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**Ionic Liquid Modified Poly (vinyl alcohol) with Improved
Thermal Processability and Excellent Electrical Conductivity**

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ABSTRACT: The combination of polymer and ionic liquid (IL) is attracting an increasing attention owing to their versatile and tunable properties. In this paper, IL 1-(2-hydroxyethyl)-3-methylimidazolium chloride ([HOEtMIM]Cl), which has complementary structure with poly (vinyl alcohol) (PVA), was adopted to act as a novel plasticizer for PVA to improve its thermal processability. The results demonstrated that the hydroxyl group and Cl⁻ in IL formed strong hydrogen bonds with the hydroxyl groups of PVA, thus efficiently confining its crystallization, decreasing its melting point and obtaining the wide thermal processing window, up to 110 °C. The resultant PVA/IL composites showed high ionic conductivity, up to 2.82×10^{-3} S/cm, and considerable flexible mechanical properties with an elongation at break of 317% when IL content was 35wt%, opening the potential applications of PVA in the field of flexible semi-solid state electric double-layer supercapacitors (EDLC) and proton exchange membrane (PEM).

Keywords: Poly (vinyl alcohol); Ionic liquid; Thermal processing; Hydrogen bonding

Introduction

Nowadays, with the shortage of oil and the aggravating environmental burden caused by the petrochemical derived polymers, utilization of biodegradable materials becomes more and more emergency for the economic sustainable development. Poly (vinyl alcohol) (PVA), one of the biodegradable polymer with multi-hydroxyl groups, has been under the spotlight and extensively applied in many fields including pharmaceuticals, membrane, fiber, and separation application, etc., ascribing to its fascinating properties such as non-toxic, water-soluble and biocompatibility.¹ However, the melting point of PVA is approximate to its thermal decomposition temperature due to the existence of a large number of strong inter- or intra-molecular hydrogen bonds among the hydroxyl groups of PVA as well as the high crystallinity of PVA, making the thermal processing of PVA quite tough and its industrial applications limited in solution processing, which is time-consuming and uneconomical, thus restricting its practical applications in a large-scale.

Up to now, considerable efforts have been devoted to achieving the thermal processing of PVA via plasticization, and various plasticizers including water, glycerin, caprolactam, polyethylene glycol, and their proper combinations, etc., have been employed.²⁻⁶ However, several drawbacks remain, e.g. volatility, thermal decomposition and instability, especially during extrusion processing, poor plasticization effect, etc., making them against the practical processing of PVA.⁷⁻⁹ Accordingly, it is quite urgent to seek a new, environmentally friendly and stable substitute.

Room temperature ionic liquids (ILs), claiming to be the “green solvents” with melting points below 100 °C, are evoking increasing attentions in recent years owing

to their appealing physicochemical properties, such as wide liquid range, good solubility, high ionic conductivity, excellent thermal stability.^{10, 11} More importantly, the properties of ILs can be readily tailored by designing the chemical structure of cations or anions to meet the requirements of the special application. For example, the combination of ILs with suitable polymers had been reported to provide a new route to fabricate polymer based functional composites, especially the ionic liquid based solid polymer electrolytes (SPEs), which have been widely used to replace the conventional liquid electrolytes ascribing to its good processibility, electrochemical stability, high ionic conductivity and operational safety.¹² The applications of SPEs have ranged from the recharge batteries to the high energy devices including electric double layer capacitors (EDLCs), electrostatic gating, proton exchange membrane fuel cells (PEMFCs) and proton exchange membrane (PDM).¹³⁻¹⁸

The aggressive ability of ILs to disrupt the extensive hydrogen-bonded networks makes them efficient processing additives for polar polymers. It has been reported recently that ILs with the anions including Cl^- , OAc^- , HCOO^- , *etc.*, the strong hydrogen bond acceptors, have high efficiency in dissolving cellulose or realizing the thermal processing of starch.^{19,20} For example, by forming new hydrogen bonding with cellulose, 1-allyl-3-methylimidazolium chloride (AMIMCl) and 1-butyl-3-methylimidazolium chloride ($[\text{C}_4\text{mim}]\text{Cl}$) could be used as non-derivative solvents for cellulose;^{21, 22} thermoplastic starch (TPS) was successfully obtained by using $[\text{C}_4\text{mim}]\text{Cl}$ as a plasticizing agent.²³ However, the contribution from cations of ILs is also indispensable.²⁴ Luo et al. confirmed that chloride anion of ILs could act as a hydrogen bond acceptor, promoting the dissolution of cellulose; while the hydroxyl group on the imidazole cation side chain was availability to form hydrogen

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3 bonding with cellulose, further weakening the inter- and intra-molecular
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5 hydrogen-bonded network of cellulose.²⁵
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8 PVA with abundant hydroxyl groups is conceivable to form hydrogen bonds with
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10 ILs. However, due to the poor thermal processability of PVA, the present PVA/IL
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12 composites such as flexible gel polymer electrolyte (FGPE),²⁶⁻²⁸ polyelectrolyte
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14 membrane (PEM)²⁹ and hydrogels for quasi-solid-state dye-sensitized solar cells³⁰
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16 are obtained by solution casting processing, which undoubtedly, to some degree,
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18 constrains the practical applications of those special composites. If thermal processing
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20 of PVA/IL composite could be realized, it would be of great significance.
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23 In this paper, based on our previous works on thermal processing of PVA,³¹⁻³⁴
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25 1-(2-hydroxyethyl)-3-methylimidazolium chloride ([HOEtMIM]Cl) with both strong
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27 hydrogen bond acceptor Cl⁻ and hydroxyl group, was chosen as an efficient plasticizer
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29 for PVA to realize its thermal processing, and simultaneously endowed PVA with high
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31 electrical conductivity. The hydrogen bonding interactions between PVA and IL, and
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33 the effects of IL on the structure and properties of PVA were systematically studied.
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35 The results from this study would open a new application for both PVA and ILs in
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37 electronic and optoelectronics areas.
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42 **EXPERIMENTAL SECTION**

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44 **Materials.** Poly(vinyl alcohol), with degree of polymerization 1750 ± 50 and degree
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46 of alcoholysis 97%, was provided by SINOPEC Sichuan Vinyon Factory, China.
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48 Ionic liquid (IL), 1-(2-hydroxyethyl)-3-methylimidazolium chloride ([HOEtMIM]Cl),
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50 was purchased from Lanzhou Institute of Chemical Physics, Chinese Academy of
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52 Sciences. Before using, IL was dried in a vacuum oven at 60 °C for 48h to remove
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54 moisture.
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Preparation of PVA/IL composites. IL (15-40 wt%) was first dissolved in distilled water to get a homogeneous IL solution. Then, PVA powders were added with fully stirring. After that, the mixture was transferred into a sealed plastic container, which was then placed in a vacuum oven at 85 °C for 2h to let IL solutions fully swelled into PVA. Subsequently, the container was opened and the oven temperature was raised to 95 °C to completely remove water. The IL content in the final mixture was 15 wt%, 25 wt%, 35 wt% and 40 wt%, respectively. PVA/IL composites were then obtained via compression molding at 165°C to 195 °C. The composites with the corresponding IL content were designated as PVA-IL-15%, PVA-IL-25%, PVA-IL-35% and PVA-IL-40%, respectively.

Characterization

Differential Scanning Calorimetry (DSC). Melting behavior and crystallization behavior of samples were tested on a TA-Q20 thermal analyzer (TA instruments Co., USA) with a heating rate of 10 °C/min from -40 °C to 250 °C and the cooling rate of 10 °C/min from 250 °C to 40 °C, respectively, under a continuous highly pure nitrogen atmosphere.

