Modified BaTiO$_3$/PVDF/Ni composites with high dielectric constant and low dielectric loss

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Abstract. Low dielectric properties of BaTiO$_3$/PVDF composites limit its application in modern microelectronics and high energy storage. In this work, three-phase composites with high dielectric properties were prepared based on the surface modification of BaTiO$_3$(BT) ceramic. The results show that, after modification of BT, the dielectric constant of the BT/PVDF composite increased by 44%, and the dielectric loss decreased by 20% at 100Hz. Nickel powder was added to the modified composites for increasing dielectric constant, when the addition of nickel powder was 20%, the dielectric constant of composites was up to 441 and the dielectric loss of composite was only 0.057.

1. Introduction
High dielectric-constant materials with low dielectric loss are widely used in the field of the capacitor [1]. BT/PVDF composites show relatively high dielectric properties and good processability, which are potentially ideal dielectric materials. However, the composites can not replace the traditional inorganic dielectric material in the use of capacitor manufacture because of the relatively low dielectric constant[2-4].

A series of methods have been taken to improve the dielectric properties of BT/PVDF composites [5] [6]. Surface modification for BT, such as surface hydroxylation, silane coupling agent modification, can enhance the dielectric properties of BT/PVDF composites, which owing to the better interface connection within composites[7-8]. But there are still some problems, such as the high dielectric loss.

In this work, BT was modified by tartaric acid, and a series of composites were fabricated. It was found that the dielectric properties of BT/PVDF composites were improved after modification. Furthermore, three-phase composites of PVDF, which are modified BT and nickel power, exhibit higher comprehensive dielectric properties.

2. Experimental

2.1 Material
Barium titanate was purchased from Nantong the new electronics co., LTD., China. Nickel powder (high purity) and Tartaric acid (AR) was obtained from Tianjin days reagent co., LTD., China.
Polyvinylidene fluoride was supplied by Shanghai Institute of Organic Fluorine, China. All chemicals were used as received.

2.2 Preparation of composites
The surface modification of BT involved several steps: (i) dissolving tartaric acid in 50ml distilled water and the solution was adjusted to pH 9, (ii) dispersing BT in the solution and put into three-necked flask, (iii) heating to 50°C and stirring for 2 hr under water bath, (iv) drying at 60°C overnight under blast oven. A series of composites were prepared by following a simple blending and hot-pressing at about 170-175°C and 10-12MPa for 30 min (Figure 1). Finally, samples were polished and slivered by sliver-paint.

2.3 Characterization
The measurement of dielectric constant and electric conductivity were carried out using a HIOKI3532-50 LCR HITESTER meter (HIOKI, Japan) in the frequency range from 100 Hz to 2MHz. The dielectric constant was calculated by using the equation (1).

\[ \varepsilon = \frac{Cd}{\varepsilon_0 S} \]  

C is the capacitance (farads), \( \varepsilon_0 \) the free space dielectric constant value \( (8.854 \times 10^{-12} \text{F/m}) \), S the capacitor area \( (\text{m}^2) \) and d the thickness \( (\text{m}) \) of the samples. Scanning electron microscope (SEM) is from a HitachiS-530 (JEOL Japan) scanning electron microscope.

3. Results and discussion
It can be seen in Figure 2(a) and (b) that the dielectric constant of BT/PVDF composites increase with the increase of BT volume fraction \( (f_{BT}) \), and the composites show low dielectric loss. The dielectric constant of the composite material increases from 121 to 174 Figure 2(a), an increase of 44%, while the dielectric loss of the system increased from 0.051 to 0.042 in Figure 2(b), decreased 18% after modification.

![Figure 1. Modified BT/PVDF/Ni composite](image)

**Figure 1.** Modified BT/PVDF/Ni composite

![Figure 2. The dielectric properties of modified BT/PVDF composites: (a), the dielectric constant of composites ;(b), the dielectric loss of composites](image)

**Figure 2.** The dielectric properties of modified BT/PVDF composites: (a), the dielectric constant of composites ;(b), the dielectric loss of composites
Nickel power is introduced into the modified BT/PVDF composites to further increase the dielectric constant owing to the percolation theory. It can be seen in Figure 3, that the addition of Nickel power can significantly improve the dielectric constant of the composites (volume fraction PVDF keep 50%). When the volume fraction of Ni arrive 22%, the system reaches a maximum dielectric constant, 894 at 100Hz Figure 3(a), when the volume faction of nickel power is 20%, the dielectric loss is only 0.057 Figure 3(b), and the dielectric constant approaches to 441, increase of 153% comparing with modified BT/PVDF composites.

Figure 3. The dielectric constant (a) and loss (b) of modified and unmodified BT/PVDF/Ni composites

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Figure 4. SEM of modified and unmodified BT/PVDF/Ni composites: A, B unmodified BT/PVDF/Ni composite; and C, D modified BT/PVDF/Ni composite
SEM images of cross section of the BT/PVDF/Ni composites with 20%Ni are shown in Figure 4. The spherical particles are given to nickel power, and the lump solid for BT, the floc is for PVDF. It can be clearly found that the dispersibility of BT in the composites is good, and the surface of BT particles becomes much rougher after modifying, even there can be some thrusting. The reason of emergence of this thrusting is that an interface layer will be formed if BT particle modified by tartaric acid, which can enhance the interface connection of the composites. Furthermore, comparing to Ni dispersion before and after modification, it can be known that the agglomeration of Ni is reduced. The percolation threshold value increase a lot with the reduction of agglomeration. It can be known that modification can increase the dielectric constant of the composites.

4. Conclusion
Modified BT/PVDF composites which have higher dielectric constant and lower dielectric loss were prepared. When the volume fraction of modified BT was 70%, dielectric constant was increased from 121 to 174, up 44%, dielectric loss was decreased from 0.05 to 0.04 at 100Hz. Modified BT/PVDF/Ni composites were fabricated, higher dielectric constant of 441 is observed at 100Hz with 20 vol% of Nickel powder, increased by 153% comparing with to modified BT/PVDF composites, and the dielectric loss is only 0.057; Modified BT/PVDF/Ni composites show excellent comprehensive dielectric properties due to good dispersibility of BT and Ni particles, and interface reaction mechanism will be studied in further.

5. References
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