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Short communication

1-Allyl-3-methylimidazolium chloride plasticized-corn starch as solid biopolymer electrolytes

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ABSTRACT

Ionic liquids (ILs), 1-allyl-3-methylimidazolium chloride ([amim]Cl) is found to be a novel plasticizer for cornstarch. [Amim]Cl-plasticized starch film also has a potential application as solid biopolymer electrolytes. In this study, different proportional [amim]Cl/glycerol mixtures are used to plasticize starch by casting. Atomic force microscopy (AFM) finds the diameter of residual starch granules existed in [amim]Cl or glycerol-plasticized starch films is only about 10 nm. However, glycerol can form more intensive hydrogen bond with starch than [amim]Cl detected by Fourier transform infrared (FT-IR) spectroscopy. So some novel ILs with high concentration and active hydrogen bond acceptors are necessary. Moreover, high [amim]Cl content can improve the water absorption and conductance of TPS film simultaneously. The conductance of TPS film with 30 wt% [amim]Cl content can achieve to $10^{-1.6}$ S cm^{-1} at 14.5 wt% water content.

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1. Introduction

ILs are salts that remain in the liquid state over a wide temperature range. They have gained in interest because of their unique properties including non-volatility, non-flammability, low viscosity, and chemical and electrochemical stability (Kubisa, 2004; Singh & Sekhon, 2005; Welton, 1999). Some ILs have been proved to dissolve carbohydrate polymers effectively (Cuissinat, Navard, & Heinze, 2008). Because high chloride ion concentration and activity of these ILs can break the extensive hydrogenbonding network and interact with hydroxyl groups of carbohydrate polymers (Swatloski, Spear, Holbrey, & Rogers, 2002). Moreover, ILs also display high ionic conductivity as a result of their high mobility and high concentration of carrier ions. ILs are expected to act as non-volatile and non-flammable electrolyte solutions (Singh & Sekhon, 2005).

Polymer electrolytes obtained from natural polymers such as starch, cellulose, chitosan, pectin and so on, have attracted attention in recent years because of their superior mechanical and electrical properties (Finkenstadt & Willett, 2005). In addition, the efficient utilization of biodegradable polymers from renewable sources is becoming increasingly important due to diminishing resources of fossil fuels as well as white pollution. In the presence of water and plasticizers, starch can be processed into thermoplastic starch (TPS) (Shogren, 1992). Moreover, TPS doped with alkali metal chlorides (LiCl, NaCl and KCl) by using melt extrusion has been prepared as SPE (Ma, Yu, & He, 2006). Starch–glycerol–$LiClO_4$ films prepared by casting also exhibit conductance of around 10^{-5} S cm^{-1} (Lopes, Dragunski, Pawlicka, & Donoso, 2003).

In this study, [amim]Cl is used as a novel plasticizer for cornstarch. With increasing [amim]Cl content, the plasticization of corn starch is discussed with AFM and FT-IR spectroscopy. The relationship between conductive properties of TPS films and [amim]Cl content and water absorption are also studied.

2. Experimental

2.1. Materials

Cornstarch was obtained from Langfang Starch Company (Langfang, Hebei, China). Glycerol and allyl chloride (analytical reagent) were purchased from Tianjin Chemical Reagent Factory (Tianjin, China). 3-methylimidazole (purity >99%, Kaile Chemical Factory, Zhejiang, China) was distilled prior to use. [Amim]Cl was synthesized according to previous report (Wu, Zhang, Zhang, He, Ren, & Guo, 2004) with a melting point of 52 °C: δH (300 MHz, CDCl3) 4.06 (3H, s), 4.94 (2H, d), 5.40 (1H, d), 5.91–5.97 (1H, m), 7.42 (1H, s), 7.65 (1H, s), 10.44 (1H, s).

2.2. Film preparation

The conductive films were prepared by casting. Cornstarch (5 g, dry basis) and 1.5 g plasticizers (the mass ratio of glycerol/[amim]Cl was 1.5/0, 1.0/0.5, 0.5/1.0 and 0/1.5, the relative film

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was named as TPS1, TPS2, TPS3 and TPS4, respectively) were directly mixed with distilled water (100 ml). The mixture was heat at 75 °C with a constant stirring for 30 min. The mixtures were cast into polytetrafluoroethylene plates and placed in an air-circulating oven at 55 °C until dry (about 8 h). The average thickness of dry films was about 0.15 mm. All samples were stored airtight under room temperature immediately.

2.3. Characterization

Agilent 5500 AFM (Agilent Technologies, Tempe, AZ) with 200 μm sharpened Si_3N_4 tips. Small pieces of TPS films ($10 \times 10\ mm^2$) were cut and placed on sample stubs. All images (256×256 pixels) were measured in air in the tapping mode.

FT-IR spectroscopy was obtained at 2 cm^{-1} resolution with BIO-RAD FTS3000 IR Spectrum Scanner (Hercules, USA). Typically, 64 scans were signal-averaged to reduce spectral noise. The samples were tested by attenuated total reflection measurements.

