Crystallinity and morphology of barium titanate filled poly(vinylidene fluoride) nanocomposites

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ABSTRACT： In this study, crystallization behavior and micro-morphology of barium titanate ($BaTiO_3$, or BT) filled poly(vinylidene fluoride) (PVDF) nanocomposites were investigated based on Fourier-transform infrared spectroscopy (FTIR), polarized optical microscopy (POM), differential scanning calorimetry (DSC), and X-ray diffractometry (XRD). BT/PVDF nanocomposite films with different concentrations of BT nanoparticles were prepared by solution casting method. The results revealed that the electrical conductivity and Seebeck coefficient of PVDF were improved by the incorporation BT nanoparticles. When 2 wt% of BT was loaded into the PVDF matrix, it mediated the β-phase crystallization in PVDF. Furthermore, the β-phase crystals could be transformed into α-phase after the samples were isothermally crystallized at 155 °C for 20 minutes. The results of DSC and POM suggest that BT nanoparticles could act as nucleation agents, promoting the crystallization activity of PVDF in a non-isothermal crystallization process. The crystal phase is influential to the electrical properties of PVDF, therefore the findings of this study is useful for the development of new applications based on BT/PVDF nanocomposites, such as high-performance thermoelectric devices or systems.

INTRODUCTION

Pure poly (vinylidene fluoride) (PVDF) is known to exist in five crystal forms: α, β, γ, δ and ε phases depending on the processing conditions [1-6]. The non-polar α-phase and the polar β-phase are the most common. The α-phase (trans-gauche bond conformation TGTG′) is formed by cooling from the melt or solvent casting at temperatures above 120 °C [2,3]. The β-phase (all trans-planar zigzag conformation TTTT) is obtained by solution casting from polar solvents under controlled operating conditions plus mechanical stretching of α-phase films between 70 °C and 100 °C and at stretch ratios between 3 to 5 [5]. Due to the piezoelectricity and pyroelectricity in the crystalline form of the β-phase, PVDF stands out from other polymeric materials for its application of sensors and actuators and its excellent dielectric and ferroelectric performance, and in contrast to other polymers, it has promising applications for energy storage materials. Some researchers have reported that electroactive β-phase PVDF can be nucleated by some fillers, such as ferrite nanoparticles [2], halloysite nanotubes [3] and graphite nanosheets [4]. Martins et al. (2012) studied the crystallization kinetics of ferrite/PVDF and found large amounts of β-phase for $CoFe_2O_4$/PVDF and $Ni_{0.5}Zn_{0.5}Fe_2O_4$/PVDF nanocomposites [2]. Mendes et al. (2009) discussed the effect of ceramic grain size and concentration on the dynamic mechanical and dielectric behavior of PVDF/$Pb\ (Zr_{0.53}Ti_{0.47})\ O_3$ composites [1].

Barium titanate (BT) particles, as a typical dielectric material with a perovskite crystal structure, possess excellent electrical properties in addition to ferroelectric, piezoelectric and positive temperature coefficient effects [7]. Thus, the incorporation of BT can enhance the PVDF's permittivity [8]. Many attempts have been made to modify the surface of BT particles to improve their dispersion within the PVDF matrix, enhance the dielectric permittivity of PVDF ($\varepsilon = 12$) [9] and prevent current leakage. For example, Fe_3O_4-coated BT particles could greatly enhance the dielectric constant of PVDF and suppress the dielectric loss [10]. Whereas a typical range of dielectric permittivity for BT/PVDF composites is 32 to 65 [11], Zhang et al. (2016) demonstrated that BT-Fe_3O_4/PVDF also exhibited high permittivity (385) when the nanocomposite was subjected to magnetic field treatments [12]. Coating the BT particle surface with an insulating layer (Al_2O_3 or TiO_2) is another promising approach to reduce current leakage by introducing a potential barrier among the fillers [13]. Although BT-modified PVDFs possess extraordinary mechanical properties, heat transfer capability, electrical conductivity and piezoelectric properties [14-16], the effect of BT on the crystallization behavior of PVDFs has rarely been studied and reported in a systematic manner.

Our previous work examined the influence of CdSe/ZnS quantum dots on the crystallization behavior of poly(lactic acid) [17]. This study investigated the influence of the BT contents and the crystallization process on the crystal structure of BT/PVDF nanocomposite films. Nanocomposite films with different BT concentrations were prepared using a solution casting method [17,18]. The microstructures and crystal structures of the prepared BT/PVDF films were explored using transmission electron microscopy, polarized optical microscopy (POM), Fourier-transform infrared (FT-IR) spectroscopy, differential scanning calorimetry (DSC) and X-ray diffraction (XRD).

