Dissolution Behavior of Maize Starch in Aqueous Ionic Liquids: Effect of Anionic Structure and Water/Ionic Liquid Ratio

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ABSTRACT: The effect of the anionic structure of ionic liquids (ILs) and water/IL ratio on the dissolution behavior of maize starch at room temperature (22−23 °C) was investigated. The ILs used were 1-ethyl-3-methylimidazolium chloride ([C2 mim][Cl]), 1-ethyl-3-methylimidazolium formate ([C2 mim][HCOO]), and 1-ethyl-3-methylimidazolium acetate ([C2 mim][CH3COO]). The structural analysis indicated that the long- and short-range molecular order in the starch after treatment with water/[C2 mim][Cl] and water/[C2 mim][HCOO] mixtures decreased with the decreasing water/IL ratio from 10:1 to 2:1 and was completely disrupted at the 2:1 ratio. However, the ordered structure of starch was disrupted completely in the water/[C2 mim][CH3COO] ratio of 5:1. The disruption extent of starch structures followed the order: [C2 mim][CH3COO] > [C2 mim][HCOO] > [C2 mim][Cl] at water/IL ratios of 10:1 and 5:1, but the opposite was observed at lower water/IL ratio (2:1). Our results clearly showed that both the nature of the anion and water/IL ratio affected the dissolution behavior of maize starch. The hydrogen bonding capacity of IL anions and viscosity of water/IL mixtures were proposed to play the key roles in the structural disruption of starch. These findings would be of great importance for rationally designing “green and sustainable” processes for the utilization of promising natural biopolymers.

INTRODUCTION

The utilization of natural biopolymers (e.g., cellulose, starch, chitosan etc.) to replace synthetic polymers for the manufacture of green materials has recently gained worldwide interest due to growing global environmental awareness, concepts of sustainability, and avoiding conflict between production of food and raw materials for industry.1 Starch is one of the most abundant, inexpensive, and renewable natural polymers that has been utilized widely in the food, chemistry, fermentation, paper, and pharmaceutical industries.5 Native starch is composed of amylose and amylopectin, which are arranged into semicrystalline granules, which are studied at structural scales ranging from nanometer to micrometer.1 The multiscale structures of starch are the major determinants of starch functionality for industrial applications.4 The insolubility of starch in most traditional solvents, due to the extensive hydrogen bonding in native granules, limits its applications.5 Conventional solvents for starch dissolution, for example, dimethyl sulfoxide, N-methylmorpholine N-oxide, and N,N-dimethylacetamide, have limitations and disadvantages, such as, volatility, flammability, and not being recyclable.6 Finding an environmentally friendly solvent for starch dissolution is an important task for expanding starch applications.

Ionic liquids (ILs), which consist of an organic cation and an organic or inorganic anion, are attracting attention as replacements for volatile organic solvents for dissolving polysaccharides because of their desirable physicochemical properties such as negligible vapor pressure, nonflammability, high chemical stability, recyclability, and miscibility.7,8 They have been called “designer solvents” because their physico-chemical properties can be tailored by appropriate selection of the cations and anions.9 ILs have been shown to dissolve starch from different sources10 with the ability to disrupt hydrogen bonds in polysaccharide molecules, which is considered the main factor for their dissolution efficacy.11,12 Carboxylate-based ILs are seen as more promising in green chemistry than commonly used chloride-containing ILs due to desirable properties of low toxicity, low corrosiveness, favorable enzyme-compatibility, and biodegradability.13−15

Over the past few years, the use of ILs in dissolution, modification, and plasticization of starch has received considerable attention.16,17 Although starch can be dissolved in pure ILs, high-energy input is still required to achieve
complete dissolution mainly due to the high viscosity of pure ILs. Hence, developing milder conditions for starch dissolution is of great importance for green and sustainable industrial applications of starch. Recently, the use of water/IL mixtures for starch dissolution at ambient temperature has attracted considerable interest. For example, maize starch was completely dissolved in mixtures of 1-ethyl-3-methylimidazolium acetate ([Emim][OAc]) and water at 28 °C and 1-ethyl- or propyl-3-methylimidazolium chloride ([Emim][Cl] or [Pmim][Cl]) and water at 22–23 °C. However, in another study, a mixture of 1-allyl-3-methylimidazolium chloride ([Amim][Cl]) and water only partially dissolved maize starch at 25 °C. Studies using undiluted ILs have shown the anionic moiety of the IL to have an important role in the dissolution of nonstarch polysaccharides. However, there are few reports that compare the effect of different anions in undiluted ILs or water/IL mixtures on the dissolution behavior of starch.

