

Changes in structure and properties of starch of four botanical sources dispersed in the ionic liquid, 1-butyl-3-methylimidazolium chloride [☆]

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Abstract

Ionic liquid (IL) has gained industry attention, especially in green chemistry. Researchers have utilized IL for dispersing cellulose, but no report using IL for other polysaccharides. In this study, corn, rice, wheat and potato starches were dispersed in hot water (DIHW) or IL, 1-butyl-3-methylimidazolium chloride and morphology, amylopectin molecular weight (APMw) and thermal properties (TP) were analyzed. For starch DIHW, corn and potato had gelatinized aggregates, whereas rice and wheat had granular clumps. Starch heat-dispersed in IL (HDIIL) had clumps composed of < 1 μm diameter particles. Starch DIHW had little effect on APMw. Cereal starches had APMw greatly reduced by HDIIL (4–6 peaks observed). Potato amylopectin was degraded less by IL (two peaks) probably because charged phosphomonoesters covalently bonded to imidazolium rings or repelled IL chloride ions and large granule size impeded IL penetration, reducing reaction efficiency. TP showed potato starch incompletely gelatinized by HDIIL. Published by Elsevier Ltd.

Keywords: Starch; Ionic liquid; Amylopectin; Imidazolium; Structure; Molecular weight; Green chemistry

1. Introduction

Ionic liquids are organic salts with melting points below 100 °C. Ionic liquids are a new technology considered to be green chemistry because of their potential use in sustainable processes as solvent replacements due to their biodegradability (Gathergood, García, & Scammells, 2004) and low toxicity (Jastorff et al., 2003; Wasserscheid, van Hal, & Bösmann, 2002). In addition to being environmental friendly by substituting for volatile organic solvents, ionic

liquids have the advantages of optimization of compound characteristics through a broad selection of anion and cation combinations (Dupont, de Souza, & Suárez, 2002), low hydrophobicity (Huddleston et al., 2001; Swatloski et al., 2001), low viscosity (Hagiwara & Ito, 2000; MacFarlane, Golding, Forsyth, Forsyth, & Deacon, 2001), electrochemical stability (Matsumoto et al., 2000), thermal stability (Kosmulski, Gustafsson, & Rosenholm, 2004), enhancement of reaction rates with higher selectivities that can achieve higher yields (Holbrey & Seddon, 1999) and are non-flammable. Due to all these advantages, there is increasing industrial interest for using ionic liquids (Freemantle, 2005).

Ionic liquids have been recently used in extraction, exploiting their hydrophobic and lipophilic nature (Bösmann et al., 2001; Fadeev & Meagher, 2001; Liu et al., 2004), separation utilizing interactions between

[☆] Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

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the ionic liquid, the stationary phase and mixture of analytes (Blanchard & Brennecke, 2001; He, Zhang, Zhao, Liu, & Jiang, 2003), and extractive distillation by altering vapor-liquid and liquid-liquid equilibria (Jork, Seiler, Beste, & Arlt, 2004). Ionic liquids have also been used in organic synthesis such as hydrogenation of aromatic compounds without high temperature (Adams, Earle, & Seddon, 1999), solvent for Friedel-Crafts (Adams, Earle, Roberts, & Seddon, 1998) and Diels-Alder (Fischer, Sethi, Welton, & Woolf, 1999) reactions, stereoselective halogenations (Chiappe, Capraro, Conté, & Pieraccini, 2001), multistep parallel synthesis (Rodríguez, Segá, & Taddei, 2003), Suzuki coupling reaction (Miao & Chan, 2003), chiral synthesis (Jessop et al., 2003) and catalysis (Hagiwara, Sugawara, Isobe, Hoshi, & Suzuki, 2004; Ley, Ramarao, & Smith, 2001). Recently, biotechnology has utilized ionic liquids, especially for biocatalysis (Sheldon, Lau, Sorgedraeger, van Rantwijk, & Seddon, 2002; Kaar, Jesionowski, Berberich, Moulton, & Russell, 2003; Park & Kazlauskas, 2003; Walker & Bruce, 2004) and synthesis of RNA and DNA oligomers (Hayakawa et al., 2001).

There have been limited studies investigating the potential of using ionic liquids to disperse or modify polysaccharides, and mostly focused on cellulose. Dissolution of cellulose using a range of ionic liquids containing 1-butyl-3-methylimidazolium cations has been studied, in which chloride containing solvents were found to be the most effective at solubilizing cellulose (Swatloski, Spear, Holbrey, & Rogers, 2002 (note title misspells cellulose); Swatloski, Rogers, & Holbrey, 2004). Acetylation of cellulose has been accomplished at room temperature using 1-allyl-3-methylimidazolium chloride (Wu et al., 2004). Recently, 1-allyl-3-methylimidazolium chloride was reported to be effective in producing regenerated cellulose by non-polluting processes (Zhang, Wu, Zhang, & He, 2005). Ionic liquids have also recently been used to produce cellulose composites (Turner, Spear, Holbrey, Daly, & Rogers, 2005; Xie, Li, & Zhang, 2005).

To our knowledge, the only report to date involving use of ionic liquids on starch is research we reported recently in which we showed 1-butyl-3-methylimidazolium chloride successfully solubilized starch and using a mixture of acetic anhydride and pyridine, high yields of acetylated starch with 0.3 to 2.6 degree of substitution was achieved (Biswas, Shogren, Stevenson, Willett, & Bhowmik, 2005). In this study, we wanted to determine if ionic liquids could successfully disperse starch molecules without altering starch structure and properties. Dispersion in ionic liquid could potentially substitute for the much less environmental friendly dimethyl sulfoxide that is frequently used to disperse starch. Based on previous findings for solubilization of cellulose (Swatloski et al., 2002; Zhang et al., 2005), we used the ionic liquid, 1-butyl-3-methylimidazolium chloride to disperse starch from four botanical sources, which we expected would not alter starch structure or properties.

