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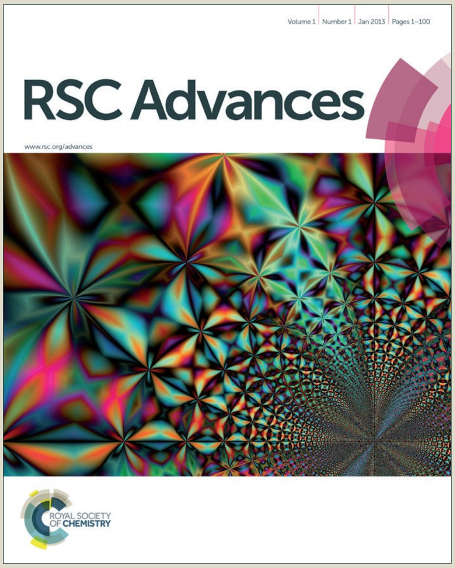

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ARTICLE TYPE

Fluorocarboxylic acid modified Barium Titanate/poly(vinylidene fluoride) composite with significantly enhanced breakdown strength and high energy density

Yujuan Niu, Ke Yu, Yuanyuan Bai, Feng Xiang, Hong Wang*

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Ceramic/polymer composites combining high permittivity fillers and high breakdown strength matrix have shown great potential applications in power system. However, the compatibility between the two phases in composite is always a key factor influencing its dielectric performance. Surface modification on fillers using traditional modifiers can improve the breakdown strength of the composites but also increase the dielectric loss at the same time, which reduces the energy efficiency of the material. In this work, we report a modifier for the surface modification of barium titanate (BT) nanoparticles, which as modifier for nanoparticles has not been demonstrated before. The poly(vinylidene fluoride) (PVDF) composites filled with the modified BT have good compatibility, high breakdown strength and low dielectric loss. Especially, the breakdown strength is much higher than that of the composites filled with unmodified BT nanoparticles. When filler volume fraction is 40%, the increase of the breakdown strength can reach 81.3%. A high energy density of 9.4 J/cm3 is achieved at 400 MV/m when the volume fraction is 10%, which is two times higher than that of the unmodified BT/PVDF composites.The abstract should be a single paragraph which summarises the content of the article.

Introduction

Capacitors are vital in nearly all modern electronic devices and electrical power systems, such as cell phones, computers, automotive vehicles, kinetic energy weapons, and high power microwave systems.[1-5] Compared with other energy storage devices (e.g., batteries, fuel cells), high energy density capacitors possess the advantage of fast charge and discharge capability.[6,7] In a dielectric material, the electric energy density is limited to $\kappa E_b 2/\ 2$, where κ is the permittivity of the material and E_b is the breakdown strength. Therefore, highly insulating materials with both large permittivity and high breakdown strength are desired for high electric energy storage.

The permittivity of organic polymers is small, so high energy density would be achieved only under extremely high electric field;[8] while ceramics with large permittivity have low breakdown strength and poor processability. Therefore composite comprising polymer matrix and ceramic fillers has become a strenuous topic of research for energy storage applications.[9,10] The idea underlying this composite approach is to integrate complementary elements, such as processability and high breakdown strength of the polymer and large permittivity from the ceramic particles, to get a substantially enhanced energy density.[11,12] However, the high surface energy of nanoparticle fillers usually leads to agglomeration and phase separation from the polymer matrix, resulting in poor interfacial interaction and high defect density. The defects in composites will make the electric field highly inhomogeneous and result in the decrease of breakdown strength.[13,14]

So far, the efforts to fight against the deficiency are mainly concentrated in two aspects, one is developing new compounding (dispersion) technology,[15] another is modifying the surface of nanoparticle fillers.[16-20] As to the latter, although many available modifiers have be used, there are still some limitations in practical use. For example most modifiers hardly diffuse into the agglomerates owing to their long molecular chains and many of them don’t have chemical specificity to the polymer matrix. In recent years, small molecule phosphonic acids are frequently used in surface modification and considered to be the most promising modifier,[21-23] since they are thought to couple to the surface of metal oxides with a high level of coverage. However, in composites, high adsorption of modifier will significantly lower the permittivity, or lead to high leakage current and dielectric loss.[24]

