用于电卡制冷的聚(偏氟乙烯-三氟乙烯) (55/45)/0.75BiFeO₃-0.25BaTiO₃复合材料的制备及热导率增强

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摘要:以聚(偏氟乙烯-三氟乙烯)(55/45)(P(VDF-TrFE) (55/45))作为聚合物基体,0.75BiFeO₃-0.25BaTiO₃(BFO-BTO)纳米纤维作为 填料以提高共聚物的热导率。结果表明,少量的BFO-BTO纳米纤维即可实现共聚物热导率的提高。在75℃时,纳米纤维含量 为2%的复合材料的热导率为0.21 W·m⁻¹·K⁻¹,几乎是P(VDF-TrFE) (55/45)共聚物膜的2倍。同时,加入纳米纤维后共聚物的电 热效应(ECE)几乎没有变化。这些结果表明少量BFO-BTO纳米纤维的加入在有效提高P(VDF-TrFE) (55/45)共聚物热导率的同 时能够保持共聚物较高的ECE。

关键词:铁电薄膜;纳米复合材料;电热效应;热导率 中图分类号:0633.4 文献标识码:A 文章编号:1001-4861(2023)04-0716-07 DOI:10.11862/CJIC.2023.035

Preparation and enhanced thermal conductivity of poly(vinylidene fluoride-trifluoroethylene) (55/45)/0.75BiFeO₃-0.25BaTiO₃ composite for electrocaloric application

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Abstract: In this work, the (P(VDF-TrFE) (55/45)) was used as polymer matrix and 0.75BiFeO₃-0.25BaTiO₃ (BFO-BTO) nanofiber was used as fillers to enhance the thermal conductivity of the copolymer. The enhanced thermal conductivity was achieved by adding a small amount of BFO-BTO nanofibers to the copolymer. A thermal conductivity of the composite film with 2% nanofibers was 0.21 W·m⁻¹·K⁻¹ at 75 °C, which was nearly twice that of the P(VDF-TrFE) (55/45) copolymer film. At the same time, the electrocaloric effect (ECE) of the copolymer almost remained unchanged after the addition of nanofibers. The results suggest that the addition of BFO-BTO nanofibers is effective to improve the thermal conductivity of P(VDF-TrFE) (55/45) copolymer while maintaining high ECE.

Keywords: ferroelectric film; nanocomposites; electrocaloric effect; thermal conductivity

Electrocaloric effect (ECE) describes the isothermal entropy change (ΔS) or adiabatic temperature change (ΔT) in polar materials induced by the polarization change under an external electric field^[1-3]. Discovered by Kobeco and Kurtschatov in Rochelle salt in the 1930s, ECE was undervalued for a long time because a small temperature change was observed in many ferroelectrics. However, giant ECE was found in PbZr_{0.95}Ti_{0.05}O₃ ceramic film at *ca*. 222 °C in 2006 and in polyvinylidene difluoride (PVDF) - based ferroelectric polymers near room temperature in 2008^[4-6]. These studies arise great interest and lay the groundwork for

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the development of solid - state refrigeration devices based on ECE. ECE is considered an emerging solid state refrigeration technology in terms of its high efficiency and environmental friendliness compared with traditional vapor compression cooling technology^[7-8].

Over the past decade, the ECE of polar polymers receives growing attention due to their flexibility, lightweight, processability, and high breakdown strength^[9-11]. However, the heat transfer efficiency of polymers is too poor to satisfy the demand of device applications^[12-13]. Therefore, to achieve larger thermal conductivity and higher ECE, composite materials have been explored^[14-16]. Fillers with high thermal conductivity can improve the heat transfer of polymers. At the same time, the interfaces between the polymer matrix and fillers may generate an interfacial coupling effect and offer an additional benefit to improve ECE^[17].

The ferroelectric - paraelectric (FE - PE) transition in ferroelectric copolymers is a first-order transition at the Curie transition. Around the Curie temperature $(T_{\rm c})$, the ECE of ferroelectric polymers is the largest. Poly(vinylidene fluoride-trifluoroethylene) (55/45)(P(VDF-TrFE) (55/45)) has the lowest $T_{\rm c}$ (73 °C) among the P(VDF - TrFE) copolymers, making it suitable for low-temperature ECE. P(VDF-TrFE) (55/45) used in this work is a typical ferroelectric polymer that is frequently investigated in the field of ECE. To enhance the thermal conductivity and ECE of P(VDF - TrFE) (55/45) ferroelectric copolymer, a small amount of 0.75BiFeO₃-0.25BaTiO₃ (BFO-BTO) nanofibers with a diameter of about 100 nm were added. The results showed that ECE was slightly enhanced by adding only 2% BFO - BTO nanofibers to the copolymer. What is more important, the thermal conductivity of the copolymer was enhanced by nearly two times by adding the nanofibers.