2. Materials and methods

2.1. Materials

Native starch from corn, potato, rice and wheat were obtained from Sigma-Aldrich (St. Louis, MO, starch product codes S4126, S4251, S7260 and S5127, respectively). The ionic liquid, 1-butyl-3-methylimidazolium chloride was obtained from Fluka (Sigma-Aldrich, St. Louis, MO, S16110).

2.2. Starch dispersion in ionic liquid

Starch (100 mg) was dispersed in 5 g of the ionic liquid, 1-butyl-3-methylimidazolium chloride, by heating starch and finely ground ionic liquid from 25 to 80 °C for 15 min, followed by heating at 100 °C for 1 h, with stirring throughout. Lower temperatures were found to not effectively disperse starch from all four botanical sources. Starch was then precipitated by adding 25 mL of 100% ethanol and centrifuged at 6800g for 15 min. Pellet was washed by adding 5 mL of deionized water with stirring for 10 min. Starch was then precipitated again using 100% ethanol and recovered by filtration using Whatman No. 5 filter paper. Starch was dried in a convection oven at 35 °C for 48 h. The same starches had the entire procedure conducted using deionized water instead of ionic liquid as a control. Three replicate of each starch dispersed separately in ionic liquid or deionized water were analyzed.

2.3. Starch morphology

Starch, spread on silver tape and mounted on a brass disk, was coated with gold/palladium (60/40) for two of the three replicate of each starch in ionic liquid or deionized water. Sample images were observed at 1500× and 5000× magnification under a scanning electron microscope (JOEL model 6400V, Tokyo, Japan).

2.4. Molecular weight distribution and gyration radius of amylopectin

Weight-average molecular weight and z-average gyration radius of amylopectin were determined using high-performance size-exclusion chromatography equipped with multi-angle laser-light scattering and refractive index detectors (HPSEC-MALLS-RI). Starch samples, duplicate measurements of each replicate of starch in ionic liquid or deionized water, were prepared as described by Yoo and Jane (2002a). The HPSEC system consisted of a HP 1050 series isocratic pump (Hewlett Packard, Valley Forge, PA), a multi-angle laser-light scattering detector (Dawn DSP-F, Wyatt Tech. Co., Santa Barbara, CA) and a HP 1047A refractive index detector (Hewlett Packard, Valley Forge, PA). To separate amylopectin from amylose, Shodex OH pak SB-G guard column and SB-806 and SB-804 analytical columns (JM Science, Grand Island, NY) were

used. Operating conditions and data analysis were described by Yoo and Jane (2002b).

2.5. Thermal properties of starch

Thermal properties of starch were determined by using a differential scanning calorimeter (DSC 2920 modulated, TA Instruments, New Castle, DE) (Jane et al., 1999). Approximately 2 mg of starch (dry starch basis, dsb) was precisely weighed in an aluminum pan, mixed with 6 mg of deionized water and sealed. The sample was equilibrated for 2 h and scanned at a rate of 10 °C/min over a temperature range of 10–120 °C. An empty pan was used as the reference. Analysis of starch thermal properties was carried out in triplicate for each replicate of each starch in ionic liquid or deionized water.

2.6. Data analysis

All statistical significance tests were calculated by using SAS (SAS Institute Inc., 1999) and applying Tukey difference test (Ramsey & Schafer, 1996).

3. Results and discussion

3.1. Starch dispersion

The dispersion of corn starch in ionic liquid or deionized water is illustrated in Fig. 1. Prior to heating, the corn starch suspension in deionized water is opaque (Fig. 1A, left) and the ionic liquid is solid (Fig. 1A, right). After heating for 15 min from 25 to 80 °C, corn starch suspension was translucent to opaque for both deionized water and ionic liquid (Fig. 1B). Corn starch dispersed in deionized water was translucent after heating at 100 °C for 1 h (Fig. 1C, left) whereas dispersion in ionic liquid under same conditions resulted in a transparent solution (Fig. 1C, right). A similar trend was observed for the other three starches. Therefore the ionic liquid, 1-butyl-3-methylimidazolium chloride was more effective at dispersing starch than deionized water.

3.2. Starch morphology

Scanning electron micrographs revealing the morphology of native corn, rice, wheat and potato starches and their dispersion in deionized water or ionic liquid are shown in Fig. 2. Heat-dispersion in either deionized water or ionic liquid (Fig. 2B–D, F–I, K–N and P–S) clearly altered structure compared with native starch (Fig. 2A, E, J and O). Corn and potato starch granules dispersed in hot deionized water fused together to form large aggregates that for corn had pores (Fig. 2B and C), whereas cracks were observed for potato (Fig. 2P and Q). Rice and wheat starch dispersed in hot deionized water were clearly different from corn and potato. While large aggregates were still formed (Fig. 2F and K), starch granules were distinguishable for rice and wheat (Fig. 2G and L). Although aggregation

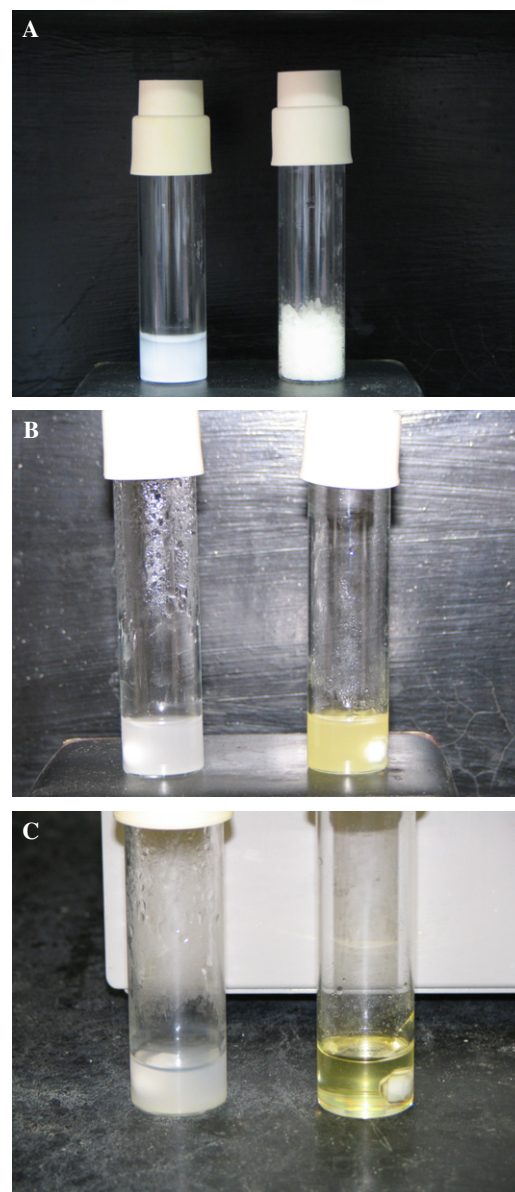


Fig. 1. Corn starch in deionized water (left) or ionic liquid (right) prior to heating (A), after heating for 15 min from 25 to 80 °C (B) and after heating for 1 h at 100 °C (C).