In this work, we use a small molecule carboxylic acid 2,3,4,5-tetrafluorobenzoic acid (F4C for short) as modifier to treat the BT nanoparticles with a low level surface coverage and find that the use of the modified BT nanoparticles (F4CBT) as filler leads to well-dispersed composite films with low dielectric loss, ultra high breakdown strength, and a high energy density of 9.4 J/cm^3. To our best knowledge, 2,3,4,5-tetrafluorobenzoic acid as the modifier for nanoparticles has not been studied before, and the improvements on breakdown strength and energy density are very significantly in the composites filled with the surface modified ceramic fillers. In our previous study, we demonstrated the

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tetrafluorophthalic acid as surface modifier could improve the breakdown strength of BT/PVDF composites.[25] Following further, the 2,3,4,5-tetrafluorobenzoic acid was used as modifier in this paper, aiming to study the influence of modifier on the dielectric performance and compatibility between the fillers and matrix, and provide further insight into the relation between the modifier structure, level of coverage and dielectric properties of the composites.

Experimental

Materials

The solvent of acetone, butanone and ethanol were purchased from Letai Co., China. PVDF powder was obtained from Shanghai 3F New Materials Ltd., China. The surface modifier 2,3,4,5-tetrafluorobenzoic acid was purchased from Alfa Co., China. BT nanoparticles with an average size about 100 nm were purchased from Sinocera Co., China. All solvents and chemicals were used as received.

Preparation of modified BT nanoparticles (F4CBT for short)

BT nanoparticles were added into an ethanol/water (95/5, v/v) solution with ultrasonic for 30 min, and then the 2,3,4,5-tetrafluorobenzoic acid was added. The mixture was ultrasonicated for 10 min, followed by stirring at 80 ℃ for 1 h. The nanoparticles were separated via centrifugation, and rinsed repeatedly with excess ethanol/water solvent, then dried overnight under vacuum at 80 ℃ to get the modified BT nanoparticles.

Fabrication of the F4CBT/PVDF composite films

2 g PVDF powder was dissolved in 15 ml mixed solvent composed of 50% acetone and 50% butanone. F4CBT nanoparticles were dispersed into the PVDF solution with different volume fractions and the suspensions were ball-milled for 4 h. After ball-milling, the homogeneous suspension was tape casting onto the PET substrate. The composite films on the substrates were standing at 80 ℃ for 30 min to evaporate the solvent followed by thermal treating at 200 ℃ for 1 h, and then immediately quenched into ice water. The thickness of the obtained composite films was 15-20 μm.

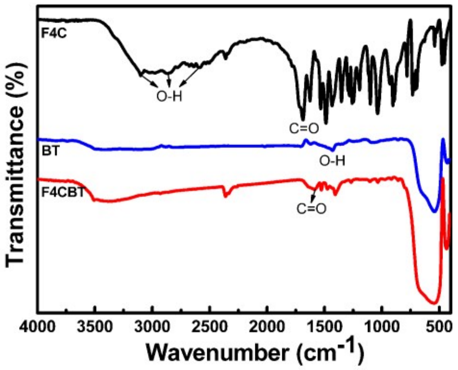

Figure 1 FTIR spectra of modifier F4C, pristine BT, and the surface modified BT with F4C.

Characterization

Fourier transform infrared (FTIR) (Bruker Tensor27) spectra and thermo gravimetric analyses (TGA) (NETZSCH STA449C) were carried out in air atmosphere for BT and modified BT nanoparticles. The microstructure of the composite was observed by a scanning electron microscopy (SEM, JSM-6460, JEOL, Tokyo, Japan). For electric measurement, gold electrodes with thickness of about 50 nm were sputtered on both sides of the film samples. Dielectric measurement covering a frequency range from 1 kHz to 10 MHz was carried out using an impedance analyzer (Agilent 4294A, Palo Alto, CA) at room temperature. The energy storage property was evaluated through the dielectric displacement-electric field (D-E) hysteresis loops measured by TF analyzer 2000 system (aix ACCT, Aachen, Germany).

