Toward a Better Understanding of Different Dissolution Behavior of Starches in Aqueous Ionic Liquids at Room Temperature

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ABSTRACT: The purpose of this study was to understand the dissolution behavior of maize and potato starches in 1-ethyl-3-methylimidazolium acetate ([Emim][OAc]):water mixtures at room temperature. With an increasing ratio of ionic liquid (IL):water, the long- and short-range ordered structures and granule morphology of both starches were disrupted progressively. The multiscale structure of maize starch was disrupted completely after treatment with the [Emim][OAc]:water mixture of 6:4, indicating good dissolution performance of this mixture for maize starch. This mixture seemed to provide a balance between the viscosity of the solvent and availability of ions to disrupt starch H-bonds. The different dissolution behaviors of maize and potato starches in [Emim][OAc]:water mixtures were attributed to structural differences of the granule surfaces. Our results showed that the dissolution behavior of starches was affected by both starch sources and properties of [Emim][OAc]:water mixtures, which may provide guidance for the development of green technology for processing of biopolymers with low energy consumption.

INTRODUCTION

Starch is an abundant, cheap, renewable, and biodegradable natural biopolymer. As the second most abundant biomass produced on Earth next to cellulose, starch is used widely in food and nonfood industries. Based on X-ray diffraction (XRD) patterns, starch is generally divided into A-, B-, and C-type crystallites, which have different functional properties. Starch mainly consists of two polymers of D-glucose linked by α(1,4) and α(1,6) bonds: lightly branched amylose, which contains approximately less than 1% α(1,6) bonds, and amylopectin with approximately 5% α(1,6) linkages. Starch granules contain an amorphous core surrounded by alternating semicrystalline and amorphous growth rings, which are studied at structural scales ranging from nano- to micrometer. Due to the strong hydrogen bonds in semicrystalline granules, starch is generally insoluble in most traditional solvents such as water and organic solvents, thus limiting its industrial applications. Dimethyl sulfoxide (DMSO) can dissolve starch completely under mild conditions, but its application has limitations due to the toxicity of the solvent. Other solvents such as N-methyl morpholine-N-oxide (NMMO) and molten imidazole have also been used to dissolve starch, but complete dissolution either requires a high temperature or may induce polymer degradation.

Ionic liquids (ILs) are salts with a melting point below 100 °C that are used as green solvents because of their nonflammability, low vapor pressure, high thermal and chemical stability, and recyclability. ILs have attracted considerable interest as solvents for polysaccharides, including cellulose, lignin, and starch, owing to their high ability to destroy the hydrogen bonds in these biopolymers. Examples of IL solvents studied in this regard include 1-ethyl-3-methylimidazolium acetate, 1-allyl-3-methylimidazolium chloride, and 1-butyl-3-methylimidazolium chloride. The [Cl]-based ILs were used initially and are more widely applied than other types of ILs. However, the [OAc]-based ILs proved to be more effective in dissolving polysaccharides and were found not to cause acid hydrolysis of glycosidic bonds due to the absence of corrosive [Cl] anions. To reduce the quantity of IL needed and to develop mild dissolution conditions, mixtures of water:ILs have been studied in the dissolution of polysaccharides at room temperature. These studies showed that starch or lignin can be dissolved in aqueous ILs at room temperature by...
modulating the structure of cations and anions or the water:IL ratio.\textsuperscript{27−29} For example, maize starch can be dissolved at room temperature in mixtures of [Emim][OAc]:water.\textsuperscript{28} The changes in morphology, crystalline lamellae, and rheological properties of maize starches were studied during dissolution in [Emim][OAc]:water mixtures.\textsuperscript{25} However, there is little information on the underlying multiscale structural changes that occur in starch when it is treated with different mass ratios of water:IL mixtures at room temperature. In our previous study, the dissolution behavior of maize starch in mixtures of water: [Cl]-based ILs was investigated by characterizing the structural changes of starch before and after dissolution.\textsuperscript{27} However, the structural changes of maize starch and the dissolution behavior of other starches in aqueous [OAc]-based ILs have not been studied. Therefore, the aim of this work was to investigate the multiscale structural changes of normal maize and potato starches during dissolution in [Emim][OAc]:water mixtures. These two starches were chosen because of their different structures and properties and wide industrial applications. The results contribute to a more comprehensive understanding of the dissolution behavior of starches in different [Emim][OAc]:water mixtures. This knowledge will help underpin the design of starch-based materials with desirable functional properties, leading to novel green chemistry applications for this important natural biopolymer.

