Performance of Ba$_{0.95}$Ca$_{0.05}$Zr$_{0.15}$Ti$_{0.85}$O$_3$/PVDF composite flexible films

Yueping WANG and Zhijian PENG

School of Engineering and Technology, China University of Geosciences, Beijing 100083, PR China

Calcium barium zirconate titanate (Ba$_{0.95}$Ca$_{0.05}$Zr$_{0.15}$Ti$_{0.85}$O$_3$, BCZT) ceramic particles were obtained by conventional ceramic processing method. BCZT powders were modified by dopamine through chemical coating method. The composite films based on dopamine@BCZT and polyvinylidene fluoride were fabricated by solution casting method. The microstructure and morphology were characterized by X-ray diffraction, high-resolution transmission electron microscopy, and field emission scanning electron microscope. The impedance analyzer and dielectric withstand voltage test were used to test the dielectric constant, loss tangent, and breakdown strength. TEM results displayed that dopamine was coated on the surface of BCZT particles uniformly with an average thickness of 20 nm. SEM results revealed that the ceramic particles were dispersed homogeneously in the matrix. The dielectric constant increased with the increasing of BCZT contents, while the loss tangent remained constant in the frequency range of $10^3$ to $10^5$ Hz.

Key-words : Dielectric properties, Ceramic-polymer composites, BCZT, PVDF

1. Introduction

For the past few years, the polymer-ceramic composites have been receiving a lot attention because of their excellent physical properties such as high-energy storage density, high dielectric constant, and low dielectric loss, which have potential application in many fields like sensors, embedded capacitors, energy storage devices and gate dielectrics applied in electronic and electrical industry. Ferroelectric ceramics have been the soul of several multibillion dollar industries, ranging from high dielectric constant capacitors to later fast developments in piezoelectric transducers, positive temperature coefficient devices, and electro-optic light valves, since the phenomenon of ferroelectricity was found in 1940s. However, they generally suffer from low dielectric breakdown strength, and processing difficult despite the high dielectric constant. On the other hand, the polymer matrix possesses large breakdown strength, easy to process and great mechanical strength, though have a very low dielectric constant, which is usually less than 10. So, integrating the ferroelectric ceramics into the polymer matrix, a novel composites with high capacitor, high energy storage density, and small volume can be fabricated. Currently, the ferroelectric ceramic fillers used into the polymer matrix are CaCu$_3$Ti$_4$O$_{12}$ (CCTO), BaTiO$_3$ (BT), etc. Barium titanate, as a material which is environmentally friendly, plays an important role in manufacturing the MLCCs due to its high permittivity and low losses, and in electric devices and thermostors because of its good dielectric characteristics. 

Nevertheless, the application in certain areas of pure barium titanate ceramic is limited due to the stable range working temperature and high loss tangent. To improve the ferroelectric properties, researchers concentrate their attention on the doping of metal ions into BaTiO$_3$ crystal. Metal oxides-doped BaTiO$_3$ ceramics have been found to possess a significant improvement in dielectric properties, as well as an interesting dielectric relaxation behavior. Li et al. doped a small amount of CuO into BaTiO$_3$ ceramics, probed into its effect on the microstructures and dielectric properties of BaTiO$_3$. It was discovered that the permittivity increases markedly for CuO doped content $x = 0.2$–0.4% and the dielectric loss decreases significantly after being doped by CuO and down to a minimum value for $x = 0.8%$. Mathibub et al. discussed the correlation between the dielectric properties and the structural characteristics of Ta$_2$O$_5$ doped BaTiO$_3$ ceramics under different sintering conditions. The results showed that dielectric properties and microstructure of BaTiO$_3$ ceramics were influenced markedly by the addition of a small amount of Ta$_2$O$_5$.