1 Experimental

1.1 Reagent

Bismuth nitrate pentahydrate (Bi(NO₃)₂•5H₂O), ferric nitrate nonahydrate (Fe(NO₃)₃•9H₂O), barium acetate (Ba(Ac)₂), tetrabutyl titanate (TTBT), citric acid (CA), acetylacetone (Hacac), glacial acetic acid (HAc), and *N*, *N* - dimethylformamide (DMF) were purchased from Sinopharm Chemical Reagent Co., Ltd. Pyrrolidone (PVP) was purchased from Tianjin Bodi Chemical Limited Industry. P(VDF-TrFE) (55/45) copolymer was purchased from Piezotech Arkema.

1.2 Preparation of composite films

BFO - BTO nanofibers^[18] were prepared using the electrospinning process. 2.985 9 g Bi(NO₃)₂·5H₂O, 2.487 0 g Fe(NO₃)₃·9H₂O, 0.698 3 g TTBT, 0.524 1 g Ba(Ac)₂, 2.480 9 g CA, 0.235 3 g Hacac, 3.589 2 g HAc, 1.973 3 g PVP, and 25 g DMF were added into a conical flask and stirred for 30 min. Subsequently, 1.973 3 g PVP was added to the mixture and stirred overnight to obtain a homogeneous precursor solution. The electrospinning process was carried out using a custom - made electrospinning machine. The applied voltage of the electrospinning process was about 20 kV. Raw nanofibers were collected and dried at 200 °C for 1 h and 350 °C for 2 h before being calcined at 600 °C for 2 h to obtain BFO-BTO nanofibers.

1.6 g P(VDF - TrFE) (55/45) powders and 5 mL DMF were mixed and stirred for 2 h. After that, BFO-BTO nanofibers were mixed into the copolymer solution. The fibers were broken down into smaller sizes and dispersed in the solution with the help of ultrasound and violent stirring. The homogeneous suspension was cast on a glass plate and dried in an oven at 70 °C for 2 h. The dried film was peeled off from the glass plate and treated in a vacuum oven at 135 °C for 5 h to eliminate the residual solvent and promote crystallinity. The volume fractions^[19] of BFO - BTO nanofibers in the composite films were 0%, 1%, 1.5%, 2%, and 2.5%, respectively. The thickness of the films was about 20 μ m.

1.3 Characterization

The morphologies of BFO-BTO nanofibers, copolymer, and composite films were analyzed by a scanning electron microscope (SEM, SU8200, HITACHI, Japan, the testing voltage was 1.5 kV) and a field emission transmission electron microscopy (FETEM, JEM-2100F, JEOL, Japan, the accelerating speed was 200 kV). The crystal structure of the specimens was examined by X-ray diffraction (XRD) using an X-ray diffractometer

(Ultima IV, Rigaku, Japan, the incident source was Cu $K\alpha$, λ = 0.154 187 nm, the operating voltage and current were 40 kV and 40 mA, respectively, the scanning range was 10° - 60° , and the scanning speed was $10 (^{\circ})$. min⁻¹). The chain conformation of the copolymer and composite films was investigated by an attenuated total reflectance-Fourier transform infrared spectrophotometer (ATR-FTIR, Nicolet 8700, Thermo Nicolet, USA). The specific heat capacity (c_p) of the films was measured by differential scanning calorimetry (DSC, 204F1 Phoenix, NETZSCH, Germany, N2 atmosphere, and the heating and cooling speed was 10 $^{\circ}$ C \cdot min⁻¹). The thermal conductivity of the films was measured by a laser flash diffusivity apparatus (LAF467, NETZSCH, Germany). For electrical tests, gold electrodes with diameters of 6 mm (for dielectric tests) or 3 mm (for ferroelectric tests) were coated on the upper and bottom surfaces of the films in a sputter coater (EMS150T, Electron Microscopy Sciences, USA). The frequency and temperature dependence of the dielectric properties of the materials were measured using an LCR meter (E4980, Agilent Technology, USA) equipped with a furnace (The testing temperature range was 30-140 $^{\circ}$ C, and the heating and cooling speed was 2 $^{\circ}$ C \cdot min⁻¹). The polarization vs electric filed hysteresis curves (P-E loops) were studied using a modified Sawyer-Tower circuit (Polyktech, State College, USA, the testing frequency was 1 000 Hz).