\section*{Materials and Methods}

\textbf{Materials.} Native maize starch (NMS, 10.2% moisture, 26.5% amylose content) was purchased from Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China). Normal potato starch (NPS, 12.2% moisture, 21.3% amylose content) was obtained from Sigma-Aldrich Chemical Co. (St. Louis, Missouri, U.S.A.). High-purity (95%, ≤ 0.5% moisture content) 1-ethyl-3-methylimidazolium acetate ([Emim]-[OAc]) was purchased from Nuowei Chemical Technology Co., Ltd. (Wuhu, Anhui, China). The chemical structure and \textsuperscript{1}H and \textsuperscript{13}C NMR spectra of [Emim][OAc] are shown in the appendices. Deionized water was used in all experiments. All other chemical reagents were of analytical grade.

\textbf{Treatment of Starch in Different IL/Water Mixtures.} The 10% (w/w) starch suspensions were prepared by dispersing starches in respective aqueous ionic liquid systems ([Emim][OAc]:water mass ratios of 2:8, 4:6, 5:5, 6:4, 8:2, and 10:0). The suspensions were stirred magnetically for 2 h at room temperature (22−23 °C), and after which, four volumes of absolute ethanol were added with stirring. The starch suspensions were centrifuged at 4500g for 15 min, and the precipitated starch was washed three times using absolute ethanol to remove the residual [Emim][OAc]. The resulting starch suspensions were dispersed in an oven at 30 °C for 24 h, ground into a powder, and passed through a 100 mesh sieve. The starch samples were referred to as MAC- or PAC-n:m, representing maize or potato starch that was treated in [Emim][OAc]:water mixtures at a mass ratio of n:m.

\textbf{Wide-Angle X-ray Diffraction (WAXD).} The crystallinity of starch samples was examined using an X-ray diffractometer (D8 ADVANCE, Bruker, Germany) operating at 40 kV and 40 mA. The starch samples were equilibrated in a chamber over saturated NaCl solution at 25 °C for one week before analysis. The starch samples were scanned from 4° to 40° (2θ) at a speed of 1 °C/min and step size of 0.02°. The relative crystallinity was quantified using TOPAS 5.0 software (Bruker, Germany), as described by Shang et al.\textsuperscript{30}

\textbf{Scanning Electron Microscopy (SEM).} The morphology of starch samples was observed by a scanning electron microscope (SU1510, Hitachi, Japan). The specimens were attached to an aluminum stub using conductive tape and coated with gold before imaging. The accelerating voltage was 5 kV.

\textbf{Light Microscopy (LM).} A light microscope (DM-400 M-LED, Leica, Germany) was used to observe the starch samples under normal and polarized light modes. Approximately 10 mg of each sample was weighed into a plastic tube, and 1 mL of deionized water was added to suspend the sample. One drop of the suspension was applied onto a microscope slide and covered with a coverslip for imaging.

\textbf{Differential Scanning Calorimetry (DSC).} The thermal properties of starch samples were performed using a differential scanning calorimeter (200 F3, Netzsch, Germany) equipped with a thermal analysis data station. The sample preparation and heating procedures were as described in Wang and Copeland.\textsuperscript{31} A starch sample (3 mg, dry base) was weighed into an aluminum pan, and then distilled water was added to obtain a sample:water ratio of 1:3 (w/w). The sample pan was sealed, equilibrated at room temperature for 12 h, and scanned from 20 to 100 °C at a heating rate of 10 °C/min. An empty pan was used as the reference. The onset temperatures (T_onset), peak temperatures (T_peak), conclusion temperatures (T_conc), and melting enthalpy (ΔH) were calculated using Proteus analysis software.

