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N, *N*-dimethylacetamide/lithium chloride plasticized starch as solid biopolymer electrolytes

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ABSTRACT

In this study, *N*, *N*-dimethylacetamide (DMAc) with certain concentration ranges of lithium chloride (LiCl) was used to plasticize starch by melting extrusion. Solid state ionic conductors, DMAc-plasticized starch containing LiCl also had a potential application as solid biopolymer electrolytes. Scanning electron microscope (SEM) showed that many remanent starch granules embed in DMAc-plasticized starch matrix. With increasing LiCl content, the number of remanent starch granules decreased dramatically and homogeneous thermoplastic starch (TPS) could be achieved. Moreover, Fourier Transform infrared (FT-IR) spectroscopy revealed that LiCl could increase the interaction between starch and plasticizers. In addition, the supermolecular structure of starch was destructed by LiCl detected by wide-angle X-ray scattering (WAXS) and thermogravimetric analysis (TGA) respectively. Finally, LiCl not only could increase the water absorption of TPS, but also improved the conductance of TPS. The conductance of TPS with 18 wt% LiCl content could achieve to $10^{-0.5}$ S cm^{-1} at 18 wt% water content.

1. Introduction

Solid polymer electrolytes (SPEs) have attracted many attentions as solid state ionic conductors, because of their advantages such as high energy density, electrochemical stability, and easy processing. Moreover, SPEs can be applied as electrical devices such as lithium batteries, electrochemical capacitors and fuel cells (Stephan & Nahm, 2006). Poly(ethylene oxide) (PEO) has been intensively studied as a matrix because of its ability to dissolve a variety of salts, beneficial structure for supporting ion transport, flexibility, high electrochemical stability, ease of preparation and processing into different geometries, and good electrolyte–electrode contact (Florjanczyk, Marcinek, Wieczorek & Langwald, 2004; Stephan & Nahm, 2006). However, the most significant disadvantage of the PEO-based polymer electrolytes is its poor ionic conductivity at ambient temperature. So considerable researches have been paid to find other polymers to overcome the disadvantage of PEO-based SPEs. The room temperature conductance of SPEs based on branched polymers can reach to 10^{-5} S cm^{-1}, which is attributed to its lower crystalline degree (Wang, Chen, Hong & Tang, 2001).

SPEs obtained from starch have attracted attentions in recent years because of its abundant, renewable, low price, biodegradable and biocompatible (Lopes, Dragunski, Pawlicka & Donoso, 2003; Ma, Yu & He, 2006). Native starch can be processed to thermoplastic starch (TPS) by melting extrusion or casting (Averous, 2004). TPS doped with alkali metals offer a promising alternative for the development of novel SPEs. As previous report, the conductance of glycerol plasticized amylopectin-rich starch doped with $LiClO_4$ is around 10^{-5} S cm^{-1} (Lopes et al., 2003). Moreover, high environment humidity can dramatically improve the conductance of metal halides doped TPS-based SPEs (Ma et al., 2006). At the same time, the development of novel plasticizers for starch, not only increase the performance of TPS, but also unexpected property can be achieved. In our previous work, ionic liquids, 1-allyl-3-methylimidazolium chloride has been used to prepare solid biopolymer electrolytes based on starch (Wang, Zhang, Liu, & He, in press).

DMAc within certain concentration ranges of LiCl is a solvent system that has been utilized to dissolve natural crystalline polysaccharides (Poirier & Charlet, 2002; Sjoholm, Gustafsson, Eriksson, Brown & Colmsjo, 2000). A generally accepted dissolution mechanism as following: Li^+ is tightly linked with the carbonyl group of DMAc while the Cl^- is left unencumbered. Thereby Cl^- is highly active as nucleophilic base and plays a major role by breaking up the inter- and intra-hydrogen bonds existed in nature polymers (Dupont, 2003). So in this study, DMAc and DMAc/LiCl mixtures with different LiCl contents are used as a novel plasticizer to prepare ionic conductive TPS by melting extrusion. With increasing LiCl content, the plasticization of starch is discussed with SEM and FT-IR spectroscopy. The supermolecular structure and thermal stability of extruded TPS are also characterized by WAXS and TGA, respectively. The relationship between conductive properties of TPS and water absorption are studied.