Thermogravimetric analysis (TGA). TGA curves were carried out on a TA Q50 thermogravimetric analyzer (TA Instrument, Co., USA) under a nitrogen atmosphere with a flow rate of 60 ml/min. The sample (approx. 8~10 mg) was heated at a Pt pan at a constant heating rate of 10 °C /min from 40 °C to 600 °C.

Wide-Angle X-ray Diffraction (WXR). Crystallization behavior of PVA/IL system was obtained by using a DX-1000 diffractometer (Dandong Fangyuan Instrument Co., Ltd., China) from $2\theta = 5^\circ$ to 40° with Ni-filtered Cu K α radiation ($\lambda = 0.1542$ nm, 40 kV, 200 mA) at a scanning rate of $1^\circ/\text{min}$ and a step interval of 0.02° .

Fourier transform infrared spectroscopy (FTIR). FTIR spectra were recorded on a Nicolet 6700 FT-IR spectrometer (Thermo Scientific Company, USA) in the ATR mode from 4000 to 400 cm^{-1} at 2 cm^{-1} resolution and 32 scans at room temperature. The tested PVA/IL films were obtained by hot pressing, and PVA film was prepared by solution casting.

X-ray photoelectron spectroscopy (XPS). XPS was carried out using a Shimadzu/Kratos AXIS Ultra DLD multifunctional X-ray photoelectron spectrometer (Manchester, UK), employing Al K^{α} excitation radiation.

Dynamical rheological behavior. Rheological test was conducted on a TA SRES strain controlled Rheometer (TA instruments Co., USA) in nitrogen atmosphere. The samples with 25 mm in diameter and 2.0 mm in thickness were obtained by hot pressing PVA/IL mixtures at 175 $^{\circ}\text{C}$ under 20 MPa on a Plate Vulcanization Machine. The gap was adjusted to 1.5 mm after the sample was loaded into the rheometer. The frequency was from 0.01 to 100 rad/s and the strain was 1%. The dynamic temperature ramps (with 1.0 HZ frequency and 1% strain) were performed from 160 $^{\circ}\text{C}$ to 230 $^{\circ}\text{C}$ at a heating rate of 1 $^{\circ}\text{C}/\text{min}$ and a constant frequency rate of 1 rad/s.

Electrical conductivity test. The electrical conductivity was measured using a two-probe method on a picoammeter (Keithley 2400, Keithely Instruments Inc., USA). Rectangular sample with a size of 10mm \times 30mm \times 2mm was cut from the compression molded composites. To ensure good contact, silver paste was painted on the surface in contact with the electrodes at both ends of the sample. The conductivity σ was calculated using the following equation:

$$\sigma = d/RS$$

Where d is the distance between two measuring electrodes, R is the given values of the resistance, and S is the effective area.

Mechanical performance. Mechanical performance of the dumbbell shaped sample was measured on a universal test instrument (5576, Instron Instruments, U.S.A) according to ASTM D-638 with a crosshead speed of 10 mm/min. The size of a specimen was 75mm \times 4mm \times 2mm (length \times width \times thickness). Five specimens were tested to obtain the average value.

Scanning electron microscopy (SEM). The surface morphologies of PVA/IL composites were observed by using an Inspect F field-emission SEM (FEI Co., Ltd., USA) with a high voltage of 20KV. All samples were fractured in liquid nitrogen and sputtered with gold under vacuum for testing.

Results and discussion

Effect of IL on the thermal performance of PVA

PVA is a multi-hydroxyl polymer with strong intra- and inter-molecular hydrogen bonding as well as high crystallinity, thus having quite high melting point, closing to its decomposition temperature, making its thermal processing very difficult. The key to obtain the thermal processing window of PVA is weakening its original intra- and inter-hydrogen bonding to decrease its melting point or/and increase its decomposition temperature.

Figure 1 (a) presents the DSC curves of pure PVA, IL and PVA with various IL content. Evidently, IL shows a melting peak at 80 °C, while the melting point of PVA is quite high, up to 217.3 °C. With the addition of IL, the melting peak of PVA/IL composites becomes weaker and broader, and gradually shifts to lower temperature, from 217.3 °C to 146.3 °C. This could be attributed to the new-formed hydrogen

bonds between IL and PVA, which effectively weakened the originally strong hydrogen bonds among the hydroxyl groups of PVA and improved the mobility of PVA molecular chains. The existence of IL in modified system also disturbed the regular arrangement of PVA molecular chains during cooling process, significantly inhibiting the crystallization of PVA. As revealed in Figure 1(b), the melt crystallization temperature (T_c) of the composites significantly decreased from 166 °C of pure PVA to 78 °C of PVA-IL-35 wt% .

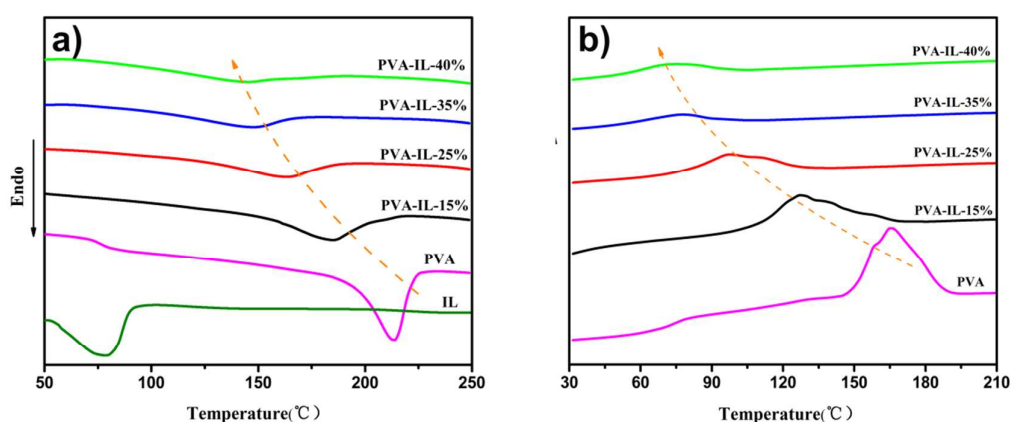


Figure 1. DSC heating (a) and cooling (b) curves of pure PVA, IL and PVA/IL composites

The influence of IL on the chain mobility of PVA can also be identified by the changes of the glass transition behaviors of PVA/IL composites, as shown in Figure 2. Clearly, ascribing to the new hydrogen bonds formed between IL and PVA, IL could effectively play its plasticizing role on PVA, remarkably reducing the T_g of PVA, e.g. from 76.6 °C of pure PVA to 11.4 °C of the composite with 35 wt% IL.

