Direct writing of PVDF piezoelectric film based on near electric field added by [Emim]BF₄

Linchen Liao¹, Caifeng Chen¹, Jilong Qian¹, Youming Zhang², Ruifang Zhang² and Jiaguang Zhu¹

¹ School of Materials Science and Engineering, Jiangsu University, Zhenjiang 212013, People’s Republic of China
² School of Mechanical Engineering, Jiangsu University, Zhenjiang 212013, People’s Republic of China
³ Author to whom any correspondence should be addressed.

E-mail: ccf@ujs.edu.cn

Keywords: PVDF, 3D printing, [Emim]BF₄, piezoelectric film

Abstract
PVDF/IL piezoelectric film based on [Emim]BF₄-added was prepared by near electric field direct writing. The β-phase content and its electric property of the film were analyzed. The results showed that the content of β crystal phase of PVDF film was improved by the synergistic effect of IL ([Emim]BF₄) and near electric field. When the amount of [Emim]BF₄ added was 1.5 wt%, the relative β-phase content of PVDF film reached 85.09%, and the crystallinity is 47.84%. Increase in [Emim]BF₄ content resulted in a significant increase in the relative dielectric constant of the film, from 6 to 285, but also accompanied by a sharp increase in dielectric loss. The d₃₃ value of the film can be as high as −10 pC/N, and the output voltage from the cantilever beam vibration feedback indicates that the voltage strength of the [Emim]BF₄-added film is greatly improved compared with the pure PVDF film.

Introduction
Polyvinylidene fluoride (PVDF) has been widely studied since its inception in the late 1960s. Compared to traditional piezoelectric materials, PVDF piezoelectric films have high sensitivity, thin thickness, good impact resistance, wide frequency response range, close to the acoustic impedance of water, good stability and easy processing. As a sensor and actuator, it is widely used in mechanics, acoustics, electronics, healthcare, military, transportation, hydroacoustic measurement, geological exploration, etc [1, 2]. PVDF usually has four crystal phases of α, β, γ and δ [3]. Generally, the α-phase is achieved under crystallization conditions because the molecular potential energy is the lowest and it is a thermodynamically stable phase [4]. The α-phase having a helical conformation TGTG is arranged in anti-parallel and has no polarity. The phase of the β-phase of all-trans TTT conformation is oriented and the electroactive is the strongest. Therefore, increasing the content of β-phase is crucial for improving the electrical properties of PVDF piezoelectric film [5, 6].

PVDF piezoelectric film with high β-phase content can be prepared by stretching method [7], spin coating method [8], solution casting [9] and traditional electrosprining [10]. However, these methods are not suitable for the preparation of PVDF piezoelectric film with complex shapes. Customized PVDF film with special shapes still requires subsequent cutting and other processes. In order to solve the above problem, and accurate customization of any shape of the film some scholars use a new near-field direct writing method to prepare customizable-PVDF piezoelectric film [11]. Kameoka et al [12] proposed a near-field direct writing technique with a scanning tip. The distance from the tip to the collector is 0.5 ~ 1 cm, which can control the deposition orientation of polymer nanofibers, but the precision is low. Sun et al [13] developed a near electric field direct writing technique by further reducing the tip-to-collector distance to sub-millimeters, with a tip-to-collector distance h ranging from 50 mm to 3 mm. Gupta et al [14] used a tube connected to the reservoir to resolve the solution limit and installed a collector under the tip guide electrode to improve positioning. This near electric field direct writing method can promote the formation of β-phase to a certain extent, and greatly reduces the working voltage [15], avoiding the unstable bending motion stage of the electrosprining Taylor cone ejecting jet.
This achieves accurate writing of the jet on the collecting plate, which saves resources and can produce films of various shapes.