occurred for all starches dispersed in ionic liquid (Fig. 2D, H, M and R), wheat and potato starch still had some starch granules that were not gelatinized (Fig. 2M and R) and all starches consisted of clumps of particles 1 µm or less in diameter (Fig. 2D, I, N and S) that was not observed for any of the starches dispersed in hot deionized water. Ionic liquid-dispersed starch, exhibiting clumping of small particles, would be expected to have greater solubility than deionized water-dispersed starch that has aggregates with little partition.

3.3. Molecular weight and gyration radius of amylopectin

Weight-average molecular weight (M_w), polydispersity, gyration radius (R_z) and density of amylopectin of corn,

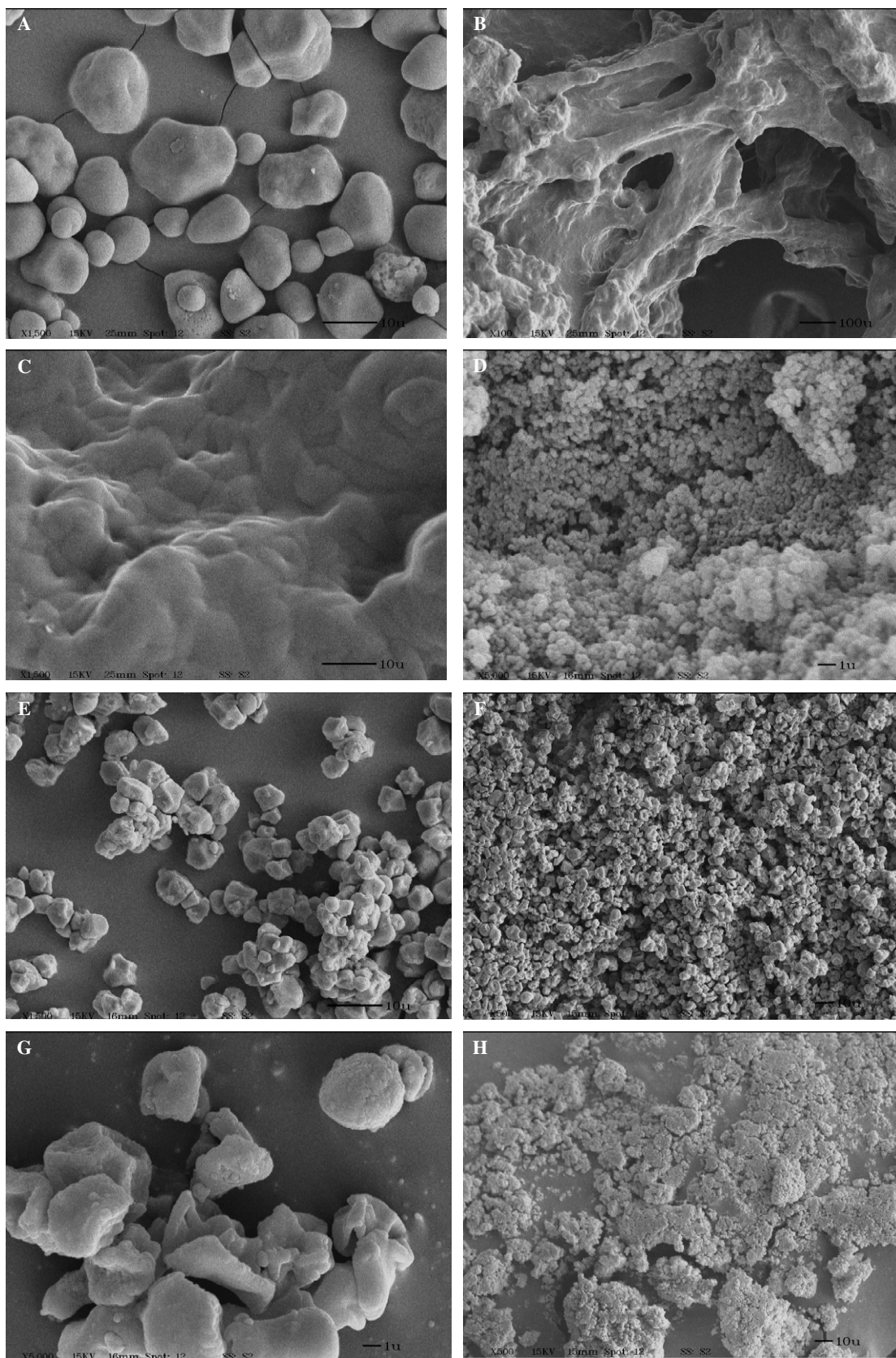


Fig. 2. Scanning electron micrographs of native corn, rice, wheat and potato starch (A, E, J and O, respectively), dispersed in hot deionized water (B–C, F–G, K–L and P–Q, respectively) and heat-dispersed in ionic liquid (D, H–I, M–N and R–S, respectively). Image magnification is 100 \times for B and K, 500 \times for F, H, O, P and R, 1500 \times for A, C, E, J, L and M and 5000 \times for D, G, I, N, Q and S.