\textbf{Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) Spectroscopy.} The ATR-FTIR spectra of starch samples were obtained using a Tensor FT-IR spectrometer (ISS50, Thermo Fisher Scientific, U.S.A.) equipped with a DLaTGS detector. The sample preparation and operation conditions were mentioned in Wang, et al.\textsuperscript{32} with minor modifications. Spectra were recorded from 4000 to 400 cm\textsuperscript{-1} against an empty cell as background, with an accumulation of 64 scans and a resolution of 4 cm\textsuperscript{-1}. The ratio of absorbances at 1047/1022 cm\textsuperscript{-1}, calculated using software OMNIC 9.2, was used to estimate the short-range molecular order of starch samples.

\textbf{Laser Confocal Micro-Raman (LCM-Raman) Spectroscopy.} The Raman spectra of starch samples were determined using a Renishaw Invia Raman microscope system (Renishaw, Gloucestershire, United Kingdom) equipped with a Leica microscope (Leica Biosystems, Wetzlar, Germany). A 785 nm green diode laser source was used.\textsuperscript{33} Spectra in the range of 3200−100 cm\textsuperscript{-1} were collected with a resolution of approximately 7 cm\textsuperscript{-1}. The full width at half-maximum (FWHM) of the band at 480 cm\textsuperscript{-1}, which was used to characterize the short-range ordered structure of starch, was obtained by software WiRE 2.0.

\textbf{Viscosity of [Emim][OAc]:Water Mixtures.} Rheological measurements of aqueous ionic liquid solutions were performed on a MCR 302 rheometer (Anton Paar GmbH, Austria). The sample preparation and operation conditions were according to Liu and Budtova\textsuperscript{18} with minor modifications. The measuring system had a cone-plate geometry with a diameter of 40 mm and cone angle of 4°. The steady-state viscosity of each solution was determined as a function of shear rate from 10 to 500 s\textsuperscript{-1} at 23 °C. In order to prevent the absorption and evaporation of water vapor, the silicone oil was placed around the edge of the measuring cell.
Low-Field Nuclear Magnetic Resonance (LF-NMR).

The LF-NMR experiments were performed on a 0.53 T (20 MHz) NMI20-025 V-I NMR analyzer (Niumag, Shanghai, China) as described by Li et al. with minor modifications. Approximately 4.5 g of the aqueous ionic liquid mixtures was placed in 15 mm NMR glass tubes before moving to the NMR probe. Transverse relaxation ($T_2$) was measured by the Carr−Purcell−Meiboom−Gill (CPMG) sequence at 32 °C with a time of 500 μs between 90 and 180° pulses ($\tau$-value). Data was acquired from 15000 echoes at four scan repetitions, and the repetition time between two successive scans was set to 15 s.

Statistical Analysis. All experiments 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 conducted. The analysis of variance (ANOVA) followed by Duncan’s tests ($P < 0.05$) was conducted using the SPSS 19.0 statistical software program (SPSS Inc. Chicago, Illinois, U.S.A.).

RESULTS AND DISCUSSION

Long-Range Ordered Structure of Starch Samples Determined by XRD. Native maize starch exhibited a typical A-type diffraction pattern with strong diffraction peaks at 15°, 17°, 18°, and 23° ($2\theta$) (Figure 1A, NMS). The weak diffraction peak at around 20° ($2\theta$) was assigned to the endogenous starch−lipid complex. Maize starch treated with the [Emim][OAc]:water mixture of 6:4 showed an amorphous diffraction pattern (Figure 1A, MAC-6:4), indicating complete disruption of the long-range crystallinity of the starch by this solvent mixture. Similar results were also observed in a previous study. In contrast, the XRD patterns of maize starch after treatment with the other [Emim][OAc]:water mixtures were similar to that of native starch, although there were small gradual decreases in crystallinity from 22.8% for native starch to 18.3% for starch treated with undiluted IL (Table 1).

