Improved Dielectric Properties of Polypropylene Nanocomposites with BaTiO₃ Nanoparticles

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Abstract. Polymer nanocomposites with improved dielectric permittivity are extremely desirable for the power capacitors. With the existing capacitor polypropylene (PP) film as the substrate, the surface of PP film is coated with a layer of BaTiO₃ (BT) with high dielectric constant of nanoparticles. Through the BT layer with high dielectric constant, the dielectric constant of the whole composite dielectric film is improved, and the dielectric loss is controlled at a relatively low level. The organic solvent system of BT paste coating and water system of BT paste coating research were prepared. Two kind of composite dielectric films which are PP/PVDF/BT and PP/BT were prepared by coating. The permittivity of PP/BT nano-composites with 50 wt% fillers at 1000 Hz was up to 4.49, which was nearly 2 times higher than that of pure PP film. According to the method, a pilot experiment was carried out. The strategy could be extended to a variety of inorganic fillers to improve the dielectric properties of polymer nano-composites for power capacitors.

1. Introduction

With the development of UHVDC transmission technology [¹-³], a lot of research has been done on long-distance high-capacity transmission [⁴,⁵]. In order to reduce energy loss, the transmission voltage level of the power grid is getting higher and higher. At present, the DC transmission level of Zhangbei Project has reached ±800KV to realize 100% green energy for the 2022 Winter Olympic Games. As an important part of DC power network, DC capacitor has attracted more and more attention. How to make capacitors with high energy density, miniaturization, safety and stability and low cost is still a hot issue. In the past...
few decades, great efforts have been made to develop flexible polymer nano-composites with high dielectric permittivity [6,7]. Polymers have good properties such as low dielectric loss, high breakdown strength, low cost and easy to process [8]. Compared with inorganic fillers, the dielectric permittivity of polymers is relatively lower. Therefore, high performance nano-composites can be prepared by combining the easily machined properties of polymers and the high dielectric properties of inorganic materials.

Recently, there has been a wealth of research on the preparation of inorganic fillers into polymer matrix. [9] However, the compatibility and dispersion between inorganic and polymer is an intractable issue. In addition to blends, coating the inorganic nano-fillers on the surface of the polymer substrate is a potential solution for industrialization to prepare the nano-composite capacitor film with high dielectric properties and high power density.

2. Materials and Methods
The excellent compatibility of inorganic fillers and polymer substrate is the crucial issue for the design of high performance capacitor. The compatibility has a huge influence on the dielectric permittivity and dielectric loss of the composites. In order to reduce the distortion points in the composite, in this study, coating routes were chosen to be studied. With the 8 μm commercial capacitor PP film from Borealis as the substrate, a homemade BT particles layer with high dielectric constant is coated on the surface of PP film. Through the BT layer with high dielectric constant, the dielectric constant of the whole composite dielectric film is improved, and the dielectric loss is controlled at a relatively low level. We mainly carried out the research of BT paste coating of organic solvent system and BT paste coating of water system. Through the two coating systems, PP/PVDF/BT and PP/BT composite dielectric film were prepared successfully. The dielectric properties of PP/PVDF/BT and PP/BT composite dielectric films were comparative studied.

3. Results & Discussion
3.1. Organic solvent system BT slurry coating
BT organic solvent system was studied with butanone as solvent and PVDF (polyvinylidene fluoride) with high dielectric constant as binder. 100nm BT particles with specific surface area of 13.5m²/g and a density of 5.86g/cm³ were prepared. As the specific surface area and density of BT particles are large, they are easy to aggregate and easy to settle. The surface of BT is chemically modified for better dispersion. Firstly, BT particles were modified with hydrogen peroxide by surface hydroxyl, and then reacted with phosphonyl butane tricarboxylic acid to form an organic modified BT with negative carboxyl charge. The reaction formula is shown in Figure 1 below:

![Figure 1](image)

Figure 1 Organic modification of BT nanoparticles.

