+PDA) composite film was successfully functionalized to the surface of BaTiO_3. Then, the grafting ratio was further determined with TGA analysis, illustrating as TGA curves in Fig.3b. It could be identified from curves that BaTiO_3 remained constant within the 800\(^\circ\)C, exhibiting superior thermostability. After coated BaTiO_3 with (MPDS+PDA) composite film via co-modification method, the curve of BaTiO_3@(MPDS+PDA) show a sharp weight loss of 17 wt.\% in the range from 200\(^\circ\)C to 300\(^\circ\)C. These was resulted from the decomposition of (MPDS+PDA) composite, which further suggested the successful modification of the organic film on BaTiO_3.

Then thermal behaviour of BaTiO_3@(MPDS+PDA)/PEN composite films with different filler ratio was characterized by TGA and DSC analysis under the protection of nitrogen condition. As shown in Fig.3a, the decomposition temperature of pure BaTiO_3 contained PEN composite reached 512.2\(^\circ\)C, which exceeded approximately 32\(^\circ\)C higher than the neat PEN (480.3\(^\circ\)C). After incorporating with the BaTiO_3@(MPDS+PDA) nanofillers, the BaTiO_3@(MPDS+PDA)/PEN composite films showed a decline on decomposition temperature of 10\(^\circ\)C with a decrease on mass of residual char compared to BaTiO_3/PEN composites with different filler ratio. This phenomenon was owing to the organic group on the film fabricated through the co-modification that weakened the overall thermostability of BaTiO_3@(MPDS+PDA)/PEN composite films \[10\]. Besides, it could be identified from the DSC curves (Fig.3b) that the T_g of pure PEN approximately reached 172\(^\circ\)C, possessing preferable endurance to high temperature. As the BaTiO_3 was introduced into PEN, the T_g of BaTiO_3/PEN showed an escalated trend with the filler ratio increased, contributing to the incorporation of nanofillers which further hindered the movement of PEN molecular chain \[11\]. Furthermore, the T_g of BaTiO_3@(MPDS+PDA)/PEN...
composites shifted to 177.6°C and 181.2°C within the filler ratio of 10 wt.% and 20 wt.%, displaying a slight increase in comparison with BaTiO₃/PEN of the same ratio. The trend was explained by the enhanced dispersibility of BaTiO₃@(MPDS+PDA) in PEN matrix that can limit the movement of molecular chain to further degree.

The dielectric properties of BaTiO₃@(MPDS+PDA)/PEN composites were checked in the frequency scope of 10² Hz to 10⁶ Hz and plotted as Fig.4. As observed in Fig.4a, the dielectric constant of BaTiO₃/PEN gradually increased from 3.68 to 8.43 at 10³ Hz with the additive amount of BaTiO₃ raised from 0 wt.% to 20 wt.%, ascribing to the introduction of BaTiO₃ that enhanced the polarization of PEN network. After coated with (MPDS+PDA) composite film on BaTiO₃, the dispersion of BaTiO₃@(MPDS+PDA) in PEN matrix was notable improved, leading to the more formation of micro-capacitor and polarized interface [12]. As the result, dielectric constant of BaTiO₃@(MPDS+PDA)/PEN composite films showed a slight increment compared to the same additive ratio of BaTiO₃/PEN. Moreover, it can be observed from Fig.4b that the dielectric loss of the PEN composites slightly increased with more amount of BaTiO₃ nanofillers incorporated, which was ascribed to the higher polarization after the introduction of more BaTiO₃ nanofillers. Besides, the dielectric loss of the BaTiO₃@(MPDS+PDA)/PEN show less rate by contrast to BaTiO₃/PEN with same ratio. This could be explained by that BaTiO₃@(MPDS+PDA) obtained more polarization interfacial surfaces with PEN matrix, which efficiently impeded the leakage of current and alleviate dielectric relaxation.

**4. Conclusion**

In conclusion, the BaTiO₃@(MPDS+PDA) was successfully synthesized through MPDS and DA basing on the co-modification method. Then the PEN composite films containing BaTiO₃@(MPDS+PDA)
were prepared via solution casting method. The results confirmed that the $T_g$ and dielectric properties of PEN composite films acquired obvious promotion with the introduction of the BaTiO$_3$@(MPDS+PDA) nanofillers. It’s believable that BaTiO$_3$@(MPDS+PDA)/PEN composite films would be a potential candidate to be applied in dielectric field.

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