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ORIGINAL PAPER

Microstructure and morphology in the PVDF films doped with $BiCl_3$

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Abstract Polyvinylidene fluoride (PVDF) thick films doped with $BiCl_3$ were fabricated by solvent casting method, and their physical properties were systematically investigated, respectively, by X-ray diffraction (XRD), Fourier transform Infrared (FTIR), and scanning electron microscopy (SEM) in this article. It revealed that the degree of crystallinity increased with the increase of the mass fraction of $BiCl_3$, and the maximum β-phase content was achieved if the mass fraction was 2%. When 2% $BiCl_3$ was added, the films became compact and the character morphology of β-phase of spherulitic crystal was proved by the typical organic material with snow-shaped structures. The experimental results suggested that a complex was formed due to the electric ions ionized by $BiCl_3$ and the free radicals with electric charge, destroyed the structure around the lattice, and returned some free radicals to their original positions, thus enhancing the degree of crystallization of β-phase PVDF. The relative dielectric constant and loss became greater as the mass fraction of $BiCl_3$ increased, but the loss decreased at 2% $BiCl_3$. The relationship between the microstructure and dielectric properties was discussed.

Keywords PVDF · $BiCl_3$ · FTIR · XRD · SEM · Dielectric properties

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Introduction

Polyvinylidene fluoride (PVDF) and its copolymers have been extensively studied due to their excellent pyroelectric and piezoelectric properties over the last three decades [1–3]. PVDF is famous for its multiple characters with four different crystalline forms, i.e., α, β, γ, and δ, which were also known as II, I, III, and IV, respectively. These crystalline phases could be transformed into each other under specific conditions, such as the application of mechanical milling or high temperature electrostatic field [4–6]. In all phases, the β-PVDF exhibits very good piezoelectric, pyroelectric, and dielectric properties so it is utilized to fabricate high β-phase PVDF for being used in sensors and actuators. In general, β-PVDF is obtained by uniaxial stretching, elevated pressure crystallization, high electric field polarization, and solution crystallization [7–15]. Recent researches have contributed to the development of methods convenient for the formation of PVDF β-phase, e.g., PVDF–Clay composites, electro-spinning based methods, and PVDF–Metal salt composites [16–18].

However, these methods often caused the structural deformation of PVDF or non-densification of material, which resulted in limited application of sensors and storage devices. Recently, it was reported that β-phase PVDF could be obtained by the crystallization of PVDF from solution with high polar solvents, such as ***N*****,** ***N***-dimethylformamide (DMF) or dimethylacetamide (DMA). This method was demonstrated to be promising for the fabrication of polymer piezoelectric and pyroelectric materials. It was a simple and low-cost method to induce the β-crystalline phase of PVDF films and able to extend the application of PVDF [19, 20]. As indicated by recent work [21], the addition of $BiCl_3$ produced β-phase and strengthened the electric conductivity.

Up to now, the working mechanism of $BiCl_3$ has not been reported yet, hence this article will give a detailed analysis about it. Our work focuses on the impact of $BiCl_3$ filler on the increment of β-phase, as well as the structural and physical properties of PVDF thick films.

Experiment

PVDF films with different amounts of $BiCl_3$ as filler were prepared by the solvent casting method as described in [21]. The PVDF powder was produced by Academic of Sichuan Chenguang Chemical Center, China. The DMA solvent and $BiCl_3$ powder were both bought from Senopharm Chemical Reagent Co., Ltd., China. PVDF powder and different mass fractions of $BiCl_3$ were added to pure DMF, respectively, and then these two solutions were mixed to form dissolved polymer with a suitable viscosity. Then a stirring state was kept to ensure well-mixed, and an ultrasonic vibration lasted for 15 min in order to remove the bubble. The mixture was placed into a balanced labware of about 5 cm^2 and kept in a vacuum oven at 70 °C for 4 h to remove the solvent completely. The thickness of the films was about 100 μm. PVDF films were prepared with the mass fraction of $BiCl_3$ of 0.0, 1, 2, 4, and 6%.

The crystalline structure analysis was performed at room temperature by an X-ray diffractometer (PANalytical B.V) with rotating anode using Cu K_α radiation and Fourier transform infrared (FTIR) spectroscopy (VERTEX 70, BRUKER, Germany). The surface and section morphology were examined by using a scanning electron microscope (SEM, FEI Co.Holand). The dielectric property was measured by an impedance analyzer (HP4192A).