Results and discussions

The FTIR spectra of modifier F4C, pristine BT and modified BT nanoparticles are shown in Fig. 1. The spectrum of dried BT nanoparticles exhibits a absorption peak at 1434 cm^{-1}, which is assigned to the stretching of O-H.[26] The BT nanoparticles were synthesized by hydrothermal method, so there are some hydroxyl groups (-OH) on the surface of the BT nanoparticles.[27] As shown in Fig. 1, the FTIR spectrum of the modifier F4C shows the characteristic peaks at 1730-1685 cm^{-1}, which are attributed to the C=O vibrations.[28] The bands appearing at 3000, 2800 and 2600 cm^{-1} are assigned to the O-H vibrations, which derive from the carboxylic acid group. However, after coupling to the surface of BT nanoparticles, the characteristic peak of C=O vibration disappear and presents a new peak at 1594 cm^{-1} in the spectrum of F4CBT, which attributed to the C=O vibration from carboxylate group.[29] The characteristic peak changes from carboxyl group to carboxylate group in the FTIR spectra may indicate the formation of chemical bonds between the modifier and the BT nanoparticles. Otherwise, the F4CBT nanoparticles have more surface oxygen functional groups compared with pristine BT nanoparticle.

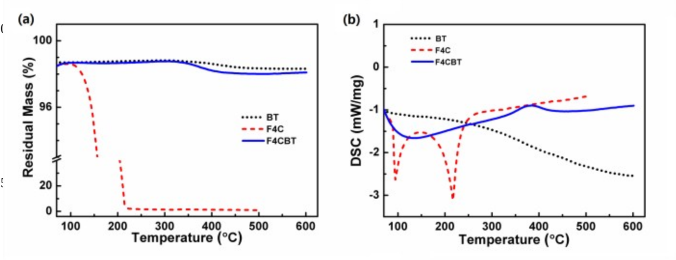

Figure 2 (a) TGA and (b) DSC curves of BT, F4C, and F4CBT measured in air atmosphere.

The thermo-gravimetric analysis (TGA) and differential scanning calorimeter (DSC) curves of BT, F4C, and F4CBT are shown in Fig. 2. As shown in Fig. 2a, the pristine BT has a negligible weight loss in the tested temperature range, which derives from the adsorbed water and the bonded hydroxyl group on the surface of the BT nanoparticles. The weight loss of F4C is complete below 300 ℃, accompanied by two sharp exothermic peaks on DSC curve (Fig. 2b), which can be deduced that the modifier has experienced a combustion reaction. In the TGA curve of F4CBT, there is a small weight loss (about 0.80%) at temperature range from 310℃ to 470 ℃. The weight loss is close to a theoretical monolayer surface coverage,[30] but it is lower than that of the conventional modifiers since the influence of molecule

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structre.[17-21] At the same time, there is an endothermic peak on the DSC curve of F4CBT, corresponding to the TGA plot change, which presents a degradation process of F4C from the BT surface.[29]

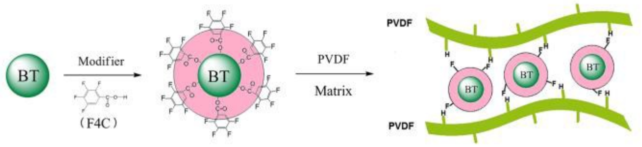

Figure 3 Mechanism for synthesis of F4CBT/PVDF composites.