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2. Experimental

2.1. Materials

Cornstarch (25 wt% amylose and 13 wt% water content) was obtained from Langfang Starch Company (Langfang, Hebei, China). DMAc and LiCl (analytical reagent) were purchased from Tianjin Chemical Reagent Factory (Tianjin, China).

2.2. Samples preparation

LiCl was oven-dried and stored in a desiccator over drier ($CaCl_2$). DMAc mixed with different LiCl contents (3, 6, 9, 12, 15 and 18 wt% based on DMAc) were heat up to 80 °C to form homogeneous viscous solution. The hot DMAc/LiCl mixtures were blended (3000 rpm, 2 min) with starch by using of High Speed Mixer GH-100Y (Beijing, China) immediately. The mixtures stored airtight until homogeneous systems were obtained. The sample codes and components were listed in Table 1. The conductive TPS were prepared as following: the mixtures were fed into the single-screw plastic extruder SJ-25(s) (Screw Ratio L/D = 25:1, Beijing, China). The screw speed was 10 rpm. The temperature profile along the extruder barrel was 130, 140, 150, and 130 °C (from feed zone to die). The die was metal plate of 10 mm thick with eight holes of 3 mm diameter. The samples were stored airtight immediately. When the samples reached room temperature (about 25 °C), the extruded strips were pressed into sheets with Flat Sulfuration Machine (Tianjin, China) and cut into tensile bars with certain size and stored in desiccator under room temperature immediately. The properties test would go on after 1 week.

2.3. Characterization

SEM was used to characterize the microstructure of SPEs. SEM was performed with a Quanta 200 microscope (FEI Company, USA). The samples were cooled in liquid nitrogen, and then broken. The fracture faces were coated with gold under vacuum for SEM observation.

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.

TGA was carried out on STA409PC thermal analysis instrument (Netzsch, Germany). TPS was cut into small pieces. The samples were about 5–10 mg in a sealed aluminum pan; the range of testing temperature was from room temperature to 600 °C at a heating rate of 15 °C min^{-1}.

WAXS patterns were measured using a Rigaku D/Max 2500V PC X-ray diffractometer (Rigaku, Tokyo, Japan) (40 kV, 100 mA) equipped with a Ni-filtered Cu radiation and a curved graphite crystal monochromator. The diffractometer was equipped with 1° divergence slit, a 0.16 mm receiving slit and a 1° scatter slit.

The water absorptions of TPS were determined gravimetrically by storing small pieces of TPS at 50% relative humidity (35.64 wt% $CaCl_2$ solution) for a period of time, its water content was calculated on the basis of its original weight and its current weight, respectively.

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.

Table 1
The symbols and composition of solid biopolymer electrolytes.

Code	Starch (wt%)	DMAC (wt%)	LiCl (wt%)
TPS0	200	60	–
TPS1	200	60	1.8
TPS2	200	60	3.6
TPS3	200	60	5.4
TPS4	200	60	7.2
TPS5	200	60	9.0
TPS6	200	60	10.8

3. Results and discussion

Native cornstarch exists in the form of solid granules (the diameter is about 10 μm) and cannot be processed as a thermoplastic material because of its strong inter- and intra-molecular hydrogen bonds (Wang, Yu, Ma & Han, 2007). Fig. 1a–d shows SEM images of TPS0, TPS2, TPS4 and TPS6, respectively. As shown in Fig. 1a–d, TPS presented a continuous phase after melting extrusion. However, most starch granules were only partly destroyed and embedded in a partially plasticized starch matrix under high shear rates and high temperature as shown in Fig. 1a. So DMAc could be recognized as a less effective plasticizer for starch. Formamide has been used to plasticize starch effectively in previous report (Ma & Yu, 2004). Therefore, DMAc combined with LiCl was used as a complex plasticizer for starch in this paper.

