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Understanding the destructuration of starch in water/ionic liquid mixtures

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Abstract

The destructuration of native maize starch in mixtures of water and ionic liquids (IL) containing acetate anions was studied in dynamic heating conditions, combining calorimetry, rheology, microscopy and chromatographic techniques. A phase diagram of starch in water/IL solutions was established. The phase transitions undergone by starch include the typical endothermic gelatinization phenomenon for IL/water ratios lower than 0.5, while for higher ionic liquid content a complex exothermic phenomenon combining mild degradation and solubilization takes place. This results in an optimum destructuration temperature as low as 40-50 °C for an IL/water ratio close to 0.7. In addition, specific macromolecular chain breakings appear to take place, depending on the nature of the cations present, resulting in different macromolecular structures of recovered starch. These results suggest the possibility of solvent media design for a controlled modification of starch macromolecular characteristics.

1. Introduction

As renewable resources are becoming essential for the industry, the creative design and application of innovative technology for the optimization of such resources is a research topic raising a huge interest since the past decade.[1] Among all polysaccharides investigated as potential alternatives to conventional oil based plastics, starch has attracted a large amount of attention.[2] Starch is one of the most abundant biopolymers

in nature, and considering its low cost, renewability, and biodegradability, it can be considered as a raw material for the elaboration of biologically degradable materials.

Starch is composed of two different glucose polymers: amylose, a predominantly linear macromolecule formed from α(1→4) linkages with a molar mass ~10^5 - 10^6 g mol^{-1}, and amylopectin, a massive multiply branched polymer containing both α(1→4) and α(1→6) linkages with a molar mass ~10^7 - 10^9 g mol^{-1}. Starch is synthesized in the form of densely packed granules, containing both amorphous and crystalline regions.[3] Given its granular structure, starch shows low solubility in any conventional solvent in spite of being highly hydrophilic. However, when suspended and heated in excess water, starch undergoes an order-disorder transition called gelatinization. During this phenomenon, starch granules swell and amylose progressively leaches out of the granule, and the semi-crystalline structure is disrupted. Although some starch molecules are readily solubilized in water, some granule remnants may still be present even after gelatinization has occurred. Thus, starch insolubility represents a problem when trying to obtain homogeneous amorphous materials.

In the last years, the performance of ionic liquids (ILs) as solvents for biopolymers has generated lots of interest. ILs are room-temperature molten salts; since they present high thermal stability and are not volatile, it has been reported that they offer an alternative to common organic solvents. For this and because they are easily recyclable and even some of them are biodegradable,[4] they have been classified as 'green solvents'. For these reasons, they have attracted enormous attention over the past decade, becoming a very fertile area of research.[5] Over the last years, the use of ILs to dissolve and process starch has been reported.[6-10] While first reports focused on ionic liquids containing chlorine anions showed strong depolymerisation of starch, limiting the potential applications,[9] more recent works on acetate based ionic liquids are more promising,[8] despite no clear

evaluation of starch degradation in such systems has been communicated by the authors. In presence of chlorine anions, the macromolecular degradation of starch has been related to acidic hydrolysis of glycosidic bonds.[6,9,11-13] According to Mateyawa *et al*.[8] the presence of acetate based ionic liquid is likely to avoid such phenomena. The same authors also reported an exothermic transition when starch was heated in pure and concentrated 1-ethyl 3-methylimidazolium acetate (EMIMAc) water solutions and it was proposed that this exothermic transition was due to starch dissolution, without gelatinization. Stevenson *et al*.[9] reported no enthalpic transition when analysing recovered starch, previously treated with 1-butyl-3-methylimidazolium chloride, suggesting that after heated in ILs, starch is destructured and no further gelatinization can be observed when re-heating in water.

As recalled by Brennecke *et al*.[14] one of the major advantages of ILs is that they offer the possibility of being tailored by modifying the chemical structure of the cation and anion moieties. Consequently, in the present work, we propose to focus on the influence of the cation by comparing the thermal destructuration of starch mixed with water and two acetate based ionic liquids: EMIMAc and Cholinium Acetate. This latter presents the advantage of a very low toxicity, choline being an essential nutrient and thus biocompatible.

2. Experimental

2.1. Materials

Regular corn starch (Maritena 100) was purchased from Tate & Lyle (Paris, France), with an initial moisture content of 12%. EMIMAc was produced by BASF, and supplied by Sigma-Aldrich. Before use, both materials were dried with P_2O_5 under vacuum at room temperature for one week. After this time, starch moisture was lower than 3%.

Cholinium acetate (CholAc) was synthesized by metathesis reaction.[15] Equivalent amounts (0.06 mol each) of cholinium chloride and potassium acetate (both purchased from Aldrich) were dissolved in absolute ethanol, mixed and stirred for 1 hour at room temperature. A white precipitate of potassium was formed and removed by filtration. Ethanol was evaporated on a rotary evaporator. The CholAc thus produced was freeze-dried prior to use. After purification and freeze-drying, CholAc melting point was 83 °C. For analysis, starch was suspended in aqueous solutions of varying IL concentration (from 0% w/w to 100% w/w IL). Since different starch concentrations were also studied, a phase diagram was prepared.

ILs are known to be highly hygroscopic thus sample preparation was carried out in a glove box under dry gas purge.

2.2. Methodology

2.2.1. Micro differential scanning calorimetry (µDSC). Mixtures of 20% w/w starch in different solvents were prepared. Solvent composition varied from 0% ILs (pure water), to 100% EMIMAc or 95% CholAc (due to its high melting point, 5% water was added to CholAc; the melting point of CholAc 95% was 53 °C). Appropriate amounts of IL and water were weighted and thoroughly mixed before starch addition. A reference cell was prepared by adding the same water content than in the sample cell. Sample was stirred (50 rpm at room temperature) for 1 h before being heated from 20 °C to 120 °C and cooled from 120 °C to 20 °C in the µDSC (µDSC7evo, Setaram, Caluire, France) at a heating/cooling rate of 1 °C min^{-1}. The onset (To), peak (Tp) and conclusion temperatures (Tc), and the enthalpy of the transition (ΔH) were determined using Calisto software (Calisto v1.32 DB v1.33). All mixtures were analysed in duplicates.