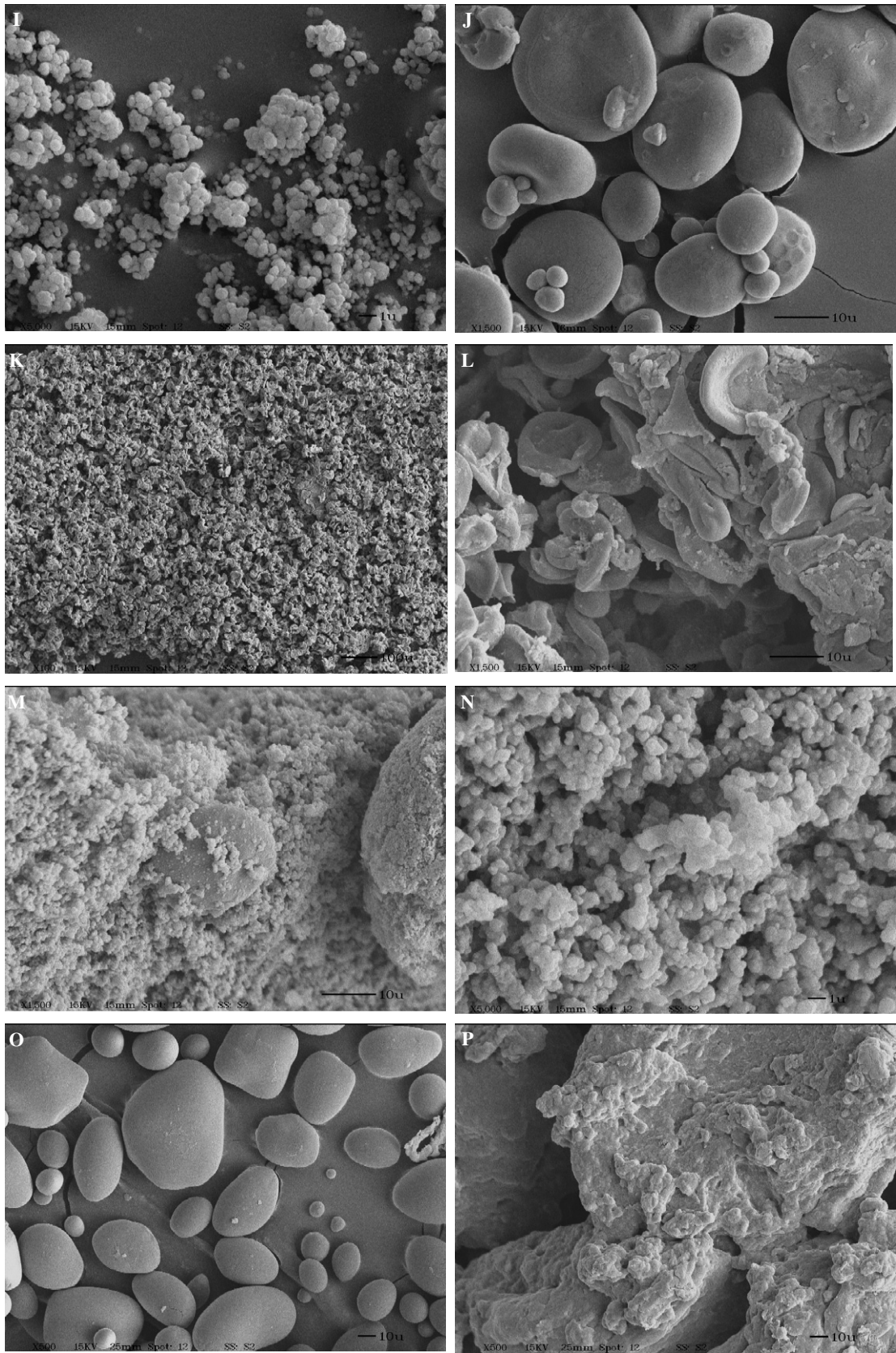


Fig. 2 (continued)

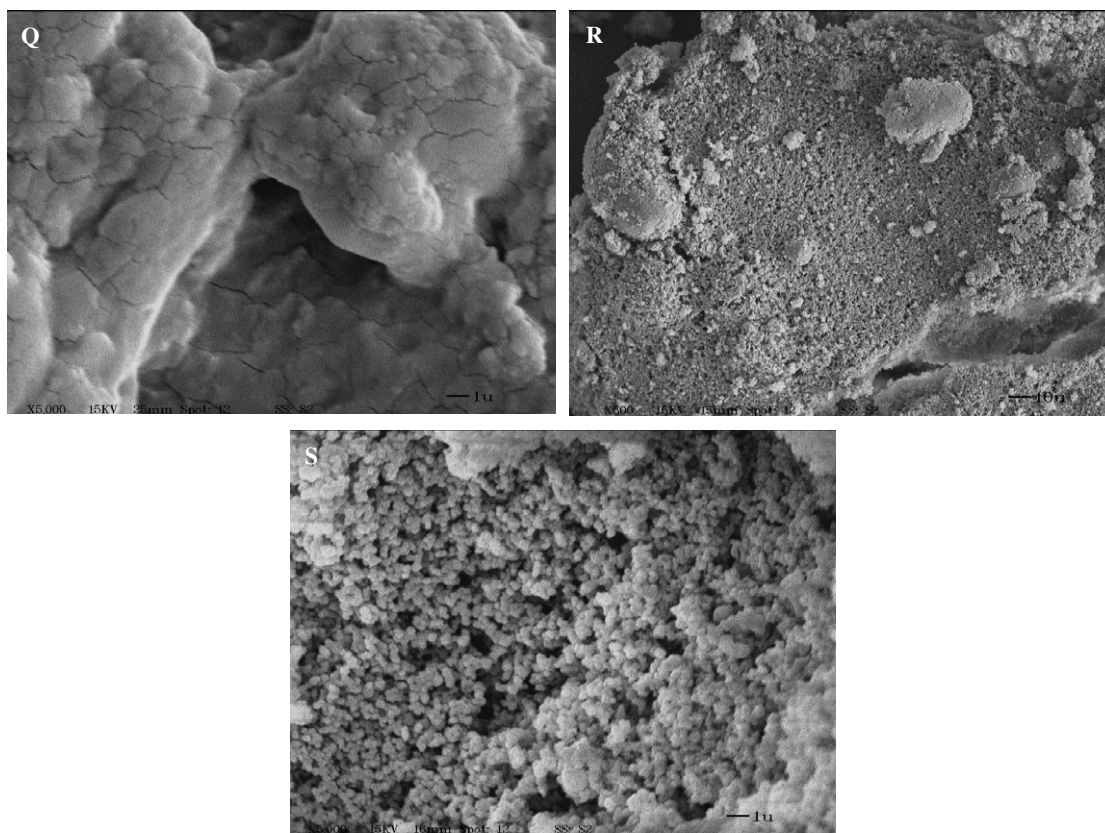


Fig. 2 (continued)

