

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

Chen Long, Wu Xiao, Zhang Xiao-Fang, Zhang Jian-Ming

Cite this article as:

Chen Long, Wu Xiao, Zhang Xiao-Fang, Zhang Jian-Ming. Enhanced Reproducibility of Positive Temperature Coefficient Effect of CB/HDPE/PVDF Composites with the Addition of Ionic Liquid[J]. *Chinese J. Polym. Sci.*, 2021, 39(2): 228-236. doi: 10.1007/s10118-020-2475-x

View online: <https://doi.org/10.1007/s10118-020-2475-x>

Articles you may be interested in

ELECTRICAL PROPERTIES OF CONDUCTIVE POLYMER COMPOSITES PREPARED BY AN INNOVATIONAL METHOD

Chinese J. Polym. Sci. 2010, 28(6): 869 <https://doi.org/10.1007/s10118-010-9157-z>

Polymerizable Ionic Liquid Copolymer P(MMA-co-BVIm-Br) and Its Effect on the Surface Wettability of PVDF Blend Membranes

Chinese J. Polym. Sci. 2015, 33(6): 857 <https://doi.org/10.1007/s10118-015-1634-y>

Enhanced Crystallization Kinetics of PLLA by Ethoxycarbonyl Ionic Liquid Modified Graphene

Chinese J. Polym. Sci. 2019, 37(3): 243 <https://doi.org/10.1007/s10118-019-2192-5>

具有高灵敏性且稳定可重复的正温度系数效应的PVDF/CF导电复合材料

PVDF/CF Conductive Composites with High Sensitivity and Stable Reproducibility of Positive Temperature Coefficient Effect
高分子学报. 2017(8): 1215 <https://doi.org/10.11777/j.issn1000-3304.2017.17090>

Ni@C/HDPE复合材料的制备及其正温度系数性能研究

PREPARATION OF Ni@C/HDPE CONDUCTIVE COMPOSITES AND THEIR POSITIVE TEMPERATURE COEFFICIENT PERFORMANCE

高分子学报. 2013(9): 1159 <https://doi.org/10.3724/SP.J.1105.2013.12395>

iPP/HDPE/CB三元导电复合材料的导电与流变行为

CONDUCTIVE AND RHEOLOGICAL BEHAVIORS OF emPP/HDPE/CB TERNARY COMPOSITES

高分子学报. 2012(12): 1371 <https://doi.org/10.3724/SP.J.1105.2012.12196>

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

Long Chen, Xiao Wu, Xiao-Fang Zhang, and Jian-Ming Zhang*

Key Laboratory of Rubber-Plastics, Ministry of Education/Shandong Provincial Key Laboratory of Rubber-plastics, Qingdao University of Science & Technology, Qingdao 266042, China

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

Citation: Chen, L.; Wu, X.; Zhang, X. F.; Zhang, J. M. Enhanced reproducibility of positive temperature coefficient effect of CB/HDPE/PVDF composites with the addition of ionic liquid. *Chinese J. Polym. Sci.* 2021, 39, 228–236.

INTRODUCTION

Conductive polymer composites (CPCs)^[1–5] 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.^[6–10] 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.^[11] 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 prosperous application of them in broader fields.^[12] To address these issues, great efforts including modification of fillers,^[13,14] crosslinking of polymer,^[15,16] hybridizations of fillers^[17–20] and application of binary matrix^[21,22] 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.^[23–25] 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.^[25–27] 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.^[22,28,29] 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.^[12]

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.^[30,31] Jeon *et al.* have developed binary polymer based PTC material with a co-continuous structure.^[32] 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.^[31] 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

* Corresponding author, E-mail: zjm@qust.edu.cn

Received April 28, 2020; Accepted June 29, 2020; Published online September 1, 2020

phase). These studies suggested that the following factors are important for improving PTC reproducibility: (i) the confinement effect of the matrix with high melting point (T_m) promotes the reconstruction of both the morphology of polymer and the conductive network in it; (ii) the continuous phase structure of the polymer matrix with high T_m is the necessary prerequisite to provide confinement. Overall, a preferable reproducibility of PTC can be achieved *via* a stronger confinement delivering from the high T_m matrix with continuous structure.

The ionic liquids (ILs), proposed as “green solvents”, have been widely used in polymer composites because of their multifunctional roles, such as working as flame retardant, compatibilizer and plasticizer.^[33–35] If a kind of IL of good compatibility with PVDF is introduced into typical HDPE/PVDF based PTC composites, the preferable PTC reproducibility might be achieved. Firstly, due to the plasticization effect to adjust the viscosity, the HDPE phase domain will be reduced to produce more interfaces for confinement. Secondly, stemming from the dilution effect^[36,37] in decreasing the crystallization rate of PVDF, the more overlaps of the sharp volume shrinkage process will be obtained between HDPE and PVDF melt. That is to say, before PVDF matrix is fixed due to crystallization, it has more time to shrink surrounding HDPE for coping with the simultaneous volume shrinkage of HDPE. Therefore, the interface gap between HDPE and PVDF will diminish to facilitate stronger confinement. Herein, to testify this hypothesis, we introduced [OMIm][NTf₂] into CB/HDPE/PVDF composites to explore its effect on the PTC reproducibility of CB/HDPE/PVDF composites.