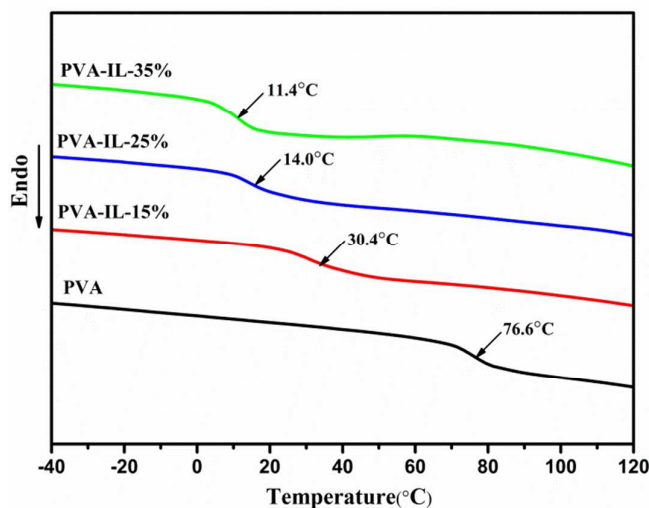


Figure 2. Glass transition Temperature of PVA/IL composites

Figure 3 shows the TG curves of pure PVA, IL and PVA/IL composites. As could be seen, PVA presents three weight loss stages, i.e. the first stage in the region of 25 °C to 125 °C, ascribing to the evaporation of small amount of water absorbed in PVA; the second stage in the field of 200 °C to 300°C, mainly involving the elimination of the side-groups of PVA; and the third stage in the range from 350 °C to 400 °C, which is dominated by the breakdown of PVA backbone.³⁵ Obviously, within the proper IL content (<35 wt%), the PVA/IL composite presents higher initial decomposition temperature (T_i , the temperature at 5 % mass loss) and less weight loss, compared with pure PVA (The inset of Figure 3), indicating the improved thermal stability of the composites, possibly attributing to the hydrogen bonds formed between PVA and IL, which shields the hydroxyl groups of PVA to a certain extent, thus retarding the elimination of the sides-groups of PVA. However, when IL content reached 35 wt%, T_i of PVA/IL composite contrarily decreases, owing to the high concentration of chloride in IL, which could destabilize the adjacent C–H bonds of PVA chains and therefore led to the worse thermal stability.

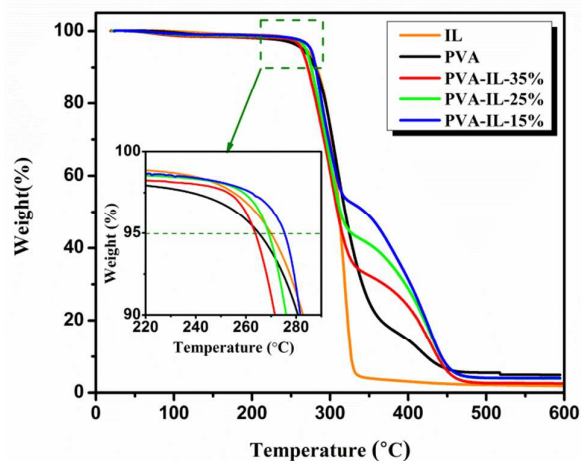


Figure 3. TGA curves of PVA, IL and PVA/IL composites

Based on DSC and TGA analysis, the thermal processing window for PVA/IL composite was calculated by using following equation, and the results were shown in Figure 4.

$$\Delta T = T_i - T_{end}$$

Where T_i is the initial decomposing temperature, i.e. the temperature at 5% mass loss obtained from TGA, T_{end} is the temperature at the end of the melting peak of PVA/IL composite obtained from DSC.

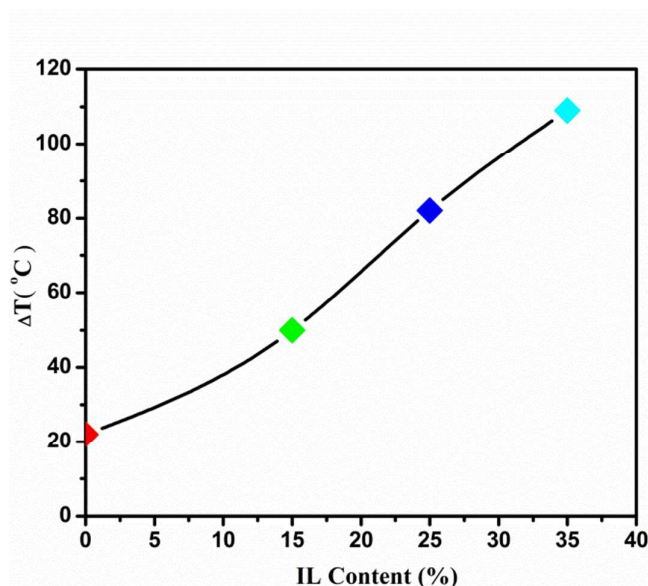


Figure 4. Thermal processing windows of PVA/IL composites

As clearly shown in Figure 4, the thermal processing window remarkably expands with the addition of IL, e.g. when IL content reaches 35 wt%, the thermal processing window of the composite is up to 110 °C, about 5 times than that of neat PVA, further confirming the plasticization effect of IL on PVA.

Effect of IL on crystalline structure of PVA

The effect of IL on the crystalline structure of PVA was analyzed by X-ray diffraction, as shown in Figure 5. PVA is a semi-crystalline polymer with four X-ray diffraction peaks,³⁶ respectively corresponding to (001) at $2\theta \approx 11.5^\circ$, (10 $\bar{1}$) at $2\theta \approx 19.5^\circ$, (101) at $2\theta \approx 20.0^\circ$ and (200) at $2\theta \approx 22.7^\circ$. Clearly, the presence of IL has a prominent effect on crystalline structure of PVA. With the addition of IL, the diffraction peaks of PVA gradually weaken, and almost disappear when IL content is up to 35 wt%, indicating the lowering crystallinity of PVA. By using MDI jade 5.0 software, the interplanar spacing as well as the crystallinity of each sample were obtained, as listed in Table 1. Evidently, with the increase of IL content, the interplanar spacing of PVA increases, while the crystallinity of PVA decreases. The (101) diffraction of PVA crystal is closely related to the intermolecular interference between PVA chains in the direction of the intermolecular hydrogen bonding,³⁷ so the enlarged (101) interplanar spacing suggests the weakened hydrogen bonding between PVA chains ascribing to the insertion of IL. The decreased crystallinity is beneficial to the thermal processing of PVA.

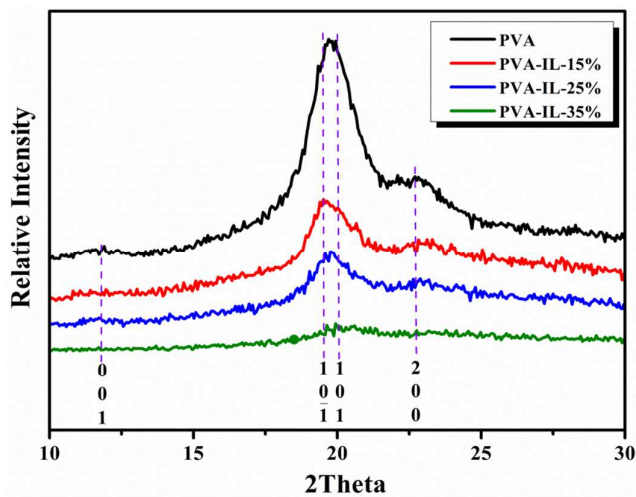


Figure 5. XRD patterns of neat PVA and PVA/IL composites

Table 1 Interplanar spacing of PVA and PVA/IL composites

Sample		PVA	PVA/IL-15%	PVA/IL-25%	PVA/IL-35%
d (Å)	001	7.59	7.64	7.66	8.37
	101	4.49	4.49	4.51	4.53
	200	3.89	3.86	3.89	3.92
Crystallinity (%)		45.43	29.84	18.00	15.13

Interactions between PVA and IL

To specify the possible interactions between PVA and IL, FTIR and XPS were carried out and the results were presented in Figure 6 and Figure 7, respectively. It could be seen from Figure 6 that PVA presents a fairly broad band within the range of 3000-3800 cm^{-1} , relating to O-H stretching vibration, while IL displays several characteristic peaks in the same range, i.e. O-H stretching vibration at 3400 cm^{-1} , $\text{C}_{4,5}\text{-H}$ and $\text{C}_2\text{-H}$ symmetric stretching vibrational of imidazolium ring at 3153 and 3089 cm^{-1} .^{38, 39} Compared with pure PVA, the O-H stretching bands of PVA/IL composites gradually shifts to higher wavenumbers, e.g. by about 19 cm^{-1} with IL content increasing to 35 wt%, confirming the formation of the hydrogen bonding between IL and PVA. The peaks at 1141 and 1093 cm^{-1} are respectively assigned to the C-O stretching vibrations in crystalline and amorphous regions of PVA.⁴⁰ With the

increase of IL content, the intensity of the peak at 1141 cm^{-1} reduces, and the medium sharp peak at 1093 cm^{-1} gradually mutually-overlapped with the C-O stretching vibration of IL at 1068 cm^{-1} to a broad double peak, indicating that IL could seep into both the crystalline and amorphous regions of PVA. All these changes in wavenumber, peak intensity and shape are based on the interactions between IL and PVA matrix.