Table 1
Molecular weight, polydispersity, gyration radii and density of amylopectin observed for native starch and starch dispersed in hot water

	$M_w (\times 10^8)^c$	Polydispersity ^d	R_z^e	Density ^f
<i>Native starch</i>				
Corn	11.30 ± 0.57	1.38 ± 0.05	382 ± 8	20.2 ± 0.2
Rice	8.53 ± 0.20	1.59 ± 0.13	355 ± 8	19.0 ± 0.8
Wheat	10.10 ± 0.15	1.64 ± 0.03	368 ± 5	20.1 ± 0.5
Potato	1.43 ± 0.75	1.35 ± 0.25	323 ± 115	5.1 ± 2.5
<i>Dispersed in water</i>				
Corn	6.76 ± 1.75	1.87 ± 0.10	360 ± 35	12.7 ± 1.3
Rice	6.51 ± 0.60	1.66 ± 0.03	342 ± 16	16.3 ± 1.0
Wheat	9.79 ± 2.59	2.01 ± 0.19	460 ± 86	11.8 ± 3.3
Potato	1.84 ± 0.07	1.62 ± 0.01	357 ± 16	4.2 ± 0.3
<i>Dispersed in ionic liquid^g</i>				
Corn	0.82 ± 0.12	1.23 ± 0.02	162 ± 10	34.0 ± 3.7
Rice	0.40 ± 0.04	1.50 ± 0.04	144 ± 11	18.2 ± 1.9
Wheat	0.24 ± 0.03	1.46 ± 0.05	182 ± 12	22.3 ± 1.8
Potato	4.06 ± 0.05	1.43 ± 0.09	198 ± 7	7.4 ± 0.2

Additionally, average molecular weight of all peaks observed with factoring for concentration for starch heat-dispersed in the ionic liquid, 1-butyl-3-methyl imidazolium chloride, and polydispersity, gyration radii and density of the highest molecular weight peak observed for starch (except corn starch where second highest molecular weight peak is reported) dispersed in ionic liquid^{a,b}. Values after ± represent the standard error of the mean.

^a Data were obtained from two injections for each of three replicate.

^b All samples were dissolved in 90% DMSO solution and precipitated with 5 vol. ethanol; freshly prepared starch aqueous solution (100 μL; 0.5 mg/mL) was injected to HPSEC system.

^c Weight-average molecular weight.

^d Polydispersity (M_w/M_n).

^e z-Average radius of gyration.

^f Density is equal to M_w/R_z^3 . Values for density may not correspond directly to data in table due to rounding of M_w and R_z .

^g Average molecular weight of all peaks observed with factoring for proportion of each peak based on peak height. Polydispersity, R_z and density are reported for the highest molecular weight peak except for corn starch in which the second highest molecular weight peak is reported (disregarding the small high molecular weight peak).

rice, wheat and potato starches in native state and heat-dispersed in water or ionic liquid is shown in Table 1. Corn and rice starches dispersed in deionized water had a substantial decrease in amylopectin M_w , but wheat and potato starch M_w was unaffected. A previous study found temperature degraded amylopectin polymers of maize amylopectin and high-amylose maize (Bello-Pérez, Roger, Baud, & Colonna, 1998) and dissolution of corn starch in hot water was found to lower amylopectin M_w relative to autoclaving and microwave heat treatments (You & Lim, 2000). Rice starch heated at 80 °C for 1 h (Mizukami, Takeda, & Hizukuri, 1999) or soaked for 2 h at 40 °C followed by steaming (Lu, Chen, & Lii, 1996) resulted in amylopectin degradation. The degradation of corn and rice amylopectin, but not wheat or potato, when starch was heat-dispersed in deionized water could be due to differences in amylopectin branch chain-length distribution (Hanashiro, Abe, & Hizukuri, 1996; Jane et al., 1999). Polydispersity of deionized water-dispersed rice amylopectin was unaltered compared with native starch amylopectin, but the other three starches observed a decrease in amylopectin

uniformity. The R_z of wheat amylopectin increased after dispersion in deionized water, whereas R_z of the other three starches were unchanged. Amylopectin density of the three dense A-type cereal starches decreased considerably after dispersion in deionized water, whereas the relatively less dense B-type potato starch was unaffected. Despite the sophisticated analytical instruments capability to detect structural changes in amylopectin molecular weight, chromatograms of the starch molecular weight distribution show the predominant amylopectin peak is not greatly altered by dispersion in hot deionized water (Figs. 3A, 4A, 5A and 6A versus Figs. 3B, 4B, 5B and 6B).