EXPERIMENTAL

Materials

Conductive CB (particle size ≈ 40 nm, dibutyl phthalate adsorption value ≈ 255 mL/100g) was obtained from Jiaozuo City Hexing 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 9.0 vol% of HDPE 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 (R_{room}) of the samples was measured by the four-probe method with a digital multi-meter (VC9806+) when the resistance was lower than $10^8 \Omega$, and a high resistance meter (ZC36) was used above that value. The volume resistivity (ρ) was calculated according to the formula $\rho = RS/d$, in which the sample resistance *R*, area *S*, and thickness *d* were definite

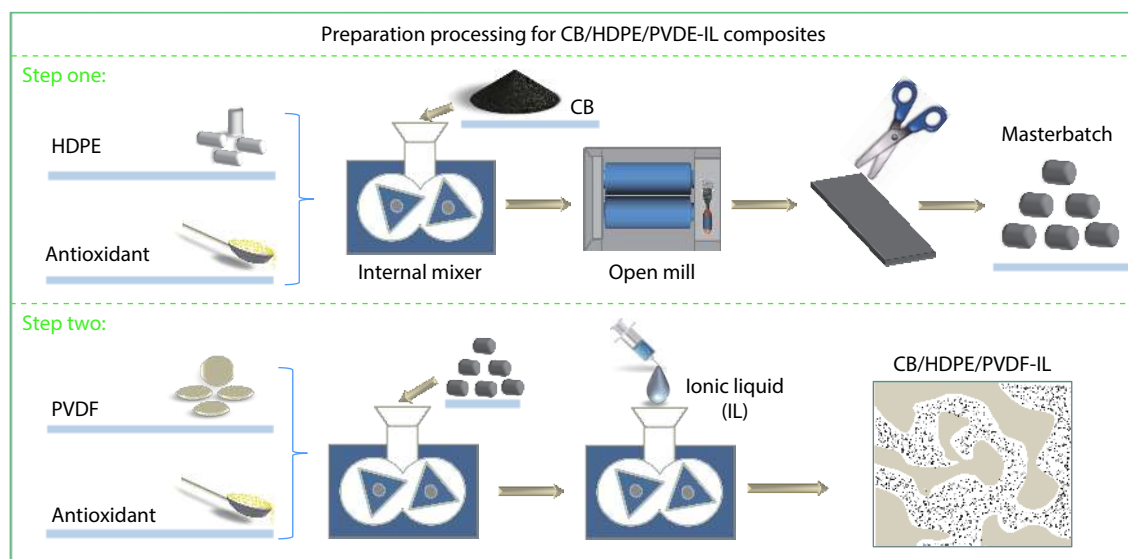


Fig. 1 Graphical illustration of the preparation processing for CB/HDPE/PVDF-IL composites.

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-K α X-ray beam ($\lambda=0.154$ 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:^[25]

$$\omega_a = \frac{\gamma_{CA} - \gamma_{CB}}{\gamma_{AB}} \quad (1)$$

where ω_a is the wetting coefficient. γ_{CA} , γ_{CB} and γ_{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 $\omega_{PE-PVDF} < -1$, 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. 3(a). 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