Fig. 3 shows the synthesis mechanism of F4CBT/PVDF composites, the possible chemical structure of modified filler F4CBT and interfacial interaction in the composites. The modifier molecules are anchored on the surface of BT nanoparticles through chemical bonds between the carboxyl group and metal oxide, forming an organic shell. On the other hand, the aromatic fluorine groups in the modifier molecule generate electrostatic interactions and may form hydroxyl bonds with the PVDF matrix.

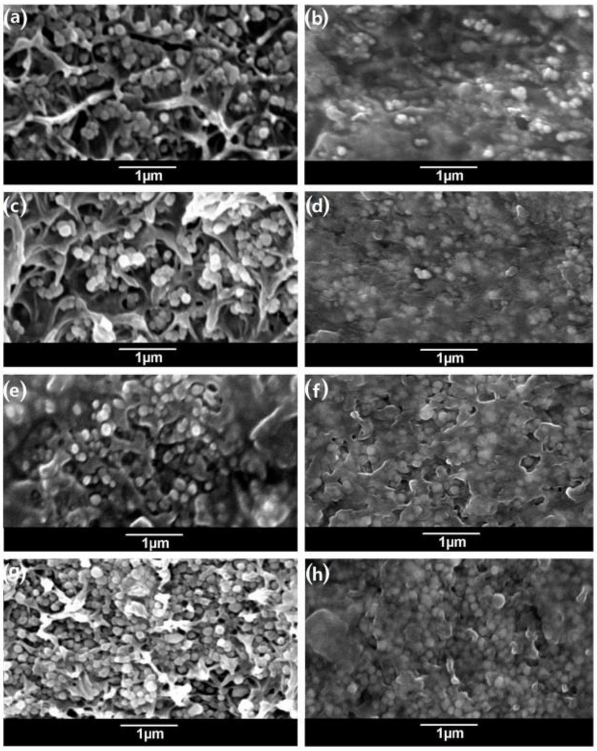

Figure 4 Morphology of PVDF composites filled with pristine BT and F4CBT, (a) 10% BT, (c) 20% BT, (e) 30%, (g) 40%; (b) 10% F4CBT, (d) 20% F4CBT, (f) 30% F4CBT, (h) 40% F4CBT.

The fracture surface morphology of the composites filled with pristine BT and F4CBT is investigated by SEM (Fig. 4). As shown in the SEM images of F4CBT/PVDF composite (Fig. 4(b), (d), (f), (h)), the nanoparticles are uniformly embedded in the polymer matrix, and well compatible with the PVDF matrix without phase separation. On the other hand, the composites filled with pristine BT nanoparticles (Fig. 4(a), (c), (e), (g)) also show good distributions of the filler in PVDF matrix due to using the ball-milling technology,[15] but the compatibility between them is poor. Although there are some -OH groups bonded on the pristine BT surface, its effectiveness is limited, large amount of the BT nanoparticles are still found to be free from the matrix. The results indicate that although few F4C are introduced onto the surface of BT nanoparticles, the compatibility of the composites still significantly improved. The main reason lies in that the fluorinated aryl group in the modifier molecule can generate electrostatic interactions and may form hydroxyl bonds with the PVDF matrix (as shown in Fig. 3)[27], so the interfacial interaction between the modified filler and the matrix is stronger than that in the composites filled with pristine BT, the compatibility of the composites F4CBT/PVDF is also significantly improved.