In our previous work, the effect of alkyl chain length of cations in undiluted or water/IL mixtures on the dissolution behavior of maize starch was studied at ambient temperature. The aim of the present study was to investigate the effect of the anion moiety of ILs and water/IL ratio on the dissolution behavior of starch. To better understand the dissolution progression, the changes of multiscale structures of maize starch before and after treatment in different water/IL mixtures were characterized, as was the effect of the viscosity of water/IL mixtures.

## RESULTS AND DISCUSSION

### Dissolution of Starch in Different Water/IL Mixtures

The extent of starch dissolution in water/[C2mim][Cl] and water/[C2mim][HCOO] mixtures increased with decreasing water/IL ratio. No undissolved starch was observed in these two mixtures at a water/IL ratio of 2:1 (Figure 2), indicating that the starch was completely dissolved. In contrast, no undissolved starch was observed in the 5:1 water/[C2mim]-[CH3COO] mixture, whereas in other two mixtures of 10:1 and 2:1, starch granules were still visible clearly. This indicated that the starch was completely dissolved in water/[C2mim]-[CH3COO] mixture of 5:1, but not in the 10:1 and 2:1 mixesures (Figure 2).

### Long-Range Crystalline Structure of Starch

The X-ray diffraction (XRD) patterns and relative crystallinity of native starch and starch samples after treatment with water/IL mixtures are presented in Figure 3 and Table 1, respectively. Native maize starch displayed a typical A-type diffraction pattern, with relative crystallinity of 28.5%. After treatment with water/[C2mim][Cl] and water/[C2mim][HCOO] mixtures, the main diffraction peaks of starch crystallites gradually became weaker and then disappeared as the water/IL ratio decreased from 10:1 to 2:1. Interestingly, the starch treated with water/[C2mim][CH3COO] mixture did not show a similar trend. Starch showed an amorphous XRD pattern after treatment with water/[C2mim][CH3COO] mixture of 5:1 (Figure 3), but some crystallinity, albeit a lower value, was still evident after treatment with water/[C2mim][CH3COO] mixtures of 10:1 (10.7%) and 2:1 (20.9%). Thus, at water/IL ratios of 10:1 and 5:1, the extent of disruption of starch crystallinity followed the order [C2mim][CH3COO] > [C2mim][HCOO] > [C2mim][Cl], whereas at a water/IL ratio of 2:1, no crystallinity was detected in starch treated with water/[C2mim][Cl] and water/[C2mim][HCOO] mixtures, but crystallinity was still present in starch after treatment with water/[C2mim][CH3COO] mixture (Figure 3).

### Thermal Properties of Starch

Native maize starch displayed a typical A-type diffraction pattern, with relative crystallinity of 28.5%. After treatment with water/[C2mim][Cl] and water/[C2mim][HCOO] mixtures, the main diffraction peaks of starch crystallites gradually became weaker and then disappeared as the water/IL ratio decreased from 10:1 to 2:1. Interestingly, the starch treated with water/[C2mim][CH3COO] mixture did not show a similar trend. Starch showed an amorphous XRD pattern after treatment with water/[C2mim][CH3COO] mixture of 5:1 (Figure 3), but some crystallinity, albeit a lower value, was still evident after treatment with water/[C2mim][CH3COO] mixtures of 10:1 (10.7%) and 2:1 (20.9%). Thus, at water/IL ratios of 10:1 and 5:1, the extent of disruption of starch crystallinity followed the order [C2mim][CH3COO] > [C2mim][HCOO] > [C2mim][Cl], whereas at a water/IL ratio of 2:1, no crystallinity was detected in starch treated with water/[C2mim][Cl] and water/[C2mim][HCOO] mixtures, but crystallinity was still present in starch after treatment with water/[C2mim][CH3COO] mixture (Figure 3).