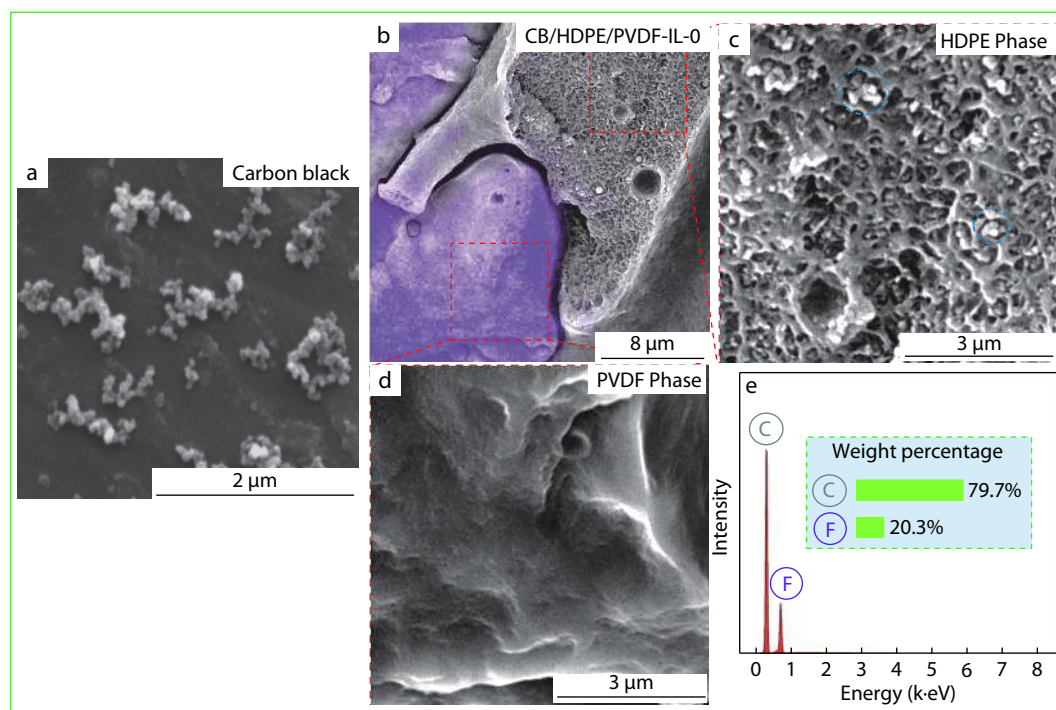


Fig. 2 The distribution of CB in HDPE/PVDF blends. (a) The SEM image of original CB particle. (b) The SEM morphology of CB/HDPE/PVDF-IL-0 integrated with EDS image of fluorine atom (the purple area). (c, d) The partial enlargement of (c) PVDF and (d) HDPE phase. The blue dotted cycles show the CB particles. (e) The EDS analysis of PVDF phase in CB/HDPE/PVDF-IL-0.

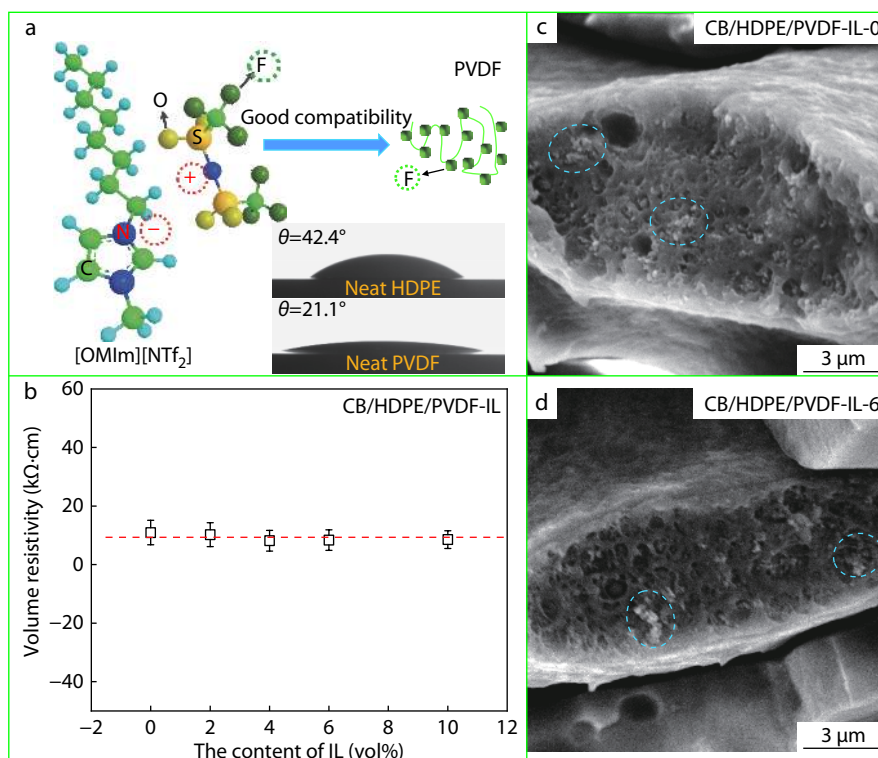


Fig. 3 (a) The molecular structure of IL and its contact angle with neat PVDF and neat HDPE. (b) Volume resistivity of CB/HDPE/PVDF-IL at room temperature with different IL loading. SEM morphology comparison of the CB particles dispersion in (c) CB/HDPE/PVDF-IL-0 and (d) CB/HDPE/PVDF-IL-6. The blue dotted cycles show the aggregates of CB particles.

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 locating 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.

$$\log \eta_s = N_1 \log \eta_1 + N_2 \log \eta_2 \quad (2)$$

where η_s , η_1 , and η_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:

$$\eta_s = e^{(\log \eta_1 - \log \eta_2)N_1 + \log \eta_2} \quad (3)$$

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:

$$\eta'_s = (\log \eta_1 - \log \eta_2) e^{(\log \eta_1 - \log \eta_2)N_1} \quad (4)$$

From Eq. (4), the first derivative of η_s (η'_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

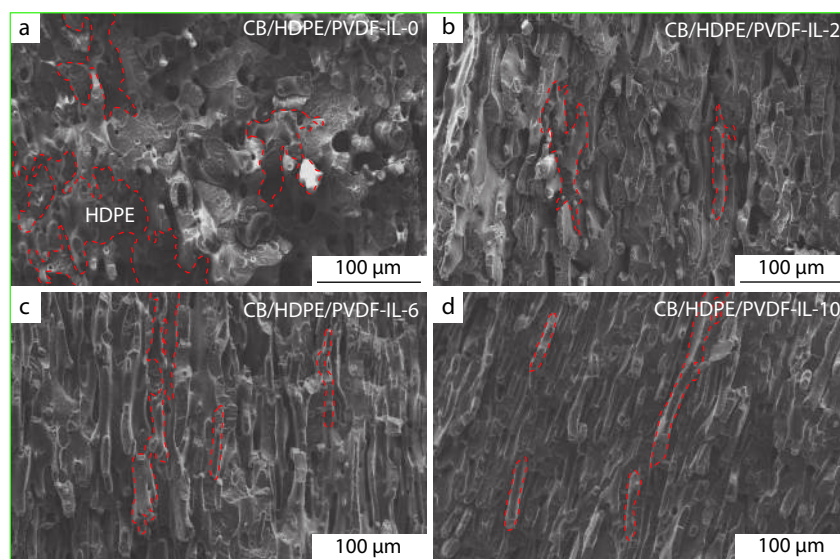


Fig. 4 Influence of IL loading on the phase morphology evolution of CB/HDPE/PVDF-IL blend characterized by SEM. The red dotted zone shows the HDPE phase.