In order to further improve the electrical properties of PVDF piezoelectric film, it is common practice to add some additives such as clay, salts, nanoparticles, ionic liquids, etc to the solution [16]. 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim]BF₄) is a hydrophilic ionic liquid (IL) at room temperature, with low vapor pressure, non-flammable, and a strong solvency, high conductivity and stability. Ionic liquids play an active role in improving the uniformity of spinning and promoting the formation of β-phase in PVDF. Seo [17] prepared a certain concentration of PLLA chloroform solution, and then a certain amount of [HMIM]Cl was added for electrospinning. It was noted that the addition of ionic liquid resulted in a sharp decrease in fiber diameter, the pore diameter on the PLLA fiber decreased with the addition of the ionic liquid, and the fiber diameter was reduced and more uniform. Pei et al. [18] prepared different proportions of PVDF/IL composites by solution casting method with IL([PhCH₂MIm]PF₆) as nucleating agent. The results showed that IL could be uniformly dispersed in PVDF. The α crystal form of PVDF is significantly decreased or even disappeared compared with pure PVDF, and the content of polar phase (β-phase and γ-phase) is increased, and PVDF/IL composite material mainly based on β crystal form is obtained. Lopes et al. [19] prepared PVDF films with 0 wt%, 5 wt% and 10 wt% of [Emim]BF₄ by solvent casting method. And the content of β-phase was significantly improved. When the addition amount was 10 wt%, the β content exceeded 60%.

However, the current reports mainly focus on the preparation of high-content IL-added polymer fibers by electrospinning, and the preparation of high-content IL-added PVDF films by casting. With the near electric direct writing method, under the premise of ensuring the smooth progress of the preparation process, there are not many researches on the effect of the addition of trace IL on the β crystal phase of PVDF film.

In this paper, we have prepared a series of IL-added PVDF piezoelectric films by near electric direct writing method, and reported the preparation process and performance characterization of the films.

Experiment

The raw materials are PVDF (Arkema 721, 99.5%), 1-methyl-2-pyrrolidone (NMP, 99.5%, Shanghai Aladdin Biochemical Technology Co., Ltd), liquid ionic [Emim]BF₄ (98%, Shanghai Maclean Biochemical Technology Co., Ltd), Acetone (Acetone, 99.5%, Sinopharm Chemical Reagent Co., Ltd), tetrabutylammonium chloride (TBAC, Shanghai Maclean Biochemical Technology Co., Ltd). 10 g of printing solution was prepared, wherein the NMP content was 77–79.5 wt%, the PVDF content was 15 wt%, the Acetone content was 5 wt%, and the added [Emim] BF₄ content was 0 wt%, 0.5 wt%, 1.0 wt%, 1.5 wt%, 2.0 wt%, and 2.5 wt%. A certain amount of ionic liquid [Emim]BF₄ (0 g, 0.05 g, 0.10 g, 0.15 g, 0.20 g, 0.25 g) and tetrabutylammonium chloride (0.05 g TBAC) were added to NMP (7.70–7.95 g) solvent and sonicated at room temperature for 30 min PVDF powder (1.5 g) was added, dissolved in the mixed solution, ultrasonically for 1 h to fully dissolve them, add acetone (0.5 g), and continue ultrasonication for 30 min to obtain a uniform printing solution. Figure 1 is a schematic view of the diagram. A syringe containing 1 ml of print solution is attached to the 3D printer nozzle. The distance between the printing nozzle and the writing bed is 2 mm, and the voltage of the DC power supply is set to 6 kV. The heating bed is attached to the copper plate, and the upper side of the copper plate is writing bed. The temperature was set to 70 °C and the running speed was 15 mm s⁻¹. The printing nozzle first moves in the horizontal x direction, then moves in the vertical y direction, and the deposited semi-solid PVDF fibers are dried in the air, and the 20 × 20 mm film is woven after 70 layers of printing. Finally, a gold electrode is plated on both sides of the film by sputtering.

The surface morphology of the sample was analyzed by a thermal field emission scanning electron microscope (JSM-7001F, Japan), and the crystal phase structure was measured by an x-ray diffractometer.

Figure 1. Printing diagram.
Crystallization properties of films were studied using differential scanning calorimetry (STA 449 F3 Jupiter, Germany). A heating rate of 10 °C min⁻¹ over the temperature range of 50 °C–200 °C, all the experiments were performed under a nitrogen environment. A Fourier transform infrared spectrometer (Nicolet 6700, Nicolet, USA) was utilized to scan and analyze the relative content of the β-phase of the film. The piezoelectric constant (d33) were measured by quasi-static piezoelectric strain constant measuring instrument (ZJ-6A, China) and the electric signal feedback of PVDF films was detected by manganese steel cantilever beams. As showed in figure 2, the distance from the PZT driver to the cantilever beam is 15 cm, and the distance from the PVDF piezoelectric film to the PZT driver is 7 cm. The voltage and frequency generated by the PZT drive is controlled by the signal generator. The PVDF piezoelectric film captures the vibration signal on the beam and amplifies and analyzes the captured signal to show the amplitude and frequency of the input vibration signal.

