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LETTER

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# Improving Dielectric Properties of $BaTiO_3$/Ferroelectric Polymer Composites by Employing Surface Hydroxylated $BaTiO_3$ Nanoparticles

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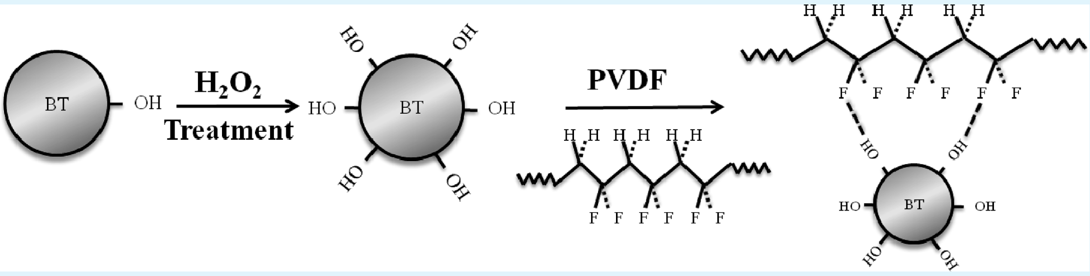
S Supporting Information

**ABSTRACT:**



Dielectric properties of poly(vinylidene fluoride) (PVDF) based nanocomposites filled with surface hydroxylated $BaTiO_3$ (h-BT) nanoparticles were reported. The h-BT fillers were prepared from crude $BaTiO_3$ (c-BT) in aqueous solution of $H_2O_2$. Results showed that the dielectric properties of the h-BT/PVDF nanocomposites had weaker temperature and frequency dependences than that of c-BT/PVDF nanocomposites. Meanwhile, the h-BT/PVDF composites showed lower loss tangent and higher dielectric strength. It is suggested that the strong interaction between h-BT fillers and PVDF matrix is the main reason for the improved dielectric properties.

**KEYWORDS:** barium titanate, hydroxylation, dielectric property, nanocomposites

## 1. INTRODUCTION

High dielectric-permittivity materials (known as high-K materials) are much desirable in the electric industry.[1] In the past decade, great efforts have been made to develop flexible ceramic/polymer nanocomposites with high permittivity, which can be potentially utilized for preparing embedded microcapacitors to meet the requirement of miniaturization trend of integrated circuits.[2−5] The introduction of ceramic particles with high dielectric constant could increase composites' dielectric constants. Meanwhile, the nature of easy processing and flexibility of the polymer host can be mostly preserved. Besides, in the recent years, some work has been focused on high-K ceramic/polymer nanocomposites by using a ferroelectric polymer, such as poly(vinylidene fluoride) (PVDF), poly(vinylidene-fluoride-trifluoroethylene) [P(VDF-TrFE)], and poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) [P(VDF-TrFE-CFE)] as a host material because of their fairly high dielectric constants.[6−10] However, these ferroelectric polymers-based nanocomposites have their limitations. First, their dielectrics constant show poor temperature stability. Usually, the dielectric constants of the ferroelectric polymer-based composites increase remarkably with the increase of the temperature. Second, the dielectric loss of these polymer composites is large, which might produce a great deal of heat that could influence composites' performance.[9,11]

Although a great deal of work has been done on mixing various polymers with different kinds of fillers to endow the composites with high performance including high dielectric constant, low loss tangent and good thermal stability, little research focuses on the effect of the interface between fillers and polymer matrix on the dielectric performance of the nanocomposites.[12−16] In fact, the interface could significantly influence the dielectric performance of the composites. In this letter, the surface of BT particles was chemically modified by $H_2O_2$ to introduce plenty of hydroxyl groups.[17] The PVDF-based nanocomposites filled with c-BT particles and h-BT

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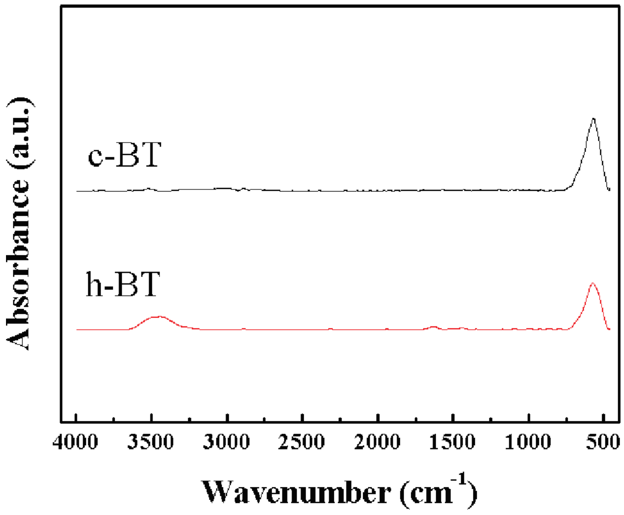


**Figure 1.** FTIR spectra of c-BT and h-BT nanoparticles.

particles were prepared and a comparison was made between them. It was found that the dielectric permittivity of the h-BT/PVDF nanocomposites had higher stability than c-BT/PVDF nanocomposites at temperatures between 20 and 150 °C. Higher dielectric breakdown strength was also found in the h-BT/PVDF nanocomposites. The hydrogen bond which leads stronger interaction between the h-BT fillers and the PVDF matrix might be the reason.