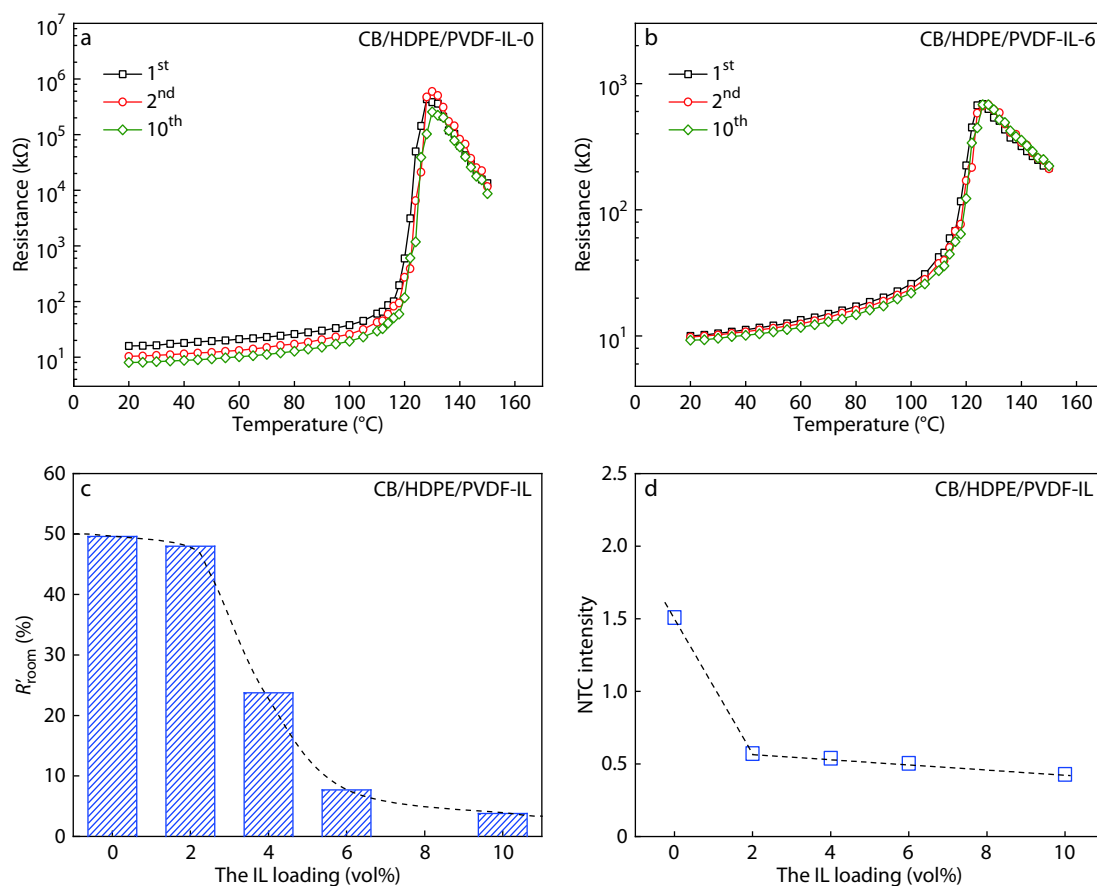


Fig. 5 PTC reproducibility of (a) CB/HDPE/PVDF-IL-0 and (b) CB/HDPE/PVDF-IL-6. (c) The change rate of the room temperature resistance (R'_{room}) undergoing ten heating and cooling cycles against loading of IL. (d) The NTC intensity (I_{NTC}) of CB/HDPE/PVDF-IL composites against loading of IL.

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'_{room}) is calculated according to: $R'_{room} =$

$(R_{room}^{1st} - R_{room}^{10th}) / R_{room}^{1st}$ and gives the value less than 7% even undergoing multiple repeated temperature cycles (Fig. 5c). For showing the NTC inhibition effect of binary polymer

matrixes as reported in other literatures, the NTC intensity (according to the equation: $I_{\text{NTC}} = \log(R_{\text{max}}/R_{150^\circ\text{C}})$) is also demonstrated as Fig. 5(d). A distinct decrease of I_{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 I_{NTC} change may be attributed to the morphology evolution of HDPE phase.