Results and discussion

Surface topography of the PVDF thin films

Figure 3 is a scanning electron micrograph of a pure PVDF film (a), a PVDF film with 0.5 wt% [Emim]BF₄ added (b), a PVDF film with 1.5 wt% [Emim]BF₄ added (c), and a PVDF film with 2.5 wt% [Emim]BF₄ added (d). As can be seen from the figure, the thickness of the spherulites of the [Emim]BF₄-added PVDF film is much smaller and denser than each other compared to the pure PVDF film. This may be because the ionic liquid [Emim]BF₄ is less volatile, forming fewer pores, and some of the [Emim]BF₄ is also encapsulated in the pores. Due to the high conductivity caused by the addition of [Emim]BF₄, the greater the conductivity of the solution when the jet breaks the surface of the Taylor cone, the stronger the electric field force acting on the jet of the solution, resulting in a lower jet radius and faster drying of the solution. PVDF crystallization time becomes shorter, and the growth of the spherulites is suppressed. These effects only need to add a small amount of [Emim]BF₄, for example, the addition of 0.5 wt% of [Emim]BF₄ can greatly change its morphology. The surface topography between the samples added in an amount of 0.5 wt%, 1 wt%, 1.5 wt%, 2 wt%, and 2.5 wt% tends to be flattened, and the spherulites become smaller.

Thermal analysis of PVDF film with [Emim]BF₄ added

The DSC curves (heating) of the PVDF film is shown in figure 4. It can be seen that the melting temperature (T_m) of PVDF films with different [Emim]BF₄ concentrations have peaks from 158.6 to 167.7 °C, with onset at approximately 140 °C.
The DSC curve can be used to calculate the crystallinity of the sample ($\chi_c$) with the following formula [20]:

$$\chi_c = \frac{\Delta H_f}{\Delta H_f^c}$$

Where $H_f$ and $\Delta H_f^c$ represents the melting enthalpy of samples and the enthalpy of fusion of the 100% PVDF crystalline sample whose value is 104.7 J·g$^{-1}$.

The $T_m$ and crystallinity of every sample are presented in table 1. The $T_m$ of pure PVDF film without added [Emim]BF$_4$ is 167.7 °C. When the added amount of [Emim]BF$_4$ is 0.5 wt%, the $T_m$ is reduced to 166.9 °C. With the increase of the [Emim]BF$_4$ content, the $T_m$ of PVDF film decreases gradually. The main reason is that incorporation of [Emim]BF$_4$ into the polymer matrix significantly reduces the spherulites size of the films. And the [Emim]BF$_4$ in the print solution also acts as a plasticizer, which weakens the attraction between the PVDF...
molecular chains and increases the mobility of the molecular chains, thereby increasing the flexibility of the film and lowering the melting point, but this also slightly reduces the crystallinity of the film.

Compared with pure PVDF mentioned in related literature [21], the film prepared by direct writing has lower crystallinity. In the process of the direct writing process, the writing solution are rapidly solidified when exposed to air, which will hinder the crystallinity, that is, PVDF molecular chains do not have enough time to fully form crystals before solidification. Although the electrostatic interaction between PVDF and [Emim]BF₄ can induce the α-phase to β-phase transition, it also hinders the crystallization process, resulting in less stable crystalline phase and increased amorphous phase.

From table 1, we can see that the crystallinity also decreases slightly with the increase in the amount of [Emim]BF₄ added, but there is an abnormally increased value at 1.5 wt%. Related studies have demonstrated that the direct addition of ionic liquids in casting methods is often accompanied by a slight decrease in crystallinity [22]. However, in the work, the comprehensive influence of factors such as the electric field, the thickness and stability of the jet are not static. Since [Emim]BF₄ itself is conductive, its addition will affect the writing process. From this point of view, the addition of ionic liquids in this experiment has a positive effect on the degree of crystallinity. However, when the amount of ionic liquid is more than 1.5 wt%, the jet flow is unstable because of the high conductivity under the action of electric field. This affects the uniformity of the film, further reduces the crystallization time, and decreases the crystallinity.

| IL content | T_m/°C | H_f (J · g⁻¹) | χ_c(%) |
|------------|--------|--------------|--------|
| 0 wt%      | 167.7  | 39.22        | 37.46  |
| 0.5 wt%    | 166.9  | 42.97        | 41.04  |
| 1.0 wt%    | 163.7  | 42.31        | 40.41  |
| 1.5 wt%    | 160.9  | 47.84        | 45.69  |
| 2.0 wt%    | 160.7  | 39.20        | 37.44  |
| 2.5 wt%    | 158.6  | 38.61        | 36.88  |

Figure 5. XRD pattern of PVDF film with different contents [Emim]BF₄.

