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Green Chemistry

TUTORIAL REVIEWS

Applications of ionic liquids in starch chemistry: a review

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Recently, the utilization of starch to replace synthetic polymers for the manufacture of green materials has gained extensive interest, due to its renewability, biodegradability, abundance and low cost. On the other hand, ionic liquids (ILs) have been widely recognized as promising "green solvents" to replace the volatile organic solvents for polysaccharides processing. Over the past few years, ILs have been increasingly demonstrated to serve as excellent media for the dissolution, plasticization and derivatization of starch. This allows the synthesis of chemically modified starches with high degrees of substitution (DS) and the development of various starch-based materials such as thermoplastic starch, composite films, solid polymer electrolytes, nanoparticles and drug carriers. The main objective of this review is to present an overview of the roles of ILs in starch dissolution, gelatinization, modification and plasticization, and their industrial applications. Moreover, this review is intended to provide a comprehensive understanding of the mechanisms behind the IL-processing of starch and to provide insights into the rational development of novel starch-based materials with ILs.

Keywords: starch, ionic liquids, dissolution, phase transition, modification, application

1 Introduction

The use of petroleum-based materials and their current processing techniques have been recognized as a threat to the energy and the environment.[1] Sustainable and green chemistries are directing the development of next-generation polymer materials. Biodegradable materials can be generated from renewable biomass feedstock, which are regarded as promising alternatives to replace synthetic polymers and to reduce the global dependence on the limited fossil fuel sources.[2] Starch is the main energy storage in plants, and it is one of the most abundant polysaccharides extracted mainly from tubers (potato, cassava) and cereals (wheat, maize, rice).[3] Starch is utilized largely in food, chemistry, material, fermentation, paper, and pharmaceutical industries because of its low-price, renewability and biodegradability.[3]

The sustainability in materials chemistry depends upon not only the selection of renewable raw materials for their manufacturing, but also on the development of mild pretreatment methods that can reduce the energy consumption and avoid the use or generation of hazardous substances.[4] The critical challenge to extend the applications of biopolymers for manufacturing bio-composite materials is to destroy the strong inter- and intra-molecular hydrogen bonds in these biopolymers.[1] Consequently, considerable efforts have been devoted to disrupting the hydrogen bonds in the biopolymers for enhancing their processability.

Recently, ionic liquids (ILs) have been utilized widely as promising "green solvents" to replace the volatile organic solvents for polysaccharides processing.[5] Over the past few years, ILs have been used as excellent media for the dissolution, plasticization and derivatization of starch,[6] facilitating the synthesis of chemically modified starches with high degrees of substitution (DS),[3] and the development of starch-based materials such as thermoplastic starch,[7, 8] composite films,[9] solid polymer electrolytes,[10, 11] nanoparticles[12] and drug carriers[13-15] (**Fig. 1**).
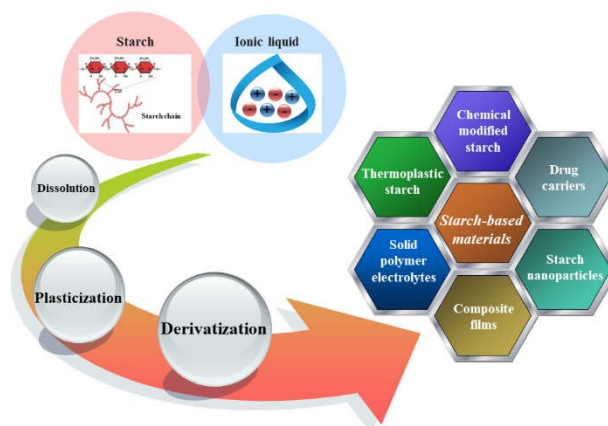

Fig. 1. Overview of the applications of ionic liquids in starch chemistry.

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In recent years, there have been several reviews documenting the advances in cellulose dissolution in ILs.[16-18] To the best of our knowledge, there is only one review paper in 2011 summarizing the applications of ILs in starch.[6] Considering the rapid development of ILs in starch applications especially the novel sustainable engineering

techniques in the treatment of starch using ILs, it is worthwhile to provide a most updated survey of the recent advances in these important aspects. This review presents an overview of the roles of ILs in starch dissolution, gelatinization, modification, plasticization, and wider applications of ILs in starch. Moreover, current discrepancies in the mechanisms regarding the starch-IL interactions are critically examined.

