The preparation of PVDF-BTO composite film and the influence of polarization intensity on the piezoelectric properties of composite film

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Abstract. In this study, the PVDF-BTO composite film was prepared by the casting method. Through FTIR, SEM and other phase structure and microstructure analysis of the composite film, it was found that the introduction of BTO can promote the growth of β-PVDF. The relative content of β-PVDF in PVDF-BTO composite film reached 62.7%, indicating that BTO acts as a nucleating agent in PVDF. PVDF-BTO composite piezoelectric film is obtained after high temperature stretching and field polarization. After testing the electrical properties of the composite piezoelectric film, it is found that the piezoelectric performance of the PVDF-BTO composite film is higher than that of the pure PVDF film. It shows that the blending of BTO and PVDF to prepare the film promotes the deflection of the electrical properties of the film to the inherent electrical properties of BTO. The influence of different polarization intensities on the piezoelectric properties of composite materials was studied. The results show that the optimal polarization intensity of the PVDF-BTO composite piezoelectric film is 30 KV/mm, and the highest piezoelectric constant d33 is 13 pC/N.

1. Introduction

According to research, traditional piezoelectric materials, such as lead-containing piezoelectric materials represented by lead zirconate titanate (PZT) and environment-friendly perovskite materials represented by barium titanate, hinder the development of wearable electronic devices and portable electronic devices due to poor flexibility, short service life, environmental pollution and other factors [1-3]. Therefore, it is urgent to develop flexible materials with good flexibility, low cost and high reliability. In recent years, PVDF has attracted great attention due to excellent dielectric, piezoelectric and ferroelectric properties in polymers [4]. The piezoelectricity generated by the strong molecular dipole in polymer chain can directly convert the mechanical energy in the form of vibration into electrical energy, which makes PVDF an ideal material for making sensors, actuators and energy collectors. For example, the composite film prepared by adding barium strontium titanate nanoparticles into PVDF greatly improves the energy collection efficiency of the flexible piezoelectric energy collector. Ye Yang [5] et al. Used polydopamine modified pvdf-bto composite piezoelectric film to prepare flexible pressure sensor at 70 MΩ. It can also output 0.122 μW/cm² under high load resistance. Compared with the pure PVDF piezoelectric thin film sensor, its piezoelectric output performance is obviously enhanced. Jing Fu [6] and others designed a flexible piezoelectric generator with ultra-high power generation capacity by using sandwich structure, that is, the corresponding pvdf-ftn / pvdf-pvdf (p-ftnx-p) compact composite was prepared by hot pressing technology. The test
results show that the flexible piezoelectric generator has 110 μW/cm³ high power density and 75 μC/m². The charge density greatly promotes the development of flexible devices. Congran Jin[7] et al. Found that the flexible piezoelectric nano generator made of CO, Na, Ag and Li doped ZnO/PVDF films, in terms of voltage generation, 5% Li doping shows the best piezoelectric output performance, and its voltage output is 9 times higher than that of ZnO/PVDF device. Qiu Ying Zhao[8] reported a piezoelectric hybrid elastic film that the film consists of PVDF and MnO2 nanorods. It was found that the combination of MnO2 and PVDF greatly enhanced the piezoelectric properties and output activity of PVDF. According to the present research, the addition of modified PVDF has become the main measure to improve the piezoelectric properties of PVDF based films. In this study, a kind of barium titanate (BTO) modified PVDF composite film is reported. Compared with PVDF pure film, PVDF-BTO composite film has better piezoelectric properties. The polarization test of the composite film is carried out, and the best polarization electric field strength of PVDF-BTO composite film is obtained.