As shown in Fig. 1b–d, the fracture surfaces of TPS became smooth with increasing LiCl contents. At the same time, the number of residual starch granules in TPS decreased dramatically. Finally, a homogeneous TPS6 could be achieved (Fig. 1d). This was attributed to LiCl could form macro-cation complexation with DMAc and left the Cl^- free. It was more effective than DMAc to interrupt the inter- and intra-molecular hydrogen bonding existed in starch. Therefore, a high plasticized starch could be achieved by extrusion.

In order to identify the complex interactions in DMAc/LiCl plasticized starch, FT-IR analysis was used. In addition, formation of homogeneous TPS was a result of strong interactions between starch and plasticizers. The analysis of FT-IR spectra of these blends enabled the interactions to be identified (Wang, Yu, Chang & Ma, 2008). FT-IR spectra for DMAc-plasticized starch with different LiCl contents 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, 1020 and 990 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 wavenumbers, because DMAc containing different LiCl contents had different hydrogen bond-forming abilities with both O of C–O–H groups and O of O–C anhydroglucose ring groups in TPS. 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). These characteristic peaks of TPS with high LiCl content were situated at lower wavenumber. It suggested that increasing LiCl content could improve the hydrogen bonding interaction in TPS. Because Li^+ could complexes with the carbonyl atoms of DMAc molecules to produce a macro-cation and left the Cl^- free to hydrogen bond with the hydroxyl or carbonyl of starch. This competitive hydrogen bond formation served to disrupt the intra- and inter-molecular hydrogen bonding existed in starch.

TGA and derivative thermogravimetry (DTG) curves were performed to detect the thermal stability of DMAc/LiCl plasticized starch. As shown in Fig. 3, the thermal decomposition of TPS followed three decomposition steps at about 100, 160 and 300 °C corresponding to the water loss, DMAc evaporation (the evaporation point of DMAc is about 164 °C) and polysaccharide thermal