Table 1. Effect of IL addition on crystallinity of samples.

β-phase characterization of PVDF film with [Emim]BF₄ added
The XRD diffraction pattern of PVDF film with different content of ionic liquid [Emim]BF₄ is shown in figure 5. In the figure, the main crystallization peak of the α-phase of PVDF is 2θ = 18.4° (corresponding to (020) crystal plane), and the main crystallization peak of the β-phase of PVDF is 2θ=20.6° (corresponding to (110) crystal plane) [23]. It can be observed that the addition of the ionic liquid [Emim]BF₄ causes the peak intensity corresponding to α-phase to decrease, even disappear. And enhances the peak intensity corresponding to the β-phase. This indicates that the addition of the ionic liquid [Emim]BF₄ induces the transformation of the α-phase to the β-phase, and this leads to a decrease in the α-phase content of PVDF and an increase in the β-phase content.
As shown in figure 6(a), PVDF is a homopolymer whose molecular chain is tightly entangled. Due to the applied electric field, Emim$^+$ has a certain degree of distribution with directionality. The functional group CF$_2$ has a large electronegativity, and the taste ring of [Emim]BF$_4$ is a positively charged planar cation. CF$_2$ and Emim$^+$, these two substances with a large difference in electronegativity interacted have a strong interaction, which promotes the rotation and rearrangement of PVDF molecular chains. As a plasticizer, TBAC's unique sterically hindered structure can reduce the interaction between PVDF’s own molecules and promote the movement of PVDF chains, as shown in figures 6(b) and (c). In addition, [Emim]BF$_4$ itself can also act as a heterogeneous nucleation point. Under the guidance of the electric field and the stretching of the jet, the rotation and rearrangement of the PVDF molecular chain are synergistically induced to change from a non-polar α-phase to a polar β-phase. It causes a decrease in the α-phase and an increase in the β-phase.

The infrared spectrum of the PVDF film with different contents of [Emim]BF$_4$ is illustrated in figure 7. The dotted line corresponds to the characteristic peaks of the α-phase and the β-phase. In the FTIR spectrum, the corresponding absorption peak positions of α of PVDF is 763 cm$^{-1}$ (CF$_2$ bending and skeletal bending); the corresponding absorption peak position of β-phase are: 840 cm$^{-1}$ (CH$_2$ rocking) and 1279 cm$^{-1}$ (CF out-of-plane deformation) [24–27]. 875 cm$^{-1}$ represents the stretching vibration of functional groups CF$_2$ in the amorphous component of pure PVDF. For the thin film sample with [Emim]BF$_4$ added, the stretching vibration peaks of CF$_2$ shifted, which indicates that the CF$_2$ and Emim$^+$ have electrostatic effects.

The relative content of the β-phase (F(β)) present in the sample is calculated by the following formula [28]:

$$F(\beta) = \frac{A_\beta}{(K_\beta/K_\alpha)A_\alpha + A_\beta}$$

Where F(β) represents the relative content of the β-phase; $A_\alpha$ and $A_\beta$ are at 763 cm$^{-1}$ (α-phase characteristic peak corresponding to CF$_2$ bending and skeleton bending) and 840 cm$^{-1}$ (β-phase characteristic peak corresponding to CF$_2$ sway) Integral area; $K_\alpha$ and $K_\beta$ represent absorption coefficients at 763 cm$^{-1}$ and $840$ cm$^{-1}$, respectively. $K_\alpha = 6.1 \times 10^6$ cm$^2$ mol$^{-1}$, $K_\beta = 7.7 \times 10^4$ cm$^2$ mol$^{-1}$[29].
Table 2 shows the effect of different amounts of [Emim]BF$_4$ on the relative content of $\beta$-phase (F($\beta$)). The addition of [Emim]BF$_4$ does obvious increase the F($\beta$). As the amount of addition increased, the F($\beta$) first increased and then decreased, and reached a maximum at the addition amount of 1.5 wt%, which was 85.09%. And from 0 wt% to 1.5 wt%, the $\beta$-phase relative content is increased, from 1.5 wt% to 2.5 wt%, and the $\beta$-phase relative content is decreased. This may be when the amount added is 1.5 wt%, its role as a heterogeneous nucleation point synergistic electric field and other factors inducing the formation of the $\beta$-phase in PVDF have tended to be saturated. It reaches its maximum at 1.5 wt% of the addition, and more added amount did not further improve the $\beta$-phase relative content, and even acts as an impurity, the F($\beta$) is reduced instead.

Dielectric and piezoelectric properties of PVDF film added with [Emim]BF$_4$ added

Figure 8 and figure 9 show the frequency dependence of the relative dielectric constant ($\varepsilon'$) and dielectric loss (tan$\delta$) of the PVDF/[Emim]BF$_4$ film. Compared with pure PVDF film, $\varepsilon'$ and tan$\delta$ of the sample containing [Emim]BF$_4$ were strongly improved. And as the [Emim]BF$_4$ content increases, the $\varepsilon'$ increases from 6 to 285 because of the [Emim]BF$_4$ slight plasticizing effect leading to chain motion and high ion conductivity, but at the same time the tan$\delta$ also increases significantly. The large value of films at low frequencies are due to the electrode polarization effect, which is due to the conduction loss caused by the radial and tangential diffusion of free charges or ions near the electrode surface. The dielectric strength of PVDF/[Emim]BF$_4$ film at higher frequency is controlled by the Maxwell–Wager–Sillars (MWS) interface polarization. The good solubility of [Emim]BF$_4$ in solution leads to a large heterogeneous interface, when the sample is applied with an electric field, the space charge to generate large phase-to-phase accumulation because of the large difference in conductivity between [Emim]BF$_4$ phase and PVDF phase. This movement and accumulation of charge carriers in the interface causes the material to produce a large dielectric constant [30], while accumulating induced charges, losses are also produced [31].

As the frequency increases, $\varepsilon'$ and tan$\delta$ decrease dramatically. This is caused by the decrease in interface polarization as the frequency increases. Since the movement and accumulation process of charge carriers in [Emim]BF$_4$ takes a certain time, and the alternating electric field changes slowly at low frequencies, the interface between [Emim]BF$_4$ and PVDF has sufficient time to accumulate a large amount of the induced charge. However, when the frequency is increased, the rate at which the interface accumulates the induced charge can not keep up with the electric field change, and the induced charge is reduced, so that the interfacial polarization effect is weakened at high frequencies, and the $\varepsilon'$ and tan$\delta$ are reduced.

Table 3 shows the $d_{33}$ values of PVDF films with different [Emim] BF$_4$ contents. It can be observed that the $d_{33}$ value of the PVDF/[Emim] BF$_4$ film has increased to some extent compared to the pure PVDF film sample.

**Table 2.** Effect of different [Emim]BF$_4$ additions on the relative content of $\beta$.

| [Emim]BF$_4$ addition (wt%) | 0    | 0.5  | 1    | 1.5  | 2    | 2.5  |
|-----------------------------|------|------|------|------|------|------|
| Relative content of $\beta$-phase (%) | 78.36| 84.19| 84.25| 85.09| 84.57| 83.60|

**Figure 8.** [Emim]BF$_4$ different relative amounts of film relative dielectric constant.
The PVDF film without [Emim]BF₄ addition has a d₃₃ value of −3 pC/N, and when the added amount reaches 1.5 wt%, the d₃₃ value reaches a maximum of −10 pC/N. Therefore, combined with the previous phase structure analysis of PVDF film, d₃₃ value is related to the content of β-phase in PVDF film. When the addition amount of [Emim] BF₄ is 1.5 wt%, the content of β-phase is the highest, which shows good piezoelectric property.