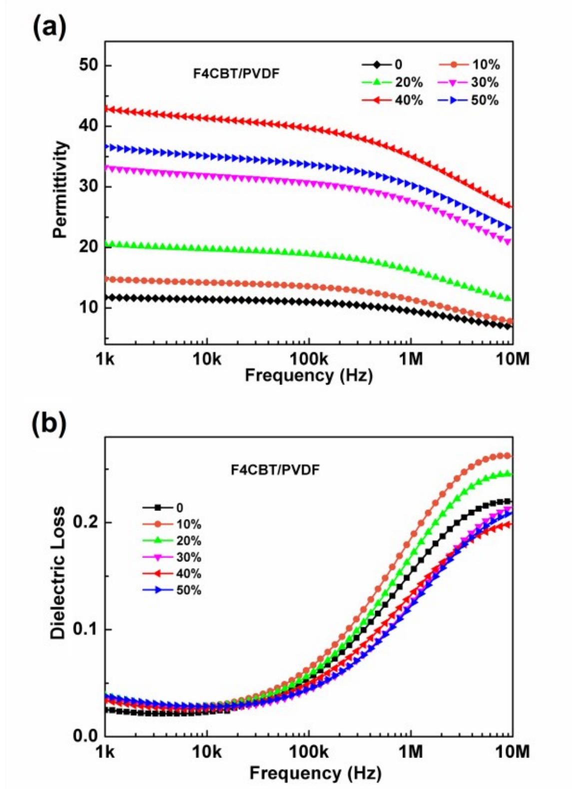

Figure 5 Frequency dependences of (a) permittivity and (b) dielectric loss of the F4CBT/PVDF composites.

The dielectric properties of the PVDF-based composites are shown in Fig. 5. As shown in Fig. 5a, the permittivity of the composites exhibits nearly independence on frequency up to 1 MHz, and then decreases especially when the volume fraction of F4CBT is increasing, which mainly due to the dielectric response of BT at high frequency.[31] The permittivity increases steadily as the filler volume fraction increasing until 40%. After that, further addition of filler particles leads to a gradual decrease in the permittivity, which can be attributed to the voids and interfacial defects induced by agglomeration between excess fillers.[32] The loss tangent (Fig. 5b) exhibits little variation in the frequency range from 1 kHz to 1 MHz and then increases to a sharp peak, which is attributed to the glass transition relaxation of the PVDF polymer matrix.[33]

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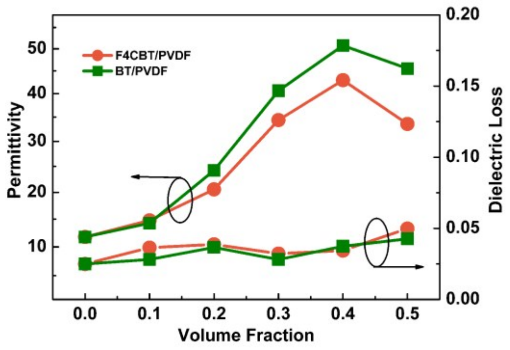

Figure 6 Comparison of the dielectric properties of the BT/PVDF and F4CBT/PVDF composites with different volume fractions at 1 kHz.

The comparisons of the permittivity and loss tangent of the composites filled with F4CBT and BT nanoparticles are shown in Fig. 6. As seen that the permittivity of the F4CBT/PVDF composite is lower than that of the composite filled with pristine BT particles. As the volume fraction of filler increases, the permittivity of the composites filled with F4CBT nanoparticles gets lower than that of the composites with untreated BT nanoparticles. The result is caused by the modifiers coated on the surface of BT nanoparticles, which act as a passivation layer, have negative influences on the interfacial polarization, and then might decrease the dielectric permittivity of the composites.[34] On the other hand, dipole polarization is a dominant factor in determining the composite permittivity compared with the interfacial polarization. The modifier layer may weaken the intensity of dipole polarization.[35] However, the diminution of the permittivity is limited when compared with that of the composites modified by tetrafluorophthalic acid and other conventional modifiers due to the molecule structure and low surface coverage of F4C. It is noteworthy that the dielectric loss is almost independent of the filler content, indicating a minimized agglomeration of the filler in the composites.[12] Compared with BT/PVDF composites, the dielectric losses of F4CBT/PVDF composites don’t deteriorate, further indicating that unlike traditional modifies, F4C does not cause more leakage current in composites. Dielectric measurement results indicate that the interfacial areas of the composites have been influenced by the modifier on the surface BT nanoparticles.