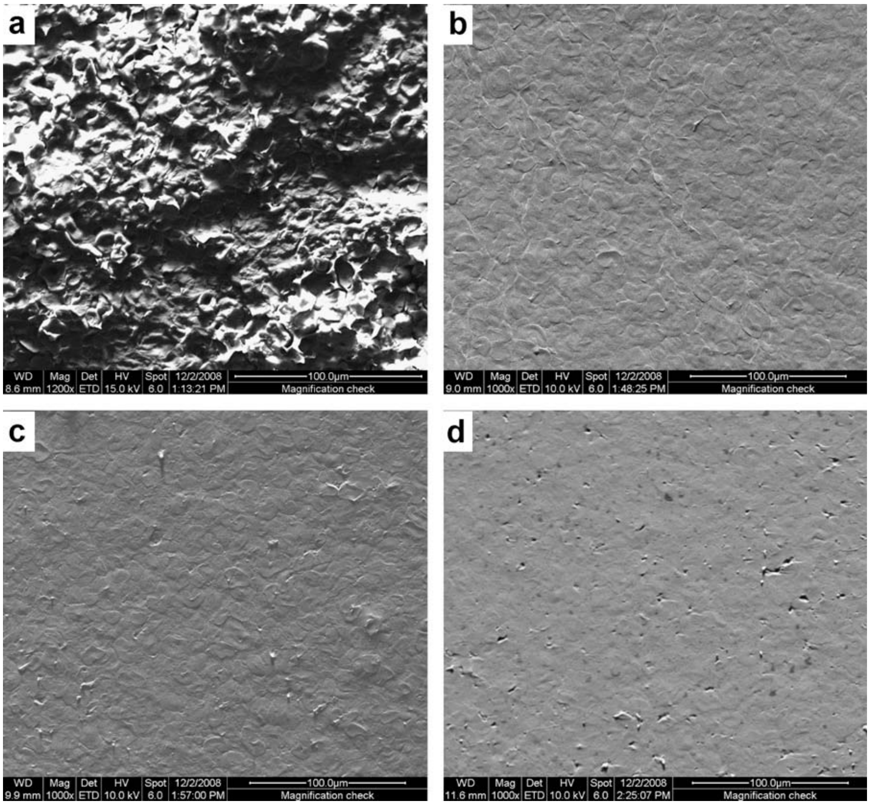

Fig. 1. The SEM photographs of TPS0, TPS2, TPS4 and TPS6. (a) TPS0; (b) TPS2; (c) TPS4; and (d) TPS6.

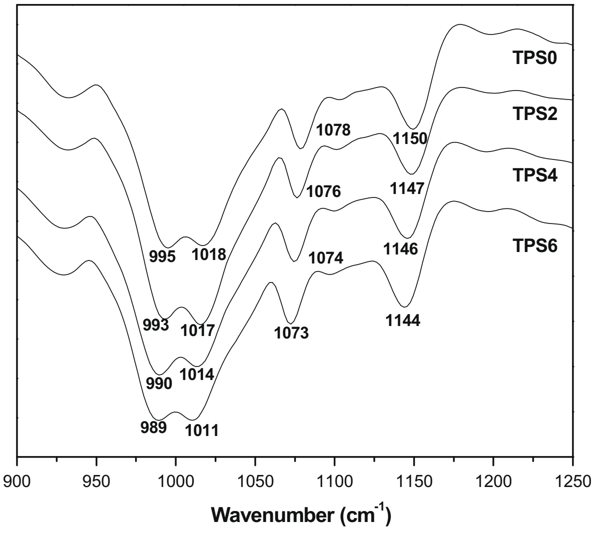

Fig. 2. FT-IR spectra of SPEs based on TPS.

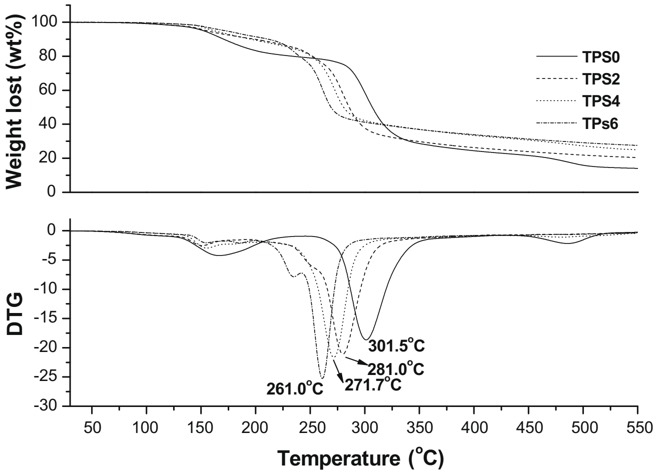

Fig. 3. TGA for TPS0, TPS2 TPS4 and TPS6.

depolymerization, respectively. As shown in Fig. 3, LiCl could dramatically decrease the evaporation of DMAc. It attributed to DMAc complexes with Li^+ to form macro-cation in TPS.

Moreover, the maximum decomposition temperature ($T_{\max}$, determined from the max peak of DTG curve in Fig. 3) of TPS shifted to low temperature with increasing LiCl content. It attributed to DMAc/LiCl depolymerized starch after melting extrusion, especially TPS6 with the highest LiCl concentration. As previous report (Potthast, Rosenau, Sixta & Kosma, 2002a), the depolymerization of cellulose becomes more pronounced as temperature and LiCl content increased, and becomes rather severe at temperatures near the boiling point of DMAc. Because DMAc reacts with the reducing ends in pulp to produce furan structures at temperatures above approx 80 °C. At higher temperatures above 130 °C, these furan structures are released as *N*, *N*-dimethyl-[2-methyl-5-(1, 2, 3, 4-tetrahydroxybutyl)-3-furyl]formamide, which is able to cleave glycosidic bonds. So high LiCl concentration could cause starch degradation and influence the molecular weight distribution of TPS during melting extrusion.