EXPERIMENTAL

Materials

PVDF pellet (Solef 1015; melting temperature, 173 °C; melt mass-flow rate, 0.2 g/10 min; tensile modulus, 2200 MPa) was supplied by Solvay. BT nanoparticle (molecular formula, $Ba_{1.001}TiO_3$; 100 nm) was acquired from Sinocera Functional Material Co. Ltd. N,N-dimethylformamide (DMF) (molecular formula, C_3H_7NO; AR; molecular weight, 73.09) was supplied by Sinopharm Chemical Reagent Co. Ltd.

Preparation of BT/PVDF nanocomposite films

The BT/PVDF samples were prepared as films by solution casting [17,18]. To produce a homogeneous film, 8 wt% of polymer solution was prepared. First, the PVDF pellet was dissolved in the DMF solvent with magnetic stirring at 60 °C to obtain a completely transparent and homogenous solution. Different weight ratios of BT nanoparticles were then dispersed into this solution and ultrasonicated for 20 minutes. The mixture was placed on a glass substrate and the solvent was removed through evaporation in an oven set at 60 °C. Finally, The BT/PVDF composite films (0wt%, 0.5wt%, 1wt%, 1.5wt% and 2 wt %), were obtained and designated as PVDF, 05BT/PVDF, 1BT/PVDF, 15BT/PVDF and 2BT/PVDF, respectively.

Characterization

After dissolving the previously prepared BT/PVDF composite films obtained in the DMF solution, a small amount of the solution was dropped onto a copper net using a syringe. The morphology of the membranes on the copper net were then studied via transmission electron microscopy (JEOL 2010 HT, Japan) at an operating voltage of 200 kV. After adding a drop of the DMF solution with BT/PVDF films to salt tablets of potassium bromide, the crystalline phases of the samples could be detected with FT-IR (NICOLET 6700, Thermo Scientific). The fraction for the β–phase of the film samples was determined from the FT-IR spectra as

$$F\left(\beta\right) = \frac{A_{\beta}}{1.3A_{\alpha} + A_{\beta}} \qquad (1)$$

where $F(\beta)$, represents the β –phase content; A_α and A_β are the absorbances at 766 and 840 cm^{-1} respectively [5,19]. The crystalline phases were also studied using a diffractometer (D8 Advance, Bruker) with CuKα radiation (λ=1.5406 nm) at a scanning rate of 2°/min from 10 to

70, a voltage of 40 kV and a current of 30 mA. The melting temperature and degree of crystallinity of the membranes were obtained through calorimetric measurement using a DSC (8000, Perkin-Elmer) at a heating rate of 10 °C/min in N_2 atmosphere. Crystalline morphologies of the membranes were studied using POM (DM2500P, Leica) with a thermal platform (THMS600 Linkam). The electrical conductivity and Seebeck coefficient of the membranes were investigated using a multifunctional meter (2400, Keithley Instruments).

RESULTS AND DISCUSSION

The transmission electron microscopic images of the BT/PVDF nanocomposite are shown in Figures 1(a) – (d). Figure 1(a) shows good dispersion of the BT nanoparticles within the PVDF matrix without any observable aggregation. The average initial size of the BT nanoparticles was around 100 nm as shown in Figure 1(b). Figure 1(c) depicts the d-spacing of the crystals, which can be calculated as 0.28 nm and 0.40 nm, corresponding to the (110) and (100) reflections of face-centred cubic (fcc) platinum, respectively. The BT nanoparticles exhibited a single crystalline structure, identified by the selected area electron diffraction pattern (Figure 1(d)) [20].

The interaction between BT and the PVDF matrix was identified via the FT-IR spectra, as shown in Figures 2(a) and (b). The unfilled PVDF and BT/PVDF nanocomposite films were investigated in the region of 4000 to 500 cm^{-1}. By monitoring the bands at 3024 and 2980 cm^{-1}, the asymmetric stretching vibration and symmetric stretching vibration of $–CH_2–$ respectively could be detected. Bands at 1406 and 879 cm^{-1} could be assigned to the outer surface and inner surface deformation vibration of CH_2 linked with CF_2, respectively. The stretching vibration of CF_2 could be revealed by the band at 1180 cm^{-1}, because the characterization peak of the bifluoride compound was located at a band of 1250 to 1050 cm^{-1} and split into two peaks [21]. The peak at 1074 cm^{-1} is attributed to the C–C stretching vibration. The absorption bands corresponding to the crystalline phases are indicated as dotted lines in Figures 2(a) and (b). Absorption bands at 980, 798, 763, 613, 532, 482 and 411 cm^{-1} correspond to the á phase, whereas the bands at 763 and 613 cm^{-1} are attributed to the non-planar rocking vibration and plane rocking vibration of the CF_2 groups in the PVDF chain [22, 23]. The â crystal phase is characterized by bands at 839, 512 and 437 cm^{-1} [24] in Fig. 2a. The absorption peaks of the inorganic filler (i.e. BT) were so weak that they were not detectable compared with those of the predominant PVDF signals. Therefore, there was no significant difference between the spectra of unfilled PVDF and BT/PVDF nanocomposites. Figure 2(a) shows the FT-IR spectra of the samples prepared through solution casting. When the content of the BT nanoparticles increased, the peaks of the â-phase (i.e. 839, 512 and 437 cm^{-1}) became stronger than the á-phase peaks, suggesting that introducing BT nanoparticles could promote the formation of â-phase crystals [25]. These results also showed that polymer chains were aligned on the surface of the BT particles in the TTTT conformation and therefore, in the â-phase, produced a strong interaction between the CH_2 of the PVDF chains and the BT [4].