2. Experiment

2.1. Preparation of PVDF-BTO composite film
Polyvinylidene fluoride uses Shanghai Sanaifu FR904 powder; solvent is N, N-dimethylformamide (Tianjin Tianli Chemical Reagent Co, Ltd, analytical pure); additive is nano-barium titanate (particle size is 100 nm, the purity is 99.9%). In this study, a composite membrane with 10% (mass fraction) BTO content was prepared for experimental analysis. The PVDF powder and the N, N-dimethylformamide solution are mixed and magnetically stirred at a ratio of 1:9. After the PVDF is fully dissolved, the PVDF solution is obtained. Add PVDF particles to N, N-dimethylformamide, first mix with magnetic stirring, then add BTO powder to the solution at a mass ratio of 9:1 according to the mass ratio of PVDF to BTO, and continue to stir until the BTO is evenly dispersed in the PVDF solution. Then, the PVDF-BTO mixed solution is obtained. Then sends the processed solution was placed on a glass plate, dried in oven temperature (25 ℃), to be N, N-dimethylformamide after complete evaporation, to obtain the pure PVDF and PVDF-BTO film composite film.

2.2. Performance characterization
The morphology of pvdf-bto composite films was characterized by field emission scanning electron microscopy (SEM) of Nippon science S4800, and the accelerating voltage was 5 KV. The crystal phase of the material was quantitatively analyzed by the Vertex70 Fourier transform infrared spectrometer (FTIR) of Brooke company in Germany. The analysis wavelength was 400-1400 cm⁻¹, and the resolution was 10 cm⁻¹. The tensile test was carried out on AI-7000-NGD servo material multifunctional high and low temperature control testing machine of gotwell (Dongguan) Co., Ltd. The sample size of tensile test is 20mm × 20mm, tensile test is carried out at a rate of 5 mm/min and 80 ℃. The piezoelectric constant d33 of piezoelectric film is obtained by ZJ-6 quasi-static piezoelectric constant tester. When testing the piezoelectric constant, firstly, electrode coating is carried out on both sides of the film with a size of 20mm×20mm, and then the electric field is polarized. The polarization temperature is 80 ℃, the polarization time is 30 min, and the polarization intensity is chosen to increase gradually. Perform piezoelectric constant test.

3. Performance characterization of PVDF-BTO composite film
The microscopic morphology of the prepared film was characterized as shown in Figure.1 Figure.1(a) and Figure.1(b) show that the unstretched film has a spherical morphology, and the prepared piezoelectric film has a uniform BTO dispersion, low porosity, and good film quality. Figure.1(c) and Figure.1(d) are the microscopic morphology of the film after stretching. The film has a fibrous morphology oriented parallel to the stretching direction. This is because PVDF film and PVDF-BTO composite film are subjected to tensile stress, which leads to the transformation of α phase to β phase in PVDF. It can be seen from Fig.1 (a) ~ (d) that during the stretching process of PVDF, the morphology of PVDF crystal changes from spherical shape to microfibril shape, and necking
phenomenon occurs, which leads to the formation of all trans planar zigzag conformation of PVDF(β phase) [9-10].

![SEM image of PVDF pure membrane and PVDF-BTO composite membrane: (a) PVDF pure membrane; (b) PVDF-BTO membrane; (c) PVDF pure film stretching; (d) PVDF-BTO composite film stretching](image)

Figure 1. SEM image of PVDF pure membrane and PVDF-BTO composite membrane: (a) PVDF pure membrane; (b) PVDF-BTO membrane; (c) PVDF pure film stretching; (d) PVDF-BTO composite film stretching

The Fourier transform infrared spectroscopy experiment can quantitatively analyze the material phase and characterize the relative content of the material phase. The relative content \( F(\beta) \) of β-PVDF can be calculated by Beer-Lambert law:

\[
F(\beta) = \frac{A_\beta}{(K_\beta / K_\alpha)A_\alpha + A_\beta}
\]  

(1)

Where the arguments are as follows: \( K_\beta = 7.7 \times 10^4 \text{ cm}^2/\text{mol}, \ K_\alpha = 6.1 \times 10^4 \text{ cm}^2/\text{mol}, \ K_\beta / K_\alpha = 1.262 \). \( A_\beta \) is the absorption peak intensity of β-PVDF, and the characteristic peak around 840 cm\(^{-1}\) is taken for integration calculation; \( A_\alpha \) is the absorption peak intensity of α-PVDF, and the characteristic peak around 760 cm\(^{-1}\) is taken for integration calculation [11].