Results and discussion

X-ray diffraction

The crystal structures of the films are revealed by the XRD patterns, as shown in Fig. 1. The spectra indicate the presence of semi-crystalline structures. The assigned crystalline peaks are listed in Table 1. XRD patterns indicate that the α and β-crystalline phases exist in the materials. The spectra of the pure PVDF show four prominent diffraction peaks at $2\theta = 18.46°$, 20.08°, 26.77°, and 38.68°, and the characteristic peak of β-phase shows at $2\theta = 20.08°$, the others are the characteristic peaks of α-phase [20, 21]. The four prominent diffraction peaks almost disappear and β-phase characteristic peak appears at $2\theta = 20.5°$ when PVDF is doped with $BiCl_3$. This phenomenon indicates that the crystalline structures of PVDF thick films have changed and form new crystalline phases.

Compared with the standard spectra, there exist no peaks corresponding to the pure $BiCl_3$. It is suggested that the $BiCl_3$ molecule is completely dispersed in the polymer matrix, and it is difficult to detect the corresponding peak due to small mass fraction of $BiCl_3$. When 2 wt% $BiCl_3$ is added, the characteristic peak of β-phase reaches its maximum, and the intensity decreases with the increasing $BiCl_3$. The intensity of characteristic peak of β-phase decreases because excessive $BiCl_3$

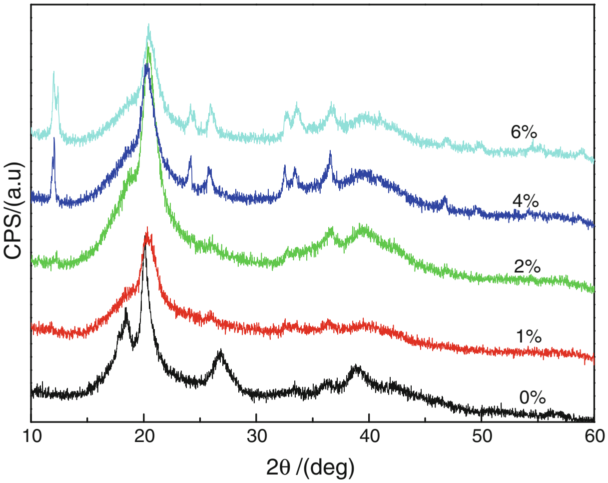

Fig. 1 XRD patterns of the PVDF films doped with different mass fractions of $BiCl_3$

Table 1 Assigned XRD peaks characterizing α- and β-crystalline phases

$BiCl_3$ (wt%)	2θ (degrees)	Assignment
0.0	18.46	(020) α
	20.08	(110) β
	26.77	(021) α
	38.68	(002) α
1.0	20.43	(110) β
	26.23	(021) α
2.0	18.67	(020) α
	20.55	(110) β
	39.11	(002) α
4.0	20.48	(110) β
	25.9	(021) α
	33.05	(130) α
	39.4	(002) α
6.0	20.48	(110) β
	25.95	(021) α
	33.51	(130) α
	39.34	(002) α

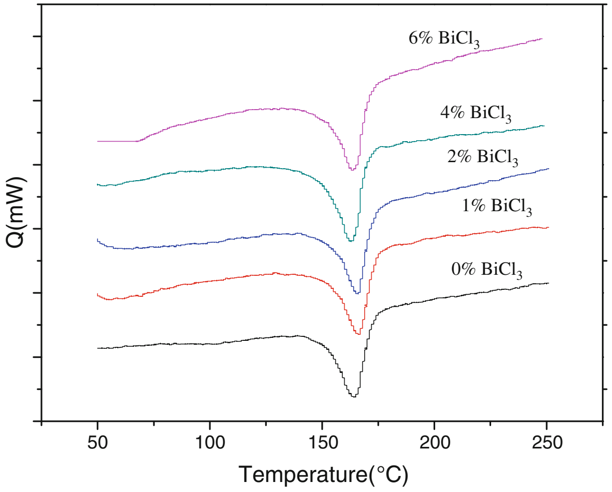

Fig. 2 DSC scans obtained for the PVDF thick films with the filling content

molecules attach to PVDF chain via fluorine bridges and influence the crystal of β-phase of PVDF.