2.2.2. Macromolecular characterization of samples. High Performance Size Exclusion Chromatography coupled with Multi-Angle Laser Light Scattering, (HPSEC–MALLS) was used. Starch was suspended in IL/water solutions, and stirred for 1 h. These suspensions were then heated in an oil bath (Ministat 240, Huber, Offenburg, Germany) used to mimic the dynamic heating performed with the µDSC: from 20 °C to 120 °C at 1 °C min^{-1}. After this thermal treatment, samples were DMSO-pretreated, precipitated with ethanol, dried and solubilized by microwave heating under pressure, as previously described by Rolland-Sabaté *et al*.[16] Each sample suspension in water at a concentration of 0.5 g L^{-1} was heated for 40 s (maximal internal temperature reached: 152 °C) at 900 W. Starch solutions were then filtered through 5 µm Durapore TM membranes (Waters, Bedford, MA, USA). Carbohydrate concentrations were determined by the sulphuric acid-orcinol colorimetric method described by Planchot *et al*.[17] Sample recoveries were calculated from the ratio of the initial mass and the mass after filtration. Solutions were immediately injected into the HPSEC–MALLS–system. The equipment and the method used were the same as that described previously.[18] The SEC column was Shodex® KW-802.5 (8 mm ID×30 cm) together with a KW-G guard column (6 mm ID×5 cm) both from Showa Denko K.K. (Tokyo, Japan). They were maintained at 30 °C. The two on-line detectors were a Dawn® Heleos® MALLS system fitted with a K5 flow cell and a GaAs laser, (λ = 658 nm), supplied by Wyatt Technology Corporation (Santa Barbara, CA, USA,) and a RID-10A refractometer from Shimadzu (Kyoto, Japan). The eluent (Millipore water containing 0.2 g L^{-1} of sodium azide) was carefully degassed and filtered on-line through Durapore GV (0.1µm) membranes from Millipore (Millipore, Bedford, MA, USA), and eluted at 0.5 mL min^{-1}. Sample recovery rates were calculated from the ratio of the mass eluted from the column (integration of

the refractometric signal) and the injected mass. These last ones were determined using the sulfuric acid-orcinol colorimetric method.[17]

$\overline{M}_n$, $\overline{M}_w$, the dispersity ($\overline{M}_w$ / $\overline{M}_n$), the radius of gyration $\overline{R}_G$ (nm) were established using ASTRA® software from WTC (version 6.1 for PC), as previously described by Rolland-Sabaté *et al*.[16,18] A value of 0.146 ml g^{-1} was used as the refractive index increment (dn/dc) for glucans and the normalization of photodiodes was achieved using a low molar mass pullulan standard (P20).

2.2.3. Rapid Visco Analyser (RVA). Viscosity properties of starch in different solutions were studied with a Rapid Visco Analyser (RVA-3, Newport Scientific Pty. Ltd., Australia). Starch suspensions (7.5% w/w) were prepared by weighting the solvent in a canister and adding starch slowly while stirring. The slurry was heated from 20 °C to 95 °C while being stirred at 960 rpm for the first 10 s and then at 160 rpm until the assay was completed. The heating rate was 10 °C min^{-1}. It was held at 95 °C for 10 min, and finally cooled to 20 °C at a cooling rate of 6.7 °C min^{-1}. Pasting temperature (Tp), peak viscosity (PV), final viscosity (FV), breakdown (BD) and setback (SB) were obtained from the pasting curve. Samples were assessed in duplicate.

2.2.4. Microscopy. The microstructure of the starch suspended in different ILs solutions before and after the enthalpic transitions was analysed with a light microscope LEICA DMRD. Light, polarized light and differential interference contrast images were obtained. Starch suspensions were prepared in the same way than samples analysed by µDSC. The appropriate amount of IL, water (when required) and starch were weighted. These mixtures were stirred for 1 h and then heated in an oil bath (Ministat 240, Huber, Offenburg, Germany) at 1 °C min^{-1} until the corresponding temperature was reached.

Samples were then removed from the bath and cooled in an ice bath. The samples were immediately observed under the microscope.

2.2.5. Statistical analysis. Data obtained were statistically treated by variance analysis, while means were compared by the Fisher LSD test at a significance level of 0.05 (INFOSTAT statistical software, Facultad de Ciencias Agropecuarias, Universidad Nacional de Cordoba, Argentina).

3. Results and discussion

3.1. Differential Scanning Calorimetry (µDSC)

The thermal behaviour of starch mixed with aqueous ILs solutions of different concentrations was monitored by µDSC (Figure 1). Increasing concentrations of ILs were used from the bottom to the top of the Figure. When IL concentration was low, starch underwent a typical gelatinization, represented by an endothermic transition (a second endothermic transition can be observed at around 100 °C, and it is ascribed to the melting of amylose-lipid complexes). The fact that gelatinization shifts to higher temperatures with increasing IL concentration is consistent with the previously described effect of the presence of different salts in aqueous solution.[19,20] The effect of salts on starch gelatinization has been found to follow the Hofmeister series, with kosmotropes (structure making, salting-out) delaying gelatinization and chaotropes (structure breaker, salting-in) accelerating it. Acetate is a well-known kosmotrope, so it was expected to produce a shift of gelatinization toward higher temperatures. Nevertheless, a further increase in IL concentration (up to 50% for EMIMAc and 60% for CholAc) led to a decrease in gelatinization temperature. This trend will be discussed below (see *Macromolecular characteristics*).

If we now consider high ILs concentrations (from the top to the bottom, Figure 1) an exothermic transition is present (the highest CholAc concentration studied was 95%, but these results were not included in the Figure since the exothermic peak was not complete at 120 °C, which is the upper limit for the µDSC, but peak onset temperature can be observed in Table 1). This exotherm starts at lower temperatures when water is added, and the heat released (ΔH) is also decreased. There is a critical concentration (depending on the IL used) were both transitions (exo and endothermic) take place: CholAc 70% and EMIMAc 60%. In the former case, both transitions can be observed, but in the latter both phenomena seem to happen at very close temperatures thus probably cancelling one another.

The same behaviour was also observed by Mateyawa *et al*.[8] working with EMIMAc and by Koganti et al.[21] using N-methyl morpholine N-oxide (NMMO). These authors attributed the exothermic transition to starch dissolution in these solvents. Enthalpy values for the exotherm for normal corn starch in NMMO were 17.5 J g^{-1} (no enthalpy change was observed when increasing NMMO concentration from 70 to 78%), whereas Mateyawa *et al*.[8] did not provide any ΔH value. In the present study, ΔH of exothermic transition ranged between 17.3 J g^{-1} (70% EMIMAc) and 180.7 J g^{-1} (100% EMIMAc) (Table 1). Moreover, when heating at low rates (0.1 °C min^{-1}), two peaks were clearly observed by µDSC (data presented in supplementary material section, Figure S1); this finding indicates that more than a single phenomenon would be responsible for the exothermic transition. The same trends were observed at different starch/solvent ratio (data not shown).

3.2. Macromolecular characterization of treated starches

In order to understand the phenomena underlying the exothermic transition, macromolecular properties of starch treated with ILs were studied using HPSEC-MALLS system. To this end, starch was treated with different IL/water solutions, recovered and DMSO-pre-treated. The

DMSO pre-treatment recoveries were between 95 and 100% for all samples. DMSO pre-treatment is known to remove the polysaccharide oligomers with degree of polymerization (DP) lower than 12. Thus, this high recovery percentage shows that the heating of samples in different IL solutions does not induce the apparition of sugars with DP smaller than 12. The solubilisation recovery rates and the elution recoveries of starches were higher than 90%. The high sample recovery values obtained here indicate that the fractionation response was quantitative for all the samples. Overall, this solubilisation procedure was thus considered as enabling the structural characterization of these samples.

