An enhancement on the dielectric performance of poly(vinylidene fluoride)-based composite with graphene oxide-BaTiO₃ hybrid

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ABSTRACT

In this work, a novel two-dimensional graphene oxide-BaTiO₃ (GO-BT) hybrid, via covalent bonding between animated BaTiO₃ nanoparticles (BT-NH₂) and graphene oxide (GO), have been prepared. Then the graphene oxide-BaTiO₃ (GO-BT) hybrid is introduced into poly(vinylidene fluoride) (PVDF) matrix to obtain composites with a high-dielectric property. The microstructure and the dielectric property of the composites were investigated. The resulting composites filled with only 1 wt% GO-BT hybrids possess an excellent dielectric constant of 61 at 100 Hz, which is nearly 2.5 times that of neat PVDF. Surprisingly, the dielectric loss of the composites with 1 wt% GO-BT hybrids are as low as that of PVDF. These research results provide an effective method into the fabrication of advanced PVDF-based dielectric nanocomposites with low content of the GO-BT hybrids.

GRAPHICAL ABSTRACT

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1. Introduction

Polymer composites with high dielectric constant (εr) have drawn intensive research for their wide applications in modern nanoelectronics from high-energy storage devices to artificial muscles, etc. The high εr ceramic filling approach, such as barium titanate (BT) and lead zirconium titanate (PZT), always dramatically improves the energy storage density and dielectric property of polymer composites [1–3]. However, this approach generally reminds a high concentration of ceramic fillers to obtain high-performance composite. Furthermore, the huge surface energy of inorganic nanofillers might lead to the agglomeration of nanofillers. Thirdly, the poor interface interaction between nanofillers and polymer is hard to avoid owing to the incompatible property between the organic matrix and inorganic fillers.
To overcome these shortcomings, an attractive approach is to tailor the polymer/ceramic interface to enhance the interface adhesion between the fillers and matrix. Therefore, several methods have been used to functionalize the surface of ceramic nanoparticles: (i) modification of nanoparticles by hydroxylation, such as $\text{H}_2\text{O}_2^4$; (ii) Introducing functional groups including $-\text{COOH}$, $-\text{COO}^-$, $-\text{NH}_2$, and $-\text{NHCO}$ onto the surface of nanofiller via reaction with hydroxyl BT, such as dopamine, ethylenediamine, silane-coupling agents, phosphoric acid, and its derivatives [1]; (iii) Modifying the nanoparticle surfaces by the polymer chains with functionalized end groups via grafting to, grafting from or in situ polymerization [4–7]. The dispersion of ceramic nanoparticles in the polymer matrix and the interface interaction between ceramic nanoparticles and polymer have been significantly promoted by the functional groups modified surface of ceramic nanoparticles.

Another possible proposal is introducing conductive filler into poly(vinylidene fluoride) (PVDF)/ceramic nanocomposites to obtain high-performance dielectric composites. The conductive fillers include metal, such as Ag [8], Ni [9,10], and carbon-based materials, such as carbon nanotubes [11], and graphene [12]. This method has been widely accepted for its synergetic effects on the improvement in dielectric constant, reducing filling concentration and enhancement of interfacial adhesion with the polymer matrix. PVDF-based composites coupling with the BaTiO$_3$-conductive filler have been reported superior electrical and mechanical properties, to be useful in various kinds of optoelectronic devices. Zhang et al. [13] fabricated a BaTiO$_3$-graphene nanoplatelets (BTG) hybrid by a sol–gel process to improve the permittivity of PVDF-based composites to 50 at 100 kHz. The mixture was transferred to an appropriate petri dish, and stirred for 12 h at 50 °C. The modiﬁed Hummer’s method. The GO sheets were added into DMF, and then dispersed under ultra sonication until a uniform brown suspension was obtained. Then the excess BT-NH$_2$ nanoparticles were added to GO were 5:1, 10:1, and 20:1, respectively. The obtained mixture was transferred to an appropriate petri dish, followed by drying in an oven at 60 °C for 12 h. The name of GO-BT hybrids was BT-NH$_2$.

Graphene oxide (GO) was prepared by a modiﬁed Hummer’s method. The GO sheets were added into DMF, and then dispersed under ultra sonication until a uniform brown suspension was obtained. Then the excess BT-NH$_2$ nanoparticles were added to GO were 5:1, 10:1, and 20:1, respectively. The obtained mixture was sonicated to form a uniform suspension, and stirred for 12 h at 50 °C.

