



# Enhanced dc conductivity and conductivity relaxation in PVDF/ionic liquid composites



Pei Xu\*, Weijia Fu, Xiao Luo, Yunsheng Ding\*

Department of Polymer Science and Engineering, School of Chemistry and Chemical Engineering, and Anhui Key Laboratory of Advanced Functional Materials and Devices, Hefei University of Technology, Hefei 230009, China

## ARTICLE INFO

### Article history:

Received 24 April 2017

Received in revised form 3 June 2017

Accepted 23 June 2017

Available online 24 June 2017

### Keywords:

Polymeric composites

PVDF

Dielectrics

Ionic liquid

Conductivity

## ABSTRACT

To investigate the effects of 1-benzyl-3-methylimidazolium hexafluorophosphate on the crystal phase, morphology and dielectric relaxation behavior of poly(vinylidene fluoride) (PVDF), a series of PVDF/IL composites have been prepared using solution-cast method. The interaction between ILs and  $>CF_2$  groups of PVDF can facilitate the PVDF chains in amorphous area to form more polar phase for PVDF composites. In the frequency spectra of PVDF composites, MWS interfacial polarization, electrode polarization and dc conductivity resulted in high values of dielectric permittivity. The incorporation of ILs into the matrix can accelerate dc conductivity. The effect of IL on charge carrier movement mechanism was resulted from the increase of ion mobility induced by polar phase crystal and ion concentration.

© 2017 Elsevier B.V. All rights reserved.

## 1. Introduction

Poly(vinylidene fluoride) (PVDF) has gained scientific and technological attention because of its chemical stabilities, mechanical properties, weatherability, and high dielectric permittivity [1–5]. PVDF has five distinct crystal phases including nonpolar  $\alpha$ -phase, polar  $\beta$ - and  $\gamma$ -phase,  $\delta$ - and  $\epsilon$ -phase, and the different crystal phases have difference properties [6]. The key applications for PVDF such as solid polymer-based electrolytes for batteries, capacitors, sensors and actuators, are related to the strong polar crystal phases of PVDF, which have all-trans conformation (TTTT) for the  $\beta$ -phase and (TTTG) for the  $\gamma$ -phase [7–9].

There are many strategies to control and improve the content of  $\beta$ -phase or  $\gamma$ -phase of PVDF [3,8]. Ionic liquids (ILs) which are composed of organic cations and anions, can promote the formation of  $\beta$ -phase by dipolar-imidazolium cation interactions between PVDF chain-molecules and the ILs during melt crystallization [10–12]. There are two successive events: the structure and morphology of PVDF/IL composites and then the dielectric properties of composites [13]. Because ILs have many excellent properties such as low volatility, high chemical stability, high thermal stability, excellent ionic conductivity [14]. In order to examine how the addition of ILs affect the alignment of dipoles and migration of space charges of PVDF for electrolytes applications, crystallization behav-

ior and dielectric polarization of PVDF/IL composites were investigated by using FTIR, XRD and dielectric relaxation spectroscopy (DRS) measurements.

## 2. Experimental

PVDF was purchased from Shanghai 3F New Material Co., China with a weight average molecular mass ( $M_w$ ) of  $2.2 \times 10^5$  g/mol and a polydispersity index of 2. The ionic liquid (IL), 1-Benzyl-3-methylimidazolium hexafluorophosphate, was obtained from Lanzhou Greenchem ILs, China. The melting point of IL is 130 °C.

The PVDF/IL composites were prepared as follows. PVDF and IL were dissolved in DMF by vigorous mechanical stirring. Afterwards, the mixture was heated to 70 °C for 8 h to remove the solvent completely and molded by hot-pressing at 175 °C and 10 MPa subsequently.

The crystal phases of samples were also characterized by X'Port, PRO MPD, Holland. The machine was operated at a 40 kV voltage and 40 mA current. FTIR-ATR spectra were carried out to analyze the crystal phases by Nicolet 67, Thermo Nicolet, USA. The morphology of PVDF/IL was investigated by field emission scanning electron microscopy (FESEM, Hitachi-SU8020). 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.