In butanone, organic modified BT and PVDF were configured into organic slurry to study the dielectric behavior of three composite films when the mass fraction of BT was 10%, 25% and 50%. In Figure 2, with the increase of BT content in the coating, the dielectric constant increased from 2.38 to 3.08, while the dielectric loss increased significantly from 0.024 to 0.595. (Table 2) Increasing the dielectric constant can increase the capacitor's energy storage density, but high dielectric loss will generate too much heat and reduce the breakdown voltage of the material, resulting in the damage of the capacitor. Therefore, the BT content in the coating should be maintained at a reasonable level.
Table.1  Permittivity and dielectric loss at 1kHz in PP/PVDF/BT composite films

| BT content (wt%) | At 1kHz (Cons.) | Loss |
|------------------|-----------------|------|
| 10               | 2.38            | 0.024|
| 25               | 2.80            | 0.541|
| 50               | 3.08            | 0.595|

3.2. Waterborne system BT slurry coating

3.2.1 Research on BT waterborne coating slurry

When using BT directly to prepare water-dispersing slurry, due to its high density and serious agglomeration, BT is easy to settle and stratify in water, so uniform dispersion solution cannot be obtained. After directly shearing and dispersing solution is placed for 5 min, the settlement is basically complete (as shown in figure 3a). Therefore, the influence of different dispersants on the dispersion performance of BT was studied. The dispersion properties of different dispersants, such as PVP (poly vinyl pyrrolidone), PVA (poly vinyl acetate), PAA (poly acrylic acid) and PMA (poly methyl acrylate) were investigated. It was found that PMA had a good dispersion effect on BT, and there was no obvious stratification of the slurry after 24h of standing (as shown in Figure 3B), indicating that BT particles in the slurry had relatively uniform dispersion. The size test of the slurry showed that BT was very evenly dispersed, including D10=120nm, D50=556nm and D90=1.54um, indicating that a small part of BT particles in the slurry were monodispersed particles and most of them were small aggregates formed by the agglomeration of three or four primary particles (Figure 3c).

The paste was coated on the surface of PP capacitor film. The liquid film immediately contracted after coating, and the paste could not form a uniform coating on the surface of PP film (as shown in figure 4a). Different types of surface wetting agent (SDS, SDBS, OP, and 4000S) composition of slurry wettability were investigated. 4000S and OP composite wetting agent components can effectively improve the wettability of the thick liquid material. It form uniform liquid film on the surface of PP film, and form a uniform coating after drying (as shown in figure 4b).
PP as a low surface energy material, the coating is easy to fall off on the surface. The influence of different types of binders, such as polyurethane, poly acrylate and polyvinyl alcohol, was studied on the coating performance. When polyvinyl alcohol was used as a binder, the coating can be peeled off in pieces with a light adhesive tape. For polyurethane, the adhesion is slightly improved, and the adhesion is also weak. When using poly acrylic acid binder, the adhesion of the coating is obviously improved. When the amount of binder added is 5wt%, the peeling strength of the coating formed by different types of binder on the PP film surface is shown in Table 2. The peel strength of the coating with poly acrylate was the highest, reaching about 23N/cm, which was much higher than that of the other two types of binder, indicating that poly acrylate could be used as a binder well for BT dielectric coating. Through the research, we obtained a stable and uniform BT coating dispersion, coating slurry can be evenly spread on the surface of PP dielectric film, forming a strong binding coating.

| Binder  | Polyurethane | Polyacrylate | Polyvinylalcohol |
|---------|--------------|--------------|-----------------|
| Coating peel strength, | 15 N/cm | 23 N/cm | Figure 8 N/cm |

### 3.2.2. Morphology and dielectric properties of PP/BT composite films

By adjusting the proportion of BT and binder in coating slurry, the composite film with different BT content was prepared. The composite films with BT weight content of 50%, 25% and 10% were prepared. The surface morphology of the films was observed by scanning electron microscopy (SEM) (figure 5). It can be seen that when BT content is 50%, although a layer of continuous coating is formed, the surface porosity is very high. High porosity will increase dielectric loss, which is not conducive to obtaining composite dielectric thin films with low dielectric loss. When the BT content was reduced to 25%, the binder formed some continuous areas (figure 5b), but the porosity was still very high. When the content of BT is 10%, the binder forms a continuous phase and BT forms a dispersed phase embedded in the layer (Figure 5c). In this case, the coating structure is relatively dense and the porosity is relatively low, which should be conducive to reducing the dielectric loss.