## 2. EXPERIMENTAL SECTION

The c-BT particles (85−100 nm) were chosen as the functional fillers (see Figure S1 in the Supporting Information). To prepare the h-BT particles, were refluxed 15 g of c-BT particles in an aqueous solution of $H_2O_2$ (35%, 350 mL) at 106 °C for 6 h, and then centrifuged and baked the solution in an oven at 80 °C for 12 h. The nanocomposites were prepared by employing a solution method. The BT particles were ultrasonically dispersed in *N*,*N*-dimethylformamide for 0.5 h. Then PVDF powder was added into the system with mechanical stir for 2 h at 70 °C. Then the mixture was cast on clean glass plates and dried at 80 °C for 4 h in an oven. The prepared nanocomposites loaded with various filler concentration and thickness of 55−70 $\mu$m were collected for test. Fourier transform infrared (FTIR) spectra (Nicolet 5DX) was used to check the effect of surface hydroxylation of the BT particles. Scanning electron microscope (SEM) (Zeiss JSM-6700F) was used to observe the fractured cross-surface of nanocomposites. Impedance analyzer (Agilent 4294A) was employed to measure the dielectric properties of the nanocomposites. High-voltage instrument (CS2674A) was used to measure DC breakdown strength of the nanocomposites.

## 3. RESULTS AND DISCUSSION

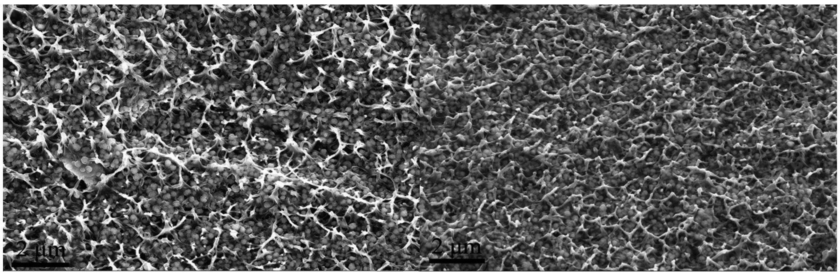
FTIR is used to testify the effect of the $H_2O_2$ treatment on the surface of the c-BT particles. As shown in Figure 1, the peak at 594 $cm^{-1}$ is assigned to the Ti−O vibration of BT. The new band at 3443 $cm^{-1}$, shown in is associated to the stretching mode of O−H, which comes from the hydroxylation of c-BT particles by the $H_2O_2$. These results indicate that the surface treatment of the c-BT nanoparticles with $H_2O_2$ could endow the c-BT particles with −OH groups.

Panels a and b in Figure 2 show the surface morphology of the fractured cross-surface of the two kinds of nanocomposites. It can be seen that the BT particles are well-dispersed in both samples. This result shows that uniform BT/PVDF nanocomposites can be obtained by solution method. However, there are much more small holes in the c-BT/PVDF composites. The holes are due to the c-BT particles being pulled out of the PVDF host during the breaking process. This result indicates there are much stronger interaction between h-BT particles and PVDF polymer than that between c-BT particles and PVDF polymer. The formation of hydrogen bond between h-BT particles and PVDF host might be the reason. As the schematic pictures show in Figure 3, quantities of hydroxyl groups are attached to the c-BT surface by its reaction with $H_2O_2$. When the h-BT particles are mixed with PVDF polymer, hydrogen bond will form between the F atoms on the PVDF and the −OH groups on the surface of the h-BT particles. As a result, strong interaction between h-BT particles and PVDF host is produced.

Figure 4 presents the dielectric constants of the c-BT/PVDF and the h-BT/PVDF nanocomposites with various filler concentration over a wide range of temperatures at 100 Hz. The dielectric constants of the PVDF were remarkably improved by introducing the two kinds of BT fillers. Stronger interfacial interaction in h-BT/PVDF composite should lead to fewer voids in the composites, and it will make the h-BT/PVDF have higher dielectric constants. In fact, the opposite results were given in Figure 4. Thermal analysis tests show hydroxylation of the BT particles rarely influence the PVDF crystal structure in the BT/PVDF nanocomposites (see Figure S2 in the Supporting Information). The dielectric properties of the nanocomposites can be explained as follows. The smaller dielectric constants were related with smaller polarization of the composites. The mobility of the polymer chain segments and the side groups in the h-BT/PVDF nanocomposites are significantly restricted because of the hydrogen bond. Consequently, smaller electrical displacements are achieved under the same electrical field, making the h-BT/PVDF nanocomposites have smaller dielectric constants.