\* Corresponding authors.

E-mail addresses: [chxuper@hfut.edu.cn](mailto:chxuper@hfut.edu.cn) (P. Xu), [dingys@hfut.edu.cn](mailto:dingys@hfut.edu.cn) (Y. Ding).

### 3. Results and discussion

As shown in Fig. 1a, in XRD patterns, Neat PVDF shows four characteristic diffraction peaks at  $2\theta = 17.8, 18.5, 19.9,$  and  $26.6^\circ$ , which are assigned to the (020), (100), (110), and (020) reflections of the  $\alpha$ -phase crystal [6]. However the XRD patterns of all PVDF/IL composites have a distinctly different feature compared with the neat PVDF. The peak at  $2\theta = 17.8, 18.5$  and  $26.6^\circ$  completely disappear and the peak at  $2\theta = 19.9^\circ$  becomes very weak. Moreover, there is a broad peak appears at  $2\theta = 20.4^\circ$  which can be attributed to the  $\beta$ -phase of PVDF. In addition, the peak at  $18.1^\circ$  is attributed to IL crystal as IL content increases. Thus, the XRD results imply that the addition of ILs could substantially induce  $\beta$ -phase of PVDF. In FTIR-ATR spectra, the characteristics vibration bands at  $766, 795, 855,$  and  $976\text{ cm}^{-1}$  can be attributed to the  $\alpha$ -phase of PVDF. However, the characteristics vibration bands of the crystalline  $\beta$ -phase are at  $840, 1279\text{ cm}^{-1}$ ; and for  $\gamma$ -phase at  $1234\text{ cm}^{-1}$ . As shown in Fig. 1b for neat PVDF, the bands at  $766, 795, 855$  and  $976\text{ cm}^{-1}$  are clearly observed. However for the PVDF/IL composites, with the addition of IL, the intensity of the bands at  $766, 795, 855$  and  $976\text{ cm}^{-1}$  are markedly weakened and even disappear while the intensity of the band at  $840\text{ cm}^{-1}$  significantly increase and a small absorption band at  $1279\text{ cm}^{-1}$  appeared. Therefore whether XRD or FTIR-ATR all prove the formation of  $\beta$ -phase [15].

Fig. 2 shows the morphologies of pure PVDF and PVDF/IL composites. As can be seen from the micrographs, with a small amount of IL content (2% and 4%), IL is distributed homogeneously in the polymer matrix, it shows that IL has good compatibility with polymer matrix. And with increasing of IL content to 8%, there is a slight aggregation of IL in polymer matrix because of the formation of IL crystal.

The dielectric permittivity and loss of pure PVDF and PVDF/IL composites are presented in Fig. 3. Electrode and MWS interfacial polarization processes in the PVDF/IL composites are clearly visible in the frequency window of Fig. 3a and b. The large values of these composites at low frequencies are due to the electrode polarization effect because of the radial and tangential diffusion of ions near the electrodes surfaces [16]. It can be clearly observed that the dielectric permittivity of the composites gradually increased with the increase of IL content. The dielectric strength of the composites at middle frequency region from 100 Hz to 10 kHz is governed by the MWS interfacial polarization. Disparity in the constituents permittivity or/and conductivity between different components at various length scales leads to interfacial blocking of charges, whose polarization manifests as a dielectric MWS interfacial polarization

peak. IL can induce polar crystal phase of PVDF (Fig. 1) and result in disparity in the constituents permittivity or/and conductivity between crystalline region and amorphous area of PVDF (Figs. 3 and 4). There is significant alteration in the strength of ion-dipolar interactions and the dipolar ordering of polar crystal in the composites with increase of IL concentration.