Native potato starch displayed a typical B-type XRD pattern with five clear peaks at 5.6°, 15°, 17°, 21.9°, and 23.7° ($2\theta$) (Figure 1B, NPS). The crystallinity of potato starch decreased gradually from 35.1 to 24.2% with increasing IL:water ratio,

Table 1. Ratios of 1047/1022 cm$^{-1}$, FWHMs of the Band at 480 cm$^{-1}$, and Relative Crystallinity of Starch Samples$^{a,b}$

| samples          | IR ratio of absorbances at 1047/1022 cm$^{-1}$ | FWHM at 480 cm$^{-1}$ | relative crystallinity (%) |
|------------------|-----------------------------------------------|-----------------------|---------------------------|
|                  | maize starch                                  | potato starch         | maize starch              | potato starch              | maize starch              | potato starch              |
| native Starch    | 0.73 ± 0.02c                                   | 0.82 ± 0.02b          | 16.82 ± 0.07a             | 16.18 ± 0.08a             | 22.8                      | 35.1                      |
| IL:water 2:8     | 0.71 ± 0.00c                                   | 0.79 ± 0.01b          | 17.20 ± 0.06c             | 16.49 ± 0.15bc            | 22.4                      | 33.1                      |
| IL:water 4:6     | 0.70 ± 0.02c                                   | 0.78 ± 0.04b          | 17.30 ± 0.02e             | 16.53 ± 0.05 cd           | 21.8                      | 32.5                      |
| IL:water 5:5     | 0.69 ± 0.02c                                   | 0.74 ± 0.03a          | 17.34 ± 0.08d             | 16.67 ± 0.14de            | 20.9                      | 31.5                      |
| IL:water 6:4     | 0.54 ± 0.01a                                   | 0.73 ± 0.01a          | 20.59 ± 0.09f             | 16.73 ± 0.12ef            | 0.0                       | 29.4                      |
| IL:water 8:2     | 0.65 ± 0.00b                                   | 0.72 ± 0.02a          | 17.39 ± 0.04d             | 16.80 ± 0.07ef            | 19.6                      | 27.1                      |
| IL:water 10:0    | 0.63 ± 0.00b                                   | 0.70 ± 0.00a          | 17.57 ± 0.10e             | 16.87 ± 0.08f             | 18.3                      | 24.2                      |

$^{a}$Values are means ± SD. The different lowercase letters represent significant differences between the data in the same column ($p < 0.05$).

$^{b}$FWHM: full width at half maximum.
demonstrating a gradual disruption of the long-range ordered structure in potato starch.

The crystalline structural changes of starches after treatment with [Emim][OAc]:water mixtures were also confirmed by the 2D views of XRD diffraction patterns (Figure 1C,D). With increasing [Emim][OAc]:water ratio, the intensity of diffraction peaks of maize (Figure 1C) and potato starches (Figure 1D) gradually weakened, with the exception of the absence of diffraction peaks of maize starch after treatment with the [Emim][OAc]:water mixture of 6:4.