Recently, much attention has been paid to poly(vinylidene fluoride) (PVDF) due to the high breakdown strength, better thermal stability and easy to process. PVDF, also a nontoxic material, is a semi-crystalline polymer exists in four different crystalline forms depending on the preparation conditions such as method of casting, melt temperature, annealing conditions and stretching of thin films. The $\beta$-phase is the desirable phase on account of its ferroelectric nature. So, dielectric composites based on PVDF matrix have been attracting more attention. Thomas et al. prepared the Poly(vinylidene fluoride)/CaCu$_3$Ti$_4$O$_{12}$ (CCTO) nanocrystal composite films (~85 mm) with relatively high dielectric permittivity (90 at 100 Hz) by the solution casting followed by spin-coating technique. Kobayashi et al. obtained BaTiO$_3$ polymer composite films by polyvinylidene fluoride (PVDF) and siloxane-modified polyamidimide (SPAI) as host polymers respectively. It was discovered that the dielectric constant reached 31.8 for the 30 vol % –BaTiO$_3$-PVDF film with the BaTiO$_3$ crystal size of 27.3 nm, that was four times larger than the dielectric constant of the PVDF film without BaTiO$_3$ and corresponded to a capacitance density as large as 0.63 nF/mm$^2$.

As we know, no previous work had reported the dielectric composite films integrating Ba$_{0.95}$Ca$_{0.05}$Zr$_{0.15}$Ti$_{0.85}$O$_3$ filler and PVDF matrix, so the aim is to make the Ba$_{0.95}$Ca$_{0.05}$Zr$_{0.15}$Ti$_{0.85}$O$_3$/PVDF composite films. However, dispersing the filler
uniformly in the matrix especially at higher volume is a difficult problem, as account of the discrepancy in the surface characteristics between the inorganic filler and the organic matrix. To improve the interface fusion between the inorganic filler and the organic matrix, many coupling agents have been applied to improve the properties of filled polymers. Yang et al.\textsuperscript{14} obtained CCTO/Si69/PVDF composites through treating the surface of CCTO by the silane coupling agent bis[3-(triethoxysilyl) propyl] tetrasulfide (Si69), and discussed the interface effect on the dielectric properties of CCTO/PVDF composites. Lin et al\textsuperscript{15} investigated the surface functionalization of BaTiO$_3$ nanoparticles by dopamine, so as to improve its compatibility with the polyvinylidene fluoride polymer matrix. It was found the dielectric constant could be increased to 56.8 with low dielectric loss. Song et al.\textsuperscript{16} studied the effect of dopamine on the dielectric properties of Ba$_{0.95}$Ca$_{0.05}$Zr$_{0.15}$Ti$_{0.85}$O$_3$/PVDF composites. Also, Song et al. fabricated a flexible poly(vinylidene fluoride-trifluoroethylene) nanocomposites with dopamine-modified BaTiO$_3$ nanofibers as the filler and the dielectric and ferroelectric properties of composites were found to be enhanced.\textsuperscript{17} In this report, we study the performance of Ba$_{0.95}$Ca$_{0.05}$Zr$_{0.15}$Ti$_{0.85}$O$_3$/PVDF composite films with dopamine as a coupling agent. The effects of inorganic filler on the microstructure, and the dielectric properties were investigated.

2. Experimental

2.1 Preparation of BCZT and Dopamine@BCZT powders

Submicron-sized BCZT polycrystalline powders were fabricated by conventional method. Stoichiometric quantities of BaCO$_3$, CaCO$_3$, TiO$_2$, and ZrO$_2$ powders were weighed accurately and mixed. Then, the mixture was put into ball grinder with moderate of zirconia balls and deionized water. After grinding for 24 h, the slurry was sand milled for 6 h, which can crush and disperse the particles further. Then, the slurry was dried at 120°C and sintered for 2 h at 1150°C. The BCZT powders with the particle size of 200–300 nm were synthesized.

In order to surface modification, dopamine@BCZT powders were prepared by chemical coating method. At first, the BCZT powders were dispersed in ethanol/water and stirred for 1 h in order to add the OH functional group to the surface of BCZT powders. After drying, the powders were dispersed into 0.03 mol·L$^{-1}$ of dopamine hydrochloride (99%, Alfa Aesar). Then the suspension was stirred for 24 h at 60°C. Next, the suspension was dried at 60°C in a vacuum oven. After the powders sieved, dopamine@BCZT powders were obtained.