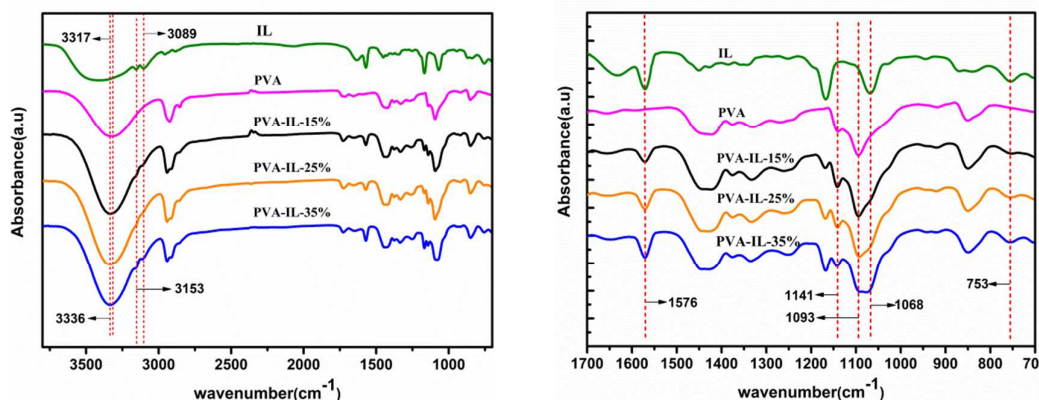


Figure 6. FTIR spectra of PVA and PVA/IL composites

As shown in Figure 7 and table 2, the Cl 2p_{3/2} of IL gives rise to an overlapping peak of the dissociative chloride ion at 196.7 eV and the combinative chloride ion with special interaction such as ionic and H-bonding at 198.2 eV. While for PVA/IL composites, the Cl 2p_{3/2} peak gradually shifts to higher binding energy, and a major increase of about 1.0 eV on the binding energy (BE) value is observed when IL content is up to 35 wt%, revealing that the chemical environment of chloride changes, which also provides an evidence for the hydrogen bonds between the Cl anions of IL and H atoms of PVA. Owing to its high polarity and small volume, Cl anions tend to be active and highly effective in breaking the extensive original hydrogen bonds in PVA, thus decreasing the electron cloud density of Cl anions and leading to the increase of the binding energy.

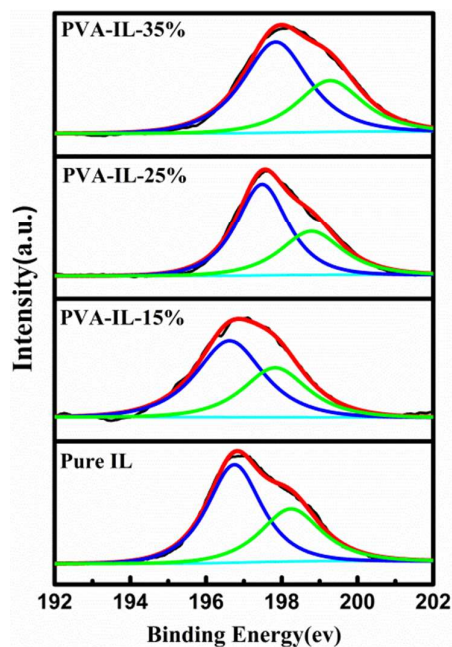


Figure 7. XPS Cl 2p3/2 spectra of pure IL and PVA/IL composites

Table 2 Binding Energies of Cl 2p3/2 of IL and PVA/IL composites

Sample	Peak 0(EV)	Peak 1(EV)
IL	196.7	198.2
PVA-IL-15%	197.5	198.8
PVA-IL-25%	197.6	198.8
PVA-IL-35%	197.8	199.3

Based on the analyses of FTIR and XPS, two kinds of hydrogen bonds between PVA and IL could be proposed, i.e. hydrogen bond between Cl anions of IL and hydroxyl groups of PVA (type I), and hydrogen bond between hydroxyl group of IL and that of PVA (type II). In the composite system, IL is surrounded by PVA chains and multiple hydrogen bonds are formed between IL and PVA. These hydrogen bonds make IL an effective physical cross-linker in system, as illustrated in Figure 8, thus taking great influence on thermal, crystallization behaviors, etc., of PVA.

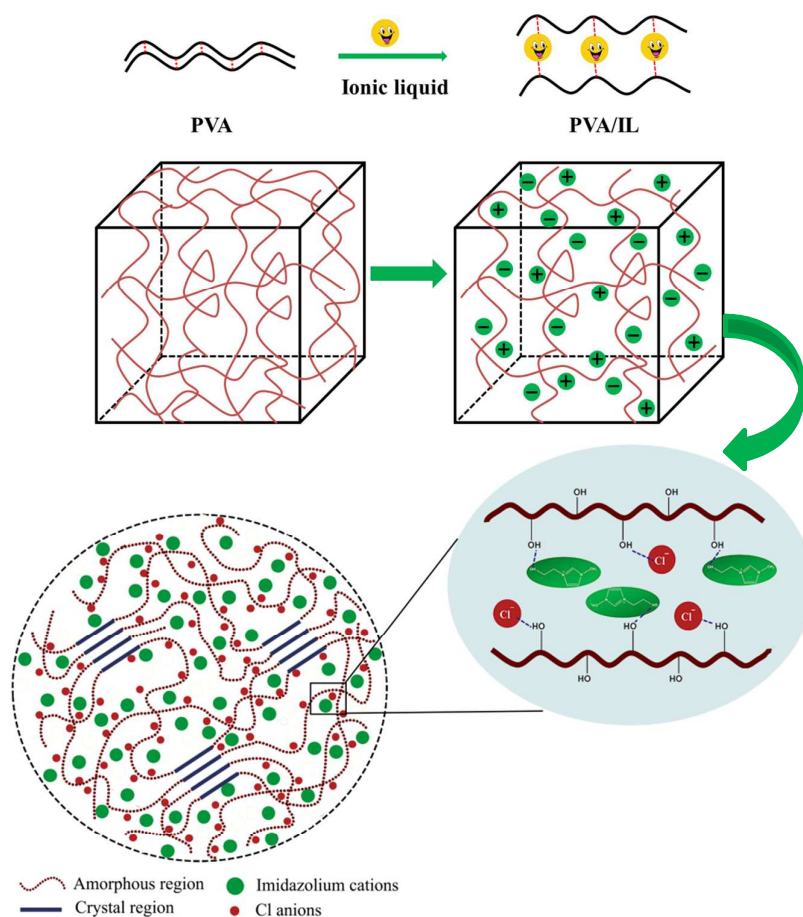


Figure 8. Schematic illustration of the hydrogen bonding between PVA and IL

The hydrogen bonds formed between PVA and IL could also be confirmed by calculating the interaction parameter between them via Nishi-Wang (polymer-diluent system) equation,⁴¹ as follows:

$$\frac{1}{T_{m,composites}^0} - \frac{1}{T_m^0} = -\frac{B \cdot V_{2u}}{\Delta H_{2u}} \cdot \frac{\phi_1^2}{T_{m,composites}^0} + \frac{R \cdot V_{2u}}{\Delta H_{2u} \cdot V_{1u}} \cdot \phi_1$$

$$\chi_{12} = \frac{B \cdot V_{1u}}{RT}$$

Where $T_{m,mixers}^0$ and T_m^0 represent the equilibrium melting point of the crystals in PVA/IL and pure PVA, respectively. B is the interaction energy density, V_{1u} and V_{2u} are the molar volumes of the repeating unit of the IL and PVA, respectively. ΔH_{2u} is the enthalpy of fusion per mole of repeating unit of PVA, ϕ_1 is the volume fraction of IL, and χ_{12} is the Flory-Huggins interaction parameter.