Output voltage signal test added with [Emim]BF₄

The piezoelectric film electrical signal detecting device shown in figure 2 is used to detect the output voltage signal of the film. The signal generator is connected with the PZT driver, and PZT drives the vibration of the cantilever beam, so that the PVDF piezoelectric film generates an electrical signal, which is filtered and displayed on the oscilloscope. Figure 10 shows the results of the test. It can be seen that after inputting 10 V/20 Hz sine
wave, the PVDF film produces an output signal. Compared with the output voltage of 96 mV of pure PVDF film, the output voltage of PVDF film added by 1.5 wt% [Emim]BF₄ reaches 332 mV, which is a huge upgrade. It can also be seen from the figure that when the [Emim]BF₄ content is between 0 wt% (pure) and 1.5 wt%, the output voltage increases, reaching the highest at 1.5 wt%, and decreasing at 2 wt% to 2.5 wt%, which is consistent with the previous phase content analysis. This shows that under the addition of [Emim]BF₄, the β-phase of the PVDF film does increase and the electrical properties are enhanced, and the film performance is best when the amount of [Emim]BF₄ added is 1.5 wt%.

Conclusion

The near electric field direct writing method is simple and suitable for applicability, and can accurately customize any shape of film. The electrical properties of the PVDF film are enhanced by adding a microscale amount of ionic liquid [Emim]BF₄ and inducing the multiple influencing factors of the β-phase formation. The introduction of [Emim]BF₄ greatly changed the surface morphology of the PVDF film, the spherulite radius was greatly reduced, and the density of the film was increased. When the addition amount of [Emim]BF₄ is 1.5 wt%, the relative β-phase content of PVDF film reached 85.09%, and the crystallinity is 47.84%. The addition of [Emim]BF₄ increases the dielectric and piezoelectric constant of the film. As the [Emim]BF₄ content increases, the ε’ increases from 6 to 285, the d₃₃ value of the film is as high as −10 pC/N, and the output voltage is greatly improved compared with the pure PVDF film.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No.51102118); and the Opening Fund of National Center for International Research on Structural Health Management of Critical Components (KFJ20–04N).