More attractively, dissimilar to the variation of I_{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 phe-

nomenon 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 μm between the surfaces of HDPE and PVDF (Fig. 7a), while the interface gaps become obviously reduced (about 0.25 μm) 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 $^\circ\text{C}$. So, the ob-

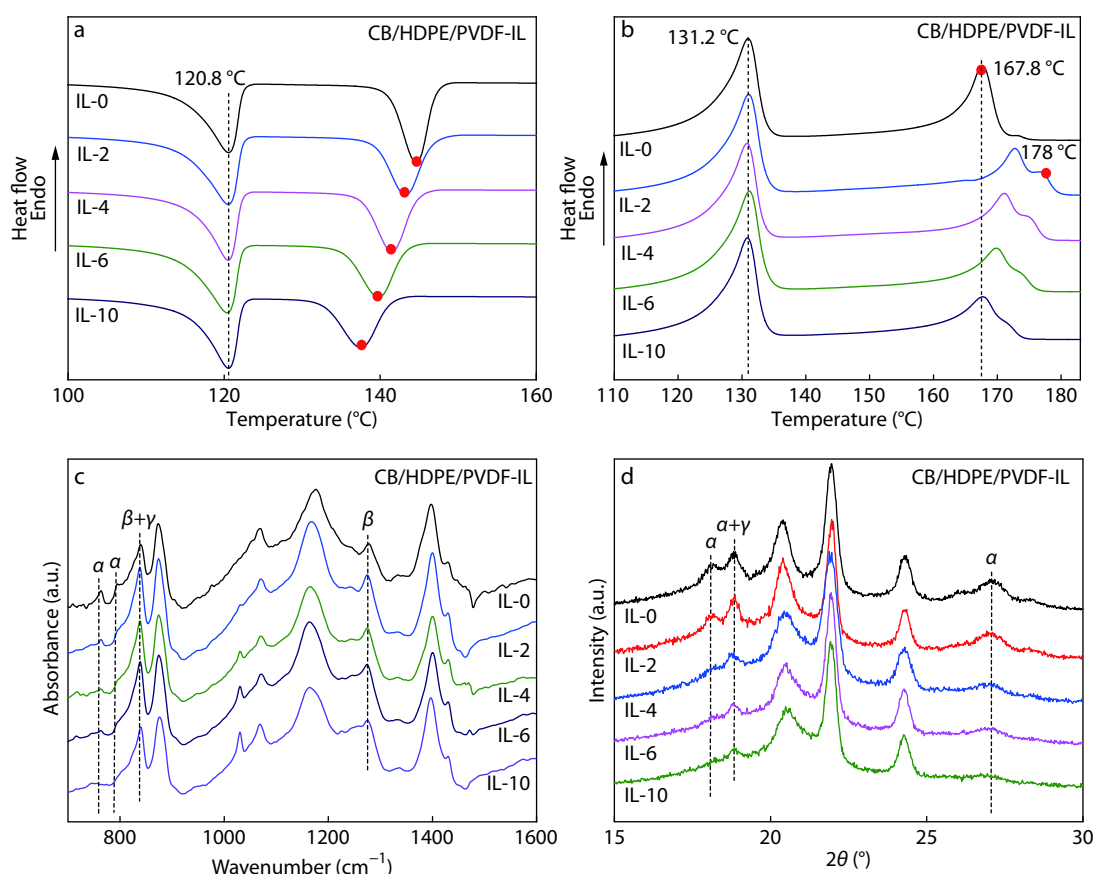


Fig. 6 Effect of the IL loading on thermodynamic phase transition behavior of CB/HDPE/PVDF-IL composites. DSC curves of PVDF/HDPE-IL during the 1st cooling (a) and the 2nd heating (b). Microstructure characterization of PVDF/HDPE-IL by (c) FTIR spectroscopy and (d) WAXD to identify the crystal type of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