Fig.2 is a Fourier Transform Infrared Spectroscopy. Among them, the absorption peaks of α-PVDF are at 610, 760, 490, and 976 cm\(^{-1}\), and the absorption peaks of β-PVDF are at about 480, 511, 840, and 879 cm\(^{-1}\). According to Figure 2, combined with formula (1), the introduction of BTO increased the relative content of β-PVDF from 56.5% to 62.7%, it shows that the introduction of BTO can enhance the relative content of β-PVDF and act as a nucleating agent in PVDF. After the film is stretched at high temperature, there is only a very weak α-PVDF peak in PVDF, while the β-PVDF peak is very obvious. The analysis shows that after the PVDF film is stretched at high temperature, the relative content of β-PVDF rises from 56.5% to 86.9%. After PVDF-BTO composite film is stretched at high temperature, the relative content of β-PVDF rises from 62.7% to 92.6%. This shows that high temperature stretching can promote the increase of the relative content of β-PVDF. Comparing PVDF
pure film and PVDF-BTO composite film after high temperature stretching, the composite film has a relatively high β-PVDF content. This is because BTO forms the core for the directional adsorption of PVDF and directly induces the production of β-PVDF, which not only makes β-The relative content of PVDF increases, and it also directly increases the crystallinity of PVDF.

Figure 2. Analysis of the relative content of crystal phase of PVDF pure film and PVDF-BTO composite film

4. The influence of polarization strength on the piezoelectric properties of PVDF-BTO composite film

The piezoelectric constant characterization test of the composite piezoelectric film found that after the introduction of BTO, the piezoelectric constant of the film increased from 2 pC/N to 13 pC/N. It is speculated that there are two factors contributing to the improvement of the piezoelectric performance of the composite piezoelectric film: On one hand, BTO has better piezoelectric properties than PVDF. Therefore, after BTO is introduced into PVDF, the performance of the piezoelectric film will be deflected to the inherent performance of BTO, thereby improving the electrical performance of the piezoelectric film. On the other hand, as shown in Figure 3, the introduction of BTO formed the directional adsorption of large particles to small particles, acting as a nucleating agent, thereby increasing the relative content of β-PVDF, producing more dipoles in the film, and enhancing the electrical activity of the film. For the PVDF pure membrane electric polarization test, this study selects the polarization interval of 15-50 KV/mm, and the gradient interval is set to 5 KV/mm to explore the optimal polarization intensity of the PVDF-BTO composite film. Figure 4 shows the influence curve of polarization intensity on the piezoelectric properties of PVDF-BTO composite film. It can be obtained that in the range of 15-30 KV/mm, the piezoelectric constant of the PVDF-BTO composite film increases with the increase of the polarization intensity. When the polarization intensity exceeds 30 KV/mm, the PVDF-BTO piezoelectric constant is basically unchanged, indicating that the optimal polarization intensity of the PVDF-BTO composite film is 30 KV/mm. The measured PVDF-BTO composite piezoelectric film the highest piezoelectric constant of 13 pC / N.
5. Conclusion

In this study, PVDF-BTO composite piezoelectric film was prepared by solution casting method. Compared with the pure PVDF film, the prepared PVDF-BTO composite piezoelectric film has a higher relative content of β-PVDF, and the relative content of β-PVDF reaches 62.7%; the relative content of β-PVDF is as high as 92.6% after stretching. The polarization experiment of the PVDF-BTO composite film was explored, and finally the optimal polarization intensity of the PVDF-BTO composite film was 30 KV/mm, and the piezoelectric constant reached 13 pC/N. Therefore, the prepared PVDF-BTO composite film can meet the requirements of making environmentally friendly piezoelectric sensors, and has great application potential in wearable electronic devices.

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