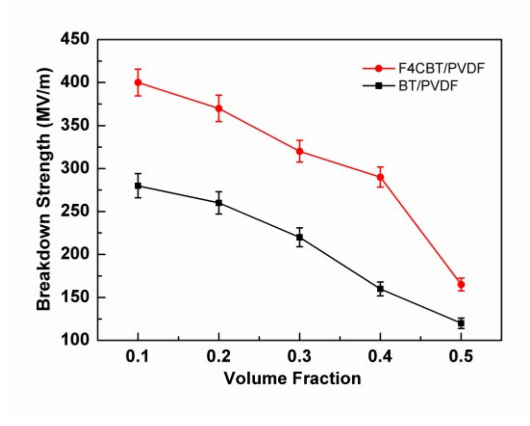

Figure 7 Comparison of breakdown strength of the composites filled with BT and F4CBT nanoparticles with various volume fractions.

The breakdown strength is a critical parameter of dielectric materials, which denotes the highest electrical field that can be applied to the films without losing their insulating property.[36] The first favorable feature of the F4CBT/PVDF composites is the significantly improved breakdown strength. The comparison of breakdown strength for composites filled with BT and F4CBT nanoparticles as function of volume fraction is shown in Fig. 7. It is worth noting that the electric breakdown strength of the composites filled with F4CBT nanoparticles are greatly enhanced compared with that of the composites filled with pristine BT nanoparticles. When the filler volume fraction is 10%, the breakdown strength of the composite with F4CBT nanoparticles can reach 400 MV/m, which increased by 42.8% compared with that of the BT/PVDF composite. When the filler volume fraction is 40%, the breakdown strength of the composite filled with F4CBT nanoparticles is 290 MV/m, about 81.3% higher than that of the composite filled with BT nanoparticles. Previous reports prove that the breakdown of composites easy to occur at the interfaces between ceramic filler and polymer matrix due to the large difference of permittivities between them will produce highly inhomogeneous electric field in composites.[37,38] In this contribution, the F4C modifiers form a transition layer between the inorganic fillers and the polymer matrix, which is a strong potential barrier where charge carriers are blocked. On the other hand, the modifier molecule bounded on the surface of BT particles extends into the PVDF matrix, which makes the influence of space charges on the breakdown strength subside.[39] Besides, the F4C modifiers serve as a surface shell layer to prevent BT nanoparticle from aggregating.[40]

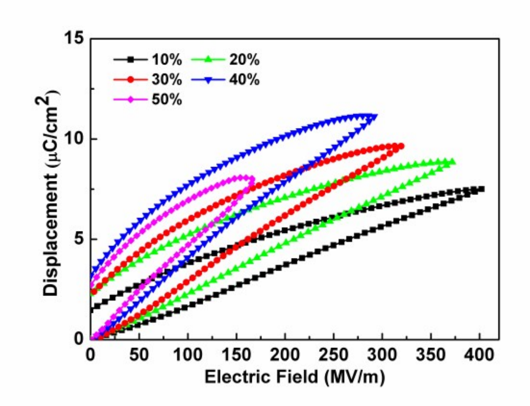

Figure 8 The D-E loops of composites F4CBT/PVDF with various volume fractions.

Except breakdown strength, the maximum polarization and remnant polarization also have important effect on the discharged energy density of the composites. As a result of the ultra high breakdown strength, the F4CBT/PVDF composites could be polarized under high electric field, leading to much increased electric displacement. As shown in the P-E loops (Fig. 8), the maximum displacement is 7.5 μC/cm^2 under 400 MV/m when the F4CBT volume fraction is 10%. Further introduction of F4CBT to 40%, the maximum displacement increases to 11.1 μC/cm^2, even though the composites is early breakdown at 290 MV/m. On the other hand, the remnant polarization increases from 1.5 μC/cm^2 to 3.2 μC/cm^2, which indicates the composites have more defects when the filler loading increase.