Short-Range Ordered Structure of Starch Samples Determined by ATR-FTIR and LCM-Raman Spectroscopy. The changes of the short-range ordered structure in starch after treatment with [Emim][OAc]:water mixtures was monitored by ATR-FTIR and LCM-Raman spectroscopy. The ATR-FTIR spectra in the range of 1200 to 800 cm\(^{-1}\) of maize and potato starches are presented in Figure 2A,B, respectively, and the ratios of absorbances at 1047/1022 cm\(^{-1}\) are shown in Table 1. Maize starch treated with the [Emim][OAc]:water mixture of 6:4 showed the lowest value of IR ratio of absorbances at 1047/1022 cm\(^{-1}\) (0.54) compared to native maize starch (0.73), indicating that the short-range ordered structure was greatly disrupted. Maize starch treated with other [Emim][OAc]:water mixtures presented decreasing IR ratios of absorbances at 1047/1022 cm\(^{-1}\) from 0.73 to 0.63 with increasing [Emim][OAc]:water ratio, indicating the gradual and lesser degree of disruption of short-range ordered structure. The ratio of the absorbances at 1047/1022 cm\(^{-1}\) of potato starch decreased slightly from 0.82 to 0.70 with increasing [Emim][OAc]:water ratio, indicating the gradual disruption of the short-range ordered structure.

The LCM-Raman spectra of samples showed five characteristic bands at 480, 865, 943, 1264, and 2900 cm\(^{-1}\) (Figure 2C,D), which are related to $\delta$ (CH\(_2\)), $\nu$ (C1–O–C4), $\nu$ (C1–O–C5), skeletal (C–C–O), and $\nu$ (C–H) modes, respectively.\(^{31,35,36}\) The band at 480 cm\(^{-1}\) is sensitive to changes of the short-range ordered structure of starch, with a smaller FWHM value indicating a greater degree of structural order.\(^{32,35–37}\) Similar to FTIR results, the short-range ordered structure of the two starch samples determined by the FWHM of the band at 480 cm\(^{-1}\) (Table 1) was disrupted increasingly with increasing [Emim][OAc]:water ratio, with the exception of maize starch treated with the [Emim][OAc]:water mixture of 6:4. A much higher FWHM value for maize starch treated with the [Emim][OAc]:water mixture of 6:4 indicated the greater disruption of the short-range ordered structure of starch.

Granular Morphology of Starch Samples. The SEM and LM images of native starch and starch samples treated with different [Emim][OAc]:water mixtures are shown in Figure 3. Native maize starch granules were irregularly shaped with a rough surface containing a few indentations (Figure 3A), whereas potato starch granules were more round with a smooth surface (Figure 3H). Under polarized light, native maize and potato starch granules displayed clear birefringent patterns with the characteristic Maltese cross (Figure 3A2,H2).

The SEM images showed that the surface morphology of maize and potato starch granules did not appear to be greatly affected by treatment with IL:water mixtures (Figure 3B–G,I–N). Birefringent granules indicative of crystallinity were observed to become increasingly blurred (maize starch) or to decrease in size (potato starch) with polarized light microscopy for both types of starch, except for maize starch treated with the 6:4 [Emim][OAc]:water mixture (Figure 3E2). No birefringent maize starch granules were evident after...
treatment with the 6:4 mixture, although the granule contours were still visible (Figures 3E1,E2).

Thermal Properties of Starch Samples. The DSC thermograms and the corresponding thermal transition parameters of starch samples are presented in Figure 4 and Table 2, respectively. Thermal transition temperatures ($T_o$, $T_p$, and $T_c$) of native maize and potato starches were 65.9, 71.5, and 76.4 °C and 61.1, 65.7, and 71.7 °C, respectively. The enthalpy changes of gelatinization were 11.5 and 16.3 J/g for maize and potato starches, respectively.

The endothermic peak ($T_p$) of maize starch shifted gradually to higher temperatures as the [Emim][OAc]:water ratio increased from 2:8 to 5:5 (Figure 4A). No peak was detected with the 6:4 IL:water mixture. The $T_p$ increased further with

Figure 3. (A−N) Representative scanning electron microscopy and light microscopy images under (A1−N1) normal and (A2−N2) polarized light modes of (A) native maize and (H) potato starch and (B−G, I−N) starch samples after treatment with different aqueous ionic liquids. (B−G) and (I−N) indicate maize and potato starch samples treated with different aqueous ionic liquids at IL:water ratios of 2:8, 4:6, 5:5, 6:4, 8:2, and 10:0, respectively.