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Maltese cross patterns (Figure 6a-1), whereas SEM showed both angular and spherical-shaped granules (Figure 6a-2). After treatment with water/[C₃mim][Cl] and water/[C₃mim][HCOO] mixtures, the granular morphology and “Maltese cross” patterns became increasingly blurred with the decreasing water/IL ratio. However, granule morphology of starch treated with water/[C₃mim][CH₃COO] mixture of 5:1 was disrupted more than starch treated with the 10:1 and 2:1 mixtures. When the “Maltese cross” patterns disappeared, no intact granules were observed for starch treated with 2:1 water/[C₃mim][CH₃COO] mixture (Figure 6d-2). However, the granule contours were still visible for the starch treated with 2:1 water/[C₃mim][HCOO] and 5:1 water/[C₃mim][CH₃COO] mixture (Figure 6g-2,i-2).

Rheological Properties of Water/IL Mixtures. The steady state viscosity of water and water/IL mixtures is shown in Figure 7. Viscosity of water/IL mixtures increased with decreasing water/IL ratio, such that the viscosity of 2:1 water/IL mixtures was 2–3 times that of the corresponding 5:1 mixtures and 4–7 times that of the corresponding 10:1 mixtures. At the same water/IL molar ratio, the viscosity of the mixtures followed the order [C₃mim][CH₃COO] > [C₃mim][Cl] > [C₃mim][HCOO].

General Discussion. In the present study, the effect of the anionic moiety of ILs and water/IL ratio on the dissolution behavior of maize starch was investigated by analyzing multiscale structural changes due to treatment with different water/IL mixtures. The extent of starch dissolution by the mixtures was determined using DSC analyses (Table 1). No enthalpy change was detected after treatment of starch with 2:1 mixtures of water/[C₃mim][Cl] and water/[C₃mim][HCOO], whereas a substantial enthalpy change of 5:1 was observed for starch treated with the 2:1 water/[C₃mim][CH₃COO] mixture. These observations were in line with the changes in relative crystallinity measured with XRD.

Short-Range Ordered Structure of Starch. The LCM-Raman spectra were obtained to characterize the short-range molecular order of native starch and starch after treatment with water/IL mixtures (Figure 5). Increases in the values of full width at half maximum (fwhm) of the band at 480 cm⁻¹ were used to assess the extent of disruption of the short-range ordered structure in starch (Table 1). The fwhm for native starch was 16.1; this value increased for starch treated with different water/IL mixtures. Therefore, greatest degree of structural disruption occurred with the 2:1 mixture being significantly less (Table 1).

Morphology of Starch Granules. The LM and scanning electron microscopy (SEM) images of native starch and starch samples after treatment with water/IL mixtures are shown in Figure 6. Under polarized light, starch granules showed clear structural order in starch (Table 1). The fwhm for native starch and starch after treatment with dihydrate water/IL mixtures (Figure 5). Increases in the values of full width at half maximum (fwhm) of the band at 480 cm⁻¹ were used to assess the extent of disruption of the short-range ordered structure in starch (Table 1). The fwhm for native starch was 16.1; this value increased for starch treated with different water/IL mixtures. Therefore, greatest degree of structural disruption occurred with the 2:1 mixture being significantly less (Table 1).

Table 1. Short- and Long-Range Ordered Structures of Native Starch and Starch after Treatment with Different Water/IL Mixtures

| samples                  | $T_c$ (°C) | $T_g$ (°C) | $T_m$ (°C) | $\Delta H$ (J/g) | relative crystallinity (%) | fwhm of the band at 480 cm⁻¹ |
|--------------------------|------------|------------|------------|-----------------|---------------------------|----------------------------|
| NMS                      | 65.1 ± 0.3¹ | 71.0 ± 0.1¹ | 76.2 ± 0.06¹ | 13.0 ± 0.5¹     | 28.5                      | 16.1 ± 0.1¹                |
| water/[C₃mim][Cl]-10:1-MS| 53.1 ± 0.6¹ | 62.0 ± 0.3³ | 70.9 ± 0.5³  | 8.1 ± 0.0³       | 22.9                      | 17.3 ± 0.1³                |
| water/[C₃mim][Cl]-5:1-MS | 56.1 ± 0.3³ | 65.8 ± 0.3⁵ | 75.7 ± 0.7⁵  | 7.1 ± 0.2³       | 20.1                      | 17.8 ± 0.0³                |
| water/[C₃mim][Cl]-2:1-MS | N.D.       | N.D.       | N.D.        | N.D.            | 0.0                       | 20.4 ± 0.1³                |
| water/[C₃mim][Cl]-5:1-MS | 51.9 ± 0.1¹ | 61.2 ± 0.1³ | 68.3 ± 0.9³  | 5.0 ± 0.1³       | 15.9                      | 18.4 ± 0.1³                |
| water/[C₃mim][HCOO]-5:1-MS| 66.5 ± 0.6² | 72.5 ± 0.1⁶ | 77.9 ± 0.0⁶  | 1.0 ± 0.0³       | 4.4                       | 18.9 ± 0.0³                |
| water/[C₃mim][HCOO]-2:1-MS| N.D.       | N.D.       | N.D.        | N.D.            | 0.0                       | 19.7 ± 0.1³                |
| water/[C₃mim][HCOO]-10:1-MS| 53.2 ± 1.0³ | 62.7 ± 0.1³ | 73.3 ± 0.3³  | 2.8 ± 0.9³       | 10.7                      | 19.0 ± 0.1³                |
| water/[C₃mim][CH₃COO]-5:1-MS| N.D.       | N.D.       | N.D.        | N.D.            | 0.0                       | 19.6 ± 0.0³                |
| water/[C₃mim][CH₃COO]-2:1-MS| 67.8 ± 0.2² | 73.0 ± 0.1³ | 78.8 ± 0.2³  | 5.8 ± 0.0³       | 20.9                      | 17.5 ± 0.0³                |

