



Effect of annealing treatment on crystalline and dielectric properties of PVDF/PEG-containing ionic liquid composites

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ABSTRACT

To investigate the effect of poly(ethylene glycol)-containing ionic liquid (IL) and thermal annealing treatment on crystallization and dielectric relaxation behavior of poly(vinylidene fluoride) (PVDF), a series of PVDF/IL composites have been prepared using a solution-cast method. The interaction between imidazolium cation of ILs and $>CF_2$ groups of PVDF can transfer nonpolar α phase to polar β and γ phase as a template at the primary crystallization, and then the interaction between PEG of ILs and $>CF_2$ groups of PVDF can facilitate the PVDF chains in amorphous region to bring more polar phase and decrease the degree of crystallization for PVDF composites according to the template under thermal annealing treatment. The experimental dielectric data were analyzed within the formalisms of complex permittivity and electric modulus. In the frequency spectra of PVDF composites, dc conductivity, electrode and Maxwell-Wagner-Sillars (MWS) interfacial polarization resulted in high values of dielectric permittivity. The incorporation of ILs into the matrix and thermal annealing treatment can accelerate dc conductivity. The temperature dependence of relaxation time of dc conductivity follows the Arrhenius equation. The effect of annealing treatment on charge carrier movement mechanism was resulted from the increase of ion mobility induced by polymer chain segmental motion and polar phase crystals.

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1. Introduction

Polyvinylidene fluoride (PVDF) has attracted considerable research activity due to its chemical, thermal and electrical stability, unique piezoelectric and pyroelectric properties [1–3]. There are several kinds of crystal phase types (α , β , γ and δ) of PVDF due to the linear structure and the mutual repulsion of fluorine atoms [4,5]. Among these crystals, α , β , and γ crystals can exist in PVDF matrix steadily. A nonpolar α phase with TGTG chain conformation is not piezoelectric, which can be easily obtained from melt crystallization. While the β and γ phases have an orthorhombic unit cell with TTTT and TTTG chain conformation that cannot form directly. The use of additives like sodium montmorillonite [6], inorganic salts [7] and ionic liquids (ILs) [8,9] is simple and cost-effective approach to induce and improve the content of polar phase. Polymeric membranes based on PVDF which consist of both crystalline and amorphous phases have drawn much research attention

because their high dielectric constant facilitates high charge dissociation and supports high concentration of charge carriers [10,11]. Addition of ceramic fillers, plasticizers such as ILs and PEG has been adopted to enhance the ionic conductivity and maintain mechanical and thermal stability of polymer electrolyte membranes [12,13].

ILs have attracted more and more attention because of its excellent physical properties such as low volatility, high ionic conductivity, nonflammability, and chemical and thermal stability [14,15]. The incorporation of ILs in the polymer matrix as flame retardant, electrolytes and efficient green plasticizer has received enormous interest because polymer/IL composites are useful in the production of solid polymer-based electrolytes for batteries, capacitors, sensors and actuators [16]. In polymer electrolyte containing IL, IL plays the role of plasticizer as well as supplier of ionic charge carrier to significantly change polymer crystallization and dielectric behavior. Li et al. reported the composite of PVDF/1-butyl-3-methylimidazolium hexafluorophosphate and found that the addition of IL drastically increased γ phase crystals of PVDF by the interaction between the $>CF_2$ and cationic ions, and the melting temperature and crystallization rate decreased with

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increasing the fraction of IL [9]. Pruvost et al. reported the composites of P(VDF-CTFE)/octadecyltriphenylphosphonium and P(VDF-CTFE)/tributyl (methyl) phosphonium methylsulfate. They found that regularly assembled ILs in the rigid amorphous fraction of P(VDF-CTFE) between crystalline lamellae can act as template to efficiently induce a complete transition of nonpolar α phase to polar phase [17].

Polyethylene glycol (PEG) as non-solvent plasticizer has been widely used in solid and gel polymer electrolyte due to the ability to decrease polymer-polymer chain interaction and solvate lithium ions, especially in PVDF composites [18,19]. Strong interaction between the C–O–C groups in PEG and the $>\text{CF}_2$ groups in PVDF chain improves the free volume/local segmental mobility of the lithium ions in PVDF/PEG/ LiTi_2O_4 membrane [20]. Do et al. fabricated core/shell (PEG/PVDF) phase-change nanofibers using coaxial electrospinning, and the PEG of the core layer was able to store and release thermal energy [21]. Hence, the PEG was selected to influence the crystal of PVDF, and the plasticizing effect and higher dielectric constant can soften the ionic interactions, and lead to ionic dissociation and mobility.

Hence, we have studied the effect of PEG-containing IL on crystal structure and transformation of PVDF under annealing treatment. The crystal structure under annealing treatment is characterized by XRD and the curves of DSC. Annealing treatment and soft PEG segment of IL can influence the crystal types and the growth mechanism. After the study on the crystal nucleating and growth, the dielectric frequency spectra can be used not only for structural characterization of the composites but also as a probe of estimating charge carrier movement mechanisms of the composites which is of great potentiality for application of polymer electrolyte.