The dispersion of BaTiO$_3$ within the PVDF was promoted by the modified dipole interaction between oxycenic groups attached on the BaTiO$_3$ and $-\text{CF}_2$– in PVDF. Also, a remarkable improvement in the dielectric constant of the PVDF/plasma-treated BaTiO$_3$ composite was observed. However, the BaTiO$_3$ concentration remains a high level of about 20 wt%. About this, our efforts were aimed at reducing the content of fillers. In this research, we fabricated a novel surface-modified BaTiO$_3$-graphene oxide (GO-BT) hybrid via covalent bonding between animated BaTiO$_3$ nanoparticles (BT-NH$_2$) and graphene oxide (GO). The morphology and dielectric property of the PVDF composites consisting of the novel GO-BT hybrids was investigated. This unique structure combines the advantages of both BT nanocomposites and GO sheets. As a consequence, the GO-BT hybrids with low filling content remarkably improve the dielectric constant of the polymer composites.

2. Experimental

To hydroxylate the BT nanoparticles, 15 g of BT nanoparticles and 160 mL of $\text{H}_2\text{O}_2$ solution were combined and sonicated for 30 min, then reﬂuxed at 105 °C for 4 h. Then the mixture was centrifuged and washed with deionized water. The BT nanoparticles were transferred to an appropriate petri dish and dried in an oven at 60 °C for 12 h. The name of hydroxylated BT nanoparticles was BT-OH.

A surface modiﬁcation of BT-OH was implemented in methylbenzene by alkoxy silane coupling agents AMMO. The hydroxylated BT nanoparticles (5 g) and alkoxy silane (2.5 g) were put into the solution of methylbenzene. The mixture was sonicated for 30 min and then reacted for 24 h at 80 °C. The BT nanoparticles were obtained by centrifugation and washed for several times. Then the obtained mixture was transferred to an appropriate petri dish, followed by drying in an oven at 60 °C for 12 h.

Graphene oxide (GO) was prepared by a modiﬁed Hummer’s method. The GO sheets were added into DMF, and then dispersed under ultra sonication until a uniform brown suspension was obtained.
obtained solution was cast into a glass mould followed by drying at 25 °C for 2 days and vacuum for 12h. The schematic illustration of the preparation process for the PVDF/GO-BT membranes is exhibited in Scheme 1. As the contrast sample, the PVDF/GO membranes were completed in the same way.

The morphology of GO-BT hybrids was characterized by Transmission electron microscopy (TEM, JEM-2010, JEOL, Japan). The groups of GO-BT nanoparticles were identified by FT-IR instrument producing the IR spectra (Bruker, model IFS 48) by the wave range of 500–4000 cm⁻¹. The dielectric constant and the dielectric loss of the nanocomposites were characterized by the Agilent 4294 A frequency response analyzer. Fractured cross sections of the PVDF/GO-BT composites were investigated by scanning electron microscopy (SEM, Inspect F, FEI) with an acceleration voltage of 20 kV.

3. Results and discussion

The transmission electron microscopy (TEM) images of GO@BT hybrids with different mass ratios of GO to BT are shown in Figure 1. The two-dimensional nanosheets with randomly folded and wrinkled structure are belonged to GO substrates. The dark particles attached on the GO nanosheets are BT nanoparticles. The GO-BT hybrids remain the two-dimensional sheet morphology. At the ratio of 1:5, the BT nanoparticles are basically spherical, and their average particle size is about 25 nm. The obvious naked areas observed on the GO sheets indicated a low-coating density of BT nanoparticles on the GO sheets. At the ratio of 1:10, it can be seen clearly that the BT nanoparticles are homogeneously immobilized on the surface of GO nanosheets. The ranges of particle sizes are roughly 15–25 nm. More nanoparticles were coated on the GO sheets as the weight ratio increased to 1:10. At the ratio of 1:20 (Figure 1(c)), the most BT particles could be observed as the aggregation of irregular shape with sizes ranging from 300 to 800 nm. Though the distribution of BT particles is poor, there are still no free BT nanoparticles in GO@BT hybrids with the ratio of 1:20, suggesting a strong interaction between the GO substrate and BaTiO₃ nanoparticles.