The original water contents of TPS were determined gravimetrically by drying small pieces of TPS at 105 °C overnight. When TPS was stored at the different relative humidity for a period of time, its water content was calculated on the basis of its original weight, its current weight, and its original water content.

Volume resistivity measurements were performed on all the samples. A Model ZL7 electrometer (SPSIC Huguang Instruments and Power Supply Branch) with a four-point test fixture was used. The strips with dimensions of $30 \times 5\ mm^2$ were measured using a Model. Each measurement was performed for five specimens and averaged.

3. Results and discussion

In native form, starch granules are insoluble in cold water. Beyond gelatinization temperature (about 60 °C), starch granules can undergo a disruption into smaller aggregates or particles in the presence of excess of water, and result in gelatinized starch (Cyras, Manfredi, Ton-That, & Vazquez, 2008). The TPS is obtained after disruption and plasticization of native starch, by temperature and in presence of water and another plasticizer.

The average diameter of native cornstarch granules (about 10 μm) had been detected in our previous study (Wang, Yu, Ma, & Han, 2007). Fig. 1a and b shows $50 \times 50\ nm^2$ AFM images of TPS1 and TPS4, respectively. As shown in Fig. 1a and b, a great deal of residual starch granules (about 10 nm) imbedded in TPS matrix, which was only one thousandth of native cornstarch granules. The destruction and plasticization of starch ascribed to the thermomechanical processing, crystal structure of native starch and the intense interaction (hydrogen bonding). However, the average diameter of residual starch granules was similar in TPS1 and TPS4.

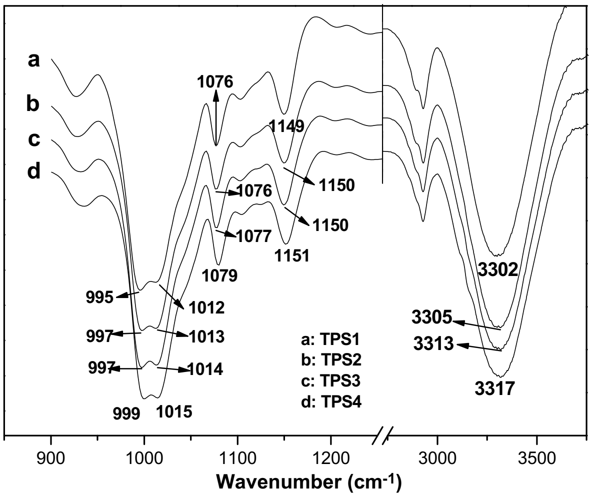

Fig. 2. FT-IR spectra of TPS films.

In addition, formation of homogeneous TPS was a result of strong interactions between starch and plasticizers. The analysis of FT-IR spectra of the blends enabled the interactions to be identified (Wang, Yu, Chang, & Ma, 2008). FT-IR spectra for TPS with different [amim]Cl content are shown in Fig. 2. Three characteristic peaks appeared between 1200 and 900 cm^{-1}, attributed to C–O bond stretching of starch. The characteristic peak at 1150 cm^{-1} was ascribed to C–O bond stretching of C–O–H group in starch, while two peaks at 1080 and 1020 cm^{-1} were attributed to C–O bond stretching of C–O–C group in the anhydroglucose ring. As shown in Fig. 2, those of TPS located at the different wavenumber, because glycerol and [amim]Cl had different hydrogen bond-forming abilities with both O of C–O–H groups and O of O–C anhydroglucose ring groups in TPS films. The lower the peak frequency of C–O group in starch was, the stronger the interaction between starch and plasticizers was (Ma et al., 2006). High glycerol content TPS films were situated at lower wavenumber at these characteristic peaks. Therefore, polyols had stronger hydrogen bond-forming abilities with starch than [amim]Cl. So, ILs contenting hydroxy groups could be used to increase the plasticization of starch.

Fig. 3 shows the water absorption of TPS with different [amim]Cl contents at 50% relative humidity. With increasing

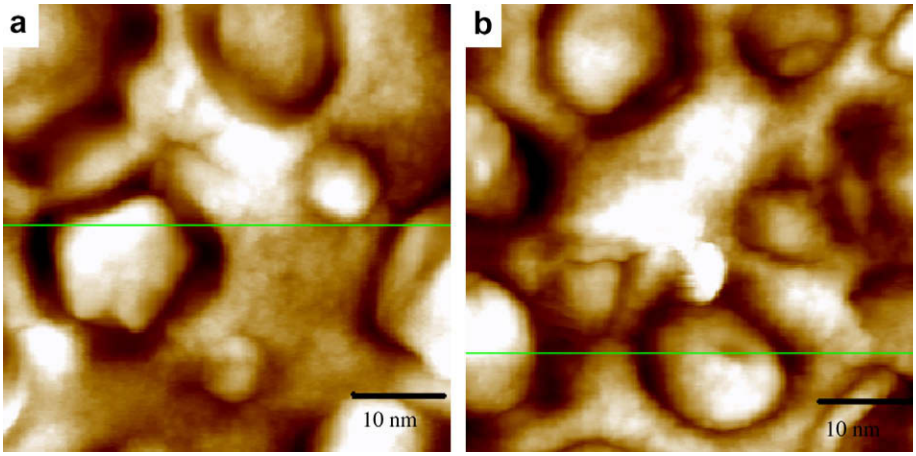

Fig. 1. Morphologies obtained by AFM at room temperature, (a) TPS1; (b) TPS4.