Figure 2a presents chromatograms for starch heated in pure water and in EMIMAc solutions. When considering starch heated in pure water, two peaks were observed for the differential refractive index signal (corresponding to chains concentration). The first and bigger one (Peak I, 5.8 mL) corresponds to amylopectin population, while the second, and smaller, to amylose (Peak II, 6.6 mL). When analysing starch/EMIMAc 100% chromatogram, two peaks are also observed; nevertheless, some important differences can be highlighted: 1) the first peak started to elute at higher volumes, indicating a lower size for these molecules as the elution volume is inversely proportional to the molecular size, 2) the second peak is bigger than the first one, and 3) no evident shift in peak II is observed. In addition the molar mass is clearly lower for each fraction of starch/EMIMAc 100% compared to starch/pure water solutions. Overall, these features indicate that amylopectin is depolymerized when heated in EMIMAc, this explains the shift of amylopectin peak (which accounts for a smaller size), while there is a co-elution of the depolymerisation products and amylose, thus explaining the increased area of the second peak. Finally, no evidence of amylose depolymerisation is found (no shift of the peak II). For samples treated with EMIMAc 70%, amylopectin also eluted at higher volumes, although the overall profile and molar mass distribution

are more similar to that of pure water. For EMIMAc 50%, no shift of amylopectin peak was observed, but the area of the peak II is bigger than for starch treated with water, indicating the presence of amylopectin depolymerisation products. Nevertheless, since mild depolymerisation occurs under these conditions (Table 2) the detector response to amylopectin is still high.

For the starch heated in 95% CholAc, only one peak could be clearly detected, while amylopectin fraction is represented by a shoulder (Figure 2b) and the molar mass is smaller for each elution volume. This accounts for the depolymerisation of amylopectin by CholAc as well. When water was added to CholAc, a shift of amylopectin elution toward higher volumes is still present, but again the overall behaviour is more similar to that of pure water.

Table 2 shows $\overline{M}_w$ values and $\overline{R}_G$ obtained by integrating the signals for the whole population of molecules present in the sample. A progressive and linear reduction in w is observed when EMIMAc concentration is increased, with a reduction % of 29, 48 and 80% for EMIMAc 50%, EMIMAc 70% and EMIMAc 100%, respectively, compared to starch heated in pure water. Interestingly, when treated in CholAc, the reduction in $\overline{M}_w$ was non-linear, and reduction % were 25, 24, 27 and 81 for CholAc 60%, CholAc 70%, CholAc 80% and CholAc 95%, respectively. The same trend was observed for $\overline{R}_G$. This indicates that both ILs have a different response in the presence of water, with rather small quantities of water (80%) reducing significantly the depolymerisation caused by CholAc.

The dispersity ($\overline{M}_w$/ $\overline{M}_n$) decrease for samples treated with ILs (from 7.56 to 7.10 and 4.48 for EMIMAc 100% and CholAc 95%, respectively) is linked to the reduction of the overall peak broadness, and explained by the reduction of the amylopectin molar mass.

Although the two acetate based ionic liquid tested do not completely avoid starch depolymerisation, the reductions of molar masses found in this study are very different to those obtained after treating starches with halide based imidazolium IL, where reductions of 1-3 order of magnitude can be observed.[6,9,12]

From Table 2 it can be observed that a slight depolymerisation takes place when treating starch with EMIMAc 50% and CholAc 60%, even though no exothermic transition was observed by µDSC. This finding may explain why gelatinization shifts to lower temperatures and ΔH decreases when starch is heated in µDSC with these IL-solutions, since this mild depolymerisation may facilitate starch swelling shifting gelatinization toward lower temperatures.

Moreover, the significantly lower molar masses observed for amylopectin populations (Peak I, Figure 2) in EMIMAc 100% and particularly in CholAc 95% treated samples compared to starch/pure water solutions account for a less dense structure (as these fractions exhibit the same size because elution volume is proportional to size in HPSEC). One can deduce that the original amylopectin population is linearized after heating in ILs, and further in CholAc.

To sum up, it is clear that starch is depolymerized when heated in IL and that the depolymerization pattern varies according to the cation nature, and not only to anion characteristics. Though at present it is not possible to propose a mechanistic explanation for this differential behavior, these results suggest the possibility of tailoring ionic liquid for a controlled modification of starch macromolecular characteristics through mild depolymerisation during destructuration.

The possible interaction between starch and IL during heating that could lead to the formation of new molecular species was monitored by FTIR and NMR. No significant

changes were found between starch heated in water or ILs. These results can be collected as Supplementary material (Figures S2 and S3).

It is also possible that the mechanism involves not only starch and LI, but also water molecules. For future studies, a possibly fruitful approach for trying to understand the interactions between these three components and their influence on the destructuration mechanism would be the use of molecular simulation. A recent paper showed the particular interest of this tool for understanding the interactions in the case of cellulose dissolution in IL/water and IL/DMSO mixtures.[22] It would also be interesting to study the destructuration of starch in IL/DMSO mixtures, since these simulations show that the co-solvent nature plays an important role in cellulose dissolution by IL.[22]

3.3. Microstructure of starch suspensions

Figure 3 presents some representative images of corn starch heated in ILs solutions under light and polarized-light (Figure 3a) microscopy, and differential interference contrast and polarized-light (Figure 3b and c) microscopy. Figure 3a presents images of samples before the enthalpic transition (depending on water content, endothermic or exothermic) for starch suspensions heated in EMIMAc solutions where a well-defined granular structure can be observed (similar images were obtained for CholAc, data not shown). Images of starch suspensions after the enthalpic transition when heated in EMIMAc and CholAc solutions are presented in Figure 3 (b,c). From these images, it can be observed that when heated in pure water, starch granules are gelatinized: swelled, deformed and with no remaining crystallinity. However, when EMIMAc is added (30 and 50%), gelatinization is not complete, since some granules are still birefringent as a result of their crystallinity. When EMIMAc reached 70%, however, no polarization was evident after heating, and neither was the presence of granular remnants, and the same was

observed for EMIMAc 100%. The absence of granular remnants may indicate that starch is not only depolymerized in concentrated EMIMAc solutions, but also it is solubilized. Both phenomena, leading to an overall starch destructuration, may account for the exothermic transitions observed by µDSC. Figure 3c shows the same behaviour when CholAc was used, but 80% of CholAc was necessary to achieve complete destructuration, since at a lower concentration (70%) granular remnants were present. Interestingly, starch suspended in EMIMAc 70% and CholAc 80% is completely destructured at 56 °C and 92 °C, respectively, and under these conditions, only mild depolymerisation is produced (Table 2).

When EMIMAc 100% and CholAc 95% were used, a few gas bubbles were observed under the microscope. These gas bubbles may indicate the formation of volatile products, but could not be identified.

These results are supported by images obtained with an Environmental Scanning Electron Microscope –ESEM- for starch heated in pure water, pure EMIMAc and CholAc 95%. In these images, the destructuration/solubilisation process is evidenced (Figure S4).