2.2 Preparation of Dopamine@BCZT/PVDF composite films

The Dopamine@BCZT/PVDF composite was obtained by solution casting method. PVDF, as the polymer matrix, was bought from Solef, and Table 1 showed the physical properties. Firstly, the PVDF polymer was dissolved in N,N-dimethyl formamide (99%, Alfa Aesar) solvent at 60°C and stirred for 1 h until the solution was transparent. Next, 4–6 vol% dopamine@BCZT powders were added to the solution. Then the mixture was stirred for 48 h at 60°C. After the solvent was evaporated at 80°C, the suspensions were concentrated. Finally, the suspensions were poured into a casting dish. The dopamine@BCZT/PVDF composite films with a thickness of 20–100 μm film were obtained. The schematic diagrams of the manufacture of dopamine@BCZT/PVDF composite films are displayed in Fig. 1.

2.3 Characteristic

The phase composition of the samples was identified by X-ray diffractometer (XRD, Rigaku D/max-2500, Cu Kα radiation, and λ = 1.5418 Å) using a continuous scanning mode with speed of 4°/min. Fourier transform infrared (FTIR) spectra of all samples were recorded in the 500–4000 cm$^{-1}$ range with a Nicolet 6700 spectrometer. The surface coatings of BCZT particles were surveyed by high-resolution transmission electron microscopy (HRTEM, JEOL, Japan). The morphology of the dopamine@BCZT/PVDF composite films was surveyed with a field emission scanning electron microscope (FESEM, LEO-1530, LEO, Oberkochen, Germany). For dielectric measurements, silver electrodes were coated on the both sides of the samples. The dielectric constant and loss tangent of the composite films were measured by HP 4294A precision impedance analyzer (Agilent) at room temperature with a frequency from 40 Hz to 10 MHz. The electric breakdown strength was obtained by a dielectric withstand voltage test (YD2013, Changzhou Yangzi Electronic Co., Ltd) with 6–8 specimens tested to increase the accuracy.

3. Results and discussion

3.1 Microstructure of surface coatings

XRD patterns of BCZT powders modified by dopamine and BCZT powders were shown in Fig. 2. It was found that the strong peaks at 2θ that corresponded to 22°(100), 31°(110), 39°(111), 45°(200), and 56°(211) were assigned to BCZT with cubic perovskite structure. No visible signal of the presence of secondary phases was observed, neither reflection splitting nor super-lattice reflections were found. After modified by dopamine, no difference was found in the X-ray patterns of BCZT. Figure 3 showed the FT-IR absorbance spectra of BCZT powders and

![Fig. 1. Schematic diagrams of manufacture of dopamine@BCZT/PVDF composite films.](image)

**Table 1. The physical properties of PVDF**

| PVDF    | Density (g/cm$^3$) | Volume resistivity (Ω·cm) | Melting point (°C) | Glass transition (°C) | Crystallizing point (°C) | Thermal stability (°C) |
|---------|-------------------|---------------------------|--------------------|-----------------------|-------------------------|------------------------|
| SOLEF  | 1.78              | >1.10$^{4}$               | 173                | -32                   | 138                     | >400                   |
dopamine@BCZT powders. After BCZT was modified by dopamine, the absorption intensity in the range of 4000–1000 cm⁻¹ wavenumbers increased. It was found that the peak locate at 3431 cm⁻¹ wavenumber was assigned to O–H stretching vibrations, which may be generated from the ethanol/water from samples. As for solid state, hydrogen bonding was formed between the neighboring hydroxyl, leading to the broader band-width and larger intensity. The absorption peak at 1050 cm⁻¹ corresponded to the C–O bending vibrations existed between benzene ring and hydroxyl. Furthermore, the absorption peaks located at 1265, 1493, and 1630 cm⁻¹ wavenumber corresponded to aromatic amine C–N stretching vibrations, aromatic C–C stretching vibrations, and N–H bending vibrations, respectively, which are generated from aromatic and amido groups, suggesting the existence dopamine.

Figure 4 showed the TEM images of Dopamine@BCZT powders. It was shown that the BCZT powders was consisted of spherical particles with the grain size of 200–300 nm. Figure 4(a) showed the aggregation between the neighboring particles, which was because that the surface free energy could be lowered greatly through the closest packing from spherical particles. As is shown in Fig. 4(b), dopamine was uniformly coated on the surface of BCZT particles with an average thickness of 20 nm revealing the good coating effect.