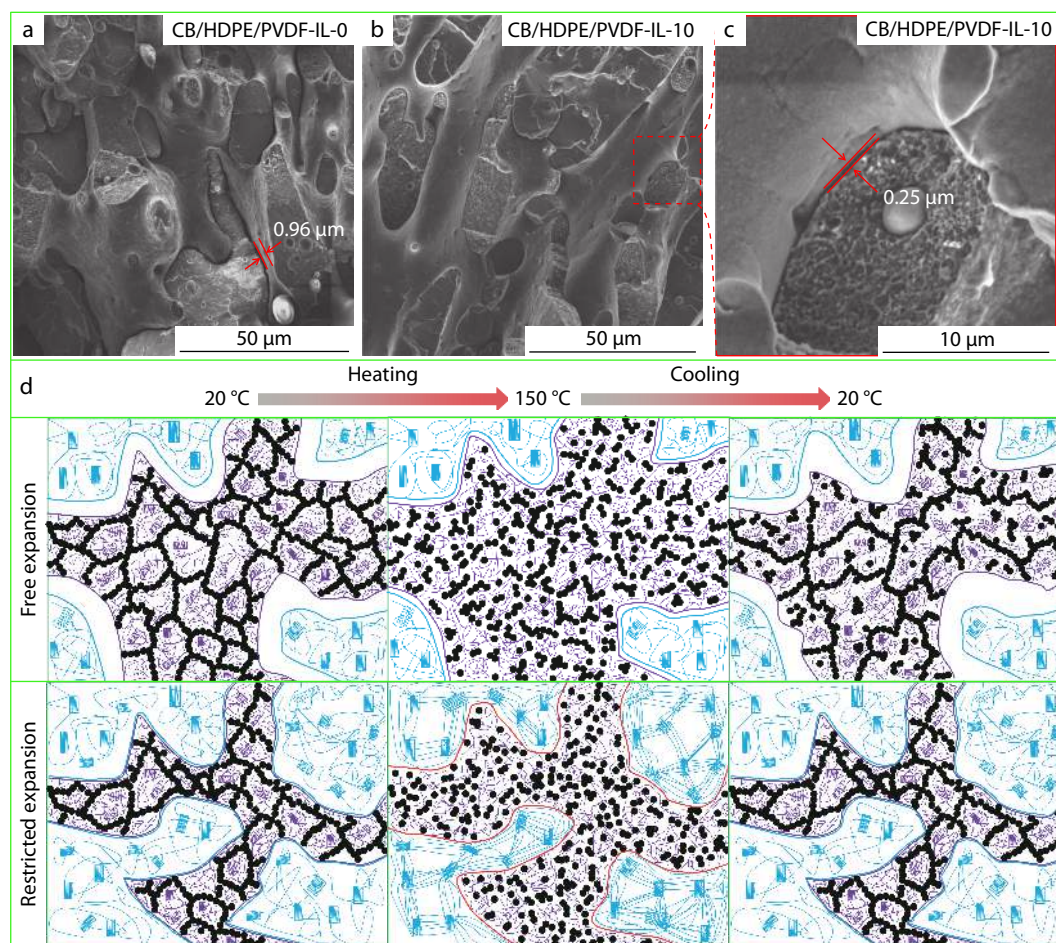


Fig. 7 SEM images of (a) CB/HDPE/PVDF-IL-0, (b) CB/HDPE/PVDF-IL-10 and (c) the corresponding magnified image. (d) The possible scheme for improving PTC reproducibility by adjusting the phase interface gap. The red line represents the complete contact of PVDF and HDPE.

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, α -phase, β -phase and γ -phase may appear in PVDF.^[45] The T_m of α -phase and β -phase are about 167–170 °C, and the T_m of γ -phase is near 179 °C. The α -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 β -phase can be identified at FTIR absorption bands of 840 and 1279 cm^{-1} . The γ -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 α - and β -phase in CB/HDPE/PVDF-IL-0. When the IL content is 2.0 vol%, the γ -

phase forms in PVDF revealing the high T_m at 178 °C in composites (Fig. 6b). With the further increase of IL, the α - and γ -phase gradually decrease to transform into β -phase because the α 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][NTf₂] with good compatibility to PVDF was introduced in CB/HDPE/PVDF composites. The phase size of HDPE was refined as the [OMIm][NTf₂] loading of 2.0 vol% due to the plasticization effect. The T_c of PVDF revealed gradual decrease with the addition of [OMIm][NTf₂] 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.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Nos. 51803103 and 21873059) and Taishan Mountain Scholar Foundation (Nos. TS20081120 and tshw20110510).