Large differences in amylopectin M_w were observed for all four starches heat-dispersed in ionic liquid (Table 1). Dispersion in ionic liquid resulted in the formation of six distinct molecular weight peaks for corn starch (Fig. 3C), four peaks for rice (Fig. 4C) and wheat (Fig. 5C) starch, and just two peaks for potato starch (Fig. 6C). M_w of heat-dispersed starch in ionic liquid was calculated by averaging the M_w of each individual peak observed and factoring in the relative proportion of each peak based on peak

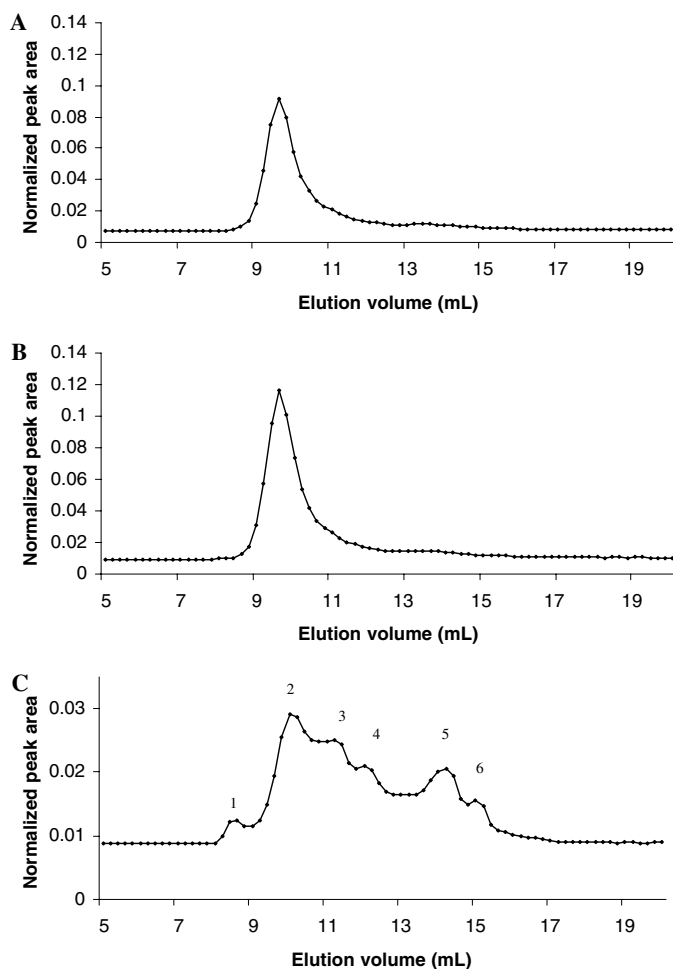


Fig. 3. Molecular weight chromatograms of corn starch in native state (A), dispersed in hot deionized water (B) and heat-dispersed in ionic liquid (C). The molecular weight of the numbered peaks in C are (1) 8.53×10^9 , (2) 2.44×10^8 , (3) 6.82×10^7 , (4) 2.67×10^7 , (5) 2.69×10^6 and (6) 9.70×10^5 .

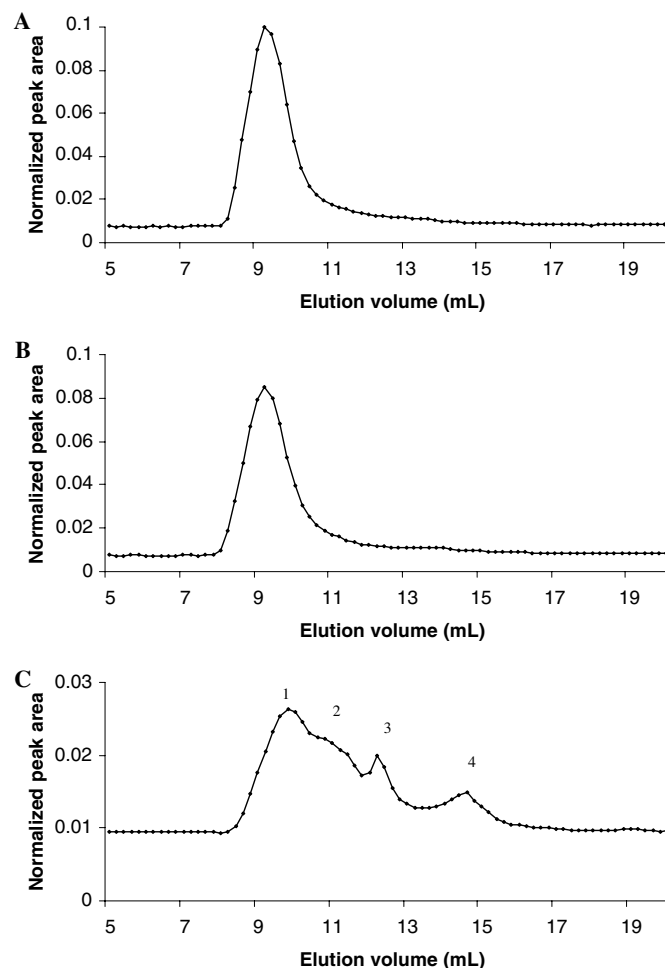


Fig. 4. Molecular weight chromatograms of rice starch in native state (A), dispersed in hot deionized water (B) and heat-dispersed in ionic liquid (C). The molecular weight of the numbered peaks in C are (1) 3.23×10^8 , (2) 9.63×10^7 , (3) 2.04×10^7 and (4) 1.30×10^6 .