According to literatures^{42, 43} and Figure 1, here, $\frac{V_{2u}}{\Delta H_{2u}} = \frac{1}{188.36} \text{ cm}^3 \text{ J}^{-1}$, $\rho_{\text{IL}} = 1.28 \text{ g cm}^{-3}$, $\rho_{\text{PVA}} = 1.26 \text{ g cm}^{-3}$, $V_{1u} = 127.05 \text{ cm}^3 \text{ mol}^{-1}$, $V_{2u} = 33.18 \text{ cm}^3 \text{ mol}^{-1}$. Then the corresponding liner relationship between $(1/T_{\text{m, composites}}^0 - 1/T_{\text{m}})/\phi_1$ and $\phi_1/T_{\text{m, composites}}^0$ was obtained, as shown in Figure 9. The slope of the line is 0.1537. Then the values of B and χ_{12} are obtained as follows: $B = -6.92 \text{ cal cm}^{-3}$, $\chi_{12} = -1.02$ at 160°C . As expected, the yield χ_{12} is negative, indicating the thermodynamic miscibility between PVA and IL ascribing to their strong hydrogen bonds. The good miscibility of PVA and IL is conducive to exert the efficient plasticizing effect of IL on PVA.

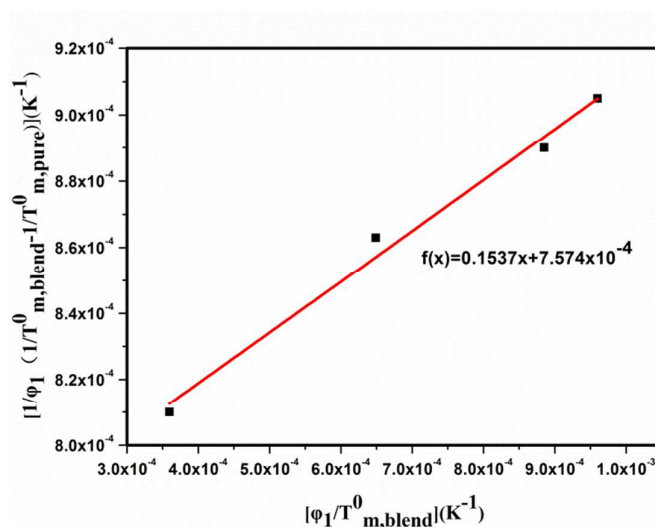


Figure 9. Plot of quantity $(1/T_{\text{m, composites}}^0 - 1/T_{\text{m}})/\phi_1$ against $\phi_1/T_{\text{m, composites}}^0$ for PVA/IL

Dynamical rheological behavior of PVA/IL composites

The distinctively useful trait of hydrogen bonding is its high directionality and reversibility, leading to the transient supramolecular structure with topologies and dynamics, which is quite sensitive to the external stimulus, e.g., temperature.^{44, 45} Rheological characterization provides good insights into the dynamics of the hydrogen-bonded networks of PVA/IL composites. Here, the PVA-IL-35% composite was explored as an example for its excellent thermal processability. Figure 10 plots

the G' and G'' as a function of angular frequency. As could be seen, both the storage modulus G' and the loss modulus G'' decrease with the increase of temperature. It is notable that a clear and broad rubbery plateau displays in the terminal region below 166 °C, revealing a solid-like behavior ($G' > G''$). To do deeper analysis, the slopes in the terminal region of G' and G'' were estimated, as shown in Figure 11 (a) and (b). The slope of G' in the terminal region is approximate to zero at temperature less than 166 °C, and approaches to 1 when temperature is over 175 °C. This is quite inconsistent with the terminal flow behavior of the perfectly homogenous polymers, whose terminal power law exponents are nearly 2 and 1 for G' and G'' respectively, according to Rouse-like model. The unusual changes of the elastic plateau of G' and G'' of our PVA/IL system in the temperature of 160 °C to 170 °C could be attributed to the dynamic changes of the special hydrogen bonding interactions between PVA and IL. At lower temperature, hydrogen bonds could act as physical cross-link points, resulting in the temporary hydrogen-bonded networks in PVA/IL composites, thus decreasing the free volume, increasing the amount of chain friction, and strongly inhibiting the long-range configurational motions, which is reflected in Figure 11 by the increase of the plateau modulus at the terminal region. While at higher temperature, hydrogen bonding between PVA and IL would be broken due to its negative forming enthalpy, causing the difficult formation of a percolated network and little influence on the rheological properties of PVA/IL composites. The similar phenomenon had been found in a series of polymers with hydrogen-bonding end groups by Yan et al.,⁴⁶ demonstrating that hydrogen bonds plays a direct role in the special rheological properties of polymers with functional chains.

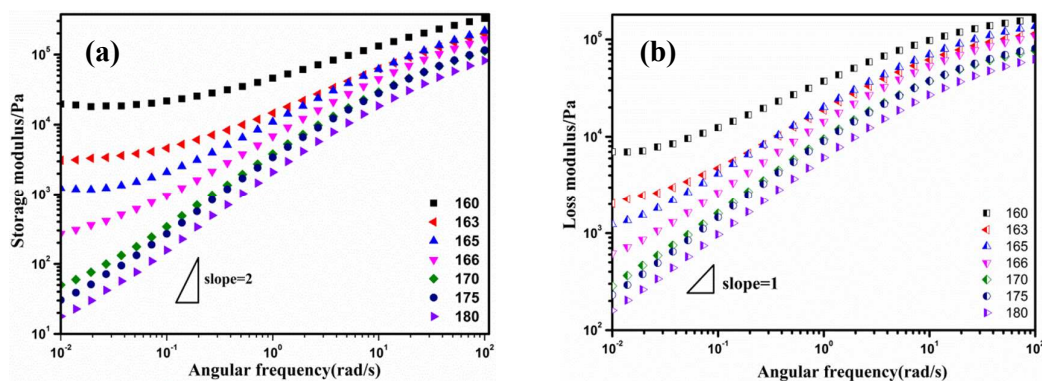


Figure 10 (a) storage modulus G' and (b) loss modulus G'' of PVA-IL-35% as a function of angular frequency at various temperature.