In order to determine the degree of crystallinity of the samples, differential scanning calorimetry (DSC) is performed and the results obtained for samples with different filling contents are shown in Fig. 2. The degree of crystallinity of PVDF films can be obtained as follows:

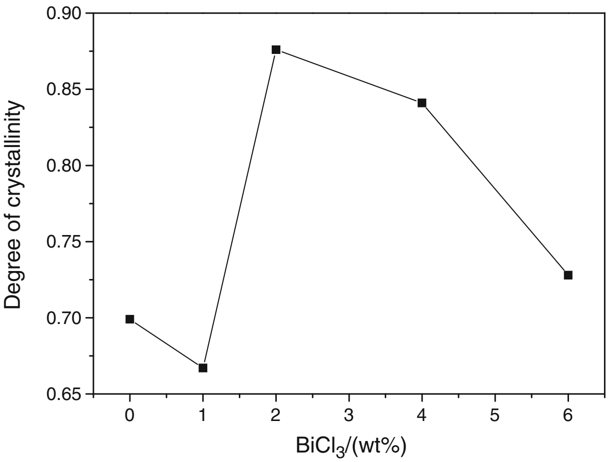

Fig. 3 Degree of crystallinity of PVDF thick films with the filling content

$$\Delta X_c = \frac{\Delta H_m}{\Delta H_{100\%,\ \text{crystalline}}} \tag{1}$$

where ΔH_m is the melting enthalpy of the samples and $\Delta H_{100\%,\ \text{crystalline}}$ is the melting enthalpy for a 100% crystallinity sample of pure PVDF, which is reported to be 104.6 J/g [22].

Figure 3 shows the degree of crystallinity of PVDF thick films with the filling content. Obviously, when 2 wt% $BiCl_3$ is added, the degree of crystallinity increases dramatically, which is 20% higher than that of undoped PVDF thick films.

Infrared analysis

Figure 4 illustrates the Fourier transform infrared (FTIR) spectroscopy results for the PVDF thick films doped with different contents of $BiCl_3$. It is clear from Fig. 4 that α-phase is dominant and has distinct unpolar characteristic absorption peaks at 610, 766, 795, and 975 cm^{-1} when the pure PVDF thick films dry at room temperature. When $BiCl_3$ is added to the solution, β-phase becomes dominant at around 600 cm^{-1}, however, four α-phases disappear. This transformation implies that the crystalline structures have changed and most of α-crystalline phases have been transformed into β-crystalline phases when $BiCl_3$ is added to the solution. When 2% $BiCl_3$ is added, the result is consistent with the XRD analysis.

Surface and cross section morphology of the films

Figure 5 shows the surface and cross section micrographs of PVDF doped with different mass fractions of $BiCl_3$. It can be seen from Fig. 5a that the porosity is large and the diameter of spherulitic crystal is about 40–50 μm. Figure 5b shows that some spherulitic crystals connect together to make the interface outlines fuzzy.

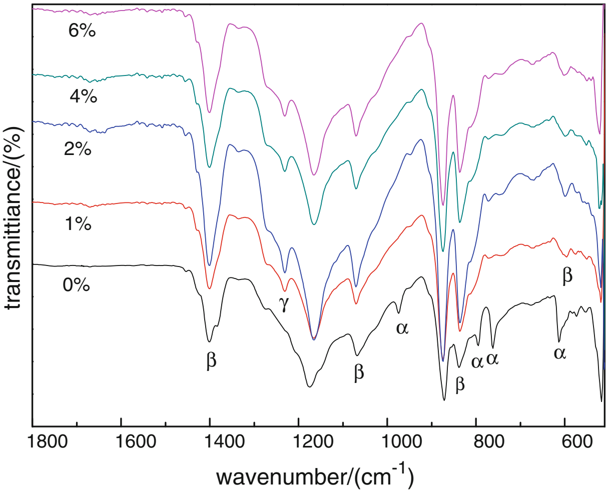

Fig. 4 IR transmittance of PVDF doped with different filling content of $BiCl_3$

Moreover, a lot of small salient is observed on the surface of spherulitic crystal. By adding 2% $BiCl_3$, the density of PVDF films increases obviously and small salient disappears, as shown in Fig. 5c and d. In addition, the diameter of spherulitic crystal is reduced to 20 μm. It can be confirmed from the comparison of Fig. 5b and d that the surface morphology of spherulitic crystal has changed after adding $BiCl_3$, and the appeared snow-shaped structure is actually the character morphology of β-phase of spherulitic crystal [23]. Figure 5e indicates that the cross-section morphology of PVDF thick films exhibits columnar structures.