Native cornstarch is of the A-style crystallinity (van Soest, Hulleman, de Wit & Vliegenthart, 1996). In the melting extrusion, plasticizers and water molecules entered into starch granules, and replaced starch inter- and intra-molecular hydrogen bonds and destructed the crystallinity of starch. Both A-style and V_H-style crystal peaks could be detected by WAXS (Fig. 4). As shown in Fig. 4, intensive residual A-style crystallinity was observed in TPS, especially in TPS0. It ascribed to the poor plasticization effect of DMAc. Many starch granules only partly destroyed and embedded in partial plasticized starch matrix had been detected by SEM (Fig. 1a). However, the intensity of A-style crystallinity decreased and some of them disappeared with increasing LiCl content. Because high concentrated LiCl could destruct the supermolecular structure of starch during melting extrusion. So DMAc was propitious to permeate into starch granules and form strong and stable hydrogen bonds with starch in the presence of LiCl. It had been proved by FT-IR analysis. In addition, the decreasing crystallinity could improve the movement of starch molecules and ionic conductivity (Ma et al., 2006).

Fig. 5 shows the water absorption of TPS with different LiCl contents at 50% relative humidity. With increasing LiCl content, the water contents of TPS improved obviously. It ascribed to the intensive hydrophilicity of LiCl. Moreover, the formed macro-cation based on DMAc could increase the hydrophilicity of DMAc in high LiCl concentration TPS. As previous report (Smits, Kruiskamp, van Soest & Vliegenthart, 2003), high water content could decrease the glass transform temperature (T_g) and improve the movement of starch molecules. So high water content could improve the ionic conductivity of TPS.

Fig. 6 mainly studies the relationship between the conductance of TPS with different LiCl contents and water absorptions. As shown in Fig. 6, the conductance of TPS was very much dependent on LiCl and water content. DMAc-plasticized starch was an insulator, even at high water content. The initial conductance of TPS1 could achieve to about $10^{-4.5}$ S cm^{-1} when 3 wt% LiCl based on DMAc was added. With increasing LiCl content, the conductance of TPS improved. The maximum conductance of TPS6 could improve to about $10^{-2.8}$ S cm^{-1}. However, the improvement of initial conductance was not obvious when LiCl content exceeded 9 wt%. As previous report (Potthast et al., 2002b), the limiting soluble concentration of LiCl in absolutely dry DMAc is 8.46 wt%. So only partial LiCl could be dissolved by remanent water existed in TPS when LiCl content exceeded 9 wt%.

Moreover, water content exerted a pronounced improvement on the conductance of TPS. It increased about 1.5–2.5 orders of magnitude from the initial water content to the max water content, respectively. So the effect of water content on the conductance of TPS was very obvious. The increasing water absorption could dissolve remanent LiCl and increase ion concentration. In addition, water could form the interaction with starch, weaken the interaction of starch molecules, and improve the movement of starch chain (Smits et al., 2003). It was advantageous to the transference of ion in TPS. At the time, the effect of water absorptions on the conductance at the low water content was more obvious than one at the high water content. It ascribed to high water absorption decreased the ion concentration excessively.