Figure 4. Thermal properties of starch samples. (A): maize starch samples and (B): potato starch samples.
Table 2. Thermal Properties of Starch Samples $^{a,b,c,d}$

| samples               | $T_o$ (°C) | $T_p$ (°C) | $T_c$ (°C) | $T_{c−T_o}$ (°C) | $\Delta H$ (J/g) |
|-----------------------|------------|------------|------------|------------------|-----------------|
| native starch         | 65.9 ± 0.1b| 71.5 ± 0.0bc| 76.4 ± 0.0e| 10.4 ± 0.0d      | 11.5 ± 0.0a     |
| IL:water 2:8          | 57.9 ± 0.1e| 70.7 ± 0.6de| 77.2 ± 0.0d| 19.3 ± 0.2a      | 10.7 ± 0.1b     |
| IL:water 4:6          | 59.4 ± 0.5d| 71.7 ± 0.0b| 78.1 ± 0.1b| 18.8 ± 0.4a      | 9.4 ± 0.5c      |
| IL:water 5:5          | 67.6 ± 1.1a| 72.0 ± 0.2b| 77.7 ± 0.1c| 10.1 ± 1.1d      | 8.9 ± 1.0d      |
| IL:water 6:4          | ND         | ND         | ND         | ND               | ND              |
| IL:water 8:2          | 64.0 ± 0.2c| 73.3 ± 0.1a| 78.6 ± 0.1a| 14.6 ± 0.2c      | 8.4 ± 0.0de     |
| IL:water 10:0         | 59.5 ± 0.1d| 70.2 ± 0.0e| 75.8 ± 0.1f| 16.3 ± 0.1b      | 8.1 ± 0.0e      |

potato starch

| samples               | $T_o$ (°C) | $T_p$ (°C) | $T_c$ (°C) | $T_{c−T_o}$ (°C) | $\Delta H$ (J/g) |
|-----------------------|------------|------------|------------|------------------|-----------------|
| native starch         | 61.1 ± 0.0a| 65.7 ± 0.0a| 71.7 ± 0.1a| 10.6 ± 0.1f      | 16.3 ± 0.1a     |
| IL:water 2:8          | 57.7 ± 0.1c| 64.5 ± 0.1c| 71.3 ± 0.1b| 13.7 ± 0.1a      | 14.2 ± 0.4b     |
| IL:water 4:6          | 57.6 ± 0.1cd| 63.8 ± 0.0d| 71.0 ± 0.1c| 13.4 ± 0.0ab     | 13.9 ± 0.2bc    |
| IL:water 5:5          | 57.3 ± 0.1cde| 63.7 ± 0.1d| 70.4 ± 0.2d| 13.0 ± 0.1bc     | 13.6 ± 0.2cd    |
| IL:water 6:4          | 57.3 ± 0.0cde| 63.4 ± 0.1e| 70.3 ± 0.1d| 12.9 ± 0.1c      | 13.2 ± 0.4d     |
| IL:water 8:2          | 57.2 ± 0.1de| 63.3 ± 0.2e| 70.1 ± 0.1d| 12.9 ± 0.1c      | 12.8 ± 0.1e     |
| IL:water 10:0         | 57.1 ± 0.5e| 62.4 ± 0.1f| 69.4 ± 0.1e| 12.3 ± 0.4d      | 12.5 ± 0.0e     |

$^a$Values are means ± SD. The different lowercase letters represent significant differences between the data in the same column ($p < 0.05$). $^b$ $T_o$: onset temperature of thermal transition. $^c$ $T_p$: peak temperature of thermal transition. $^d$ $T_c$: conclusion temperature of thermal transition. $^e$ $\Delta H$: enthalpy change of thermal transition. $^f$ ND: not detected.