β-phase increment mechanism

According to the microstructures analysis of PVDF, it is demonstrated that the crystalline state of PVDF has been changed remarkably and more β-phases are formed when $BiCl_3$ is added. During the process of solution crystallization, the polymer matrix could produce some free radicals divorced from the crystalline lattice. These free radicals with positive or negative electric charge are formed by the bond fission, such as the bond broken, the desorption treatment, the formation of hinge, and C=C double bonds. These free radicals, aggregating around the lattice, prevent the crystallization of PVDF and reduce the degree of crystallization of pure PVDF. When $BiCl_3$ is added, a complex could be formed by the electric ions ionized by $BiCl_3$ and the free radicals with electric charge, which destroy the structure around the lattice, make some free radicals return to their original positions, and consequently improve the degree of crystallization of β-phase PVDF. Another reason may be the intermolecular interactions between polymer, solvent, and filling agent as an important factor which is favorable for the formation of β-phase.

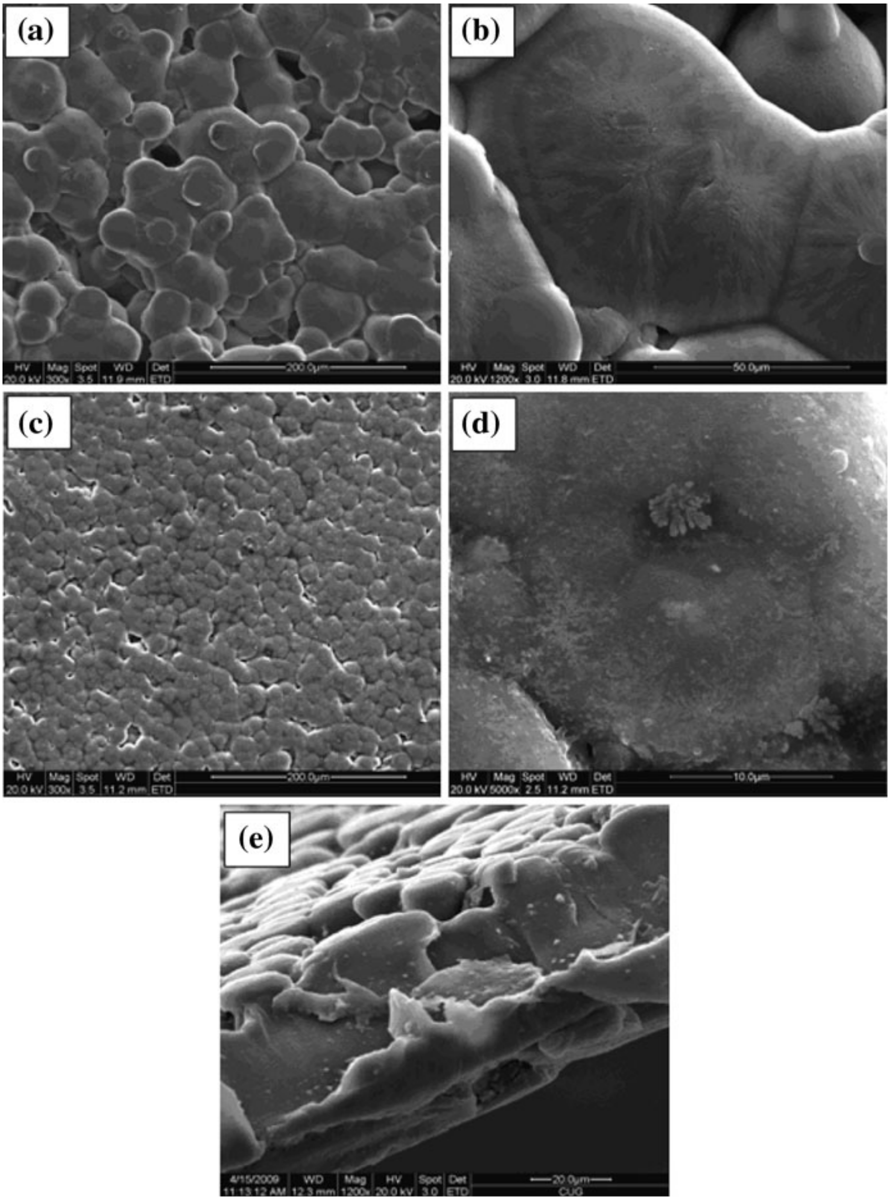

Fig. 5 SEM micrographs of PVDF doped with different fraction of $BiCl_3$. **a**, **b** Surface micrograph of pure PVDF, **c**, **d** Surface micrograph of PVDF with 2% $BiCl_3$, **e** Cross section micrograph of PVDF with 2% $BiCl_3$

Dielectric properties

Figure 6 shows the relationship between the dielectric properties (relative dielectric constant, loss) of PVDF films and different mass fractions of $BiCl_3$. With increasing

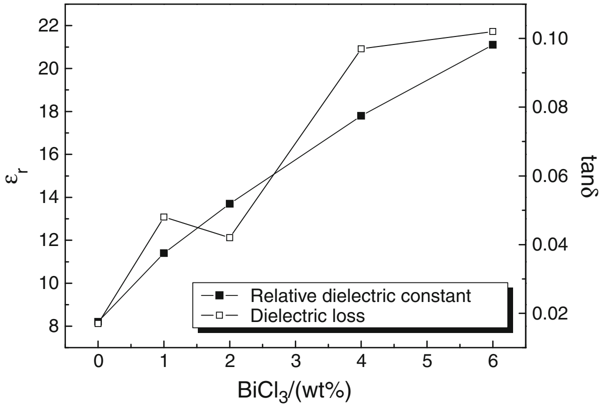

Fig. 6 Dielectric properties of the PVDF films doped with different mass fractions of $BiCl_3$

$BiCl_3$, the relative dielectric constant of the PVDF thick films almost increases as per an approximately linear relationship, and the dielectric loss also has an ascending trend with the increase of the mass fraction of $BiCl_3$. The relative permittivity increases significantly due to the enhancement of polarization as $BiCl_3$ increases. However, the loss decreases from 0.05 to 0.04 when the content of $BiCl_3$ is 2%. It is suggested