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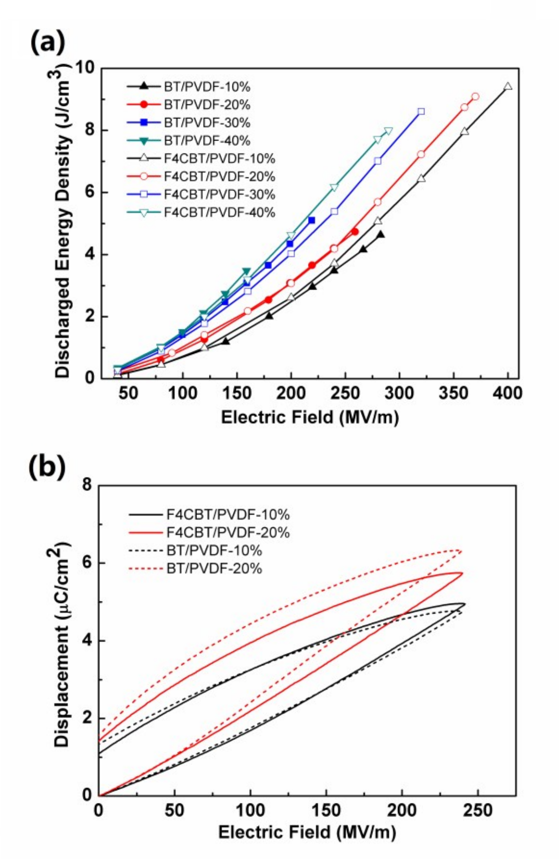

Figure 9 (a) Discharged energy density of the composites F4CBT/PVDF and BT/PVDF with different volume fractions as a function of electric field; (b) the comparison of D-E loops between the composites F4CBT/PVDF and BT/PVDF at same electric field.

Being ferroelectric in nature, the PVDF matrix could be polarized significantly under a high electric field, giving rise to a deviation from the linear behavior of the electric displacement versus the electric field for the PVDF-based composites.[41] So the energy densities of the composites are calculated from each displacement hysteresis loop by the integral,

$$U_e = \int E dD \quad (1)$$

where E is the electric field and D is the electric displacement.[25] Fig. 9a shows discharged energy density as a function of applied field for composites F4CBT/PVDF and BT/PVDF. It can be observed that the discharged energy density increases with the filler loading and electric field. As a result of the high breakdown strength, the maximum discharged energy density of 9.4 J/cm^3 is achieved at 400 MV/m in the F4CBT/PVDF film samples with 10% filler volume fraction. Compared with composites filled with unmodified BT nanoparticles, the composites F4CBT/PVDF have higher discharged energy density at low filler loading (10%) under the same electric field. As filler volume fraction increasing, the discharged energy density of BT/PVDF gradually overtakes that of F4CBT/PVDF. The discharged energy density is strongly depending on the maximum polarization and remnant polarization. As shown in Fig. 9b, the maximum polarization of composites BT/PVDF is lower than that of F4CBT/PVDF at the same electric field when the filler loading is 10%. And then increasing the filler loading to 20%, the maximum polarization of composites BT/PVDF becomes higher than that of F4CBT/PVDF. The variation trend is consistent with the performance of discharged energy density of the composites. The results indicate that the modifiers form a passivation layer at the surface of BT nanoparticle, obstruct the formation of dielectric channels and weaken the intensity of dipole polarization. At the same time, the passivation layer reduces the Maxwell–Wagner–Sillars (MWS) interfacial polarization and space charge polarization of the composites,[42] which makes the composites have lower remnant polarization than composites BT/PVDF (Fig. 9b) and able to tolerate higher voltage without breakdown.

