Enhanced Reproducibility of Positive Temperature Coefficient Effect of CB/HDPE/PVDF Composites with the Addition of Ionic Liquid

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Abstract Developing an effective method for improving the reproducibility of positive temperature coefficient (PTC) effect is of great significance for large-scale application of polymer based PTC composites, owing to its contribution to the security and reliability. Herein, we developed a carbon black (CB)/high density polyethylene (HDPE)/poly(vinylidene fluoride) (PVDF) composite with outstanding PTC reproducibility, by incorporating 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([OMIm][NTf₂]) into the composite. After multiple repeated temperature cycles, the PTC performance of as-prepared material keeps almost unchanged and the variation of resistance at room temperature is less than 7%. Our studies revealed that [OMIm][NTf₂] contributes to the improvement of PTC reproducibility in two ways: (i) it acts as an efficient plasticizer for refining the co-continuous phase morphology of HDPE/PVDF blends; (ii) it inhibits the crystallization of PVDF through the dilution effect, leading to more overlaps of the volume shrinkage process of HDPE and PVDF melt which results in the decrease of interface gap between HDPE and PVDF. This study demonstrated that ionic liquids as the multifunctional agents have great potential for improving the reproducibility in the application of the binary polymer based PTC composites.

Keywords Conductive polymer composites; Reproducibility; Positive temperature coefficient; Ionic liquid

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INTRODUCTION
Conductive polymer composites (CPCs) with PTC effect, which present the increase of resistance with temperature, hold tremendous promise for versatile applications from smart heating device to ultra-accurate intelligent temperature control system. Meanwhile, the good processing property inheriting from insulated polymer matrix and the excellent electrical conductivity deriving from conductive fillers also provide a necessary prerequisite for its large-scale application. However, the shortcomings including the negative temperature coefficient (NTC) phenomenon that presents a resistance decline with temperature and the poor electrical reproducibility after repeated temperature cycles, hinder the proper application of them in broader fields. To address these issues, great efforts including modification of fillers, crosslinking of polymer, hybridizations of fillers and application of binary matrix have been made for eliminating these negative performances.

Among them, the application of binary crystalline polymer matrix including polypropylene (PP)/ultrahigh molecular weight polyethylene (UHMPE), polyethylene (PE)/PVDF etc. has attracted a lot of attention in recent years. On the one hand, the negative temperature coefficient effect could be significantly improved due to the inhibition effect or offset of the second PTC effect of the crystalline polymer with higher melting point. On the other hand, owing to the crystal-induced volume-exclusion effect and double percolation structure of incompatible system, the percolation threshold of conductive fillers can be largely reduced. Although these attempts have improved the performance of CPCs, it still remains a challenge to achieve the excellent PTC reproducibility based on crystalline polymer matrix, which meets the rigorous requirements for long-term performance of commercial application.

To pursue desired reproducibility of PTC composites based on binary crystalline polymer matrix, both the morphology of polymer blends and distribution of conductive fillers have been investigated. Jeon et al. have developed binary polymer based PTC material with a co-continuous structure. The outstanding improvement of PTC reproducibility is attributed to the continuous second matrix (polyethylene) to maintain a reproducible morphology of another polymer during temperature cycles. In addition, Zhang et al. have designed “island-bridge” electrical conductive networks in HDPE/PVDF/carbon nanofiber (CNF) composite to improve the reproducibility of PTC. As reported, the continuous “sheath” structure of PVDF plays the critical role in enhancing PTC reproducibility, due to its confinement effect to facilitate the reconstruction of conductive networks in “island” (HDPE...
Preparation processing for CB/HDPE/PVDF-IL composites

**EXPERIMENTAL**

**Materials**
Conductive CB (particle size=40 nm, dibutyl phthalate adsorption value=255 mL/100g) was obtained from Jiaozuo City He Xing Chemical Industry Co., Ltd. (China). The commercial HDPE (L501 (5000S)) was bought from Sinopec Yangzi Petroleum Chemical Co., Ltd., China. PVDF (Solef 460) was supplied by Solvay Co., Ltd. Antioxidant (Chinox 1010), supplied by Double Bond Chemical (Shanghai) Co., Ltd., was used to prevent oxidation degradation at the content of 0.5 wt%. 1-Octyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ([OMIm][NTf₂]) was supplied by Qingdao Aolike New Material Technology Co., Ltd.