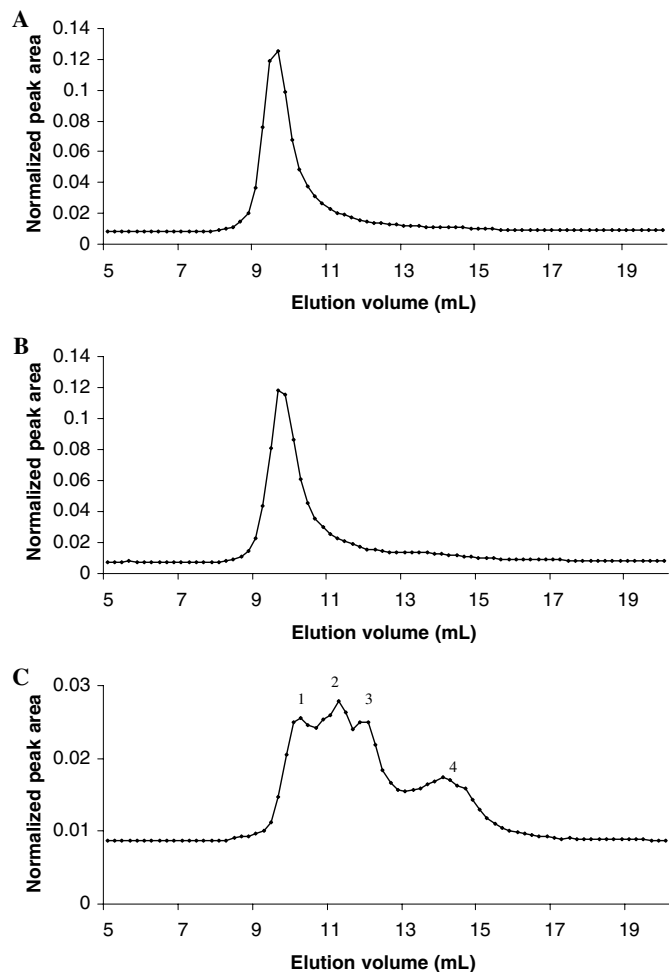


Fig. 5. Molecular weight chromatograms of wheat starch in native state (A), dispersed in deionized hot water (B) and heat-dispersed in ionic liquid (C). The molecular weight of the numbered peaks in C are (1) 2.32×10^8 , (2) 6.90×10^7 , (3) 3.10×10^7 and (4) 3.12×10^6 .

height. A substantial decrease in amylopectin M_w was observed for cereal starches dispersed in ionic liquid compared with both native starch and starch dispersed in hot deionized water, but potato starch had an increase in M_w . The increase in potato amylopectin M_w after dispersion in ionic liquid, that was not observed for the other starches, is most likely due to covalent bonding of the positively charged imidazolium ring of the ionic liquid (Chau-mont, Schurhammer, & Wipff, 2005) and the negatively charged phosphomonoesters of the potato amylopectin molecules (Posternak, 1951). The three cereal starches lack phosphomonoesters and are therefore uncharged and unable to covalently bond with the ionic liquid. The additional possibility of larger potato amylopectin molecules being less affected by ionic liquid, thereby raising the average molecular weight could not be eliminated.

While ionic liquid was effective in solubilizing starch from all four botanical sources, it clearly reduced the amylopectin molecular weight of cereal starches and produced breakdown products with varying M_w for all four starches. In addition to covalent bonding with imidazolium rings, the

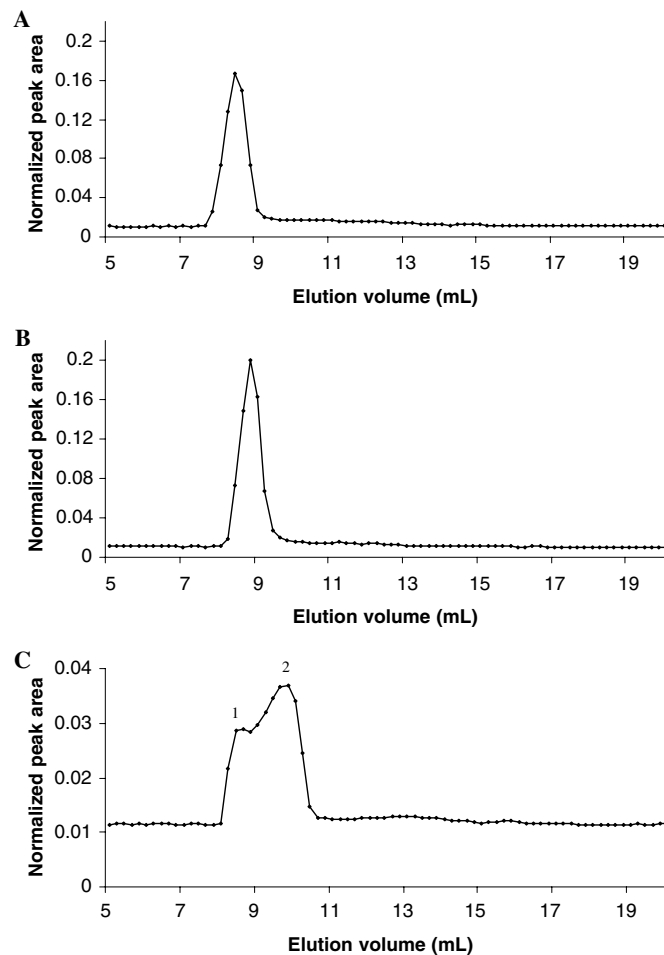


Fig. 6. Molecular weight chromatograms of potato starch in native state (A), dispersed in hot deionized water (B) and heat-dispersed in ionic liquid (C). The molecular weight of the numbered peaks in C are (1) 1.48×10^9 and (2) 3.50×10^8 .

lower degradation exhibited by potato amylopectin compared with the three cereal starches when heat-dispersed in ionic liquid could be related to the ionic liquid chloride ions. Higher chloride concentration of ionic liquids has been reported to increase the solubilization rate of cellulose, and is implicated with breaking the extensive hydrogen bonding network (Swatloski et al., 2002), but disruption of hydrogen bonding will not reduce starch M_w . The ionic liquid may produce acidic conditions that hydrolyze glycosidic bonds or produce alkaline conditions that oxidize and break glycosidic bonds. The negatively charged phosphomonoesters of potato amylopectin (Posternak, 1951) may to some extent repel the chloride ions of the ionic liquid, explaining why potato starch amylopectin has less degradation compared with the three cereal starches that have amylopectin with no phosphomonoesters and are uncharged. The charge repulsion theory is further substantiated by the fact that potato starch has amylopectin with a B-type polymorphism which has lower packing density of crystalline amylopectin double helices compared with the three cereal starches that exhibited the more densely packed A-type polymorphism. Therefore the ionic liquid would be

expected to penetrate and solubilize the potato starch more rapidly compared to the cereal starches, so it is likely the charged amylopectin molecules played a role in reducing potato amylopectin degradation. A contrasting argument could be made that potato amylopectin was less affected by ionic liquid because the much larger size of potato granules hindered ionic liquid penetration. Additionally, potato starch average amylopectin branch chain-length (DP 29.4) is considerably longer than corn (DP 24.4), rice (DP 22.7) and wheat (DP 22.7) amylopectin (Jane et al., 1999), which would require the ionic liquid to disrupt a greater amount of hydrogen bonds and Van der Waals forces in order to result in amylopectin degradation.