3.3. Rapid Visco Analyser (RVA)

RVA is an empirical study commonly performed on starch slurries to follow viscosity behaviour as the sample is heated. While heated, the starch granules start to retain solvent and swell, which results in a concomitant increase in viscosity, i.e. viscosity onset temperature. The viscosity of the suspension increases to the point where the number of swollen-intact starch granules is maximal. Peak viscosity (PV) is indicative of solvent-binding capacity. Whereas the temperature increases and the granule absorbs as much solvent as to achieve its rupture point, the viscosity decreases to a minimum. This decrease in viscosity is called breakdown (BD). When starch suspension cools, amylose

retrogrades (re-crystallizes), resulting in an increase in viscosity named setback (SB), until a gel is formed at the end of the test. In this study, viscosity onset temperature correlated with µDSC onset temperature, although the former was higher than the latter (Tables 1 and 3).

It has been established that viscosity onset is higher that gelatinization onset temperature,[23] since different techniques detect starch transitions in different ways giving slight differences in the determined parameters.

Figure 4 presents the viscosity profiles of starch in EMIMAc (Figure 4a) and CholAc (Figure 4b) solutions. ILs alone were also analysed, their viscosity was near zero and no change in viscosity was observed during heating and cooling processes. From Figure 1 it can be seen that starch heated in concentrated EMIMAc solutions (100% and 70%) undergoes an exothermic transition, related to starch depolymerisation/solubilisation; and when EMIMAc was 50% or lower, an endothermic transition - ascribed to gelatinization- took place. Figure 4a shows that when EMIMAc 100% is used, viscosity increases as depolymerisation/solubilisation take place. During cooling stage, viscosity increases significantly, probably as a consequence of the interaction between the products of depolymerisation which are smaller and less branched than amylopectin, favouring their association, and also to amylose retrogradation. As water is added (EMIMAc 70%) the viscosity onset temperature and peak viscosity are lower (in agreement with µDSC results, Table 1). The decrease in the viscosity onset temperature is related to the lower viscosity of the solvent when compared to pure EMIMAc, and its diffusion into the granule which would be faster, facilitating depolymerisation. However, starch depolymerisation is lower in EMIMAc 70%, explaining the lower viscosity value during heating when compared to pure EMIMAc (Table 3). Increasing the water content to 50% (EMIMAc 50%), the solvent diffusion into the granule

increases and the amount of water is enough to gelatinize starch. In addition, a slight depolymerisation is also observed with EMIMAc 50% (Table 2). Both phenomena may explain the higher viscosity shown by this sample (Table 3). When EMIMAc 30% is used, the pasting behaviour is closer to that of starch in pure water, although overall viscosity is higher. These results are in good agreement with Mateyawa *et al.*[8]

Figure 4b shows that starch in CholAc solutions have a different behaviour than in EMIMAc solutions. When heated in concentrated CholAc solution (CholAc 95%) two peaks are present: at the beginning of the test, CholAc is in solid state –explaining the high viscosity of the sample at this point- but as temperature increases it melts; a second increase in viscosity is observed during the cooling period. The exothermic peak (observed by µDSC) for this sample starts at around 97 °C (Table 1), this may explain the absence of a viscosity peak during heating. However, some depolymerisation may have occurred during the heating at 95 °C forming smaller and more linear molecules from amylopectin, explaining the slight increase in viscosity during cooling. CholAc 70% could not be analysed since viscosity exceeded RVA limit (10000 cP).

For CholAc 50% and 30%, an increase in viscosity was observed between 85-90 °C (Table 3), and no viscosity breakdown was found. The viscosity increase started late during heating, while the maximum temperature reached by the RVA is 95 °C. This temperature may not be sufficient to completely disrupt starch granular structure, although granules may swell and some amylose may leach out, resulting in a viscosity increase.

3.4. Phase diagram

Summarizing, Figure 5 shows corn starch phase diagram when treated in different ILs solutions. When IL concentration is high, complete loss of granular structure is observed (result supported by microscopy images), and this destructuration is accompanied by

starch depolymerisation (HPSEC-MALLS results), the degree of depolymerisation depending on water amount. When water content is sufficiently high, gelatinization occurs, instead of destructuration/solubilisation. Under these conditions, granular remnants are still observed after heating. When EMIMAc 60% is used, a partial gelatinization followed by partial destructuration/solubilisation takes place, and the same is true for CholAc 70%.

Conclusions

Results presented in this study show that two different phenomena take place when starch is heated in EMIMAc and CholAc solutions: when concentration of both ILs is low enough, gelatinization is the dominating phenomenon, whereas when concentration is higher, depolymerisation and dissolution of starch take place. The effect of both ILs on gelatinization corresponds to that of stabilizing salts.

EMIMAc and CholAc have shown to be appropriate solvents for starch destructuration when mixed with the correct amount of water (30% water for EMIMAc and 20% water for CholAc). At these concentrations, destructuration (depolymerisation + dissolution) starts at temperatures as low as 36 °C and 68 °C, respectively and, after heating at 120 °C, starch average molar mass is reduced by 27 and 48% when heated in CholAc 80% and EMIMAc 70%, respectively. This suggest that specific starch chain breakings may occur depending on the cation present in the IL, which could open the possibility of solvent media design for a controlled modification of starch macromolecular characteristics.

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Notes and references

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Electronic Supplementary Information (ESI) available: [µDSC, FTIR, 13C CP/MAS NMR results and ESEM images are provided as Supplementary Material]. See DOI: 10.1039/b000000x/

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Table 1. µDSC results for regular corn starch heated in ILs/water solutions.

Solvent	Transition	ΔH (J g^{-1})	To (°C)	Tp (°C)	Tc (°C)
0% IL (pure water)	Endo	11.9±0.2a	60.3±0.1b	67.2±0.0b	73.3±1.4d
10% CholAc	Endo	13.7±0.0b	72.5±0.5c	78.4±0.1c	84.6±0.4ef
20% CholAc	Endo	14.3±0.9bc	77.5±0.2de	82.7±0.1d	86.7±3.4fg
30% CholAc	Endo	16.2±0.0d	80.3±0.5e	85.7±0.6d	89.8±0.1g
50% CholAc	Endo	16.2±0.5d	73.9±0.4cd	78.7±0.2c	83.1±0.1e
60% CholAc	Endo	14.4±0.9bc	58.7±4.7b	65.1±3.4b	69.6±2.6c
70% CholAc	Exo+endo	nd	46.7±0.2B	nd	66.9±0.8b
80% CholAc	Exo	39.5±1.4B	68.2±2.4E	78.4±1.4CD	88.4±1.9CD
90% CholAc	Exo	67.2±12.7C	85.9±1.1F	103.7±2.7E	114.3±3.4E
95% CholAc	Exo	nd	97.8±2.5G	nd	nd
10% EMIMAc	Endo	14.0±0.3b	70.7±1.0c	76.6±0.9c	82.9±0.8d
20% EMIMAc	Endo	14.7±0.4bc	73.1±0.4cd	78.4±0.2c	84.8±0.2ef
30% EMIMAc	Endo	15.5±0.3cd	72.9±0.4c	77.7±0.5c	83.7±0.3ef
50% EMIMAc	Endo	12.5±0.6a	51.5±0.3a	56.4±0.3a	62.9±0.9a
60% EMIMAc	None	nd	nd	nd	nd
70% EMIMAc	Exo	17.3±4.5A	36.2±0.8A	46.7±0.9A	52.2±0.6A
80% EMIMAc	Exo	63.3±2.3C	48.9±1.7B	65.0±1.9B	72.5±0.8B
90% EMIMAc	Exo	110.8±5.3D	56.2±0.5C	74.8±0.5C	85.7±0.8C
100% EMIMAc	Exo	180.7±20.8E	62.3±0.6D	80.1±0.3D	92.4±0.3D

ΔH: transition enthalpy; To, onset temperature; Tp, peak temperature; Tc, conclusion temperature.