3.2 Microstructure and morphology of Dopamine@BCZT/PVDF composite films

The powder X-ray diffraction patterns of dopamine@BCZT/PVDF composite films with BCZT contents of 0–61 vol% were shown in Fig. 5. As is known, PVDF is a semi-crystalline polymer exists in four different crystalline forms depending on the preparation conditions like solvent, melt temperature, method of casting, stretching of thin films, and annealing conditions. The strongest peak at 2θ corresponding to 18.5° was assigned to α-PVDF, the peaks at 2θ corresponding to 20° and 23° were assigned to β-PVDF, and the broad peak at 2θ corresponding to 26.6° was assigned to γ-PVDF.21) After the BCZT was incorporated in PVDF matrix, the peaks assigned to PVDF shows an evident reduction in intensity. In contrast, the diffraction peaks assigned to BCZT become clearly visible. Among the peaks at 2θ corresponding to 32°(110), 39°(111), 45°(200), 56°(211), and 65°(220), there were no reflection splitting, no super-lattice reflections, and no secondary phase found indicating that the BCZT possess the cubic perovskite structure. With the addition of BCZT powders increasing, the peaks belonging to PVDF reduced gradually, while that of BCZT became sharper and stronger. When the addition of BCZT increased to 41 vol%, the peaks of PVDF were very weak because of the strong diffraction of the incorporated ceramic powders. It was also found that as the addition of inorganic components increasing, the intensity of crystallized phase peaks became stronger and the crystallinity was much greater, showing that stable solid solution was formed between BCZT and PVDF.

FT-IR spectra of dopamine@BCZT/PVDF composite films filled with various fractions of BCZT powders was shown in Fig. 6. It was found that the composite films were consisted of α-phase, β-phase, and γ-phase PVDF. The absorbance band at 765, and 613, 765, and 975 cm⁻¹ was related to α-phase. The band at 613 and 766 cm⁻¹ are the bending and wagging vibration of CF₂ groups and rocking vibration in the PVDF chain, respectively. The β-phase was observed at 840, 878, 1170, and 1232 cm⁻¹. The absorbance band at 872 cm⁻¹ was assigned to the CH₃ and CF₂ group generated from the CH₃ rocking and CF₂ stretching, while the band at 1170 and 1232 cm⁻¹ were assigned to the CH₂ group, which is attributed to the CH₂ wagging and rocking. The in-plane
bending or scissoring of CH2 was observed at 1402 cm\(^{-1}\), while the bending of C–C appeared at 1070 cm\(^{-1}\). From Fig. 6, with the increase of the contents of BCZT powders, the peaks of \(\beta\)-phase became stronger, while that of \(\alpha\)-phase became quite weak. It was concluded that the introducing of BCZT particles and the role-played by the dopamine affected the crystalline phase of PVDF from \(\alpha\)-phase to \(\beta\)-phase. The polar \(\beta\) phase is the most desirable from a technological point of view, for providing better dielectric properties.\(^{24}\)

The microstructure and morphology the dopamine@BCZT/PVDF composite films were observed by scanning electron microscopy (SEM) and the results were showed in Fig. 7. From Fig. 7(a), the pure PVDF film was clear and neat without any pores or impurities. Figures 7(b)–7(d) showed the surface morphologies of composite films filled with 9, 22 and 41 vol \% dopamine@BCZT powders, respectively. It was observed that the dark region was the PVDF matrix and the bright particles were the inorganic powders with the particle sizes of 200–300 nm. With the content of BCZT increasing, packing of particles grew denser, revealing that the excellent compatibility between poly(vinylidene fluoride) and dopamine modified BCZT particles. As the content of BCZT powders was 41 vol \% shown in Fig. 7(d), inorganic particles were dispersed homogeneously in the matrix of composite films with no obvious pores. Figure 8 showed the macroscopic images of the composites film with 41 vol \% (a) and 52 vol \% (b) of dopamine@BCZT powders. Given the good compatibility between dopamine modified BCZT powders and PVDF matrix, superior flexibility was obtained even at the high loading of BCZT powders, as shown in Fig. 8(b).