2 Ionic liquids and their related properties for biopolymer processing

Ionic liquids (ILs) refer to "liquid salts composed of ions with melting temperature below 100 °C", which are first introduced in chemical engineering applications around the turn of the 20th to 21st century.[19] Over the past decades, there has been an exponential increase in the number of publications describing the synthesis and application of ILs and there is no doubt that ILs have become a major subject of study in modern chemistry.[20] ILs have been found to efficiently dissolve cellulose without derivatization,[21] leading to the expanded use of ILs in the processing of diverse biopolymers.[3, 5, 6, 17, 22] The processing of different biopolymers (e.g., cellulose, starch, chitin, inulin, chitosan, lignin etc.) and the fabrication of the related biodegradable materials are largely determined by the physicochemical properties of ILs used.[5] Some important properties of ILs that are closely linked to biopolymer processing are illustrated in **Fig. 2** and discussed respectively in the following.
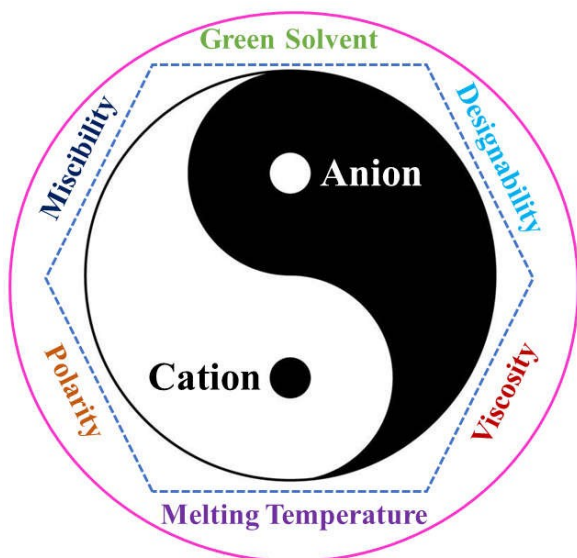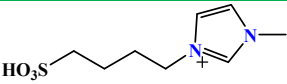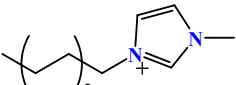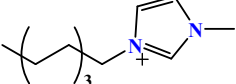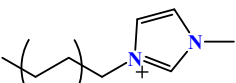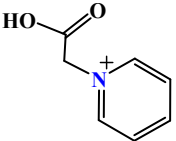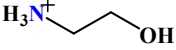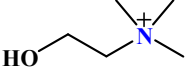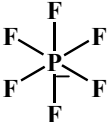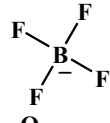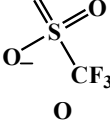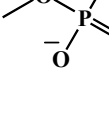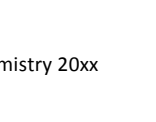

Fig. 2. Physicochemical properties of ionic liquids that are related to biopolymer processing.

Green solvents. Most importantly, ILs can be used as "green solvents" for clean and green technologies.[20] ILs have appealing and unique physicochemical properties such as negligible vapor pressures,[23, 24] non-flammability, excellent thermal and chemical stabilities,[25] notable recoverability and ionic conductivities,[26] and efficient dissolution ability for biopolymers, which make them fascinating candidates for the replacement of volatile organic compounds (VOCs) for biopolymer processing.[27]