Values followed by different lowercase letters in the same column are significantly different ($p < 0.05$).

Values followed by different uppercase letters in the same column are significantly different ($p < 0.05$).

Table 2. Weight-average molar mass ($\overline{M}_w$), dispersity ($\overline{M}_w / \overline{M}_n$) and z-average radius of gyration ($\overline{R}_G$) determined by HPSEC-MALLS for corn starch samples treated in ILs solutions.

	Whole population		
Solvent	$\overline{M}_w$ (10^7) (g mol^{-1})	$\overline{M}_w / \overline{M}_n$	$\overline{R}_G$ (nm)
Pure water	44.36±0.63	7.56±0.49	302.8±1.8
EMIMAc 50%	31.43±2.93	10.59±0.31	275.5±10.7
EMIMAc 70%	23.08±0.15	6.65±1.37	247.6±1.4
EMIMAc 100%	8.78±0.02	7.10±0.04	225.8±1.1
CholAc 60%	33.13±0.18	11.09±0.37	279.2±0.6
CholAc 70%	33.57±2.69	8.44±0.89	268.6±9.5
CholAc 80%	32.3±0.07	5.05±0.06	282.4±2.3
CholAc 95%	8.11±0.00	4.48±0.05	208.5±0.0

Table 3. RVA parameters for regular corn starch heated in ILs/water solutions.

Solvent	Peak viscosity (cP)	Trough (cP)	Breakdown (cP)	Final viscosity (cP)	Setback (cP)	Pasting temperature (°C)
0% LI (pure water)	1444±119a	1049±42ab	374±9b	2673±271b	1623±229a	72.5±0.5c
30% CholAc	2700±41b	2264±18d	nd	1740±27a	nd	90.9±0.8f
50% CholAc	5473±399d	4754±339e	nd	4332±721c	nd	84.9±0.1e
70% CholAc	nd	nd	nd	nd	nd	nd
95% CholAc	nd	nd	nd	nd	nd	nd
30% EMIMAc	3568±76c	1387±38bc	2181±38c	3994±76c	2607±38b	80.6±0.5d
50% EMIMAc	8249±20e	1548±20c	6701±0d	4289±62c	2742±42b	62.6±0.4b
70% EMIMAc	3071±95b	815±16a	2256±79c	3868±36.8c	3053±21c	55.7±0.9a
100% EMIMAc	2849±391b	2681±412d	168±22a	9939±308.6d	7255±105d	78.8±2.1d

Values followed by different lowercase letters in the same column are significantly different ($p < 0.05$).

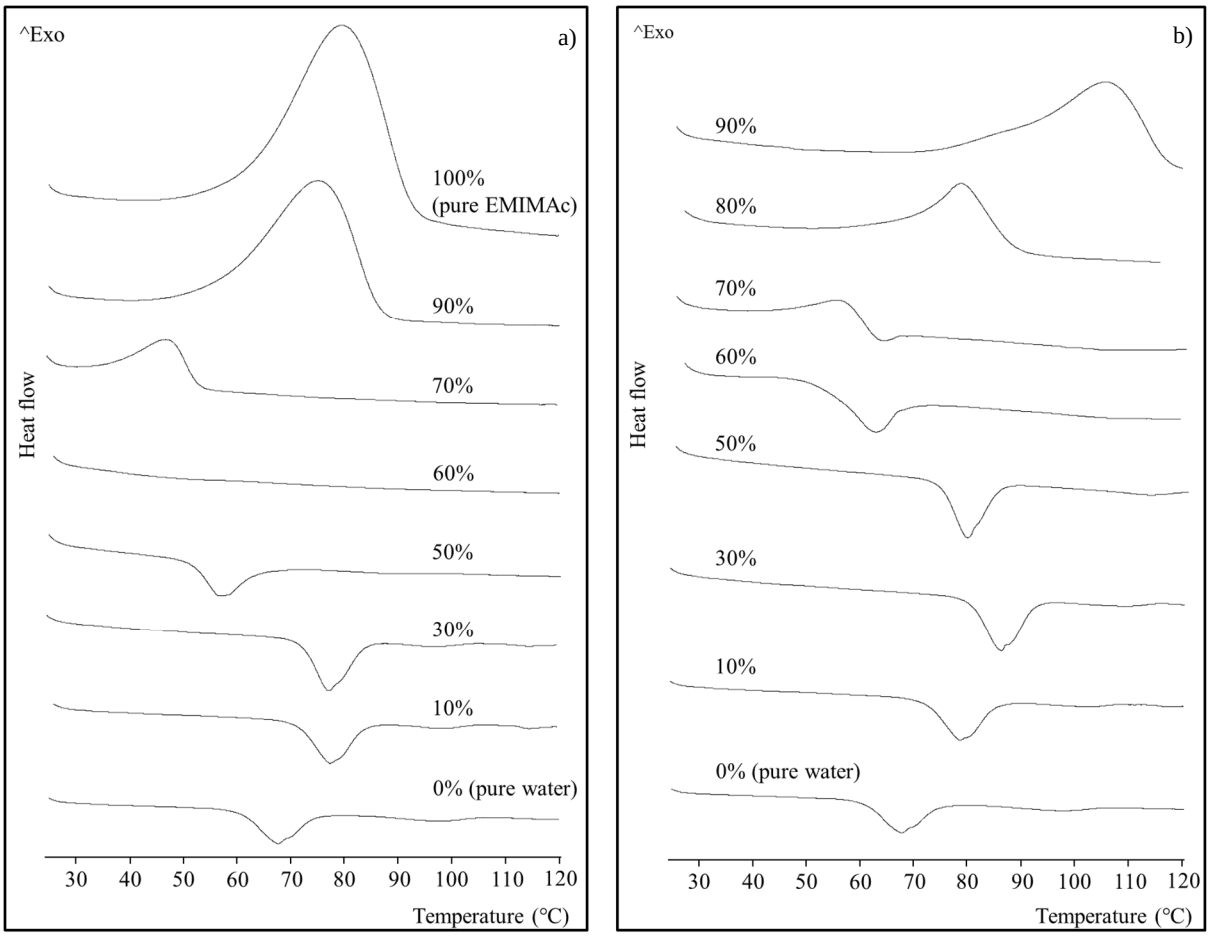
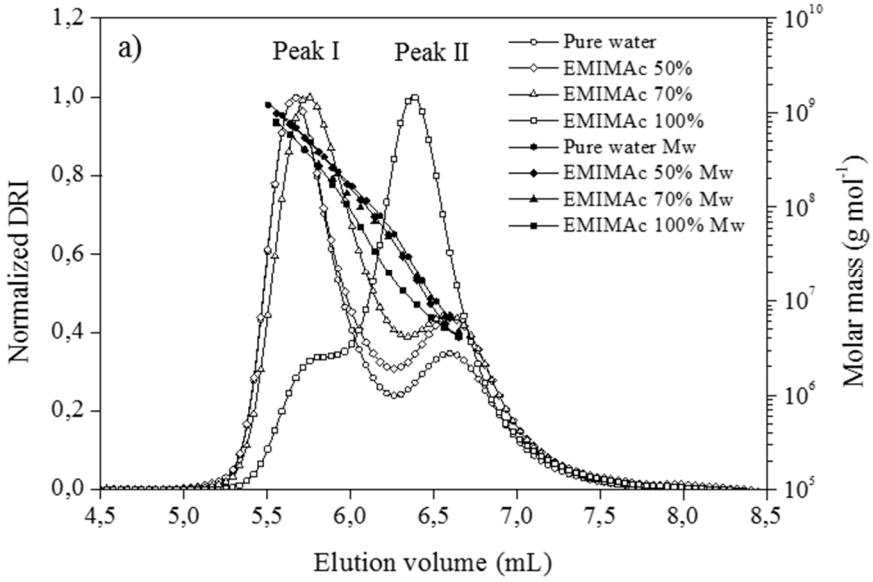