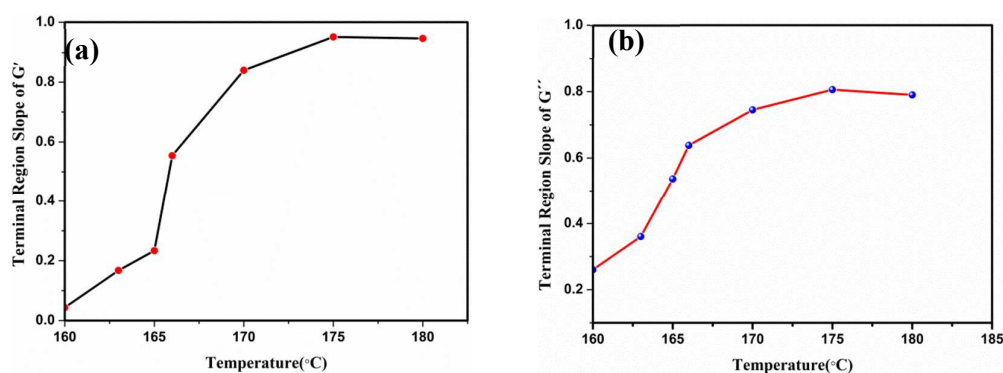


Figure 11 (a) Terminal Region Slope of G' versus temperature and (b) Terminal Region Slope of G'' versus temperature for PVA-IL-35%

The plateau modulus is closely related to the physical cross-link points caused by the hydrogen bonds. To quantify the temperature dependence of hydrogen bonds, the effective cross-link density was calculated by using the following equation of the rubber elasticity.⁴⁷ The data were shown in Table 3.

$$G' \approx G_N = \left(1 - \frac{2}{\phi}\right) RT v_e V_2^{\frac{2}{3}}$$

Where G_N is the plateau modulus, T is the temperature, v_e is the cross-link density of the hydrogen-bonded networks, R is the gas constant, V_2 is the volume fraction of polymer in the hydrogen-bonded networks and ϕ is the functionality of the cross-links, which is assumed to be 4 for an intermolecular hydrogen bonding.

Clearly, with the increase of temperature, the low-frequency modulus G_N decreases, showing a decrease in effective cross-linking density, e.g. from 14.43 mol/cm^3 to 0.23 mol/cm^3 when temperature increases from 160°C to 166°C , which undoubtedly supports the dynamic changes of the hydrogen-bonded networks driven by the hetero-complementary hydrogen bonding.

Table 3 Effective cross-links density value at various temperature

Temperature ($^\circ\text{C}$)	160	163	165	166	170~180
$\nu_e \text{ (mol/m}^3\text{)}$	14.43	2.37	0.89	0.23	—

Conductivity of PVA/IL composites

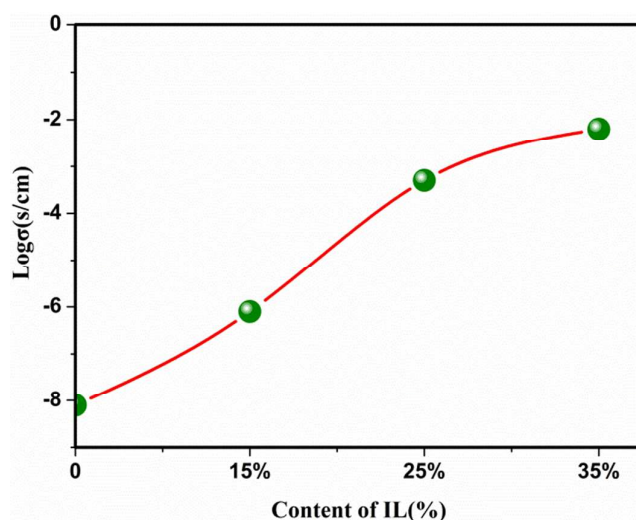


Figure 12. The electrical conductivity of PVA/IL composites

Figure 12 shows the electrical conductivity of PVA/IL composites. As expected, the addition of IL largely increases the conductivity of PVA/IL composites. When IL is 35 wt%, the conductivity of PVA/IL composites reaches $2.82 \times 10^{-3} \text{ S/cm}$, about six orders of the magnitude higher than that of pure PVA.

As well known, ILs have high ionic conductivity attributing to the migration of the detached cations and anions. In PVA/IL composite system, the strong hydrogen

bonded networks between PVA and IL construct conductive bridges for proton, facilitating its transfer, and thus leading to the conductivity of PVA/IL composites. And also from the general expression of ionic conductivity, $\sigma = \sum nqu$, where n is the concentration of the charge carrier, q is the charge of the carrier and u is the mobility of the carrier.⁴⁸ It can be seen that the concentration and the mobility of the ions are two main factors affecting its conductivity. With an increase of IL content, more ions participate in charge transfer, which is responsible in increasing the ionic conductivity of PVA/IL composites. The efficient plasticizing effect of the IL can also contribute to the ionic conductivity of PVA/IL composites since IL helps to soften the PVA backbone and improve the flexibility of its segments, providing more ionic conduction pathway and accelerating the ionic transportation.⁴⁹

Mechanical Properties of PVA/IL Composite

The effects of IL content on the mechanical properties of PVA/IL composites were shown in Figure 13, and pure PVA was absent due to its poor thermal processability. It could be seen from Figure 13 (a) that with the increase of IL content, PVA/IL composites tend to present rubber-like elasticity, and both tensile strength and Yong's modulus of the composites decreased while the elongation at break increased dramatically, e.g. with 35 wt% IL, the elongation at break of the composite increased to above 300% while the tensile strength and Yong's modulus decrease to 14MPa and 31MPa, respectively. This could be ascribed to the good miscibility between PVA and IL, which made IL an efficient plasticizer for PVA and PVA segments more flexible.

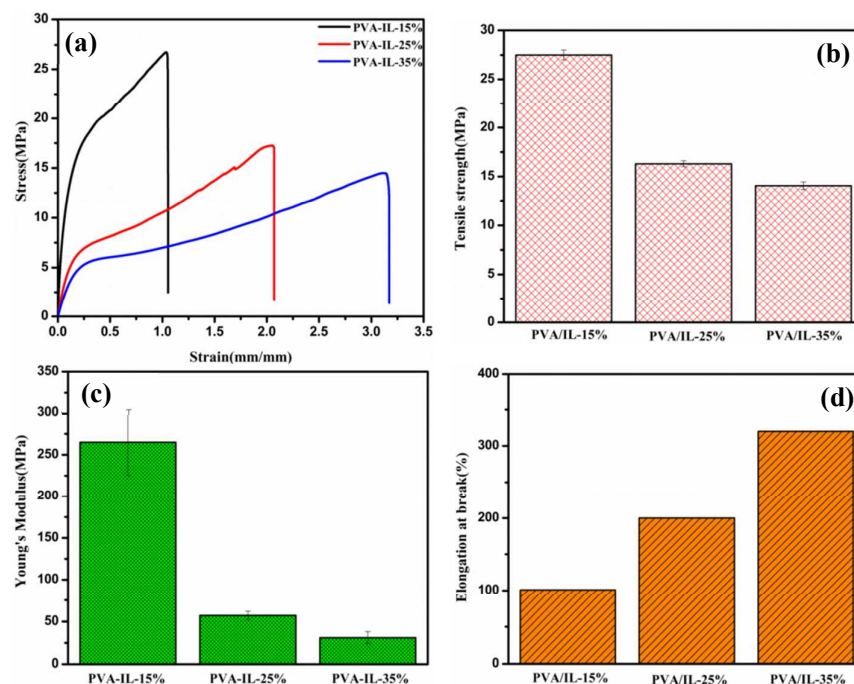


Figure 13. Stress-strain curves (a), tensile strength (b), Young's modulus (c), and the elongation at break (d) of PVA/IL composites