Additionally, all the composites experienced a monotonic decrease in the dielectric constant at elevated temperature. In fact, mobility of the PVDF molecular is significantly promoted with increasing temperature. Consequently, larger dielectric constants are achieved at higher temperature. Moreover, the dielectric permittivities of the two composites are close to each other at room temperature, while they are distinct at higher temperature. It means the c-BT/PVDF composites show weaker temperature dependence in dielectric constants. At low temperatures, it is difficult for molecules response to the applied electrical field in both kinds of composite because of the poor molecular mobility. At the high temperature, the molecular mobility is significant improved in the c-BT/PVDF nanocomposites, but the hydrogen bonds in the h-BT/PVDF nanocomposites still restrict the mobility of the molecules and consequently make the dielectric constants increase much slower with the temperature.

Dependence of dielectric constant and loss tangent of the c-BT/PVDF and h-BT/PVDF nanocomposites are shown in panels a and b in Figure 5. The dielectric constants of the h-BT/PVDF nanocomposite are smaller than that of the c-BT/PVDF nanocomposites and decrease much slower with the increasing frequency. The results suggest that the dielectric properties of the h-BT/PVDF composites possess better frequency stability. This phenomenon can be explained as follows. At high frequency, molecules in both kinds of samples do not have enough time to be polarized. However, at low frequency, the molecules in the



(a) (b)

**Figure 2.** SEM pictures of the fractured cross-surface of the (a) c-BT/PVDF and (b) h-BT/PVDF nanocomposites with the filler concentration of 30 vol %.

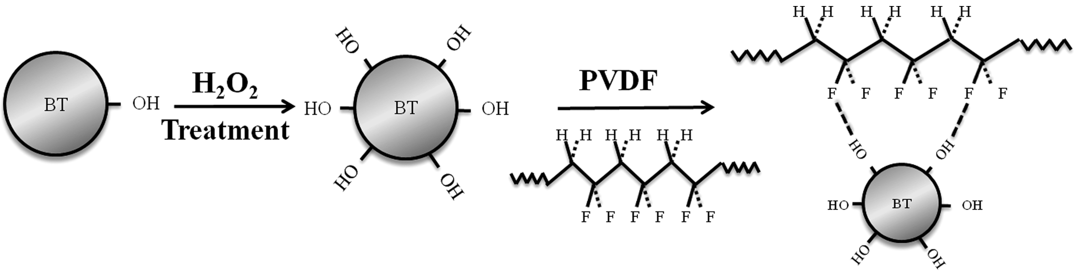


**Figure 3.** Schematic diagrams of the hydroxylation of BT particles and formation of hydrogen bond in h-BT/PVDF nanocomposites.

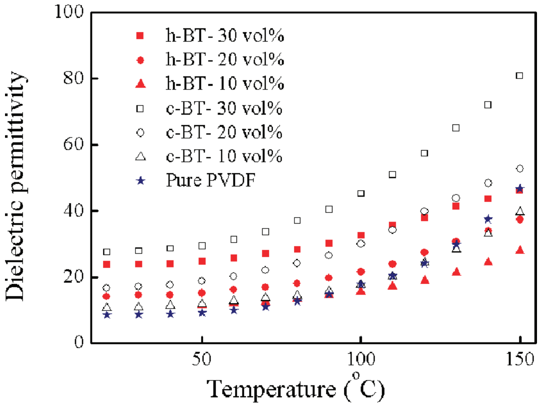


**Figure 4.** Temperature dependence of dielectric permittivity of the c-BT/PVDF and h-BT/PVDF nanocomopposites filled with various concentrations of fillers at 100 Hz.

h-BT/PVDF nanocomposites are still much refrained by the hydrogen bond, and thus the h-BT/PVDF nanocomposites shows weak dependence of dielectric constant on frequency. Additionally, the dielectric loss of the h-BT/PVDF nanocomposites is lower than that of the c-BT/PVDF nanocomposites, which makes them more attractive in application. The interaction between the h-BT filler and the PVDF matrix can be confirmed by Figure 6. The loss tangent peaks correspond to the glass transition temperature of PVDF. The loss tangent peak moving to a higher temperature in the h-BT/PVDF composites indicates the molecules in the PVDF have lower mobility. The results are in good agreement with the measured properties of the composites.