Figure 1. Micro differential scanning calorimetry thermograms for regular corn starch heated in EMIMAc/water (a) and CholAc/water (b) solutions.



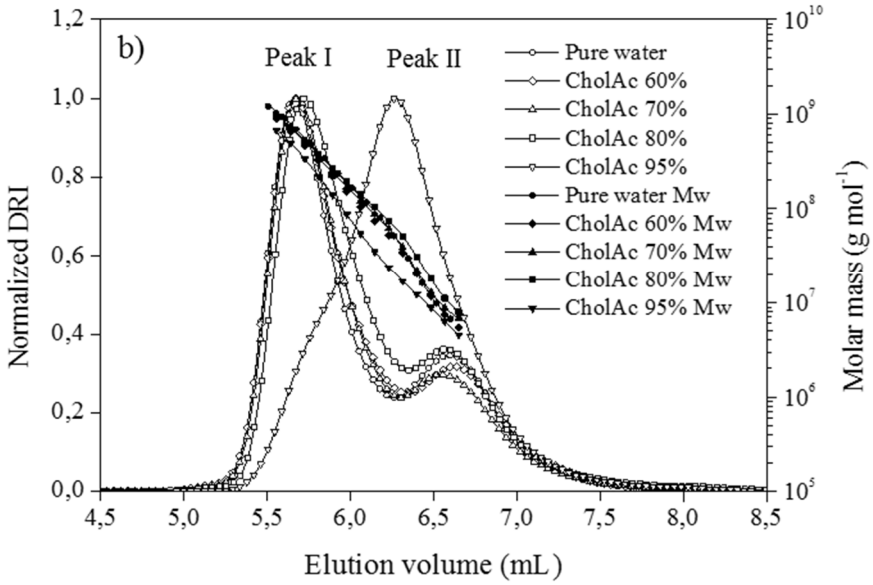


Figure 2. Chromatograms of regular corn starch treated with EMIMAc (a) and CholAc (b) solutions (differential refractive index –DRI- answer) and molar masses (M_w) versus elution volume.

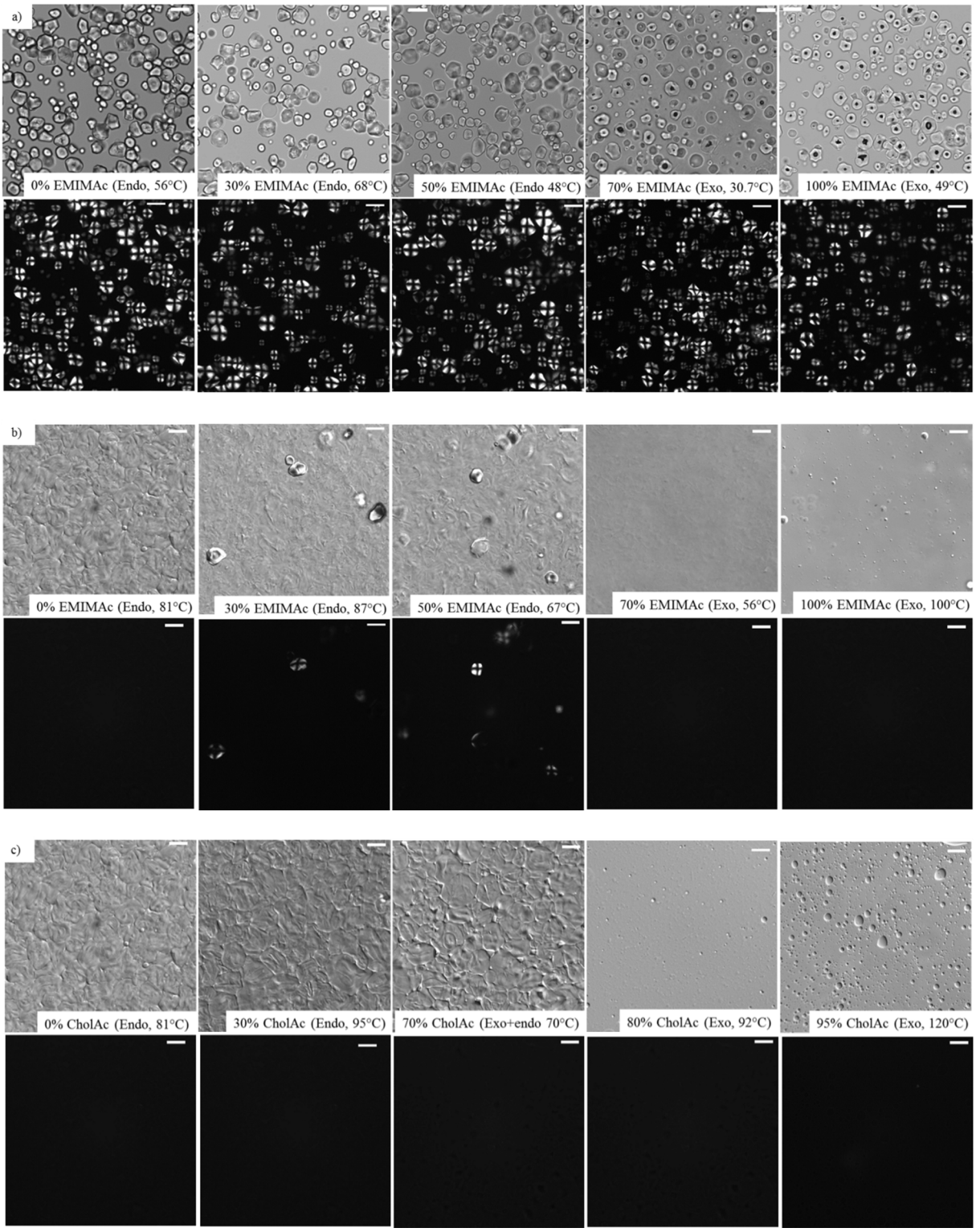


Figure 3. Light, polarized-light and differential interference contrast images for starch treated in ILs. (a) Light and polarized-light images of starch heated in EMIMAc solutions (To); (b) Differential interference contrast and polarized-light images of starch heated in EMIMAc solutions (Tc), and (c) Differential interference contrast and polarized-light images of starch heated in CholAc solutions (Tc). Bar scale: 20 µm.