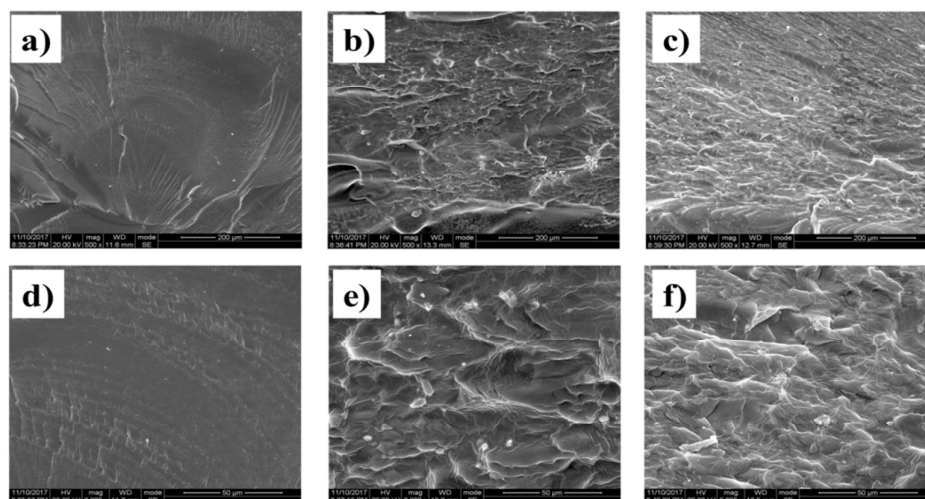


Figure 14. SEM image of PVA/IL composites (PVA-IL-15 wt%: (a) and (d); PVA-IL-25 wt%: (b) and (e); PVA-IL-35 wt%: (c) and (f))

To further illuminate the toughening effect of IL on PVA, SEM images of the fracture surface of the composites were observed, as shown in Figure 14. Apparently, the

fracture surface of PVA-IL-15% is smooth, revealing a brittle fracture. However, with the increase of IL content, more micro-protrusions, larger rough failure areas and prominent deformation appear, identifying the hydrogen bonded networks among PVA and IL, which functions as the physical crosslinking points to make PVA/IL composites of high elasticity.

Conclusions

In this work, [HOEtMIM]Cl, was adopted to improve the thermal processability of PVA. The results revealed that IL was an efficient plasticizer for PVA ascribing to the formation of the strong hydrogen bonding between Cl anions or/and hydrogen groups of IL and hydroxyl groups of PVA. With the incorporation of IL, the melting point, glass transition temperature as well as crystallinity of PVA/IL composites decreased, and wide thermal processing window, up to 110 °C, was obtained. The special hydrogen-bonded networks in PVA/IL composite made the rubbery plateau appeared in the terminal region of the composites and the high ionic conductivity of the composites, up to 2.82×10^{-3} S/cm. The composites also exhibited considerable flexible mechanical properties, with an elongation at break of 317% when IL content was 35 wt%. This study makes it possible to fabricate PVA/IL composites in a large scale via traditional melt processing and will provide a facile strategy to gain potential functional material in electronic and optoelectronics fields.

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Notes

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References

- (1) Hassan, C. M.; Peppas, N. A. Structure and applications of poly(vinyl alcohol) hydrogels produced by conventional crosslinking or by freezing/thawing methods. In *Biopolymers/Pva Hydrogels/Anionic Polymerisation Nanocomposites*; Abe, A., Ed.; Springer: Berlin, 2000; Vol. 153, pp 37-65.
- (2) Liu, P.; Chen, W.; Liu, Y.; Bai, S.; Wang, Q. Thermal melt processing to prepare halogen-free flame retardant poly (vinyl alcohol). *Polym. Degrad. Stab.* **2014**, *109*, 261-269.
- (3) Zhang, X.; Burgar, I.; Lourbakos, E.; Beh, H. The mechanical property and phase structures of wheat proteins/polyvinyl alcohol blends studied by high-resolution solid-state NMR. *Polymer* **2004**, *45* (10), 3305-3312.
- (4) Rahman, W. A. W. A.; Sin, L. T.; Rahmat, A.; Samad, A. Thermal behaviour and interactions of cassava starch filled with glycerol plasticized polyvinyl alcohol blends. *Carbohydr. Polym.* **2010**, *81* (4), 805-810.
- (5) Song, P. a.; Xu, Z.; Lu, Y.; Guo, Q. Bioinspired strategy for tuning thermal stability of PVA via hydrogen-bond crosslink. *Compos. Sci. Technol.* **2015**, *118*, 16-22.
- (6) Luo, X.; Li, J.; Lin, X., Effect of gelatinization and additives on morphology and thermal behavior of corn starch/PVA blend films. *Compos. Sci. Technol.* **2012**, *90*, (4), 1595-1600.

- (7) Zhang, W.; He, X.; Li, C.; Zhang, X.; Lu, C.; Zhang, X.; Deng, Y., High performance poly (vinyl alcohol)/cellulose nanocrystals nanocomposites manufactured by injection molding. *Cellulose* **2014**, 21, (1), 485-494.
- (8) Alexy, P.; Kachova, D.; Kršiak, M.; Bakoš, D.; Šimková, B., Poly (vinyl alcohol) stabilisation in thermoplastic processing. *Polym. Degrad. Stab.* **2002**, 78, (3), 413-421.
- (9) Zhou, X. Y.; Cui, Y. F.; Jia, D. M.; Xie, D., Effect of a complex plasticizer on the structure and properties of the thermoplastic PVA/starch blends. *Polym. Plast. Technol. Eng.* **2009**, 48, (5), 489-495.
- (10) Rogers, R. D.; Seddon, K. R., Ionic liquids--solvents of the future? *Science* **2003**, 302, (5646), 792-793.
- (11) Hayes, R.; Warr, G. G.; Atkin, R. Structure and nanostructure in ionic liquids. *Chem. Rev.* **2015**, 115 (13), 6357-6426.
- (12) Fergus, J. W., Ceramic and polymeric solid electrolytes for lithium-ion batteries. *J. Power Sources* **2010**, 195, (15), 4554-4569.
- (13) Xu, K.; Lu, H.; Kinder, E. W.; Seabaugh, A.; Fullerton-Shirey, S. K., Monolayer Solid-State Electrolyte for Electric Double Layer Gating of Graphene Field-Effect Transistors. *ACS nano* **2017**, 11, (6), 5453-5464.
- (14) Kinder, E. W.; Fuller, A.; Lin, Y.-C.; Robinson, J. A.; Fullerton-Shirey, S. K., Increasing the Room-Temperature Electric Double Layer Retention Time in Two-Dimensional Crystal FETs. *ACS Appl. Mater. Interfaces* **2017**, 9, (29), 25006-25013.
- (15) Saito, Y.; Iwasa, Y., Ambipolar insulator-to-metal transition in black phosphorus by ionic-liquid gating. *ACS nano* **2015**, 9, (3), 3192-3198.