The endothermic peak of the DSC profile of potato starch shifted gradually from 65.7 to 62.4 °C with increasing [Emim][OAc]:water ratio, and the enthalpy change of gelatinization decreased from 16.3 to 12.5 J/g. The decreased $T_p$ of potato starch after treatment suggested that the stable crystallites were disrupted preferentially, leading to the lower melting temperature of residual less stable crystallites. The changes in the $\Delta H$ value of starches after treatments were generally consistent with the results from XRD, ATR-FTIR, and LCM-Raman.

Rheological Properties of [Emim][OAc]:Water Mixtures. The viscosities of the different [Emim][OAc]:water mixtures were constant over a range of shear rates (Figure 5). As the [Emim][OAc]:water mass ratio increased from 0 to 5:5, the viscosity increased only slightly from 0.8 to 4.4 mPa·s. However, the viscosity more than doubled to 10.0 mPa·s at an [Emim][OAc]:water ratio of 6:4 and then increased again to 21.4 mPa·s at a ratio of 8:2. Undiluted [Emim][OAc] had the highest viscosity of 66.0 mPa·s.

$T_2$ Distribution of [Emim][OAc]:Water Mixtures. The state of water molecules in a solution can be differentiated from the distribution of transverse relaxation time $T_2$ into strongly bound water ($T_{2s}$, 0.01–1 ms), weakly bound water ($T_{2w}$, 1–100 ms), and free water ($T_{2f}$, 100–10000 ms). The $T_2$ distribution of [Emim][OAc]:water mixtures (Figure 6) showed a gradual decrease in the mobility of water molecules with increasing IL in the mixtures, which could be due to water...
molecules being increasingly bound by IL and the effects of higher viscosity. However, except for undiluted IL and, to a lesser extent, the IL:water mixture of 8:2, the water molecules in the aqueous IL mixtures were freely mobile.

**General Discussion.** The present study has shown from analyses at multiple scales that the structure of maize starch was disrupted completely after treatment with the [Emim][OAc]:water mixture of 6:4. As shown previously, this indicates good dissolution of maize starch in this aqueous IL solution. We propose that this 6:4 ratio of IL:water represents a "sweet spot"; at lower ratios, there is not enough IL to break sufficient hydrogen bonds in starch to cause complete structural disruption, whereas the low mobility of water molecules in high-viscosity IL:water mixtures reduces the penetration of IL into starch granules (Figures S and 6).

Similar behavior was not observed with potato starch, which could be due to its distinct surface morphology. Maize starch has many surface pores and channels, which may facilitate the penetration of the [Emim][OAc]:water mixture into granules. In contrast, potato starch granules have a smooth, hard outer surface, which may reduce the penetration of the [Emim][OAc]:water mixture. The gradual disruption of potato starch structure suggested that the dissolution occurred from the surface, as shown by the increasing degree of disruption of the starch granule surface observed by SEM (Figure 3). In addition, repulsion of acetate ions by negatively charged phosphate groups in potato starch may be another reason for differences in the dissolution behavior between potato and maize starches.

**CONCLUSIONS**

The multiscale structure of both maize and potato starches was progressively disrupted at room temperature (22–23 °C) by treatment with [Emim][OAc]:water mixtures containing increasing mass-ratio amounts of the IL. Treatment of maize starch with the [Emim][OAc]:water mixture at a ratio of 6:4 resulted in complete structural disruption of the granules. The effectiveness of this particular mixture in dissolving maize starch is attributed to surface morphology differences in maize starch, vis a vis potato starch granules, and the balance between the amount of IL versus viscosity of the various mixtures. These findings will be useful for developing protocols for the use of ILs as solvents for starch in novel applications for this important natural biopolymer.

**ASSOCIATED CONTENT**

* Supporting Information
  The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00962.

  Figure 1 and Figure 2 for Ionic liquid structure and NMR spectra (PDF)

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**Notes**

The authors declare no competing financial interest.

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