REFERENCES

- Liu, Y.; Zhang, H.; Porwal, H.; Tu, W.; Evans, J.; Bilotti, E. Universal control on pyroresistive behavior of flexible self-regulating heating devices. *Adv. Funct. Mater.* **2017**, *27*, 1702253.
- Wang, L.; Chen, L. X.; Song, P.; Lu, Y. J.; Qiu, H.; Zhang, Y. L.; Kong, J.; Gu, J. W. Fabrication on the annealed Ti₃C₂T_x MXene/epoxy nanocomposites for electromagnetic interference shielding application. *Compos. Part B Eng.* **2019**, *171*, 111–118.
- Chen, J. W.; Cui, X. H.; Sui, K. Y.; Zhu, Y. T.; Jiang, W. Balance the electrical properties and mechanical properties of carbon black filled immiscible polymer blends with a double percolation structure. *Compos. Sci. Technol.* **2017**, *140*, 99–105.
- Yilmaz, O. C.; Sen, I.; Gurses, B. Q.; Ozdemir, O.; Cetin, L.; Sarikanat, M. The effect of gold electrode thicknesses on electromechanical performance of Nafion-based ionic polymer metal composite actuators. *Compos. Part B Eng.* **2019**, *165*, 747–753.
- Radzuan, N. A. M.; Zakaria, M. Y.; Sulong, A. B.; Sahari, J. The effect of milled carbon fibre filler on electrical conductivity in highly conductive polymer composites. *Compos. Part B Eng.* **2017**, *110*, 153–160.
- Chen, Z.; Hsu, P. H.; Lopez, J.; Li, Y. Z.; To, J. W. F.; Cui, Y.; Wang, C.; Andrews, S. C.; Liu, J.; Cui, Y.; Bao, Z. N. Fast and reversible thermoresponsive polymer switching materials for safer batteries. *Nat. Energy* **2016**, *1*, 15009.
- Kang, H. S.; Sim, S.; Shin, Y. H. A numerical study on the light-weight design of PTC heater for an electric vehicle heating system. *Energies* **2018**, *11*, 1276.
- Song, P.; Liang, C. B.; Gu, H. B.; Wang, L.; Qiu, H.; Kong, J.; Gu, J. W. Obviously improved electromagnetic interference shielding performances for epoxy composites via constructing honeycomb structural reduced graphene oxide. *Compos. Sci. Technol.* **2019**, *181*, 107698.
- Liu, Y.; Zhang, H.; Porwal, H.; Tu, W.; Wan, K. N.; Evans, J.; Newton, M.; Busfield, J. J. C.; Peijs, T.; Bilotti, E. Tailored pyroresistive performance and flexibility by introducing a secondary thermoplastic elastomeric phase into graphene nanoplatelet (GNP) filled polymer composites for self-regulating heating devices. *J. Mater. Chem. C* **2018**, *6*, 2760–2768.
- Wang, X.; Sparkman, J.; Gou, J. H. Electrical actuation and shape memory behavior of polyurethane composites incorporated with printed carbon nanotube layers. *Compos. Sci. Technol.* **2017**, *141*, 8–15.
- Deng, H.; Lin, L.; Ji, M. Z.; Zhang, S. M.; Yang, M. B.; Fu, Q. Progress on the morphological control of conductive network in conductive polymer composites and the use as electroactive multifunctional materials. *Prog. Polym. Sci.* **2014**, *39*, 627–655.
- Xu, H. Positive temperature coefficient effect of polymer nanocomposites. In *Polymer nanocomposites*, Huang, X.; Zhi, C. Eds. Springer: Cham, **2016**, p. 83–110.
- Bae, S. H.; Layek, R. K.; Lee, S. H.; Kuila, T.; Kim, N. H.; Lee, J. H. Effects of the reduction of PANi-coated oxidized multiwall carbon nanotubes on the positive temperature coefficient behaviors of their carbon black/high density polyethylene composites. *Polym. Test.* **2016**, *50*, 83–93.
- He, L. X.; Tjong, S. C. Facile synthesis of silver-decorated reduced graphene oxide as a hybrid filler material for electrically conductive polymer composites. *RSC Adv.* **2015**, *5*, 15070–15076.
- Zhang, R.; Tang, P.; Shi, R.; Cheng, T.; Bin, Y.; Hu, S. Improved electrical heating properties for polymer nanocomposites by electron beam irradiation. *Polym. Bull.* **2018**, *75*, 2847–2863.
- Tang, P.; Zhang, R.; Chen, Z.; Yang, B.; Bin, Y. Effect of γ -ray irradiation on the microstructure and self-heating property of carbon fiber/polyethylene composite films. *Compos. Part A* **2015**, *78*, 174–180.
- Dang, Z. M.; Li, W. K.; Xu, H. P. High performance hybrid carbon fillers/binary-polymer nanocomposites with remarkably enhanced positive temperature coefficient effect of resistance. *J. Appl. Phys.* **2009**, *106*, 024913.
- Liang, C. B.; Song, P.; Qiu, H.; Zhang, Y. L.; Ma, X. T.; Qi, F. Q.; Gu, H. B.; Kong, J.; Cao, D. P.; Gu, J. W. Constructing interconnected spherical hollow conductive networks in silver platelets/reduced graphene oxide foam/epoxy nanocomposites for superior electromagnetic interference shielding effectiveness. *Nanoscale* **2019**, *11*, 22590–22598.
- Hu, J.; Liu, L. Q.; Xie, Y. Y.; Wu, L. M. Facile synthesis of thermal-responsive P(NIPAM-S)/SiO₂ hybrid hollow spheres and their controllable release property for fragrance. *Polym. Chem.* **2013**, *4*, 3293–3299.
- Chen, L.; Hou, J. R.; Chen, Y. W.; Wang, H. J.; Duan, Y. X.; Zhang, J. M. Synergistic effect of conductive carbon black and silica particles for improving the pyroresistive properties of high density polyethylene composites. *Compos. Part B Eng.* **2019**, *178*, 107465.
- Qu, Y.; Zhang, W.; Dai, K.; Zheng, G.; Liu, C.; Chen, J.; Shen, C. Tuning of the PTC and NTC effects of conductive CB/PA6/HDPE composite utilizing an electrically superfine electrospun network. *Mater. Lett.* **2014**, *132*, 48–51.
- Lai, F.; Wang, B. B.; Zhang, P. Enhanced positive temperature coefficient in amorphous PS/CPMWCNT composites with low percolation threshold. *J. Appl. Polym. Sci.* **2019**, *136*, 47053.
- Di, W. H.; Zhang, G.; Peng, Y.; Zhao, Z. D. Two-step PTC effect in immiscible polymer blends filled with carbon black. *J. Mater. Sci.* **2004**, *39*, 695–697.
- Wei, Y.; Li, Z.; Liu, X.; Dai, K.; Zheng, G. Q.; Liu, C. T.; Chen, J. B.; Shen, C. Y. Temperature-resistivity characteristics of a segregated