2 Results and discussion

Fig.1a shows the SEM image of the calcined BFO-BTO nanofibers, and the diameter of the nanofibers was quite uniform and was around 100 nm. The TEM image in Fig.1b shows that nanofibers consist of small crystal grains, causing the rough surface of the fibers observed in SEM images. The XRD pattern (Fig. 1c) indicates the perovskite crystal structure of nanofibers^[19].

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Fig. 2a and 2b show the surface and cross-sectional SEM images of the copolymer and composite films, a braid-like crystalline microstructure was observed on the surface of all films. For the composite films, we can see the claviform fibers were uniformly distributed in the composite films without obvious aggregation, as shown in Fig.2a. In the cross-sectional image shown in Fig.2b, only the ends of the nanofibers can be observed and the fibers were not aggregated according to the image. The XRD patterns of the copolymer and composite films are shown in Fig. 2c. The peaks at 18.7° and 19.1° are assigned to the (110) and (200) planes of β -phase of the copolymer (PDF No.42-1649), while the peaks at 22.2°, 32.6°, 39.1°, 45.4°, 51.2°, and 56.4° were associated with BFO-BTO nanofibers (PDF No.05-0626)^[20]. On the FTIR spectra shown in Fig. 2d, the peaks at 840 and 1 286 cm⁻¹, which were from $T_{\rm m}>4$ (All - trans conformation was larger than 4) and T_3G chain conformations of the copolymer, had strong intensity. The FTIR results are consistent with the XRD results that the copolymer is mainly in β -phase^[21].

Fig. 3 presents the temperature dependence and frequency dependence of the dielectric properties of the copolymer and composite films. The T_c (ca. 73 °C) did not vary with the addition of BFO-BTO nanofibers, as shown in Fig.3a. As shown in Fig.3b, as the amount of BFO-BTO nanofibers in composite films increased, the dielectric constant of the composite films was slightly enhanced. This can be ascribed to the mechanisms that the dielectric constant of BFO-BTO nanofibers was much higher than the polymer matrix and the addition of BFO - BTO nanofibers induced interfacial



Fig.1 (a) SEM image, (b) TEM image, and (c) XRD pattern of calcined BFO-BTO nanofibers



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Fig.2 (a) Surface and (b) cross-sectional SEM images, (c) XRD patterns, and (d) FTIR spectra of the copolymer and composite films



Fig.3 (a) Temperature dependence at 1 kHz and (b) frequency dependence of the dielectric properties at room temperature of the copolymer and composite films

effects in composite films, which enhanced the dielectric properties^[22].

Fig.4 shows the P-E loops of the copolymer and composite films at room temperature and around $T_{\rm c}$ measured under an electric field of 100 MV·m⁻¹. At room temperature, the films were in a ferroelectric state and the *P*-*E* loops with large hysteresis can be observed (Fig. 4a). Because only a small amount of fibers was added to the copolymer, the variation of the polarization response between these films was minor. While at a higher temperature that near and above the FE-PE transition, the P-E loops became slim, and the remanent polarization diminished, as shown in Fig. 4b-4f. From the P - E loops measured at different temperatures, the variation of the polarization with temperature can be obtained, as presented in Fig. 5a. According to the Maxwell relations, the reversible ΔS and ΔT can be deduced as^[23-24]:

$$\Delta S = \int_{E_1}^{E_2} \left(\frac{\partial D}{\partial T} \right) dE$$
(1)

$$\Delta T = -\frac{T}{\rho} \int_{E_1}^{E_2} \frac{1}{c_p} \left(\frac{\partial D}{\partial T} \right) dE$$
⁽²⁾

Herein, D is the electric displacement, which is approximately equal to P (polarization) for ferroelectric polymers; T is the temperature; E is the electric field strength; ρ is the density of the material. The c_p of the composite films with 0% and 2.5% BFO-BTO was characterized and presented in the inset in Fig.5a. The ΔS and ΔT as a function of T at 100 MV ·m⁻¹ can be calculated, as shown in Fig.5b and 5c. From 75 to 100 °C, ΔS and ΔT gradually decreased. The difference between ΔS or ΔT of the copolymer and composites was minor. For example, the copolymer film had a ΔS of 61.4 kJ·m⁻³·K⁻¹ and a ΔT of 8.1 °C under an electric field of 100 MV·m⁻¹ at 75 °C, whereas the composite film with 2% BFO-BTO had a ΔS of 67.8 kJ·m⁻³·K⁻¹ and a ΔT of 8.5 °C. Consequently, the addition of BFO-BTO nanofibers did not change or even slightly enhanced the ECE of the copolymer. This can be ascribed to the increase in dielectric constant and polarization with the addition of nanofibers, which

allows for a greater change in polarization near the $T_{\rm c}$ and thus an enhancement in the ECE.