2. Experimental

2.1. Materials and sample preparation

PVDF was obtained from Shanghai 3F New Material Co., China with a weight average molecular mass (M_w) of 2.2×10^5 g/mol and a polydispersity index of 2. PEG-containing imidazolium ionic liquid (IL) was synthesized and purified by column chromatography in our laboratory (ESI Figs. S1 and S2).

The PVDF/IL composites with different IL contents (0, 2, 4, 8, and 12 wt %) were prepared by solution mixing directly. Then IL and

PVDF were dissolved in DMF under magnetic stirring at 60 °C for 12 h in order to form uniform syrup. Afterwards, the mixture was poured into petri dish, transferred into air dry oven, and heated to 100 °C for 24 h to remove the solvent completely. Last, the mixture was molded by hot-pressing at 175 °C and 10 MPa subsequently. The samples were annealed in vacuum oven at 140 °C for 12 h.

2.2. Sample characterization

The melting process measurement was finished by differential scanning calorimeter (DSC, 821e, Mettler Toledo). The crystal forms of samples were also characterized by X'Port, PRO MPD, Holland. The machine was operated at a 40 kV voltage and 40 mA current. The wavelength of monochromated X-ray was 0.124 nm, and the beam size was ca. 400 μm . The data was recorded from $2\theta = 5\text{--}30^\circ$ at a scanning speed of $2^\circ/\text{min}$ with a step interval of 0.02° . The films were coated with silver electrodes of 10 mm in diameter for ac dielectric measurements. The dielectric permittivity was measured with Agilent E4980A LCR meter with the frequency ranging from 20 Hz to 2 MHz.

3. Results and discussion

3.1. Structural characterization of PVDF/IL composites

Annealing treatment was employed to study the influence of thermal effect on PVDF by DSC. Fig. 1a and b shows the first heating DSC curves of all samples after hot-pressing and annealing at 140 °C, respectively. Firstly, double melting peaks are observed in pure PVDF after hot-pressing and annealing at 140 °C for 12 h. It is easy to distinguish that lower melting peak in the samples resulted in the melting of the ordered structure, which were formed during the mould pressing [22]. The higher melting peak originated from the formation of perfect crystals. Secondly, three melting peaks occurred in the PVDF/2IL and PVDF/4IL without annealing treatment. The highest melting peak corresponding to polar phase originated from the crystal induction of IL because of the ion-dipole interaction between the $>\text{CF}_2$ of PVDF and the imidazolium cation of IL. But only one melting peak occurred in the samples under annealing treatment. This indicates the IL with PEG long soft chain can facilitate the PVDF chain in amorphous area to form other crystal with TTT conformation. Hence, the melting peak is around 174 °C, which corresponds to polar phase [23]. Lastly, in PVDF/8IL

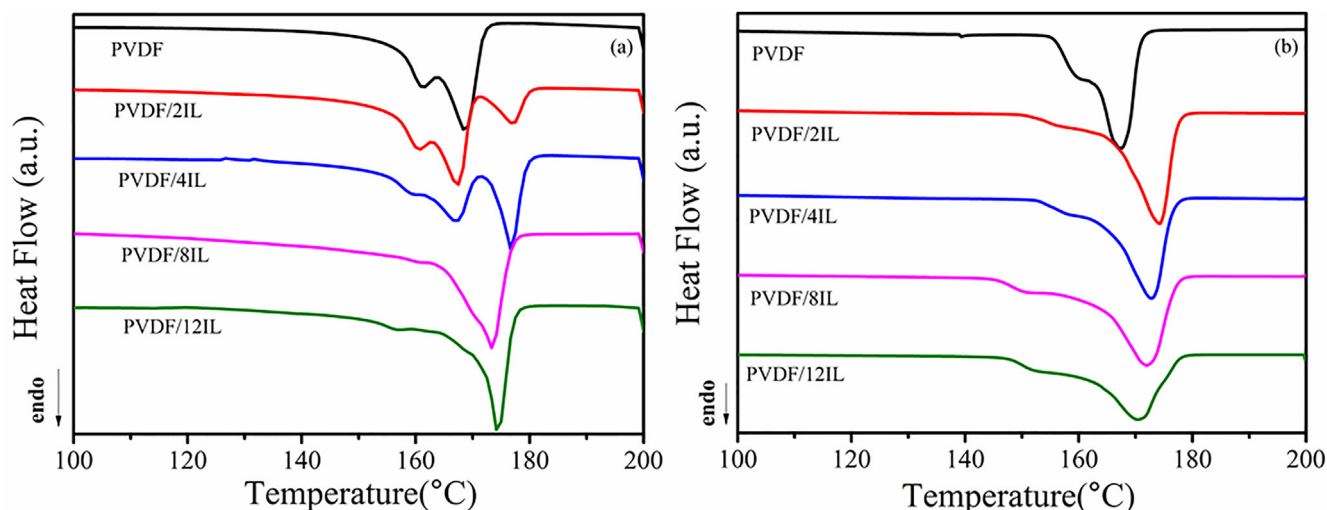


Fig. 1. (a, b) First heating DSC curves of all samples after hot-pressing and annealing at 140 °C, respectively.

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