Among the three cereal starches heat-dispersed in ionic liquid, the higher number of degradation products resulting from corn amylopectin could be due to differences in starch granule morphology. Wheat starch has a bimodal granule size distribution and granules that vary in shape from lenticular to spherical, whereas rice starch granules are compound (Jane, Kasemsuwan, Lees, Zobel, & Robyt, 1994). Corn starch neither has a bimodal starch granule size distribution, varying granule morphology or compound starch granules and therefore the ionic liquid may have penetrated and reacted with corn starch more effectively than the other cereal starches. The small high molecular weight peak observed for corn starch after dispersion in ionic liquid is most likely unmodified large corn amylopectin molecules rather than covalent bonding between starch and the ionic liquid.

The highest molecular weight peak observed for each starch after dispersion in ionic liquid, with the exception of disregarding the small high molecular weight peak

observed for corn starch, was compared with starch that was native and dispersed in hot water for amylopectin polydispersity, R_z and density. All four starches had a substantial reduction in amylopectin R_z compared with native starch and starch dispersed in hot water. Corn, wheat and potato starches heat-dispersed in ionic liquid had an increase in amylopectin density compared with starch dispersed in hot deionized water, and corn starch dispersed in ionic liquid also had considerably higher density than native starch. The ionic liquid may have allowed greater aggregation of amylopectin molecules to occur in corn starch. All four starches had an increase in amylopectin uniformity when heat-dispersed in ionic liquid compared with deionized water.

3.4. Thermal properties

The thermal properties of corn, rice, wheat and potato starch in native state, and heat-dispersed in deionized water or ionic liquid are shown in Table 2. Starch dispersed in hot deionized water was completely gelatinized for all four starches and similar findings were observed for starch heat-dispersed in ionic liquid except for potato starch that was not completely gelatinized, with a small endotherm observed. Significant differences were observed in the onset and peak temperatures for melting of the amylose–lipid complex thermal transition among the cereal starches in native state, and heat-dispersed in deionized water or ionic liquid, but these differences are very small. Although the ionic liquid reduced the enthalpy change of the amylose–lipid complex thermal transition for rice and wheat starch, the ionic liquid did not effectively reduce or eliminate this

Table 2

Thermal properties of corn, rice, wheat and potato starch in its native state and heat-dispersed in deionized water or the ionic liquid, 1-butyl-3-methylimidazolium chloride^{a,b}

	Starch transition			Amylose–lipid transition		
	T_o (°C)	T_p (°C)	ΔH (J/g)	T_o (°C)	T_p (°C)	ΔH (J/g)
<i>Native starch</i>						
Corn	62.9 ± 0.1	68.0 ± 0.1	14.9 ± 0.7	86.8 ± 0.8	91.6 ± 0.2	0.85 ± 0.17
Rice	57.6 ± 0.1	65.6 ± 0.3	11.4 ± 0.8	86.0 ± 0.3	91.5 ± 0.5	3.14 ± 0.28
Wheat	55.7 ± 0.2	60.0 ± 0.1	9.4 ± 0.5	87.5 ± 0.4	91.8 ± 0.3	2.51 ± 0.19
Potato	57.6 ± 0.1	62.1 ± 0.0	15.0 ± 0.7	no	no	no
<i>Dispersed in water</i>						
Corn	no	no	no	87.8 ± 0.3	91.6 ± 0.3	0.63 ± 0.13
Rice	no	no	no	86.8 ± 0.5	92.8 ± 1.0	2.42 ± 0.39
Wheat	no	no	no	86.7 ± 0.1	91.1 ± 0.0	2.25 ± 0.18
Potato	no	no	no	no	no	no
<i>Dispersed in ionic liquid</i>						
Corn	no	no	no	87.3 ± 0.4	91.4 ± 0.2	1.14 ± 0.01
Rice	no	no	no	86.8 ± 0.4	91.0 ± 0.2	0.98 ± 0.21
Wheat	no	no	no	87.3 ± 0.3	91.2 ± 0.2	1.01 ± 0.26
Potato	55.1 ± 0.5	59.5 ± 0.2	1.84 ± 0.7	no	no	no

Values after ± represent the standard error of the mean.

no = not observed.

^a Data were obtained from three analyses for each of three replicate.

^b Starch samples (~2.0 mg, dry starch basis) and deionized water (~6.0 mg) were used for the analysis; T_o , T_p and ΔH are onset and peak temperature, and enthalpy change, respectively.

thermal transition like ionic liquid effectively reduced or eliminated the starch gelatinization thermal transition.

4. Conclusion

Ionic liquids have shown promise in industrial applications to substitute hazardous solvents, enabling environmental friendly green processes. In this study, we evaluated the ionic liquid, 1-butyl-3-methylimidazolium chloride, to disperse corn, rice, wheat and potato starch and compared its modification in structure and thermal properties with starch dispersed in deionized water. We proposed that ionic liquids could replace dimethyl sulfoxide for dispersing starch without altering starch structure or properties, and therefore would be an improved green chemistry solvent for starch. Heat-dispersion in ionic liquid clearly degraded amylopectin to lower molecular weight molecules, with the three cereal starches degraded considerably more than potato starch which in fact had a higher average molecular weight despite the occurrence of amylopectin degradation. Starch dispersed in hot water had a small decrease in amylopectin molecular weight. Potato amylopectin structure was most likely less affected by the ionic liquid because it has phosphomonoesters, that the three cereal starches lack, which are negatively charged and can covalently link to the imidazolium rings or repel the chloride ions of the ionic liquid, and the larger potato granules impeded ionic liquid penetration. Scanning electron micrographs showed starch heat-dispersed in ionic liquid aggregated consisting of clumps with individual particles <1 µm in diameter that most likely would be more soluble than starch dispersed in water that had large aggregates with larger particle sizes or lacked partition. The lack of similarity in structure and properties of the four starches between dispersion in water or ionic liquid suggests that the particular ionic liquid we studied may have limited applications as a solvent for starch.

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