Three kinds of PP/BT composite dielectric films with different BT content were prepared and their dielectric properties were studied by broadband dielectric spectrum analyzer (BDS), as shown in Figure 6. It can be seen that when BT content is 50%, the dielectric constant at 1kHz is 4.49. When the BT content is 25% and 10%, the permittivity is 3.58 and 3.50. Both of which were higher than the PP film's
permittivity which is 2.1, indicating that it was feasible to increase the permittivity of the composite film by coating the capacitor film surface with BT material with high permittivity using water-based system.

![Dielectric constant vs Frequency](image1)

**Figure. 6** Dielectric properties of PP/BT composite films.

| BT content (wt%) | At 1kHz (Cons. Loss) |
|------------------|----------------------|
| 10               | 3.50 0.021           |
| 25               | 3.58 0.019           |
| 50               | 4.49 0.595           |

The dielectric properties of three PP/BT composite dielectric films with different BT contents are shown in Table 3. It can be seen that the BT content increased from 10% to 25%, and the increase of the dielectric constant was not particularly obvious. Therefore, we amplified the slurry with BT content of 10% to carry out the pilot study of PP/BT composite dielectric film.

3.2.3. Study on pilot test process of BT coating

After BT is prepared into coating slurry, continuous intaglio coating pilot line is used (figure 7a). The process adaptability of coating slurry continuous coating process and further optimize coating slurry system were studied. It formed evenly coated paste in the manual coating, while it appeared a lot of pinholes after shrinkage in the pilot line. SEM observation of the coating showed that the local coating was not well covered in these areas, and the bare substrate of PP film could be seen, which may be due to the low surface energy of PP film, leading to insufficient slurry infiltration. In order to increase surface energy, plasma corona equipment was used, which can improve the surface energy of PP film from 28dyn/cm to 45dyn/cm. After corona treatment, the coating is uniform without obvious pinhole defects. Although the coating is uniform, there are still many obvious pore structure on the surface. However, pore structure will increase the dielectric loss. In order to improve the adhesion between coating and PP film, the adhesion between coatings was further adjusted. Using this method, a roll of PP/BT composite dielectric film which was 580mm in width and 400m in length was produced (Figure. 7b), with BT coating thickness of 2 μm and BT content of 10wt% in the coating.

![Coated pilot test line](image2)

**Figure. 7a)** Coated pilot test line, (b) PP/BT composite dielectric film coated continuously.
The dielectric properties of the prepared PP/BT composite dielectric film were studied, as shown in Figure 8. It can be seen that the permittivity of the continuously prepared composite dielectric film is 2.38 at 1kHz, which is slightly higher than the permittivity of PP film 2.1. This shows that it is feasible to increase the permittivity of the composite diaphragm by coating the capacitor film surface with high permittivity BT material. Besides, the dielectric loss is also relatively low, which is 0.067. A continuously prepared reel of composite dielectric film will be provided to the factory for aluminizing the prototype capacitor. Next, based on the existing coating size, we will further improve and enhance the existing coating size system to prepare PP/BT composite dielectric film with higher dielectric constant and low dielectric loss.

4. Conclusions
In this paper, the existing capacitor PP film is used as the substrate, and the surface of PP film is coated with a high dielectric constant layer of BT nanoparticles. The BT layer with high dielectric constant is used to improve the dielectric constant of the whole composite dielectric film. The organic solvent system of BT paste coating and water system of BT paste coating were prepared. Two kind of composite dielectric films which are PP/PVDF/BT and PP/BT were prepared by coating. The film has good adhesion, uniform coating distribution and fewer pinholes. The dielectric properties of the composite film showed that the dielectric constant of that could be increased from 2.1 to 4.49 by coating BT nanoparticles. According to the experimental formula, several rolls of high-performance thin films with dielectric constant of 2.38 and dielectric loss of 0.067 were prepared through the pilot test. The performance of capacitors was further studied.

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