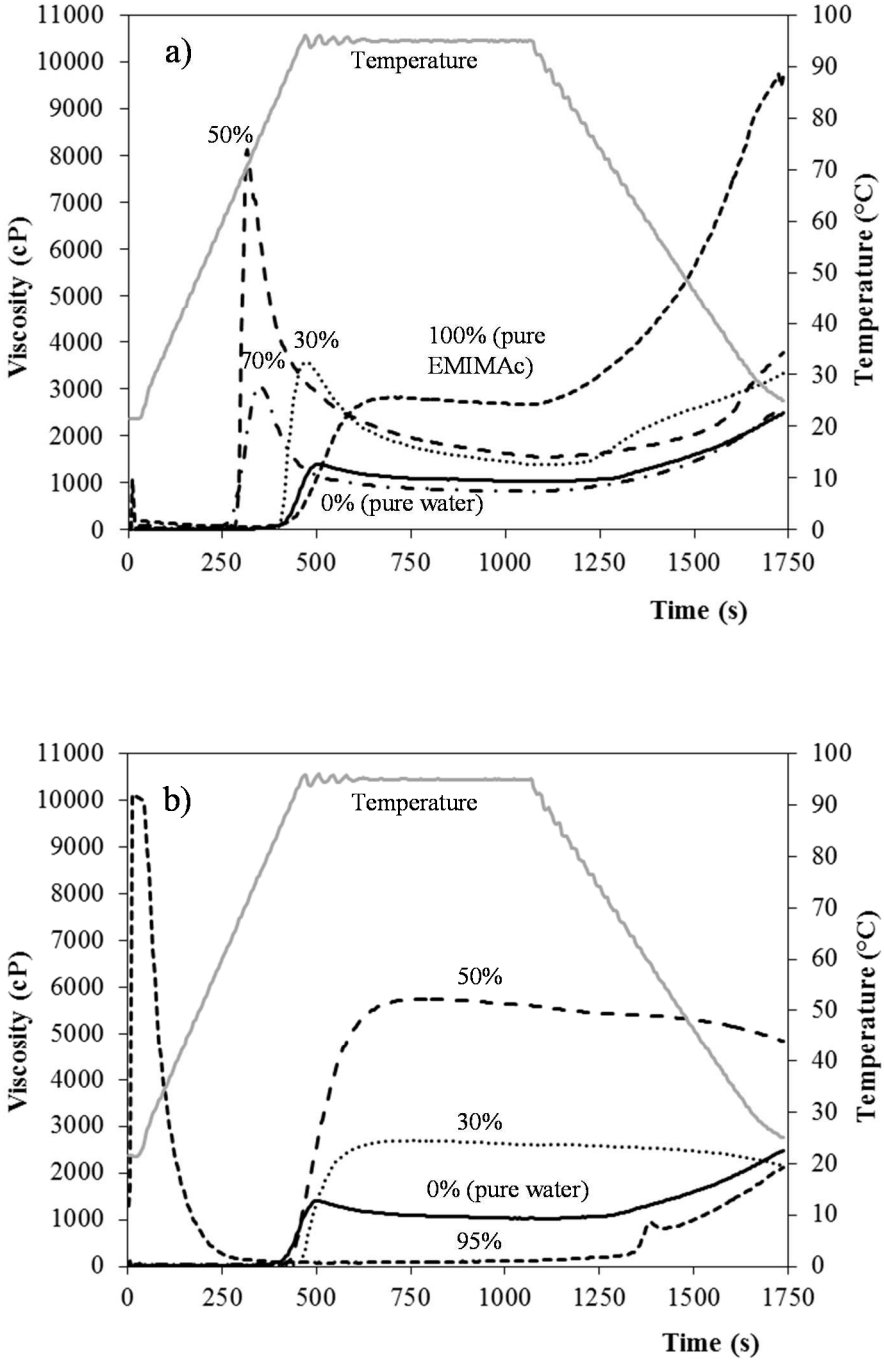


Figure 4. RVA curves for starch heated in EMIMAc (a) and CholAc (b) solutions.

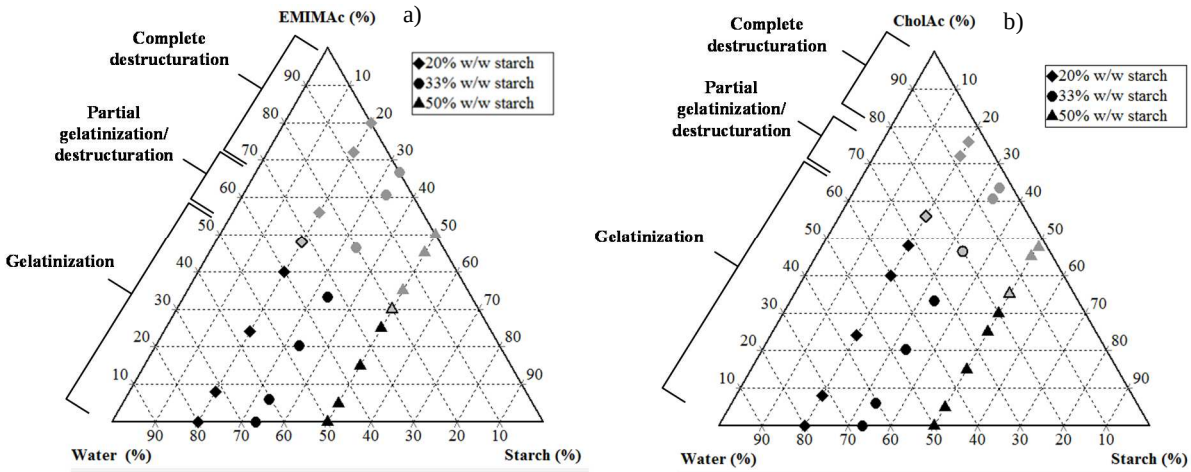


Figure 5. Phase diagrams for starch treated in solution with different ILs concentrations. (a) EMIMAc treated starch, (b) CholAc treated starch.