Nanoparticles or polymers can be immobilized on the surface of GO sheets via either the reaction between functional groups or the π–π stacking. From the FT-IR spectrum (Figure 2), two new bands at 2850 and 2920 cm⁻¹ were observed in the spectra of BT-NH₂ nanoparticles comparing to BT-OH, which could be caused by C–H stretching vibrations of the alkylated alkoxy group in the alkoxysilane. Another new peak at 1536 cm⁻¹ could be ascribed to the N–H bending vibration. Two shoulders at 920 and 1190 cm⁻¹ are characteristics of the deformation vibrations of Si–C and Si–OH, respectively. These results exhibited that the end-functionalized siloxane molecules with –NH₂ groups were attached to the BT-OH surface successfully. The spectra of GO sheets show absorption bands at 3400 and 1379 cm⁻¹, respectively, according to stretching vibration of –OH and C–O groups, which demonstrated hydroxyl groups on the surface of GO sheets. The broad adsorption at 1640 cm⁻¹ is attributed to the C=O bond stretching in the carboxyl functionality. The spectra of GO-BT hybrids present

![Scheme 1. Schematic illustration of the preparation process for the PVDF/GO-BT membrane.](image)

![Figure 1. TEM images of GO-BT hybrid with varying weight ratio: (a) 1:5; (b) 1:10; (c) 1:20.](image)
a new appearance peak at 1282 cm\(^{-1}\) attributed to stretching vibration of the C–N bond of the amide group. It is proved that the BaTiO\(_3\) nanoparticles were successfully transformed onto the surface of GO sheets via the condensation reaction between –COOH of GO sheets and –NH\(_2\) of BaTiO\(_3\) nanoparticles.

Figure 3 demonstrates the fractured cross-sections of PVDF-based composites. Clearly, some areas of aggregation of wrinkled GO could be observed in Figure 3(a). However, well-distributed BaTiO\(_3\) nanoparticles can be seen on the surface of GO sheets, and GO-BT hybrids are well dispersed within the PVDF matrix (Figure 3(b)). The immobilized BaTiO\(_3\) nanoparticles inhibited the aggregation of GO sheets, and the amino groups on BaTiO\(_3\) nanoparticles significantly improved the interaction between BaTiO\(_3\) nanoparticles and PVDF chains.

The dependence of dielectric constant on the frequency of the PVDF composites at room temperature is revealed in Figure 4(a). After introducing 1 wt% GO nanosheets into PVDF, the dielectric constant and dielectric loss of PVDF composites significantly improved compared to pure PVDF.
constant was dramatically improved in the low range frequency. The observation could be well illustrated by the Maxwell–Wagner–Sillars (MWS) interfacial polarization. The MWS polarization could dramatically improve the dielectric constant due to the entrapment of free charges at the interfaces between nanoparticle and matrix. In the case of 1 wt% GO-BT hybrids, the dielectric constant was enhanced to 61 at 100 Hz, which is nearly 2.5 times that of neat PVDF. These results are reasonable because the improvement in the permittivity of the PVDF by adding either the GO sheets or BT particles was largely observed in recent researches. The improvement in the dielectric constant was because the insulated layer BaTiO3-NH2 between the GO sheets and PVDF matrix relatively decreased the MWS interfacial polarization. Furthermore, the amino groups fixed on the BaTiO3 nanoparticles efficiently restricts the charge carrier migration in the fillers-matrices space.

Figure 4(b) presents the dependence of dielectric loss on the frequency for PVDF and its composites with different fillers. There exists a large and broad relaxation under low frequency for the composite filled with 1% GO. The reason was that the GO nanosheets were formed local conduction paths by overlapping with each other, leading to the direct current (DC) conduction (transport-related loss). However, for composites filled with 1% GO-BT hybrids, the relaxation under low frequency was almost unobservable. One possible reason is that the BT nanoparticles fixed on the GO surface effectively prevented the formation of local conductive paths with the direct current (DC) conduction (transport-related loss). Another reason is that the stronger interaction between BaTiO3-NH2 and PVDF chains restricted the dipole movement of the polymer matrix. The filler category shows little effect on the dielectric losses at high frequency in the PVDF composites. Table 1 illustrates the dielectric properties of the nanocomposites containing different kinds of fillers. The PVDF-based composites filled with 1 wt% GO-BT hybrids in this study demonstrate an observably larger dielectric constant compared with others’ results.

4. Conclusions

A novel and high-performance PVDF-based dielectric nanocomposites filled with low filler contents of GO-BT hybrids were successfully prepared. The dielectric constant was enhanced remarkably when 1 wt% GO-BT hybrids were incorporated into the PVDF matrix, and the dielectric loss is no more than that of PVDF. The results are attributed to the effective reduction of the MWS interfacial polarization by the insulated layer BaTiO3-NH2 between the GO sheets and PVDF matrix. In addition, the amino groups fixed on the BaTiO3 nanoparticles efficiently restrict the charge carrier migration in the fillers-matrices space. Overall, this research provides an effective method of fabricating high-performance dielectric nanocomposites, which have great insight into advanced dielectric devices.

Disclosure statement

No potential conflict of interest was reported by the authors.

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