**Sample Fabrication**
In order to disperse all of CB to HDPE phase, an optimized processing method was used to fabricate the composites, as shown in Fig. 1. Step one: the HDPE, antioxidant (0.5 wt% of the HDPE) and CB were firstly mixed in an internal mixer (RM-200C Mixer, Harbin Hapro Electric Technology Co., Ltd. China) at 60 r/min and 160 °C for 10 min. Then, the master-batch was cut into particles after quickly pressed into a sheet by an open mill. Step two: PVDF and antioxidant (0.5 wt% of the PVDF) were firstly mixed in the internal mixer at 60 r/min and 185 °C for completely melted. Then the master-batch was mixed for 1.5 min prior to the addition of IL for another 3 min. After compounding, the mixtures were compression-molded into sheets with thickness of around 2.0 mm at 185 °C and 10 MPa for 10 min. In addition, the volume fraction of CB was fixed at around 5 vol%. The mixture containing 0.5 wt% of PVDF and volume contents of IL were 0 vol%−10.0 vol% of PVDF. For convenience, the specimens were denoted as CB/HDPE/PVDF-IL-x, where x denotes the volume content of IL. All samples were cut into 2 mm × 20 mm × 70 mm and were rested to release stress overnight, before performing the electrical measurements.

**Characterization**
For eliminating contact resistance, all samples were fused with conductive copper mesh at both ends of them. The room-temperature resistance (Rroom) of the samples was measured by the four-probe method with a digital multi-meter (VC9806+) when the sample resistance was lower than 10⁸ Ω, and a high resistance meter (ZC36) was used above that value. The volume resistivity (ρ) was calculated according to the formula ρ = RS/d, in which the sample resistance R, area S, and thickness d were definite.

**Fig. 1** Graphical illustration of the preparation processing for CB/HDPE/PVDE-IL composites.
values. The temperature-dependence of resistivity was measured in a heating device with the rate of 2.0 °C/min. The crystal forms of polymer were explored by a RIGAKU Ultima IV X-ray diffractometer with Cu-Kα X-ray beam (λ=0.154 nm) in the range of 2θ of 5°−40°, as well as the characterization of infrared spectroscopy with reflection pattern from 600 cm$^{-1}$ to 3000 cm$^{-1}$. A differential scanning calorimeter (Q20-TA) was used to measure the thermodynamic phase transition behavior from 20 °C to 190 °C with a heating rate of 10 °C/min. The morphology characterization was investigated by a field emission scanning electron microscope (SEM, JSM-7500F) at an accelerating voltage of 10 kV and the elemental analysis was carried out by energy dispersive X-ray spectroscopy (EDX, LEICA EM UC7). Samples were covered with platinum film after fractured in liquid nitrogen before detecting morphology.

RESULTS AND DISCUSSION

The Distribution and Dispersion of Conductive CB

As to binary polymer based PTC composites, the pyroresistive property can be influenced by the factors including the location of conductive fillers in matrices, the dispersion of conductive fillers. According to classical thermodynamics, the preferential location of conductive fillers in immiscible polymer systems can be predicted by the following Young’s equation:

$$\omega_a = \frac{\gamma_{CA} - \gamma_{CB}}{\gamma_{AB}} \tag{1}$$

where $\omega_a$ is the wetting coefficient. $\gamma_{CA}, \gamma_{CB}$ and $\gamma_{AB}$ are the interfacial energies between the polymer A and filler, the polymer B and filler and between the polymer A and polymer B, respectively. $\omega_a > 1$ and $\omega_a < -1$ represent that the fillers tend to locate in polymer B and polymer A, respectively. $1 > \omega_a > -1$ indicates that the fillers will preferentially be located at their interface. Due to $\gamma_{PE-PVDF} < -1$, conductive CB prefers to distribute in PE phase of the incompatible PE/PVDF system.[25]

To determine the location of CB in composites, the SEM and EDS characterizations of composites were performed (Fig. 2). The pristine CB presents micron-scale aggregate with nano-scale original particle (Fig. 2a). After compounding, it can be easily observed in HDPE phase (Figs. 2b and 2c). In contrast, in PVDF phase distinguished by EDS to identify fluorine elements (Figs. 2b and 2e), it shows the uniform and smooth fracture morphology without the dispersion of CB particles (Figs. 2b and 2d). Consequently, the CB particles entirely locate in HDPE phase so that the concern about the CB distribution in PVDF is eliminated.