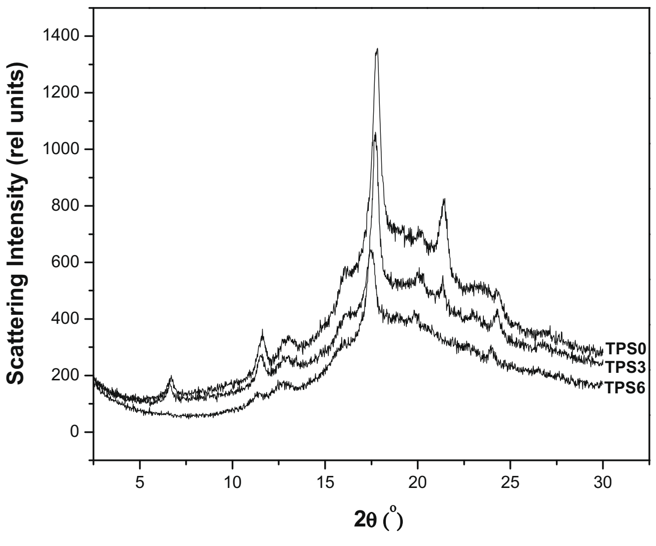

Figure 4. Wide-angle X-ray scattering curve for TPS.

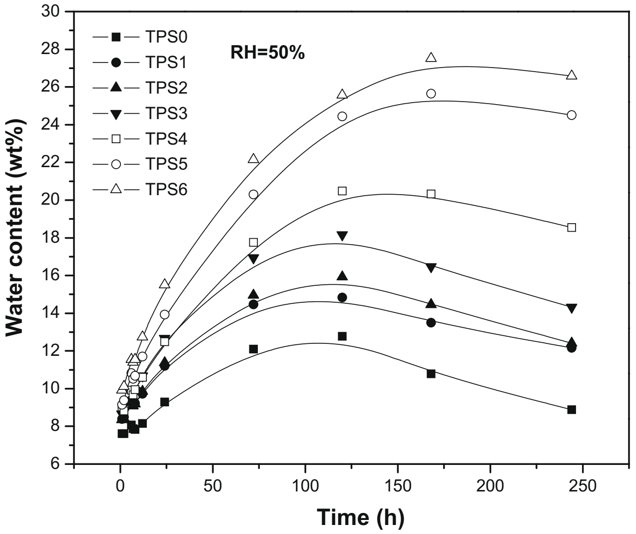

Fig. 5. The relation of water content in TPS with different LiCl content and storage time at RH = 50%.

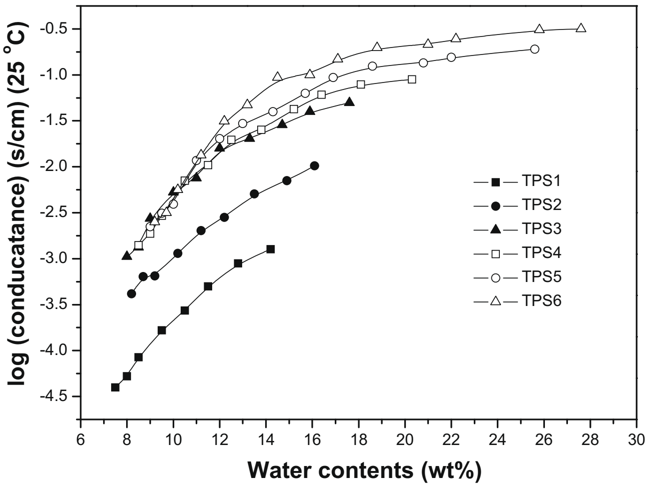

Fig. 6. The electrical conductivity of TPS with different LiCl and water contents.

4. Conclusion

DMAc was proved to be a less effective plasticizer for starch. However, DMAc containing high LiCl concentration had strong hydrogen bond-forming abilities with starch, which could plasticize starch effectively. DMAc/LiCl mixture could be used to prepare ionic conductive TPS by melting extrusion. Moreover, high concentration LiCl could improve the thermal stability of DMAc. On the other hand, the thermal depolymerization of starch became more pronounced with increasing LiCl content. LiCl could also decrease the crystallinity of TPS accompanying with the destructed supermolecular structure of starch. In addition, the improvement of LiCl content not only increased the water absorption of TPS, but also improved the conductance of TPS. At the same time, water absorption also exerted an obvious improvement on the conductance of TPS. The conductance of TPS6 increased about 2.5 orders of magnitude from the initial water content to the max water absorption. So DMAc/LiCl plasticized starch would be a promising alternative for the development of new SPEs, 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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