3.3 Dielectric constant, loss tangent of Dopa-min e@BCZT/PVDF composite films

The dielectric constants and loss of dopamine@BCZT/PVDF composite films as a function of the BCZT content were measured over the frequency range 40 Hz–10 MHz at room temperature, and the results were shown in Fig. 8. From Fig. 8(a), it was discovered that the dielectric constants increased with the increasing of dopamine@BCZT contents and slightly decreased with the increase of frequency. When the loading of BCZT particles was over 41 vol \%, the dielectric constant increase greatly with the increasing dopamine@BCZT contents. With the increasing frequency from 40 Hz to 10 MHz, the dielectric constant of composites decreases yet it could remain above 20 even at a high frequency as 10 MHz. As for 61 vol \% BCZT samples, the dielectric constant at 1000 Hz was increased to 100 from that of the neat PVDF samples which is 4. Meanwhile, the dielectric loss tangent remained quite low in the frequency range from 1000 to 105 Hz (shown in Fig. 8(b)). The dielectric loss tangent in the frequency range from 40 to 100 Hz was high conforming the existing of interfacial polarization, which originated from the signature relaxation. Little variation in the frequency range from 10^3 to 10^5 Hz and then increases to a sharp peak around 10^7 Hz, which is attributed to the glass, transition relaxation of the PVDF polymer matrix and is denoted as \(\alpha\) relaxation.

As for the increase in dielectric constants with the increase volume fractions of dopamine@BCZT powders stated above, it could be explained by the following three reasons. One was that the introduction of high dielectric constant BCZT particles led
to the average electric field enhancement in the matrix, and the more the BCZT content was introduced, the bigger the dielectric constants would be contributed to. Another one was that large amounts of charges accumulated at the interfaces of the two phase due to the difference between BCZT particles and PVDF matrix, forming the interfacial polarization. With the increasing of BCZT contents, the amounts of interfacial charges increased bringing about the enhancement of interfacial polarization density, which raised the dielectric constant of the whole materials. The third one was the surface modification of BCZT powders with dopamine. As is shown in Fig. 1, the organic layers formed by the polymerization of dopamine on the surface of BCZT powders played a critical role in the conjugation between BCZT particles and PVDF powders, which determine the dielectric performance of the composite films. Firstly, the –OH was added onto the surface of BCZT particles through the dispersing in ethanol/water, resulting in the surface activity increase. Next, the –OH was connected to the NH2 of dopamine, which made the remaining –OH of dopamine active. Finally, by the coupling of dopamine, BCZT particles were connected to the PVDF matrix.

In addition, the dielectric behavior of the dopamine@BCZT/PVDF composite films, several theoretical models have been proposed and comparisons between theoretical values and the experimental were done in order to analyze quantitatively. Modified Rother–Lichtenecker model, which is based on the Rother–Lichtenecker equation, one representation of logarithmic law of mixing for a chaotic or statistical mixture, is demonstrated as:

\[ \ln \varepsilon_{\text{eff}} = \ln \varepsilon_p + f (1 - k) (\ln \varepsilon_c - \ln \varepsilon_p) \]  

(1)

where \( k \) is the shape-dependent parameter. \( \varepsilon_p \) and \( \varepsilon_c \) represent the dielectric constant of the composite film, PVDF matrix, and BCZT, respectively. Maxwell–Wagner mixing rule is usually used to predict the effective constant for a ceramic-polymer composite incorporating distributed spherical inclusions of ceramic material, which is calculated as:

\[ \varepsilon_{\text{eff}} = \varepsilon_p + \frac{2\varepsilon_p + \varepsilon_c + 2f(\varepsilon_c - \varepsilon_p)}{2\varepsilon_p + \varepsilon_c - f(\varepsilon_c - \varepsilon_p)} \]  