To gain further insight into the effect of charge carrier movement on polarization phenomena, we detailedly investigated the variation of ac conductivity,  $\sigma_{ac}$  as a function of frequency and temperature.  $\sigma_{ac}$  can be calculated by the equation [17].

$$\sigma_{ac} = \omega \varepsilon_0 \varepsilon'' \quad (1)$$

The  $\sigma_{ac}$  in the frequency domain for PVDF and PVDF/IL composites are presented in Fig. 4a. The  $\sigma_{ac}$  values of these polymeric composites increase non-linearly with increase of frequency on logarithm scale. It has been established that the ion transportation in polymeric composites occurs on different time scale under the influence of alternating current (ac) electric field. The  $\sigma$  spectra of the investigated composites shows two regions on frequency scale; (i) the dc plateau region dominated low frequency region below 1 kHz and (ii) the power law dispersive region above 1 kHz. Further, it is observed that the  $\sigma$  increases with increasing IL content of the composites. This increase has two implications, firstly, the mobility of the ions increases due to increased dipolar ordering of polar crystal, and secondly, the ion concentration increases.

To analyze the conductivity relaxation, the  $\varepsilon^*$  data were transformed into complex electric modulus formalism  $M^*$  formalism, according to [18]

$$M^* = \frac{1}{\varepsilon^*} = \frac{1}{\varepsilon' - i\varepsilon''} = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} + j \frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2} = M' + iM'' \quad (2)$$

Fig. 4b respectively show  $M''$  of electric modulus versus frequency for PVDF/IL composites at  $30^\circ\text{C}$ . The  $M''$  spectra of the conducting composites exhibit a peak in the high frequency region corresponding to the conductivity relaxation process. With the increase of IL content, the  $M''$  dispersion have shift towards higher frequency side which reveals that the conductivity relaxation is thermally activated with the hops of charge carriers. Ion mobility induced by polar phase crystal and ion concentration can improve the ion hopping from one site to the neighboring site. The frequency  $f_{max}$  of the peak is assumed to represent a characteristic frequency of conductivity relaxation. When the frequency is lower than  $f_{max}$  the charge carrier can make long-range motion, and when the frequency is higher than  $f_{max}$  charge carriers are spatially

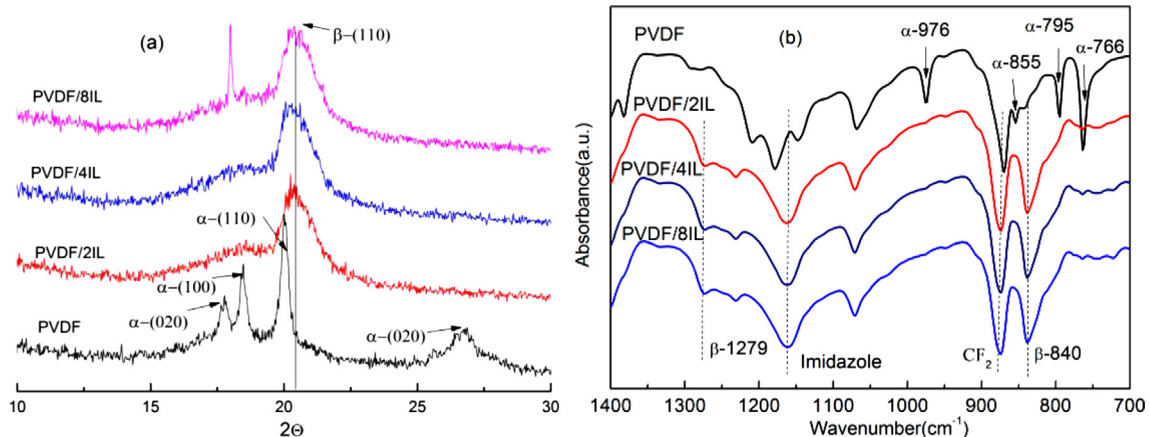


Fig. 1. (a) XRD patterns of pure PVDF and PVDF/IL composites after hot pressing; (b) FTIR-ATR spectra of all samples after hot pressing.

Download English Version:

<https://daneshyari.com/en/article/5463423>

Download Persian Version:

<https://daneshyari.com/article/5463423>

[Daneshyari.com](https://daneshyari.com)