- conductive CB/PP/UHMWPE composite. *Colloid Polym. Sci.* **2014**, *292*, 2891–2898.
- 25 Zha, J. W.; Li, W. K.; Liao, R. J.; Bai, J.; Dang, Z. M. High performance hybrid carbon fillers/binary-polymer nanocomposites with remarkably enhanced positive temperature coefficient effect of resistance. *J. Mater. Chem. A* **2013**, *1*, 843–851.
 - 26 Chan, C. M.; Feng, J. Carbon Black-Filled immiscible blends of poly(vinylidene fluoride) and high density polyethylene: the relationship between morphology and positive and negative temperature coefficient effects. *Polym. Eng. Sci.* **1999**, *39*, 1207–1215.
 - 27 Chan, C. M.; Feng, J. Double positive temperature coefficient effects of carbon black-filled polymer blends containing two semicrystalline polymers. *Polymer* **2000**, *41*, 4559–4565.
 - 28 Narkis, M.; Mironi-Harpaz, I. Thermoelectric behavior (PTC) of carbon black-containing TPX/UHMWPE and TPX/XL-UHMWPE blends. *J. Polym. Sci. Part B: Polym. Phys.* **2001**, *39*, 1415–1428.
 - 29 Xie, L.; Zhu, Y. T. Tune the phase morphology to design conductive polymer composites: a review. *Polym. Compos.* **2018**, *39*, 2985–2996.
 - 30 Bin, X.; Xu, C.; Agari, Y.; Matsuo, M. Morphology and electrical conductivity of ultrahigh molecular weight polyethylene/low molecular weight polyethylene/carbon black composites prepared by gelation/crystallization from solutions. *Colloid Polym. Sci.* **1999**, *277*, 452–461.
 - 31 Zhang, X.; Zheng, X. D.; Zou, H. Z.; Zheng, X. F.; Liu, Z. Y.; Yang, W.; Yang, M. B. Two-step positive temperature coefficient effect with favorable reproducibility achieved by specific “island-bridge” electrical conductive networks in HDPE/PVDF/CNF composite. *Compos. Part A* **2017**, *94*, 21–31.
 - 32 Jeon, J.; Lee, H. B. R.; Bao, Z. Flexible wireless temperature sensors based on Ni microparticle-filled binary polymer composites. *Adv. Mater.* **2013**, *25*, 850–855.
 - 33 Vidal, L.; Riekkola, M. L.; Canals, A. Ionic liquid-modified materials for solid-phase extraction and separation: a review. *Anal. Chim. Acta* **2012**, *715*, 19–41.
 - 34 Xu, Y.; Xu, H.; Zheng, Q. Influence of ionic liquid on glass transition, dynamic rheology, and thermal stability of poly(methyl methacrylate)/silica nanocomposites. *J. Appl. Polym. Sci.* **2019**, *136*, 48007.
 - 35 Xing, C. Y.; Li, J. Y.; Yang, C. M.; Li, Y. J. Local grafting of ionic liquid in poly(vinylidene fluoride) amorphous region and the subsequent microphase separation behavior in melt. *Macromol. Rapid Commun.* **2016**, *37*, 1559–1565.
 - 36 Wang, C.; Liao, W. P.; Wang, M. L.; Lin, C. C. Miscible blends of syndiotactic polystyrene and atactic polystyrene. Part 2. Depolarized light scattering studies and crystal growth rates. *Polymer* **2004**, *45*, 973–981.
 - 37 Meng, Q. J.; Li, W. J.; Zheng, Y. S.; Zhang, Z. C. Effect of poly(methyl methacrylate) addition on the dielectric and energy storage properties of poly(vinylidene fluoride). *J. Appl. Polym. Sci.* **2010**, *116*, 2674–2684.
 - 38 Berhan, L.; Sastry, A. M. Modeling percolation in high-aspect-ratio fiber systems. I. Soft-core versus hard-core models. *Phys. Rev. E* **2007**, *75*, 041120.
 - 39 Balberg, I.; Anderson, C. H.; Alexander, S.; Wagner, N. Excluded volume and its relation to the onset of percolation. *Phys. Rev. B* **1984**, *30*, 3933–3943.
 - 40 Grunberg, L.; Nissan, A. H. Mixture law for viscosity. *Nature* **1949**, *164*, 799–800.
 - 41 Stefanie, B.; Andreas, S.; Sven, H.; Ralf, H. Morphology formation in PC/ABS blends during thermal processing and the effect of the viscosity ratio of blend partners. *Materials* **2016**, *9*, 659.
 - 42 Pötschke, P.; Paul, D. R. Formation of co-continuous structures in melt-mixed immiscible polymer blends. *J. Macromol. Sci. Polym. Rev.* **2003**, *43*, 87–141.
 - 43 Zha, J. W.; Wu, D. H.; Yang, Y.; Wu, Y. H.; Li, R. K. Y.; Dang, Z. M. Enhanced positive temperature coefficient behavior of the high-density polyethylene composites with multi-dimensional carbon fillers and their use for temperature-sensing resistors. *RSC Adv.* **2017**, *7*, 11338–11344.
 - 44 Seo, M. K.; Rhee, K. Y.; Park, S. J. Influence of electro-beam irradiation on PTC/NTC behaviors of carbon blacks/HDPE conducting polymer composites. *Curr. Appl. Phys.* **2011**, *11*, 428–433.
 - 45 Martins, P.; Lopes, A. C.; Lanceros-Mendez, S. Electroactive phases of poly(vinylidene fluoride): determination, processing and applications. *Prog. Polym. Sci.* **2014**, *39*, 683–706.