The relative fraction of the â–phase calculated from the FT-IR spectra is shown in Table 1, which demonstrates that *F(â)* is increased with an increase of BT in PVDF. From Figure 2(b), it can be seen that the samples treated with the isothermal crystallization process only exhibited á-phase crystals, indicating that the crystallization behavior of the PVDF was greatly influenced by the heat treatment and less affected by the concentration of BT. Because the á-phase is the most stable, it is generally obtained when the material is cooled from the melt at temperatures below 160 °C [4].

XRD measurements were conducted to obtain more crystal information from unfilled PVDF and BT/PVDF samples. Figures 3(a) and 3(b) illustrate the XRD patterns of precipitated samples and isothermal crystallized samples, respectively, at 155 °C for 20 minutes. For the XRD patterns of the PVDF, peaking at 20.8° indicates the â phase and 18°, 18.6° and 20.3° indicate the á phase [26]. It can be seen from Figure 3(a) that several different forms of crystals existed in the PVDF sample, which were crystallized from the solution. With BT nanoparticles, the peaks assigned to the â phase of PVDF became more visible and outstanding when the amount of BT reached 2%. Meanwhile, by increasing the amount of BT nanoparticles, diffraction peaks for the perovskite crystal type of BT were gradually enhanced, and the XRD patterns of the BT matched well with JCPDS No. 05-0626 [27,28], supporting the existence and uniform dispersion of BT nanoparticles. In Figure 3(b), strong diffraction peaks at 18.0°, 18.6°, 20.3° and 26.9° corresponding to the á-phase crystal were found in the isothermal crystallized samples. These results are consistent with the FT-IR analysis.

The heating and cooling curves of the composite films, measured by DSC, are presented in Figure 4. The extrapolated onset melting temperature, designated as the melting point (T_{mo}), melting peak temperature (T_{mp}), extrapolated termination melting temperature (T_{me}), melting enthalpy (ΔH_{m}) and degree of crystallinity (X_{c}), were derived from Figure 4(a) and summarized in Table 2.

The formula for calculating crystallinity is shown as follows:

$$x_c = \frac{1}{x} \times \frac{\Delta H_{\mathrm{m}}}{\Delta H_{100}} \times 100\% \tag{2}$$

where x_{c} is the degree of crystallinity, x is the mass fraction of PVDF in the composite material, ΔH_{m} represents the melting enthalpy, and ΔH_{100} is the melting enthalpy of 100% crystalline polymer (i.e., 104.6 J/g for PVDF) [6,29]. The extrapolated onset crystallization temperature, designated as the melting point (T_{co}), crystallization peak temperature (T_{cp}), extrapolated termination crystallization temperature (T_{ce}) and crystal enthalpy (ΔH_{m}) were derived from Figure 4(b) and summarized in Table 3. The data from Tables 2 and 3 show that BT nanoparticles had little influence on T_{mo}, T_{mp}, T_{me}, T_{co}, T_{cp} and T_{ce}. Conversely, introducing the BT nanophase affected the melting enthalpy in both the heating and cooling processes (i.e., ΔH_m and ΔH_c). A higher concentration of BT nanoparticles led to more vigorous endothermal (heating) and exothermal (cooling) reactions during the phase transition and crystallization process. These results clearly indicate that BT nanoparticles can promote the crystallization activity of PVDF in the non-isothermal crystallization process.

POM was applied to visualise the crystallization patterns using polarised light. The POM images of the BT/PVDF composite films with different BT contents (0%, 0.5%, 1%, 1.5% and 2%), melted at 200 °C for 5 minutes and crystallised at 155 °C for 20 minutes are displayed in Figure 5. The grain size of the spherocrystals from Figure 5 is shown in Table 4. Under the same degree of magnification, the unfilled PVDF exhibited a larger size of spherocrystals (Figure 5(a)) compared to the BT/PVDF composite films with 0.0625%, 0.125%, 0.25% and 0.5% of BT nanoparticles (i.e., Figures 5(b)-5(e)). The dispersed BT nanoparticles functioned as a heterogeneous nucleating agent to accelerate the melt crystallization of PVDF, leading to the smaller size of the spherocrystals. However, as shown in Figures 5(f)-5(h), spherocrystal size increased when the BT concentration exceeded 1%. The results indicate that, for this heat treatment regime (i.e., melted at 200 °C for 5 minutes and crystallised at 155 °C for 20 minutes), nucleation is more favourable when the BT concentration is less than 1%.