ORCID iDs

Caifeng Chen https://orcid.org/0000-0002-0093-604X

References

[1] Burnham Eay E D, La T, Tarbutton JA and Ellis JD 2017 Strain characteristics of additive manufactured polyvinylidene fluoride (PVDF) actuators Sens. Actuator A-Phys. 266 65–92
[2] Manna S, Batalyal S K and Nandi A K 2006 Preparation and characterization of silver-poly(vinylidene fluoride) nanocomposites: formation of piezoelectric polymorph of poly(vinylidene fluoride) J. Phys. Chem. B 110 12318–26
[3] Tao M, Liu F, Ma B and Xue L 2013 Effect of solvent power on PVDF membrane polymorphism during phase inversion Desalination 316 137–45
[4] He X and Yao K 2006 Crystallization mechanism and piezoelectric properties of solution-derived ferroelectric poly(vinylidene fluoride) thin films Appl. Phys. Lett. 89 112909
[5] Yu J, Jiang P, Wu G, Wang L and Wu X 2011 Graphene nanocomposites based on poly(vinylidene fluoride): Structure and properties Polym. Compos. 32 1483–91
[6] He F, Sarkar M, Lau S, Fan J and Chan L H 2011 Preparation and characterization of porous poly(vinylidene fluoride-trifluoroethylene) copolymer membranes via electrospinning and further hot pressing Polym. Test. 30 436–41
[7] Mohammadi B, Yousefi A A and Bellah S M 2007 Effect of tensile strain rate and elongation on crystalline structure and piezoelectric properties of PVDF thin films Polym. Test. 26 42–50
[8] Ong W L, Gao M and Ho G W 2013 Hybrid organic PVDF-inorganic M-rGO-TiO₂ (M = Ag, Pt) nanocomposites for multifunctional volatile organic compound sensing and photocatalytic degradation-H2 production Nanoscale 5 11283–90
[9] Gregorio R and Borges D S 2008 Effect of crystallization rate on the formation of the polymorphs of solution cast poly(vinylidene fluoride) Polymer 49 4089–16
[10] Zheng J, He A, Li J and Han C C 2007 Polymorphism control of poly(vinylidene fluoride) through electrospinning Macromol. Rapid Commun. 28 2159–62
[11] Chen C, Cai F, Zhu Y, Liao L, Qian J, Yuan F and Zhang N 2019 3D printing of electroactive PVDF thin films with high β-phase content Smart Mater. Struct. 28 108071
[12] Kameoka J, Orth R, Yang Y, Czapekewski D, Mathers R, Coates G W and Craighead H G 2003 A scanning tip electrospinning source for deposition of oriented nanofibres Nanotechnology 14 1124–9
[13] Sun D, Chang C, Li S and Lin L 2006 Near-field electrospinning Nano Lett. 6 839–42
[14] Gupta A, Seifalian A M, Ahmad Z, Edrisinsinghe M J, Winslet M C and Bioact J 2007 Novel electrohydrodynamic printing of nanocomposite biopolymer scaffolds Compat. Polym. 22 265–80
[15] Andrew J S and Clarke D R 2008 Effect of electrospinning on the ferroelectric phase content of polyvinylidene difluoride fibers Langmuir 24 670–2
[16] Xing C, Zhao M, Zhao L, You J, Cao X and Li Y 2013 Ionic liquid modified poly(vinylidene fluoride): crystalline structures, miscibility, and physical properties Polym. Chem. 4 5726–34
[17] Seo J M, Arumugam G K, Khan S and Heiden P A 2009 Comparison of the effects of an ionic liquid and triethylbenzylammonium chloride on the properties of electrospun fibers, 1-Poly(lactic acid) Macromol. Mater. Eng. 294 35–44
[18] Xu P, Fu W, Luo X and Ding Y 2017 Enhanced dc conductivity and conductivity relaxation in PVDF/ionic liquid composites Mater. Lett. 206 60–3
[19] Lopes A C, Gutiérrez J and Barandiarán J M 2018 Direct fabrication of a 3D-shape film of polyvinylidene fluoride (PVDF) in the piezoelectric phase for sensor and actuator applications Eur. Polym. J. 99 111–6
[20] Gao K, Hu X, Dai C and Yi T 2006 Crystal structures of electrospun PVDF membranes and its separator application for rechargeable lithium metal cells Mater. Sci. Eng. B-Adv. Funct. Solid State 131 105–5
[21] Sharma M, Sharma S, Abraham J, Thomas S, Madras G and Bose S 2014 Flexible EMI shielding materials derived by melt blending PVDF and ionic liquid modified MWNTs Mater. Res. Express 1 035003
[22] Lins L C, Livi S, Maréchal M, Duchet-Rumeau J and Gérard J F 2018 Structural dependence of cations and anions to building the polar phase of PVDF Eur. Polym. J. 107 236–48
[23] Zhang C X et al 2005 Study on morphology of electrospun poly(vinyl alcohol) mats Eur. Polym. J. 41 423–32
[24] Yee W, Kotaki M, Liu Y and Lu X 2007 Morphology polymorphism behavior and molecular orientation of electrospun poly (vinylidene fluoride) nanofibers Polymer 48 512–21
[25] Bormashenko Y, Pogreb R and Stanevsky O 2004 Vibrational spectrum of PVDF and its interpretation Polym. Test. 23 791–6
[26] Gregorio R and Ueno E M 1999 Effect of crystalline phase, orientation and temperature on the dielectric properties of poly (vinylidene fluoride)(PVDF) J. Mater. Sci. 34 4489–500
[27] He L, Sun J, Wang X, Yao L, Li J, Song R, Hao Y, He Y and Huang W 2011 Enhancement of β-crystalline phase of poly(vinylidene fluoride) in the presence of hyperbranched copolymer wrapped multiwalled carbon nanotubes J. Colloid Interface Sci. 363 122–8
[28] Salimi A and Yousefi A A 2003 Analysis method: FTIR studies of β-phase crystal formation in stretched PVDF films. Polym. Test. 22 699–704
[29] Esterly D M and Love B J 2004 Phase transformation to poly(vinylidene fluoride) by milling J. Polym. Sci. Pt. B-Polym. Phys. 42 91–7
[30] Wang P, Xu P, Zhou Y, Yang Y and Ding Y 2018 Effect of MWCNTs and P(MMA-IL) on the crystallization and dielectric behavior of PVDF composites Eur. Polym. J. 99 58–64
[31] Thakur P, Kool A, Bagchi B, Das S and Nandy P 2014 Enhancement of β phase crystallization and dielectric behavior of kaolinite/ halloysite modified poly(vinylidene fluoride) thin films Appl. Clay Sci. 99 149–59