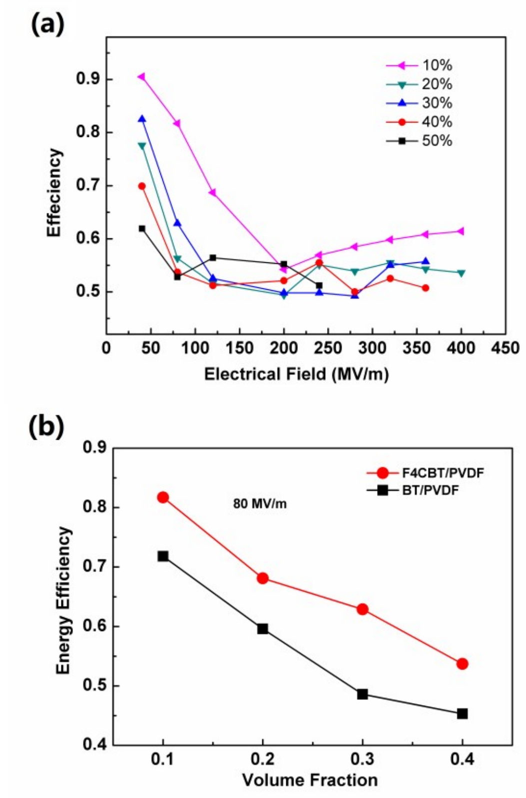

Figure 10 (a) Efficiencies of the composites F4CBT/PVDF with different volume fractions as a function of the electric field; (b) the comparison of efficiency between the composites F4CBT/PVDF and BT/PVDF at 80MV/m.

For practical applications, the composites not only need to have a high energy density, but also desired to maintain a high efficiency, since high energy loss in capacitor will lead to more heat, which destroy the performance and reliability of the whole device. The energy storage efficiency (η) could be calculated according to the formula,

$$\eta = \frac{\text{discharge energy}}{\text{charge energy}} = \frac{U_e}{U_e + U_{loss}} \quad (2)$$

where U_{loss} is the energy loss. The energy loss was calculated by the numerical integration of the closed area of the hysteresis loops.[7,43] Fig. 10a shows the efficiencies of the composites as function of electric field with different filler loading. It is clearly shown that the efficiencies decrease as electric filed increasing under low electric filed. And then the tendency of the efficiency curve tends to be flat and exhibits nearly independence on electric

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field. Below 100MV/m, the efficiencies of the composites decrease as the concentration of filler increasing. After that, the trends are not obvious as electric field increasing but they are all higher than 45% before breakdown. Fig. 10b shows the efficiency of composites F4CBT/PVDF and BT/PVDF with various volume fractions at 80MV/m. Compared with BT/PVDF composites, F4CBT/PVDF composites exhibit much higher energy efficiency within all the filler loadings. The improved efficiency is attributed to the reduction of the remnant polarization of the composites F4CBT/PVDF, which is technologically meaningful for energy storage because a low remnant polarization generally indicates low energy loss. The reduction of remnant polarization in the composites becomes more remarkable with the increase of the filler content. The results demonstrate that the composites developed here can capitalize upon the combination the large permittivity of inorganic materials and the high breakdown strength of polymers to achieve high energy density and high efficiency.

Conclusions

In summary, homogeneous composites comprising PVDF polymer and the fluorocarboxylic acid modified BT nanoparticles were prepared via a chemical route. The FTIR spectra and the thermo gravimetric analyses show that the F4C modifier shell layer was bonded to the surface of the BT nanoparticles, which provides significant effects on the resulting dielectric behaviors and energy density of the composite. Large breakdown strengths have been obtained with an increase of 81.3% compared with the composite filled with 40% unmodified BT nanoparticles; a high energy density of 9.4 J/cm^3 has been achieved at 400 MV/m with 10% volume fraction, which is two times as high as that of pristine BT/PVDF composites. The results demonstrate that the fluorocarboxylic acid as modifier can effectively improve the dielectric performance of PVDF based composites, thus providing an excellent modifier for the composites' development in pulsed power capacitors.

Acknowledgment and Notes

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Electronic Materials Research Laboratory, Key Laboratory of Ministry of Education & State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, China. Fax: +86-29-82660974; e-mail: hwang@mail.xjtu.edu.cn

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