Values are means ± standard deviation. Values with the same lowercase letters in the same column are not significantly different (p < 0.05). N.D. means not determined.

Figure 4. Differential scan calorimetry thermograms of native starch and starch samples after treatment with different water/IL mixtures.

Figure 5. LCM-Raman spectra of native starch and starch samples after treatment with different water/IL mixtures.

[¹] (Table 1). No enthalpy change was detected after treatment of starch with 2:1 mixtures of water/[C₃mim][Cl] and water/[C₃mim][HCOO], whereas a substantial enthalpy change of 5.8 J/g was observed for starch treated with the 2:1 water/[C₃mim][CH₃COO] mixture. These observations were in line with the changes in relative crystallinity measured with XRD.
water/IL mixtures was shown to be consistent with the degree of starch structural disruption. Our hypothesis to explain the dissolution behavior of starch in different water/IL mixtures is based on the capacity of the anion of the IL to form hydrogen bonds and the viscosity of the water/IL mixtures. At low concentration of ILs, the water/IL mixtures have sufficiently low viscosity to favor the ILs to penetrate into granules and disrupt hydrogen bonds in starch. With increasing concentration of ILs in the mixtures, the extent of dissolution increased due to more ILs breaking a larger amount of hydrogen bonds in starch granules. However, the reduced extent of starch dissolution in water/[C2mim][CH3COO] mixtures of 2:1 is proposed to be due to the high viscosity of this mixture impeding the penetration of ILs into granules.20

At water/IL molar ratios of 10:1 and 5:1, the extent of starch dissolution followed the order [C2mim][CH3COO] > [C2mim][HCOO] > [C2mim][Cl], consistent with the order of hydrogen bonding capacity of anions [CH3COO]− > [HCOO]− > [Cl]−.14,23 The greater hydrogen bonding capacity made the anions interact more readily with the hydroxyl groups of starch molecules to disrupt the ordered structure of granules. At low water/IL ratio (2:1), the high viscosity of water/[C2mim][CH3COO] mixture resulted in the slower penetration of the IL into starch granules, lowering the extent of disruption of starch structure.

CONCLUSIONS

Both the anionic moiety and water/IL ratios influenced the dissolution behavior of maize starch. The short- and long-range ordered structures in the starch were disrupted increasingly with decreasing water/IL ratio of water/[C2mim][Cl] and water/[C2mim][HCOO] mixtures. However, in water/[C2mim][CH3COO] mixtures, the greatest disruption of the starch structure occurred in the 5:1 mixture rather than in the 2:1 mixture. Maize starch was completely dissolved at ambient temperature in a 5:1 water/[C2mim][CH3COO] mixture and in 2:1 mixtures of water/[C2mim][HCOO] and water/[C2mim][Cl]. The hydrogen bonding capacity of the IL anions and viscosity of the water/IL mixtures were proposed to account for the differences in starch dissolution behavior. At high water/IL molar ratios, the hydrogen bonding capacity of the IL anions play a major role in starch dissolution, whereas the viscosity of the water/IL mixtures dominates starch dissolution at low water/IL ratio. These findings indicate that the dissolution ability of ILs for natural biopolymers can be modulated by selecting the anionic moiety and water/IL ratio.

