



Nature of phase transitions of waxy maize starch in water-ionic liquid mixtures

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ABSTRACT

The nature of phase transitions of waxy maize starch heated in mixtures of water and ionic liquid (IL) was elucidated using a variety of analytical methods. The transition from a single endotherm to an exotherm followed by an endotherm, and then to a single exotherm was observed with the increasing concentration of IL. The results showed that at T_o of DSC phase transition no structural disruption had occurred. Except for the water/IL ratios of 1.5:1 and 1:1, there was considerable structural disruption of starch samples that were preheated to T_p or T_{p2} of gelatinization transition. No residual structural order was observed at T_c of the gelatinization transition. An exothermic transition at water:IL ratios of 3:1 and 2:1 was attributed to the interaction of ionic liquid and amorphous regions in starch. The molecular disassembly of starch granules during gelatinization in different water:IL mixtures proceeded to completion at different rates.

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1. Introduction

Growing environmental concerns about usage of fossil fuels have prompted increasing interest in alternative and more sustainable non-petroleum based natural resources [1]. Biodegradable polymers obtained from renewable resources are seen as a viable alternative to petroleum-derived polymers due to their more ecologically-friendly properties [2]. Polysaccharides and proteins are often regarded as renewable resources that have advantages of biodegradability [3–5]. In this regard, starch is a polysaccharide receiving considerable attention as a potential alternative to traditional petroleum-based materials [6–8].

Starch is a semicrystalline polymer, which is formed by essentially linear amylose and highly branched amylopectin molecules. Despite the simple composition, starch granules in nature present as very complicated hierarchical structures, which are studied on size scales that range from nano- to micrometer [9,10]. This multi-scale structural order in granules plays a key role in determining functionality and suitability for different applications of starch as a raw material in food industries [11] and for the fabrication of biologically degradable materials [12]. There is considerable interest in developing novel and

environmentally friendly solvents or plasticizers for transforming native starch granules into versatile products with desirable end-use properties [5,13]. This involves dissolving or plasticizing the starch in various ways. Starch plasticizers in use typically include polyols (for example, glycerol, glycol, sorbitol) or amine-containing compounds (urea, amides) [12,13]. There are also various types of solvents employed to dissolve starch, of which dimethyl sulfoxide (DMSO) and strong inorganic alkalis (e.g., KOH and NaOH) are used most commonly [14]. Novel solvents, such as *N*-methylmorpholine-*N*-oxide (NMMO) [15] and molten imidazole [14] have also been considered for their potential ability to dissolve starch granules [14–17]. Understanding the structural changes of starch during phase transitions in such solvent systems will open the way for the preparation of starch solutions for applications that require well-defined starch properties.

Ionic liquids (ILs) are a class of organic salts with a melting point below 100 °C [17]. They consist of an organic cation and an organic or inorganic anion and have potential as readily recyclable alternatives to traditional organic solvents [2,18,19]. Ionic liquids have recently attracted much interest due to their efficacious dissolution of polysaccharides, such as cellulose [20–22], lignocellulosic materials [23–25], starch [26–29] and chitin and chitosan [30]. Some ILs (containing Cl^- or Ac^- anions) can disrupt hydrogen bonds between hydroxyl groups of starch and thereby disrupt the semicrystalline structure of native starch granules at room temperature [27,31–34].

There have been numerous studies on the effects of ILs or IL-water mixtures on the gelatinization behavior of starch [16,35,36].

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These studies have focused on the thermal transition profiles of starch measured by differential scanning calorimetry (DSC), but have not delved into underlying the structural changes of the starch during phase transitions. The nature of these phase transitions of starch in ILs or IL-water mixtures remains to be revealed. Hence, the aim of the present study was to elucidate for the first time the structural changes that occur during phase transitions of starch in a complete range of IL-water mixtures. The starch used was from waxy maize, which is mainly composed of amylopectin and has a higher amount of ordered structures compared with normal or high-amylose starch.

2. Materials and Methods

2.1. Materials

Waxy maize starch (WMS, 0.3% amylose and 7.6% moisture content) was kindly provided by National Starch Specialties Ltd. (Shanghai, China). *N*-Methyl-imidazole, 3-chloro-propylene was supplied by SigmaChemical Co. (St Louis, MO, USA). Other chemical reagents were all of analytical grade.

2.2. Preparation of ionic liquid [AMIM]Cl

N-Methyl-imidazole (4.11 g, 0.05 mol), 3-chloro-propylene (4.60 g, 0.06 mol) and 20 mL ethyl acetate were added into a three-necked flask equipped with a mechanical stirrer and a water condenser. The reaction was conducted at 60 °C for 6 h under nitrogen atmosphere. The excess 3-chloropropylene was removed by distillation and the unreacted *N*-methyl-imidazole was extracted with ethyl acetate. The resulting viscous yellow ionic liquid was dried under vacuum for 48 h [37,38]. The AMIMCl prepared in this way was characterized by ¹H NMR and ¹³C NMR (Supplementary Fig. 1), which showed that AMIMCl had a purity of 95% and was suitable for use in subsequent experiments.