- (16) Díaz, M.; Ortiz, A.; Ortiz, I., Progress in the use of ionic liquids as electrolyte membranes in fuel cells. *J. Membr. Sci.* **2014**, 469, 379-396.
- (17) Jiang, J.; Zhao, W.; Xue, Z.; Li, Q.; Yan, C.; Mu, T., PEGylated Quasi-Ionic Liquid Electrolytes: Fundamental Physiochemical Properties and Electrodeposition of Aluminum. *ACS Sustainable Chem. Eng.* **2016**, 4, (10), 5814-5819.
- (18) Osada, I.; de Vries, H.; Scrosati, B.; Passerini, S., Ionic - Liquid - Based Polymer Electrolytes for Battery Applications. *Angew. Chem. Int. Edit.* **2016**, 55, (2), 500-513.
- (19) Wang, H.; Gurau, G.; Rogers, R. D., Ionic liquid processing of cellulose. *Chem. Soc. Rev.* **2012**, 41, (4), 1519-1537.
- (20) Bendaoud, A.; Chalamet, Y., Effects of relative humidity and ionic liquids on the water content and glass transition of plasticized starch. *Carbohydr. Polym.* **2013**, 97, (2), 665-75.
- (21) Swatloski, R. P.; Spear, S. K.; Holbrey, J. D.; Rogers, R. D., Dissolution of cellulose with ionic liquids. *J. Am. Chem. Soc.* **2002**, 124, (18), 4974-4975.
- (22) Zhang, H.; Wu, J.; Zhang, J.; He, J., 1-Allyl-3-methylimidazolium chloride room temperature ionic liquid: a new and powerful nonderivatizing solvent for cellulose. *Macromolecules* **2005**, 38, (20), 8272-8277.
- (23) Sankri, A.; Arhaliass, A.; Dez, I.; Gaumont, A. C.; Grohens, Y.; Lourdin, D.; Pillin, I.; Rolland-Sabaté, A.; Leroy, E., Thermoplastic starch plasticized by an ionic liquid. *Carbohydr. Polym.* **2010**, 82, (2), 256-263.
- (24) Pinkert, A.; Marsh, K. N.; Pang, S.; Staiger, M. P., Ionic liquids and their interaction with cellulose. *Chem. Rev.* **2009**, 109, (12), 6712-6728.
- (25) Feng, L.; Chen, Z.-l., Research progress on dissolution and functional

modification of cellulose in ionic liquids. *J. Mol. Liq.* **2008**, 142, (1-3), 1-5.

(26) Zhang, X.; Wang, L.; Peng, J.; Cao, P.; Cai, X.; Li, J.; Zhai, M., A Flexible Ionic Liquid Gelled PVA - Li₂SO₄ Polymer Electrolyte for Semi - Solid - State Supercapacitors. *Adv. Mater. Interfaces* **2015**, 2, (15).

(27) Liew, C.-W.; Ramesh, S.; Arof, A., Good prospect of ionic liquid based-poly (vinyl alcohol) polymer electrolytes for supercapacitors with excellent electrical, electrochemical and thermal properties. *Int. J. Hydrogen Energy* **2014**, 39, (6), 2953-2963.

(28) Zhu, M.; Tan, C.; Fang, Q.; Gao, L.; Sui, G.; Yang, X., High performance and biodegradable skeleton material based on soy protein isolate for gel polymer electrolyte. *ACS Sustainable Chem. Eng.* **2016**, 4, (9), 4498-4505.

(29) Gohil, J. M.; Karamanev, D. G., Novel approach for the preparation of ionic liquid/imidazoledicarboxylic acid modified poly (vinyl alcohol) polyelectrolyte membranes. *J. Membr. Sci.* **2016**, 513, 33-39.

(30) Zhang, W.; Yuan, C.; Guo, J.; Qiu, L.; Yan, F., Supramolecular ionic liquid gels for quasi-solid-state dye-sensitized solar cells. *ACS Appl. Mater. Interfaces* **2014**, 6, (11), 8723-8728.

(31) Chen, N.; Li, L.; Wang, Q., New technology for thermal processing of poly (vinyl alcohol). *Plast. Rubber. Compos.* **2007**, 36, (7-8), 283-290.

(32) Wang, R.; Wang, Q.; Li, L., Evaporation behaviour of water and its plasticizing effect in modified poly (vinyl alcohol) systems. *Polym. Int.* **2003**, 52, (12), 1820-1826.

(33) He, P.; Bai, S.; Wang, Q., Structure and performance of Poly (vinyl alcohol)/wood powder composite prepared by thermal processing and solid state shear

milling technology. *Compos. Part B-Eng.* **2016**, 99, 373-380.

(34) Jia, Y.; Bai, S.; Park, C. B.; Wang, Q., Effect of Boric Acid on the Foaming Properties and Cell Structure of PVA Foam Prepared by Sc-CO₂ Thermoplastic Extrusion Foaming. *Ind. Eng. Chem. Res.* **2017**.

(35) Holland, B.; Hay, J., The thermal degradation of poly (vinyl alcohol). *Polymer* **2001**, 42, (16), 6775-6783.

(36) Assender, H. E.; Windle, A. H., Crystallinity in poly (vinyl alcohol). 1. An X-ray diffraction study of atactic PVOH. *Polymer* **1998**, 39, (18), 4295-4302.

(37) Assender, H. E.; Windle, A. H., Crystallinity in poly (vinyl alcohol) 2. Computer modelling of crystal structure over a range of tacticities. *Polymer* **1998**, 39, (18), 4303-4312.

(38) Vraneš, M.; Tot, A.; Armaković, S.; Armaković, S.; Gadžurić, S., Structure making properties of 1-(2-hydroxyethyl)-3-methylimidazolium chloride ionic liquid. *J. Chem. Thermodynamics* **2016**, 95, 174-179.

(39) Liew, C.-W.; Ramesh, S.; Arof, A., A novel approach on ionic liquid-based poly (vinyl alcohol) proton conductive polymer electrolytes for fuel cell applications. *Int. J. Hydrogen Energy* **2014**, 39, (6), 2917-2928.

(40) Mansur, H. S.; Sadahira, C. M.; Souza, A. N.; Mansur, A. A., FTIR spectroscopy characterization of poly (vinyl alcohol) hydrogel with different hydrolysis degree and chemically crosslinked with glutaraldehyde. *Mater. Sci. Eng., C* **2008**, 28, (4), 539-548.

(41) Nishi, T.; Wang, T., Melting point depression and kinetic effects of cooling on crystallization in poly (vinylidene fluoride)-poly (methyl methacrylate) mixtures. *Macromolecules* **1975**, 8, (6), 909-915.

- (42) Nishio, Y.; Haratani, T.; Takahashi, T.; Manley, R. S. J., Cellulose/poly (vinyl alcohol) blends: an estimation of thermodynamic polymer-polymer interaction by melting-point-depression analysis. *Macromolecules* **1989**, 22, (5), 2547-2549.
- (43) Nie, N.; Zheng, D.; Dong, L.; Li, Y., Thermodynamic properties of the water+ 1-(2-hydroxyethyl)-3-methylimidazolium chloride system. *J. Chem. Eng. Data* **2012**, 57, (12), 3598-3603.
- (44) Lewis, C. L.; Stewart, K.; Anthamatten, M., The influence of hydrogen bonding side-groups on viscoelastic behavior of linear and network polymers. *Macromolecules* **2014**, 47, (2), 729-740.
- (45) Xing, K.; Chatterjee, S.; Saito, T.; Gainaru, C.; Sokolov, A. P., Impact of Hydrogen Bonding on Dynamics of Hydroxyl-Terminated Polydimethylsiloxane. *Macromolecules* **2016**, 49, (8), 3138-3147.
- (46) Yan, T.; Schröter, K.; Herbst, F.; Binder, W. H.; Thurn-Albrecht, T., Nanostructure and rheology of hydrogen-bonding telechelic polymers in the melt: from micellar liquids and solids to supramolecular gels. *Macromolecules* **2014**, 47, (6), 2122-2130.
- (47) Mark, J. E.; Erman, B., *Rubberlike elasticity: a molecular primer*. Cambridge University Press: 2007.
- (48) Ramesh, S.; Liew, C.-W.; Ramesh, K., Evaluation and investigation on the effect of ionic liquid onto PMMA-PVC gel polymer blend electrolytes. *J. Non-Cryst. Solids* **2011**, 357, (10), 2132-2138.
- (49) Wojnarowska, Z.; Knapik, J.; Díaz, M.; Ortiz, A.; Ortiz, I.; Paluch, M., Conductivity mechanism in polymerized imidazolium-based protic ionic liquid [HSO₃-BVI_m][OTf]: dielectric relaxation studies. *Macromolecules* **2014**, 47, (12),

4056-4065.

Graphical Abstract

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