EXPERIMENTAL SECTION

Materials. Maize starch (MS, 10.1% moisture and 22.4% amylose content) was obtained from Sigma-Aldrich Chemical Co. (St. Louis, MO, USA). The ILs (1-ethyl-3-methylimidazolium chloride, [C2mim][Cl]; 1-ethyl-3-methylimidazolium formate, [C2mim][HCOO]; 1-ethyl-3-methylimidazolium acetate, [C2mim][CH3COO]) were bought from Nuowei Chemistry Co., Ltd. (Wuhu, Anhui, China) with purities >95% (water contents <5000 ppm). The chemical structures of ILs used are listed in Figure 1. Milli-Q water was used in all instances.

Starch Treatment in Water/IL Mixtures. Water/IL mixtures at different molar ratios (10:1, 5:1, and 2:1) were prepared, and the treatment of maize starch in the different mixtures was as reported elsewhere.20 Starch samples after treatment were stored in a desiccator before structural analysis. The abbreviation (water/IL-m/n-MS) is used subsequently to indicate maize starch that was treated with mixtures of molar ratios of m water/n IL.

Long-Range Crystallinity of Starch. The crystallinity of starch samples was determined using an X-ray diffractometer (D8 ADVANCE, Bruker, Germany) operating at 40 kV and 40 mA. The samples were equilibrated over a saturated NaCl solution at room temperature for 3 days before measurement. The moisture-equilibrated samples were scanned over the range of 5° to 35° (2θ) at a rate of 2°/min and a step size of 0.02°. The relative crystallinity was calculated using the software of DIFFRAC EVA (Version 3.0, Bruker, Germany).24
Thermal Properties of Starch. Thermal properties of the starch samples were measured using a differential scanning calorimeter (200 F3, Netzsch, Germany) equipped with a thermal analysis data station. Approximately 3 mg of starch samples were weighed accurately into aluminum pans, and Milli-Q water was added to obtain a starch/water ratio of 1/3 (w/v). The pans were sealed and allowed to stand for 6 h at room temperature before analysis. The samples were heated from 20 to 100 °C at a rate of 10 °C/min. An empty aluminum pan was used as the reference. The onset (T_on), peak (T_p), conclusion (T_c) temperatures, and enthalpy of gelatinization (ΔH) were obtained through a data recording software.

Short-range Molecular Order of Starch. The short-range molecular order of the starch samples was determined using Renishaw inVia Raman spectroscopy (Renishaw, Gloucestershire, United Kingdom) equipped with a Leica microscope (Leica Biosystems, Wetzlar, Germany). A 785 nm green diode laser source was used. Spectra in the range of 3200–100 cm⁻¹ were obtained with a resolution of approximately 7 cm⁻¹. The fwhm of the band at 480 cm⁻¹ was used to characterize the short-range molecular order of starch using the software of Wire 2.0.

Morphology of Starch. Morphology of the starch samples was observed using a light microscope (DM-4000M-LED, Leica, Germany) and a field-emission scanning electron microscope (SU-1510, Hitachi, Japan). For light microscopy, one drop of a 0.5% starch suspension was applied onto a glass slide and covered with a coverslip. Starch samples were imaged under polarized light modes at room temperature.

For SEM, starch samples were mounted on a stub with double-sided adhesive tape, sputter-coated with gold before imaging. An accelerating voltage of 5 kV was used.

Rheology Properties of Water/IL Mixtures. Rheological measurements of water/IL mixtures were performed in an Anton Paar MCR302 rheometer (Anton Paar GmbH, Austria) with a Peltier temperature control system. The measuring system had cone-plate geometry with a diameter of 40 mm and cone angle of 4°. For each mixture, the steady-state viscosity was measured at a shear rate from 10 to 500 s⁻¹ at constant temperature (23 °C). Silicone oil was placed around the edge of the measuring cell to prevent water evaporation.

Statistical Analysis. All analyses were performed at least in triplicate, and the results are reported as mean values and standard deviations. In the case of XRD, only one measurement was performed. One way analysis of variance (ANOVA) followed by post-hoc Duncan’s multiple range tests (p < 0.05) was conducted to determine the significant differences between mean values using the SPSS 17.0 Statistical Software Program (SPSS Inc. Chicago, IL, USA).

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S.W. conceived and designed the study. F.R. conducted the experiments. F.R and S.W. performed data analysis. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

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