Another heat treatment regime (i.e., melted at 200 °C for 5 minutes and crystallized at 165 °C for 40 minutes) was conducted on the same samples and the POM images are displayed in Figure 6. The grain size of the spherocrystals from Figure 6 are summarized in Table 4. Martins et. al. (2012) suggested that in an isothermal crystallization process, nucleation kinetics can be enhanced by the presence of nanoparticles [2]. The size of the spherocrystals of the BT/PVDF composite films were typically larger than those shown in Figure 5 at the same concentration of BT. A similar trend related to the effect of BT on the isothermal crystallization behavior of PVDF can be observed in Figure 6. The dispersed BT nanoparticles facilitated nucleation of the PVDF when the content of BT was less than 1%. The higher concentration of BT nanoparticles in the PVDF resulted in a shorter separation distance between the BT nanoparticles and enhanced their absorption of the PVDF molecular chains. The nucleation of PVDF was then inhibited because the BT nanoparticles hindered the movement of the PVDF molecular chains.

The electrical conductivity of the BT/PVDF composites with different contents of BT (with electrical conductivity ~1 S/m) [30] nanoparticles was also investigated. Figure 7 shows that the PVDF film behaved like an insulator (Curve A) due to its poor conductivity, but the electrical conductivity of the composite film increased with BT content. The BT nanoparticles, as high dielectric ceramic powders, not only possessed good electrical conductivity, but also facilitated the formation of â-phase crystals and enhanced the electron flow path in the PVDF matrix. At room temperature, the electrical conductivity of the 2BT/PVDF sample was enhanced tenfold compared with the 05 BT/PVDF. However, the BT had a positive temperature coefficient [7]; therefore, the electrical conductivity of the BT/PVDF composites showed a declining trend with an increase in the temperature.

The Seebeck coefficient of BT/PVDF composites with different BT (Seebeck coefficient ~2000 μV/K) [31] concentrations are shown in Figure 8. The Seebeck coefficient improved when the BT nanoparticles were incorporated. The Seebeck coefficients of the BT/PVDF composites increased in proportion to the concentrations of BT, and the enhancement became more remarkable at temperatures above 105 °C. The Seebeck coefficient of the BT/PVDF composites also increased commensurate with the concentration of BT because the polar â-phase crystals increased when there was more BT in the PVDF. These results agree with those of FT-IR and XRD.

It has been reported that the â-phase of polymorphic PVDF plays an important role in improving its thermoelectric performance, piezoelectric behavior, and ferroelectricity [9,32,33]. This study proposes an effective method to induce the â-phase of the polymorphic PVDF polymer via composite technology using BT nanoparticles. The nano-confined crystallization of PVDF has also been used to obtain more â-phase polymorphic PVDF. Anodic aluminum oxide with cylindrical nanopores (diameter, 20 to 400 nm) has been used as a template for confinement [33,34]. However, the structure of this type of template, usually in simple shapes, is limited by its method of construction. Two-photon polymerization technology based on direct laser writing can be integrated with computer-aided design to generate three-dimensional structures on the nanometer and micrometer scales. Templates with pre-designed micro-architecture can be produced with this method to study the effect of mechanical confinement on the crystallization behavior of PVDF in a more controlled manner. The results will provide new knowledge to better understand crystallization behavior, crystal orientation and polymorphism and to provide more detailed information to further improve the properties of PVDF. An example of this type of template, produced by using a direct laser writing system (Photonic Professional GT, Nanoscribe GmbH) is shown in Figure 9.

CONCLUSIONS

In this study, BT/PVDF nanocomposite films with an improved Seebeck coefficient were prepared. The effect of dispersed BT nanoparticles on the crystallization behavior of PVDF was also studied. It was found that the formation of the crystal phase of PVDF is greatly affected by the heating process and that the BT nanophase can promote the nucleation of PVDF up to a concentration of 0.125wt% BT. The electrical conductivity of the BT/PVDF nanocomposites can also be improved by filling the BT nanoparticles. Unfortunately, the electrical conductivity of BT/PVDF composites is reduced at higher temperatures due to the positive temperature coefficient of BT. Further work will be needed to improve the stability of the crystal phase at higher temperatures and to investigate other thermoelectric effects (e.g., the Seebeck effect).

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