For guaranteeing the unaltered CB dispersion with addition of ILs, the mixing time after adding ILs in step two was drastically reduced. Moreover, the kind of IL has been specifically selected for further diminishing its effect on the dispersion of CB in HDPE. The chemical structure of used IL with amounts of fluorine atoms in cationic group is shown in Fig. 3a. Due to the same polar elements (fluorine), it presents good compatibility with PVDF which is demonstrated by the smaller contact angle with neat PVDF (Fig. 3a). Hence, as the selected IL prefers to disperse in PVDF, the dispersion of CB in HDPE is hardly influenced by IL. Comparing the SEM morphology of composites with and without ILs (Figs. 3c and 3d), the large aggregates of CB can be observed from both of them and the dispersion of CB presents similarities. Furthermore, the volume resistivity of PVDF/HDPE-IL-0 is

![Fig. 2](https://doi.org/10.1007/s10118-020-2475-x)
about 10 kΩ·cm, and it keeps almost constant with the increase of IL (Fig. 3b). Because the dispersion of CB has a crucial influence on the conductivity of composites,[20,38,39] the unaltered dispersion of CB in CB/HDPE/PVDF-IL is further confirmed by the unchanged volume resistivity.

The Effect of IL Loading on the Phase Morphology

The phase morphologies of CB/HDPE/PVDF-IL composites with various IL loadings are exhibited in Fig. 4. The HDPE phase can be easily distinguished by the roughness of fracture surface due to the CB particles completely located in HDPE. As shown in Fig. 4, the HDPE phase in CB/HDPE/PVDF-IL-0 presents the irregular shape with domain size about 100 µm (Fig. 4a), however, the significantly smaller size of HDPE phase with rod-like shape can be observed in the case of 2.0 vol% of ILs and it keeps almost constant as the IL increases (Figs. 4b–4d).

These changes can be attributed to the plasticization effect of ILs, which reduce the viscosity of PVDF. And, the mixture law of solution viscosity[40] as following can be used to deeply expound the viscosity evolution of PVDF phase.

\[
\log \eta_s = N_1 \log \eta_1 + N_2 \log \eta_2 \tag{2}
\]

where \(\eta_s\), \(\eta_1\), and \(\eta_2\) are the viscosities of the mixture, component 1, and component 2, respectively; \(N_1\) and \(N_2\) represent the mole fractions of component 1 and component 2, respectively.

The viscosity of the solution can be further expressed as:

\[
\eta_s = e^{\left(\log \eta_1 - \log \eta_2 \right) N_1 + \log \eta_2} \tag{3}
\]

Assume that the components 1 and 2 are the IL and the PVDF melt (\(\eta_1 < \eta_2\)), respectively. For elucidating the viscosity variation of PVDF phase with the IL, the first derivative of Eq. (3) is derived as:

\[
\eta_s' = \left(\log \eta_1 - \log \eta_2\right) e^{\left(\log \eta_1 - \log \eta_2\right) N_1} \tag{4}
\]

From Eq. (4), the first derivative of \(\eta_s (\eta_s')\) is gradually approaching to zero. The influence of IL on the viscosity of PVDF tends to exponentially decline with increase of it. Hence, when the small amount of IL is introduced (2.0 vol%), the viscosity of PVDF decreases significantly. The viscosity ratio of PVDF and HDPE phase in melt state is changed[41,42] so that the better co-continuous morphology of composites can be obtained to reveal smaller size of HDPE phase. With further increase of IL, the effect on the reduction of the PVDF viscosity is sharply weakened as Eq. (4). Subsequently, the morphology of HDPE reveals almost no change. Moreover, the rod-like shape of HDPE phase may also result from the decline of PVDF viscosity which promotes its flow at high temperature and pressure during compression molding. Generally, at a constant dosage of HDPE, the smaller size of phase domain means more surface of HDPE to receive confinement from PVDF. Hence, for the purpose of receiving stronger confinement from PVDF, the sufficient surface as the prerequisite can be realized with the IL loading above 2.0 vol%.