2.3. Differential scanning calorimetry

Differential scanning calorimetry (DSC) measurements were performed using a Differential Scanning Calorimeter (200F3, Netzsch, Germany) equipped with a thermal analysis data station. Native starch (approximately 3.0 mg) was weighed accurately into the aluminum sample pans. The distilled water/IL mixtures (3 times the weight of starch) were added in the DSC pans. The pans were shaken gently to ensure complete immersion of starch in the liquid, sealed, and the DSC profile recorded immediately. The pans were heated from 20 to 120 °C at a rate of 10 °C/min. A ratio of water/IL: starch of 3:1 (w/w) was used in the DSC measurements. An empty aluminum pan was used as the reference.

The Universal Analysis 2000 software was used to analyze the single endotherm and exotherm of the DSC profiles for onset (T_o), peak (T_p), and conclusion (T_c) temperatures and enthalpy change (ΔH). The definition and determination of these parameters are described in detail in Wang & Copeland (2012) [39]. For water/IL ratios of 3:1 and 2:1, the thermograms were more complex. For these transitions, five temperatures were defined and determined. T_o is defined as the onset temperature of initial exotherm, and T_c is defined as the conclusion temperature of gelatinization subsequent endotherm. T_{p1} represents the peak temperature of exothermic peak, T_{p2} represents peak temperature of endothermic peak, and T_m represents the mid-point temperature between T_{p1} and T_{p2} .

2.4. Preparation of starch samples using the RVA instrument

To obtain sufficient material to characterize structural changes of starch during DSC phase transitions, samples were prepared by heating water/IL-starch systems in a RVA instrument without stirring under the same heating profile described above for DSC measurements [40]. For the starch-pure IL mixture, an oil bath with heating control system was used to prepare sample that was heated to T_c , because the highest heating temperature of RVA was set as 95 °C. Approximately 1 g of native starch was weighed accurately into an RVA canister and the water/IL was added with a pipette to obtain the liquid: starch ratio of 3.0 (w/w). The mixture in the canister was agitated gently with a glass rod before heating separately to T_o , T_p , and T_c with the paddle immobilized. For the mixtures of water/IL of 3:1 and 2:1, starch samples were also heated to T_{p1} , T_m and T_{p2} . After heating to the designated temperatures, starch samples were washed in 25 mL of absolute ethanol with stirring and centrifuged at 6800g for 15 min to remove the IL. This washing process was repeated two times and the residual ethanol evaporated in the fume hood overnight. After adding three volumes of deionized water, starch was freeze-dried, ground into a powder, and passed through a 100 μ m sieve. For starch-water systems, the heated starch samples were freeze-dried without washing in ethanol.

2.5. FTIR spectroscopy

The FTIR spectra of freeze-dried starch samples after RVA heating were obtained using a Tensor 27 FTIR spectrometer (Bruker, Germany) equipped with a KBr beam splitter and a DLATGS detector. The spectra were scanned in the range of 4000–400 cm^{-1} , with an accumulation of 64 scans and a resolution of 4 cm^{-1} . All spectra were automatically baseline-corrected in the range of 1200 and 800 cm^{-1} by OMNIC 8.0 before being deconvoluted with a half-band width of 19 cm^{-1} and an enhancement factor of 1.9. The ratio of absorbances at 1047/1022 cm^{-1} was used to estimate the short-range ordered structure of starch [41].

2.6. Laser confocal micro-Raman (LCM-Raman) spectroscopy

Raman spectra of freeze-dried starch samples were obtained using a Renishaw Invia Raman microscope system (Renishaw, Gloucestershire, United Kingdom) equipped with a Leica microscope (Leica Biosystems,

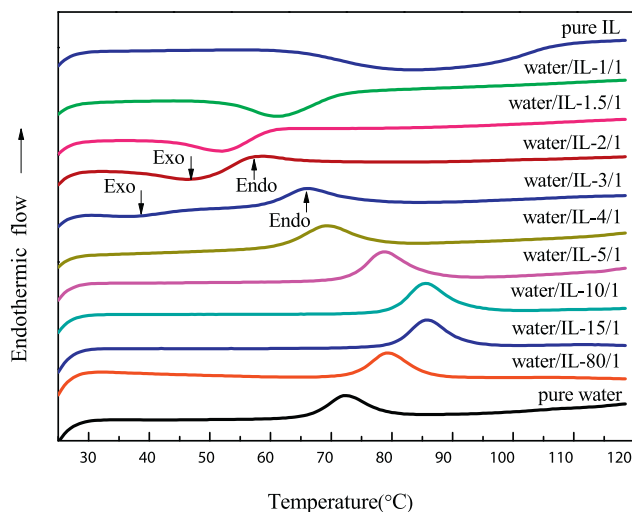


Fig. 1. DSC thermograms of waxy maize starch in water/IL mixtures. The numbers above the curves indicate the mole ratios of water/IL.

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