(2)

where \( f \) is the volume fractions of the BCZT fillers. Jayasundere and Smith deduced the following equation for the permittivity as a randomly connected state in a binary piezoelectric 0–3 composite by modifying the well-known Kerner equation including interactions between neighboring spheres:

\[ \varepsilon_{\text{eff}} = \varepsilon_p \left[ \frac{3\varepsilon_p \varepsilon_c}{2\varepsilon_p + \varepsilon_c} \left( 1 + 3 \frac{\varepsilon_c - \varepsilon_p}{\varepsilon_c + 2\varepsilon_p} \right) \right] \]  

\[ + \varepsilon_p \left[ \frac{3\varepsilon_p \varepsilon_c}{2\varepsilon_p + \varepsilon_c} \left( 1 + 3 \frac{\varepsilon_c - \varepsilon_p}{\varepsilon_c + 2\varepsilon_p} \right) \right] \]  

\[ + \frac{1}{2} \frac{2\varepsilon_p + \varepsilon_c + 2f(\varepsilon_c - \varepsilon_p)}{2\varepsilon_p + \varepsilon_c - f(\varepsilon_c - \varepsilon_p)} \]  

(3)

where \( \varepsilon_p \) and \( \varepsilon_c \) is the volume fraction of polymer and ceramic, respectively, \( \varepsilon_p + \varepsilon_c = 1 \). In this study, the value of \( \varepsilon_p \) and \( \varepsilon_c \) used 8000 and 4, respectively.

\[ \begin{array}{|c|c|c|c|c|}
\hline
\text{Model} & \text{Correlation coefficient} & \text{Maximum deviation} & \text{Mean square error} & \text{Residue standard deviation} \\
\hline
\text{Modified Rother–Lichtenecker} & k = 0.3 & 0.9834 & 15.0456 & 15.8842 & 7.1036 \\
\text{Modified Rother–Lichtenecker model (k=0.4)} & k = 0.4 & 0.8244 & 0.2154 & 38.1764 & 17.073 \\
\text{Maxwell–Wagner Model} & k = 0.3 & 0.5184 & -0.3631 & 84.1075 & 37.614 \\
\text{Jayasundere–Smith Model} & & 0.7172 & -0.3107 & 49.3784 & 22.0827 \\
\hline
\end{array} \]

**Figure 9** showed the experimental and theoretical dielectric constant predicted by Maxwell–Wagner model, Modified Rother–Lichtenecker model, and Jayasundere–Smith model at 1000 Hz and room temperature of dopamine@BCZT/PVDF composite films with different volume fractions of BCZT powder contents. From Fig. 9, it was found that the experimental data was in good accordance with Modified Rother–Lichtenecker, Jayasundere–Smith model and Maxwell–Wagner as the volume fraction of BCZT powder contents was less than 20%. But, as the volume fraction was higher, Maxwell–Wagner model started to be unfit for the experimental data and the deviation became more apparent as more content of BCZT powder was added. This can be explained that more BCZT particles would import more interfaces into the composites at higher filler concentration, however these two models just neglected the interaction. In contrast, Jayasundere–Smith model takes the interactions between neighboring spheres into account, as well as Modified Rother–Lichtenecker Model employs a shape-dependent parameter, being account for a good agreement with the with experimental data when the volume fractions of BCZT were over 30. The residue standard deviation, mean square error, correlation coefficient, and maximum deviation were applied to reflect the differences between the experimental and theoretical dielectric constant, as listed in **Table 2**. It can be found that the theoretical dielectric constant predicted by Jayasundere–Smith model had a low residue standard deviation of 0.7172 and a correlation coefficient of 0.7172, and the theoretical dielectric constant predicted by Modified Rother–Lichtenecker model had a low residue standard deviation of 7.1036 and a correlation coefficient of 0.9834. Therefore, it is concluded that the Modified Rother–Lichtenecker and Jayasundere–Smith model are much useful to predict the dielectric constant of ceramic-polymer composites, yet this model has a little limitation that it makes no difference as the dielectric constant of ceramic powder is over thousand.
4. Conclusions

$\text{Ba}_{0.95}\text{Ca}_{0.05}\text{Zr}_{0.15}\text{Ti}_{0.85}\text{O}_3$/PVDF composite flexible films with high dielectric constant and low dielectric loss were prepared through a solution casting method with dopamine@BCZT powders as filler. TEM results displayed that dopamine was uniformly coated on the surface of BCZT particles with an average thickness of 20 nm. SEM results indicated that the ceramic particles were dispersed homogeneously in the matrix. The dielectric constant increased with the increasing of BCZT contents, while the loss tangent remained constant in the frequency range of $10^3$ to $10^5$ Hz.

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