Designable solvents. ILs are comprised of an organic cation and an inorganic or organic anion. The commonly used ILs have cations such as alkylimidazolium $[R_1R_2im]^+$, alkylpyridinium $[RPy]^+$, alkylpyrrolidinium $[RPr]^+$, choline $[Ch]^+$, tetraalkylammonium $[NR_4]^+$, tetraalkylphosphonium $[PR_4]^+$ and anions such as halide, carboxylate $[RCOO]^-$, dicyanamide $[Dca]^-$, thiocyanate $[SCN]^-$, tetraflouroborate $[BF_4]^-$, hexaflourophosphate $[PF_6]^-$, methanesulfonate $[CH_3SO_3]^-$. The cations and anions of ILs considered in this review are listed in **Table 1**. The most interesting aspect of ILs in biopolymer processing is the possibility to 'design' or 'tune' a set of specific physical and chemical properties through the adjustment of the cation structure (e.g., the class of cation, the length and symmetry of substituent groups) as well as the selection of the structure and extent of charge delocalization of the anion.[28, 29] The number of potential ion combinations available reputedly equates to a million ILs, whereas just about 600 molecular solvents are in use today.[19] Considering ILs are tunable solvents, they can be designed by an appropriate combination of cations and anions for particular biopolymers, which is not possible when conventional organic solvents are concerned. Among all ILs, those with the combination of imidazolium-based cations and halide-based or carboxylate-based anions have been most commonly used for starch dissolution, plasticization and modification.[6]

Table 1 List of cations and anions of ionic liquids presented in this work.

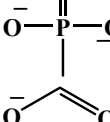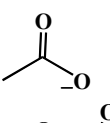| Name	Abbreviation	Structure
Cations		
1-H-3-methylimidazolium	$[Hmim]^+$	
1,3-Dimethylimdazolium	$[Mmim]^+$	
1-Ethyl-3-methylimidazolium	$[Emim]^+$	
1-Propyl-3-methylimidazolium	$[Pmim]^+$	
1-Allyl-3-methylimidazolium	$[Amim]^+$	
1-Hydroxypropyl-3-methylimidazolium	$[C_3OHmim]^+$	
1-Glycidyl-3-methylimidazolium	$[Gmim]^+$	
1-Butyl-3-methylimidazolium	$[Bmim]^+$	

Name	Abbreviation	Structure
1-(4-Sulfobutyl)-3-methylimidazolium	[SBmim]+	
1-Hexyl-3-methylimidazolium	[Hexmim]+	
1-Octyl-3-methylimidazolium	[Omim]+	
1-Hexadecyl-3-methylimidazolium	[C$_{16}$mim]+	
1-(Carboxymethyl)pyridinium	[CMPy]+	
2-Hydroxyethylammonium	[NH$_3$CH$_2$CH$_2$OH]+	
Choline	[Ch]+	
Anions		
chloride	[Cl]−	
bromide	[Br]−	
iodide	[I]−	
Nitrate	[NO$_3$]−	
Hexafluorophosphate	[PF$_6$]−	
Tetrafluoroborate	[BF$_4$]−	
Trifluoromethanesulfonate	[TfO]−	
Methylphosphonate	[(MeO)HPO$_2$]−	
Formate	[HCOO]−	
Acetate	[OAc]−	
Dimethylphosphate	[Me$_2$PO$_4$]−	

Dicyanamide	[Dca]−	

Melting temperature. The melting temperature of ILs depends significantly on the structures of cations and anions. The first reported IL (*N*-ethylpyridinum chloride) for cellulose dissolution in 1930 has limited practical use because of the relatively high melting point (120 °C).[30] The melting temperature of ILs nowadays is below 100 °C due to the design of bulky, asymmetric cations and weakly coordinating anions that destabilize the crystal lattice.[31, 32] An increasing number of carbon atoms in the side chain of the cation results in an increase in the melting temperature of ILs.[16] The alkenyl instead of saturated alkyl in the side chain of the cation decreases the melting point of ILs due to the suppressed crystallization of the ILs.[33] For example, the melting temperature of 1-allyl-3-methylimidazolium chloride ([Amim][Cl]) is 17 °C, which is much lower than that of 1-propyl-3-methylimidazolium chloride ([Pmim][Cl], 60 °C).[34] The presence or absence of strong hydrogen bonds in ILs also influences the melting temperature. The C–H···X (X = Cl, Br) interaction is very strong in alkylimidazolium halide ILs and can even possess some covalent character,[35] which make this type of ILs present higher melt temperatures (typically ≥ 60 °C) than those of conventional solvents. However, the hydrogen bonding interaction in imidazolium acetate ILs is considerably weak, resulting in a low melting point of 1-ethyl-3-methylimidazolium acetate ([Emim][OAc]) (< −20 °C).[17]