Figure 7 shows the breakdown strength of the nanocomposites. Weibull statistics was used to analyze the data of breakdown strength of the composites. The Weibull statistical distribution used for the breakdown strength is given in the following equation

$$P = 1 - \exp\left[-\left(\frac{E}{E_0}\right)^{\beta}\right] \quad (1)$$

where $P$ represents the cumulative probability of electrical failure, $E$ donates the experimental breakdown strength, $\beta$ is the shape parameter, and $E_0$ represents the breakdown strength at the cumulative failure probability of 63.2%, which is often used to compare the breakdown strength of various samples. Usually, the above equation is changed into double logarithmic transformation for plotting

$$\log[-\ln(1-P)] = \beta \log E - \beta \log E_0 \quad (2)$$

As shown in Figure 7, with increasing filler concentration, the dielectric breakdown strength of the composites becomes lower. There might be two reasons. First, introducing the high dielectric permittivity filler into the low dielectric polymer host will increase the electric field in the polymer host.[14] As a result, the dielectric breakdown strength of the composites decreases obviously. Second, more voids will be introduced into the nanocomposites with the rising filler concentration. These voids will definitely diminish the dielectric strength of the composite because of the low breakdown strength of the air. It should be noted that the h-BT/PVDF nanocomposites show higher dielectric breakdown strength than that of the c-BT/PVDF nanocomposites at the same filler concentration. It might be due to the improved compatibility between the h-BT and PVDF

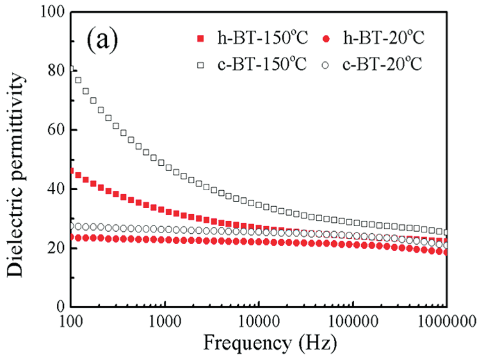


**Figure 5.** Frequency dependences of (a) dielectric permittivity and (b) loss tangent of the c-BT/PVDF and h-BT/PVDF nanocomposites loaded with 30 vol% fillers at various temperatures.

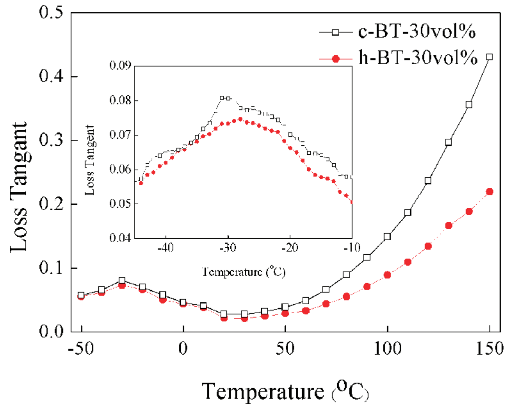


**Figure 6.** Temperature dependence of loss tangent of the c-BT/PVDF and h-BT/PVDF nanocomposites loaded with 30 vol % fillers at 1 kHz.

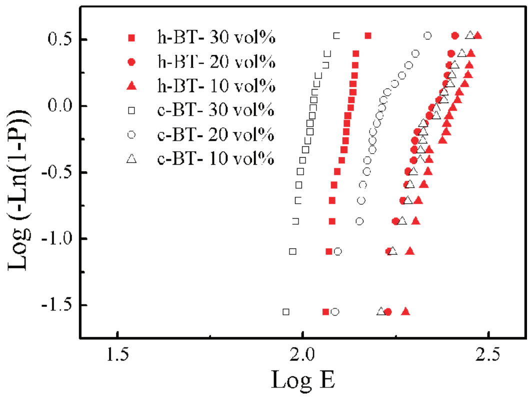


**Figure 7.** Weibull plots of the dielectric strength for c-BT/PVDF and h-BT/PVDF nanocomposites loaded with various concentrations of fillers.

host that can decrease the voids quantity in the composites, and in turn improve the dielectric breakdown strength of the composites.

## 4. CONCLUSIONS

In conclusion, hydroxylation of BT nanoparticles has been realized. BT/PVDF nanocomposite can be achieved by solution method. Compared with the c-BT/PVDF nanocomposites, the dielectric properties of the h-BT/PVDF nanocomposites show weaker temperature dependence and frequency dependence, and it also exhibits higher dielectric breakdown strength.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** TEM graph of the c-BT particles (Figure S1); DSC heating curves of the c-BT/PVDF and h-BT/PVDF nanocomposites (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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