The PTC Reproducibility and Discussion

Referring to previous reports,[43,44] the PTC performance has been measured ten cycles for exhibiting the PTC reproducibility. Comparing with the CB/HDPE/PVDF-IL-0, the composites
with IL of 6.0 vol% reveals super reproducibility (Figs. 5a and 5b). To be specific, the change rate of the room temperature resistance ($R'_{\text{room}}$) undergoing ten heating and cooling cycles against loading of IL is calculated according to: $R'_{\text{room}} = \frac{R'_{\text{room}}^{1\text{st}} - R'_{\text{room}}^{10\text{th}}}{R'_{\text{room}}^{1\text{st}}}$ and gives the value less than 7% even undergoing multiple repeated temperature cycles (Fig. 5c). For showing the NTC inhibition effect of binary polymer

Fig. 4 Influence of IL loading on the phase morphology evolution of CB/HDPE/PVDF-IL blend characterized by SEM. The red dotted zone shows the HDPE phase.

Fig. 5 PTC reproducibility of (a) CB/HDPE/PVDF-IL-0 and (b) CB/HDPE/PVDF-IL-6. (c) The change rate of the room temperature resistance ($R'_{\text{room}}$) undergoing ten heating and cooling cycles against loading of IL. (d) The NTC intensity ($I_{\text{NTC}}$) of CB/HDPE/PVDF-IL composites against loading of IL.

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matrixes as reported in other literatures, the NTC intensity (according to the equation: \( \ln(NTC) = \log(R_{\max}/R_{150^\circ C}) \)) is also demonstrated as Fig. 5(d). A distinct decrease of \( \ln(NTC) \) occurs at the IL loading of 2.0 vol% and it is almost constant with increase of IL, subsequently. This variation is consistent with the morphology evolution of HDPE phase in composites (Fig. 4). Hence, the reason for \( \ln(NTC) \) change may be attributed to the morphology evolution of HDPE phase.

More attractively, dissimilar to the variation of \( \ln(NTC) \), the \( R_{room} \) reveals an obvious decline postponed to the loading of IL between 2.0 vol% and 6.0 vol%. As the CB/HDPE/PVDF-IL composites present uniform morphology with the IL content in range of 2.0 vol%–10.0 vol%, the obvious improvement of PTC reproducibility must derive from other reason. Therefore, the characterizations of DSC, WAXD and FTIR spectroscopy have been employed to further explore the evolution of thermodynamic behavior and microstructure evolution of CB/HDPE/PVDF-IL composites (Fig. 6). Observing from Figs. 6(a) and 6(b), with the increase of IL content, the melt-crystallization behaviors of HDPE and PVDF in CB/HDPE/PVDF-IL composites significantly demonstrate different trends. As to HDPE, both melt-crystallization temperature (\( T_c \)) and the melting point (\( T_m \)) show the constant value no matter what content of IL is incorporated. This is due to the complete dispersion of IL in PVDF. In contrast, The \( T_c \) of PVDF demonstrates a steady decline with increase of IL (Fig. 6a). This phenomenon evidently reveals the dilution effect\[36,37\] that the good compatibility and strong interaction between ILs and PVDF inhibits molecular chains of PVDF to form crystal.

As we know, for crystalline polymers, the obvious specific volume-temperature behavior occurs in the cooling process. When the crystallization process is complete, the shape of crystalline polymers will be fixed by the physical cross-linked structure with the crystals acting as cross-linking point, and the variation of volume shrinkage during the subsequent descent temperature process can be ignored due to the less free volume to shrink. In the HDPE/PVDF system, the gradually decreasing \( T_c \) of PVDF with the help of IL means the increasing overlaps of the sharp volume shrinkage process between HDPE and PVDF. That is to say, in the molding process of high pressure, before PVDF was fixed by crystallization, the PVDF would have more time to flow and shrink for coping with the simultaneous volume shrinkage of HDPE. Thus, after molding, the pipe space surrounding HDPE gradually decreases to lead a diminishing interface gap, as shown in Figs. 7(a)−7(c). The interface of CB/HDPE/PVDF-IL-0 demonstrates clear gap which is about 0.96 \( \mu \)m between the surfaces of HDPE and PVDF (Fig. 7a), while the interface gaps become obviously reduced (about 0.25 \( \mu \)m) in CB/HDPE/PVDF-IL-10 (Figs. 7b and 7c). This observation suggests that, with the increase of IL, the more intensive confinement can be obtained from PVDF during repeated temperature cycles under 150 °C. So, the ob-

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**Fig. 6** Effect of the IL loading on thermodynamic phase transition behavior of CB/HDPE/PVDF-IL composites. DSC curves of PVDF/HDPE-IL during the 1st cooling (a) and the 2nd heating (b). Microstructure characterization of PVDF/HDPE-IL by (c) FTIR spectroscopy and (d) WAXD to identify the crystal type of PVDF.