The thermal conductivities of the copolymer and composite films at 75 °C were measured, as illustrated in Fig. 6. The thermal conductivity of the composite film with 0% BFO-BTO was $0.11 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$. The composite films had a thermal conductivity from 0.2 to 0.22 $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, which was nearly twice that of the composite film with 0% BFO-BTO. This may be due to the higher thermal conductivity of BFO-BTO ceramic nanofibers than copolymers, upon the addition of nanofibers to the copolymer, the nanofibers can act as a thermal path and the dispersed fibers formed a thermal conductivity.



Fig.4 (a) *P-E* loops measured at 1 kHz of the copolymer and composite films at room temperature; (b-f) *P-E* loops measured at 1 kHz of the copolymer and composite films at a temperature below, near, and above the FE-PE transition



Fig.5 (a) Polarization responses (Inset: c_p vs *T* curves of the composite films with 0% and 2.5% BFO-BTO), (b) ΔS vs *T* curves and (c) ΔT vs *T* curves of the copolymer and composite films at an electric field of 100 MV · m⁻¹

tivity network to promote heat transfer^[25]. For fiber - filled composites, their thermal conductivity of the com-

posite was given^[26]:

$$\frac{1}{k_{\rm e}} = \frac{1}{\sqrt{C(k_{\rm p} - k_{\rm f})[k_{\rm p} + B(k_{\rm f} - k_{\rm p})]}} \ln \frac{\sqrt{k_{\rm p} + B(k_{\rm f} - k_{\rm p})} + 0.5B\sqrt{C(k_{\rm p} - k_{\rm f})}}{\sqrt{k_{\rm p} + B(k_{\rm f} - k_{\rm p})} - 0.5B\sqrt{C(k_{\rm p} - k_{\rm f})}} + \frac{1 - B}{k_{\rm p}}$$
(3)

Where, $B = \sqrt{\frac{3\varphi}{2}}$, $C = -4\sqrt{\frac{2}{3\varphi}}$; $k_{\rm e}$, $k_{\rm p}$, $k_{\rm f}$ are the thermal conductivity of the composite film, polymer, and

nanofiber, respectively. φ is the volume fraction of



Fig.6 Thermal conductivity of the copolymer and composite films at 25 and 75 °C

nanofibers.

If the thermal conductivity of the polymer matrix is much smaller than that of filler materials, in the low φ range ($\varphi < 0.667$), the effective thermal conductivity of composites can be approximated by:

$$k_{\rm e} \approx \frac{k_{\rm p}}{1-B} \tag{4}$$

After substituting the thermal conductivity of the copolymer (0.17 $W \cdot m^{-1} \cdot K^{-1}$) and the nanofiber (8 $W \cdot m^{-1} \cdot K^{-1}$) into the above formula^[27], the thermal conductivity of the composite film was calculated as 0.19 $W \cdot m^{-1} \cdot K^{-1}$ when the φ was 1% and 0.20 $W \cdot m^{-1} \cdot K^{-1}$ when the φ was 2%, which was consistent with estimated values.

The thermal conductivity of copolymer and composite films at 25 °C was also measured, as shown in Fig. 6. The thermal conductivity of the copolymer film was 0.17 $W \cdot m^{-1} \cdot K^{-1}$, which is consistent with prior studies, and that of the composite films was in the range of 0.22 to 0.24 $W \cdot m^{-1} \cdot K^{-1}$ [14,28]. The results suggested that by adding only a small amount of BFO-BTO nanofibers, the thermal conductivity of the copolymer can be greatly improved. The enhancement of thermal conductivity by adding nanofibers is beneficial for electrocaloric application because good heat dissipation is necessary.

3 Conclusions

In summary, we prepared BFO-BTO nanofibers by the electrospinning process. The nanofibers consisted of small crystal grains and had a perovskite crystal structure. The diameter of nanofibers was quite uniform, which was around 100 nm. The composites of P(VDF - TrFE) (55/45) and the nanofibers were prepared by the solution casting method. Microstructure analysis indicated that the fibers were uniformly distributed in the composite film without obvious aggregation. Subsequently, the ECE values of the copolymer and composite films with BFO-BTO nanofibers were investigated. We demonstrate that the composite film with 2% BFO - BTO had the optimal ECE properties with ΔS of 67.8 kJ·m⁻³·K⁻¹ and ΔT of 8.5 °C at an electric field of 100 MV·m⁻¹. By adding a small amount of BFO-BTO nanofibers to the copolymer, the composite films had a notable enhancement (about two times) in thermal conductivity, which can be ascribed to the formation of the thermal conductivity network in composite films. Besides, the high thermal conductivity of composite films remained relatively steady as the temperature rises.

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