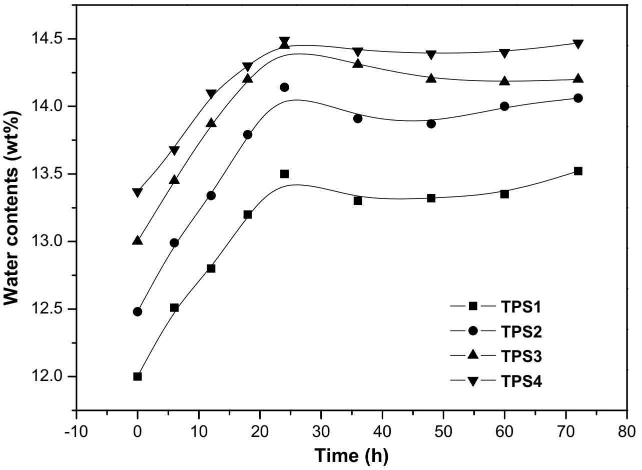

Fig. 3. The relation of water absorption in TPS films with different [amim]Cl content and storage time at RH = 50%.

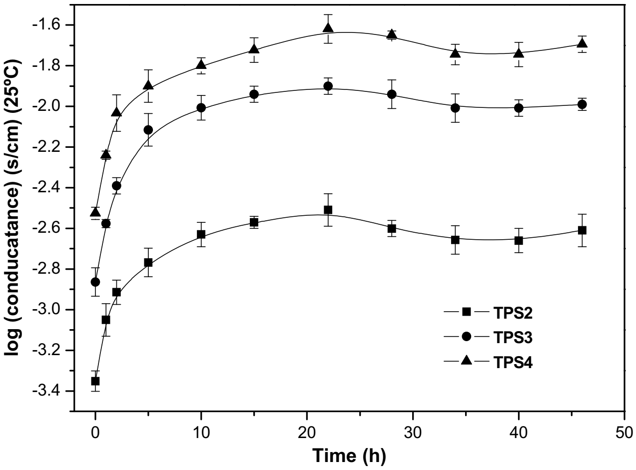

Fig. 4. The electrical conductivity of TPS films with different [amim]Cl content.

[amim]Cl content, the water contents of TPS film improved obviously. It ascribed to the intensive hydrophilicity of [amim]Cl (as shown in Fig. 2, the peak at about 3300 $\mathrm{cm^{-1}}$ ascribed to free, intermolecular, and intramolecular bound hydroxyl groups of starch, water and glycerol, was transferred to the lower frequency with increasing [amim]Cl content).

As shown in Fig. 4, the conductance of TPS was very much dependent on [amim]Cl and water content. Glycerol-plasticized-TPS film was an insulator, even at high water content. The conductance of TPS2 (10 wt% [amim]Cl content) could achieve to $10^{-3.4}\,\mathrm{S\,cm^{-1}}$ at 12 wt% water content. The conductance of TPS4 (30 wt% [amim]Cl content) increased about 1 order at 13.4 wt% water content. It indicated that increasing ion concentration could improve the conductance of TPS film effectively. Moreover, the effect of water contents on the conductance of TPS film was also very obvious. Especially, the improvement in high [amim]Cl content TPS film (from $10^{-2.5}$ to $10^{-1.6}\,\mathrm{S\,cm^{-1}}$) was more obvious than low [amim]Cl content one (from $10^{-3.4}$ to $10^{-2.7}\,\mathrm{S\,cm^{-1}}$). Because the water content increased with improving [amim]Cl content in TPS film at the same storage time as shown in Fig. 3. Water had been recognized as an effective plasticizer to weak the interaction of starch molecules and improve the movement of starch chains (Lourdin, Coignard, Bizot, & Colonna, 1997). So high water content was advantageous to the transference of anion and cation in TPS film. Compared with alkali metal doped TPS (Lopes et al., 2003; Ma et al., 2006), the conductance of ILs-plasticized TPS film was higher.

4. Conclusion

Hydrophilicity [amim]Cl containing high chloride ion concentration had strong hydrogen bond-forming abilities with starch. It could be used to plasticize cornstarch by casting. At the same time, conductive biopolymer could be achieved. Moreover, [amim]Cl and water content exerted an important influence on the conductance of TPS film. The maximum conductance of TPS film could achieve to $10^{-1.6}\,\mathrm{S\,cm^{-1}}$ at 14.5 wt% water content, which was higher than alkali metal doped TPS (Ma et al., 2006). So ILs-plasticized-starch would be a promising alternative for the development of new SPE, which had a wide variety of potential applications such as antistatic plastics, electronic shielding, biosensor, environmentally sensitive membranes and so on.

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