that the compactness of the polymer increases and dielectric loss decreases when $BiCl_3$ is added. Then, the dielectric loss increases again. It is mainly due to the increase of polarizability of the films with the addition of excessive $BiCl_3$, and in turn the increase of polarizability leads to the increase of the leakage current. Furthermore, the increase of the leakage current results in the improvement of the electric conductivity of the films. Therefore, the dielectric loss is increased [24–26]. As for the pyroelectric materials, it is very important to reduce the dielectric constant and loss, and thus improving the detectivity figure of merit of pyroelectric infrared detector.

Conclusions

The degree of crystallization of β-phase PVDF thick films doped with $BiCl_3$ was fabricated by the casting method. The impact of $BiCl_3$ on the crystal of PVDF was characterized by microstructure analysis, and the working mechanism was systematically analyzed. XRD patterns revealed a main characteristic peak at $2\theta = 20.5°$ corresponding to the β-phase, meanwhile, the characteristic peaks for the α-phase almost disappeared. It indicated that α-phase had been converted into β-phase and the crystalline form of PVDF thick films changed when the $BiCl_3$ was added. In addition, β-phase content was characterized by FTIR spectra. When the $BiCl_3$ was added, most characteristic peaks for the α-phase disappeared, meanwhile, two main characteristic peaks for the β-phase appeared at 600 and 840 cm^{-1}, respectively. It showed that the change of crystalline structure could be attributed to the addition of $BiCl_3$, moreover, partial α-phase had transformed to β-phase. During the process of solution crystallization of PVDF films, a complex was formed by the electric ions ionized by $BiCl_3$ and the free radicals with electric charge. The complex destroyed the structure around the lattice, and made some free radicals return to their original positions, thus enhancing the degree of crystallization of β-phase PVDF. The dielectric properties improved with the increasing mass fraction of $BiCl_3$, and the best property appeared at 2% $BiCl_3$.

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