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vious improvement of PTC reproducibility in range of 2.0 vol%−10.0 vol% of IL may be attributed to the more intensive confinement to effectively facilitate the reconstruction of the HDPE morphology as well as the conductive network in it.

Moreover, for maintaining the confinement of PVDF, the large difference of $T_m$ between HDPE and PVDF is valuable. As shown in Fig. 6(b), the $T_m$ of PVDF in composites after incorporating IL is not sacrificed, despite appearing of double peak and the $T_m$ evolution of a steep rise followed by a fall. To elucidate this variation, the qualitative analyses of crystal types of composites are exhibited in Figs. 6(c) and 6(d). Commonly, $\alpha$-phase, $\beta$-phase and $\gamma$-phase may appear in PVDF.\(^{[45]}\) The $T_m$ of $\alpha$-phase and $\beta$-phase are about 167−170 °C, and the $T_m$ of $\gamma$-phase is near 179 °C. The $\alpha$-phase of PVDF is most easily detected at FTIR absorption bands of 766 and 795 cm$^{-1}$, as well as the characteristic peaks of WAXD at 17.7°, 18.3° and 26.6°. The $\beta$-phase can be identified at FTIR absorption bands of 840 and 1279 cm$^{-1}$. The $\gamma$-phase can be detected at FTIR absorption bands of 840 cm$^{-1}$ and the characteristic peaks of WAXD at 18.5°. Due to the low $T_m$ (167.8 °C, Fig. 6b) and the evident FTIR absorption bands of 766, 795, and 1279 cm$^{-1}$ (Fig. 6c), the PVDF mainly reveals $\alpha$- and $\beta$-phase in CB/HDPE/PVDF-IL-0. When the IL content is 2.0 vol%, the $\gamma$-phase forms in PVDF revealing the high $T_m$ at 178 °C in composites (Fig. 6b). With the further increase of IL, the $\alpha$- and $\gamma$-phase gradually decrease to transform into $\beta$-phase because the $\alpha$ characteristic peaks of WAXD disappear (Fig. 6d) and the $T_m$ of PVDF migrates to low temperature (Fig. 6b).

From all of the above analyses, a possible scheme for improving PTC reproducibility is further proposed (Fig. 7d). Without IL, the drastic volume expansion of HDPE during melting process of CB/HDPE/PVDF composite presents freedom (free expansion). The HDPE phase hardly receives any confinement from the surrounding pipe space fixed by PVDF, except for being segmented by PVDF phase. Therefore, the CB/HDPE/PVDF-IL-0 reveals dissatisfied reproducibility of PTC. After the addition of IL (restricted expansion), due to the plasticization effect of IL, the refined size of HDPE phase is obtained which produces more interface for receiving confinement. More importantly, because of the dilution effect of IL where the good compatibility and strong interaction between ILs and PVDF inhibit molecular chains of PVDF to form crystal, the smaller interface gap between HDPE and PVDF can be realized. Consequently, during heating process, the expansion of HDPE may push the surrounding PVDF pipe to adjust molecular conformations (molecular chain orienta-
tion in amorphous region), for coping with the stress stemming from HDPE. Naturally, during cooling process, the stronger and reversible confinement of PVDF could act on the HDPE phase to preferably reshape the morphology of HDPE as well as the conductive network in it. Then, the superior PTC reproducibility can be realized.

CONCLUSIONS

In summary, the [OMIm][NTf$_2$] with good compatibility to PVDF was introduced in CB/HDPE/PVDF composites. The phase size of HDPE was refined as the [OMIm][NTf$_2$] loading of 2.0 vol% due to the plasticization effect. The $T_c$ of PVDF revealed gradual decrease with the addition of [OMIm][NTf$_2$] owing to the dilution effect. The interface gap is also significantly reduced. Thus, a stronger confinement effect from PVDF could impose on HDPE phase to preferably reconstruct the morphology of HDPE as well as the conductive network in it. The CB/HDPE/PVDF-IL composites with IL content above 4.0 vol% revealed superior PTC reproducibility. The $R_{room}$ was less than 7% even undergoing multiple repeated temperature cycles. This investigation provides a facile and efficient way for fabricating high performance PTC composites with desirable reproducibility.

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