Supplementary material

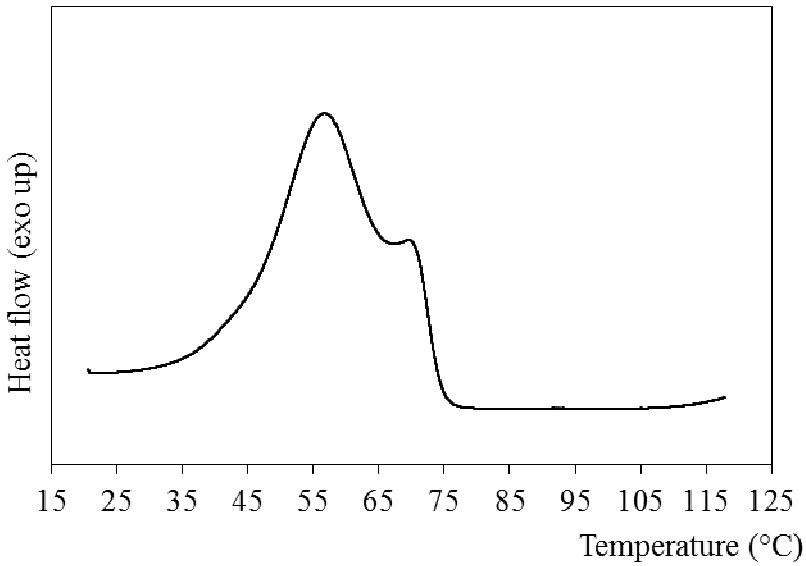


Figure S1. µDSC curve starch heated in EMIMAc at 0.1 °C min^{-1}

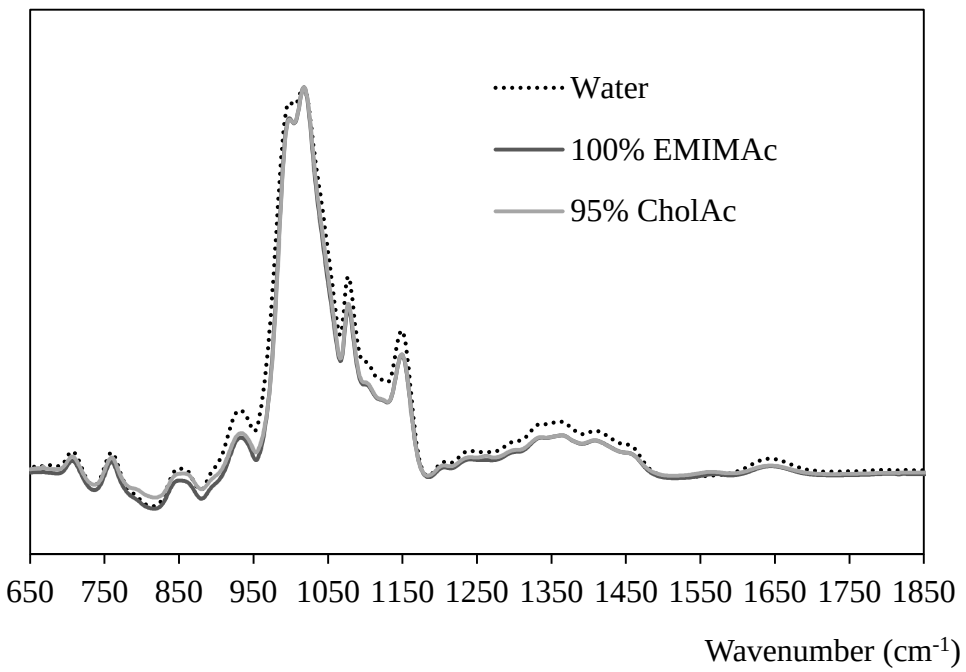


Figure S2. FTIR spectra of starch heated in pure water, EMIMAc 100% and CholAc 95% solutions.

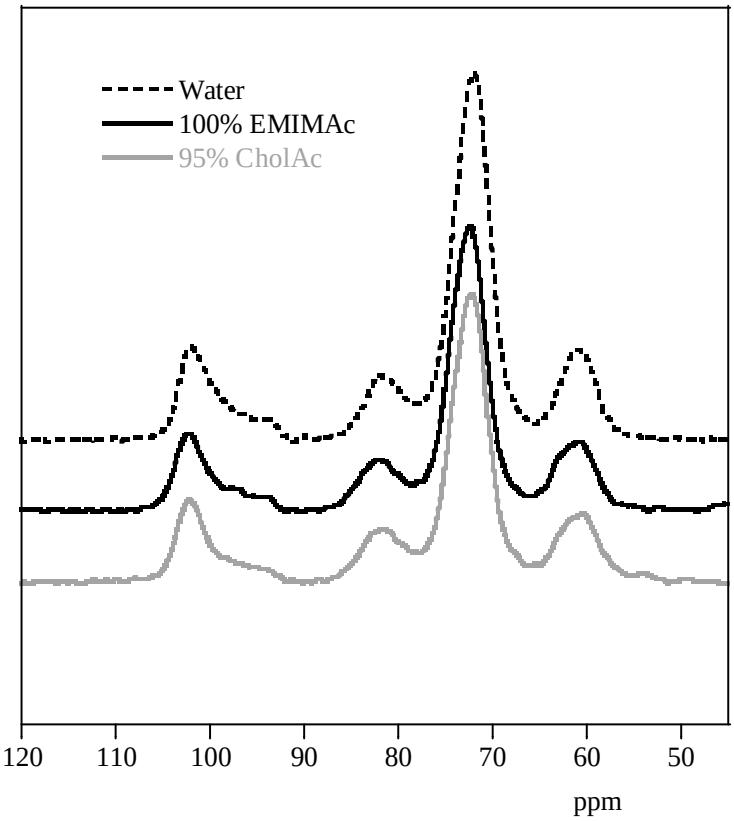


Figure S3. ^{13}C CP/MAS NMR spectra of starch heated in pure water, and EMIMAc 100% and CholAc 95% solutions.

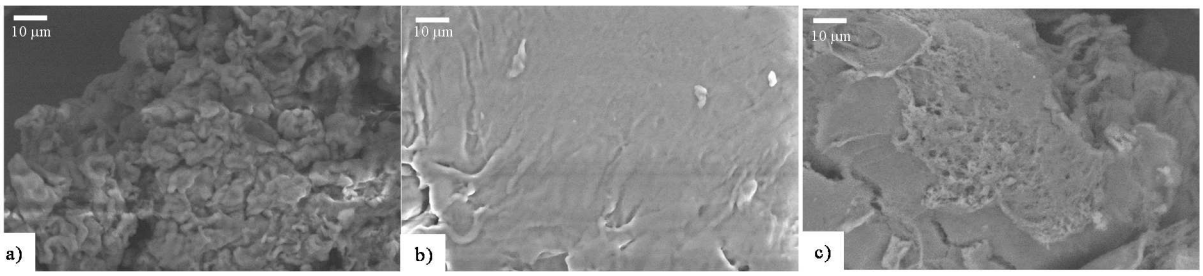


Figure S4. Environmental scanning electron microscopy (ESEM) images of corn starch heated in: pure water (a), EMIMAc 100% (b), CholAc 95% (c).