Viscosity. The viscosity of ILs, similar to oils, is higher than that of most common molecular solvents.[16] It depends on their inter-ionic interactions (e.g., Coulomb forces, hydrogen bonding, van der Waals interactions) and thus varies considerably with temperature, the chemical structure of IL, and the co-solvent(s).[5] The viscosity of alkylimidazolium-based ILs decreases with increasing temperature and increases with a longer alkyl chain of the cation.[36] Similar to the melting temperature of ILs, the viscosity of ILs is also affected by the hydrogen bonding interaction in ILs.[37, 38] For example, the acetate-based ILs have remarkably lower viscosities than the corresponding chloride-based ILs.[36] In general, the viscosity of ILs with the same cations follows the order [Cl]− > [BF$_4$]− > [PF$_6$]−.[16] For biopolymer processing, viscosity plays a major role in the dissolution of biopolymers in ILs. The high viscosity of ILs is not favorable for the dissolution of biopolymers, thus a co-solvent with low viscosity is always used. Addition of a small amount of water or some other common solvent (e.g., dimethylsulfoxide (DMSO), acetonitrile, dimethylformamide (DMF) and ethylene glycol) reduces the viscosity to almost one-half that of the pure IL.[36, 39-41] The presence of co-solvents decreases the aggregation of the IL ions (**Fig. 3**),[42-44] with the nature of the co-solvent playing a more important role than its content.[45]
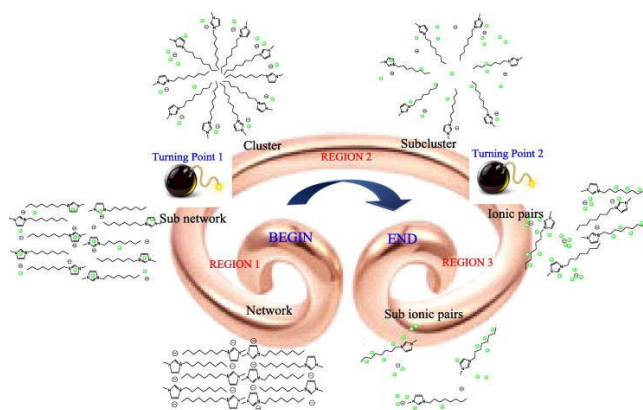
Fig. 3. Dissociation of the ionic liquid by water in an acetate-based IL and water system. The filled green circle represents water. Reproduced from Ref. [42] with permission from Elsevier Ltd. (2014).

Polarity. Many compounds that are insoluble or only partially soluble in other organic solvents can be efficiently dissolved in ILs having strong hydrogen-bond acceptors.[41, 46] Based on their solvation capabilities, ILs are classified generally as highly polar solvents. The Kamlet-Taft method[28] and solvatochromic method[17] have been applied to predict and correlate the solubility of biopolymers and biomolecules in ILs with their polarities.

Miscibility with other solvents. ILs are usually miscible with polar solvents such as ketones, alcohols and dichloromethane, but immiscible with non-polar organic solvents including ethers and alkanes.[5] Based on the solubility of ILs in water, ILs can be classified to be either hydrophilic (water-miscible) or hydrophobic (forming a biphasic system with water). The miscibility of ILs with water depends mainly on the hydrophilic nature of the anion and the hydrophobic nature of the cation.[47] The hydrophobicity of ILs increases with increasing alkyl chain length of cations.[48] ILs with $[PF_6]^-$ anion are water-immiscible, and ILs with $[OAc]^-$, $[NO_3]^-$ and halide anions are water-miscible.[16] The hydrophilic and hydrophobic nature of ILs determines their solvation properties, which in turn determines the recovery of the products by solvent extraction.[49] Generally, the biopolymers can dissolve in hydrophilic ILs but not in hydrophobic ILs.[21]

Toxicity. Toxic effects of ILs are very important for starch processing due to the starch-based products are widely used in the areas of food and biodegradable materials. The structural composition of the IL, including the cation, alkyl chain length and anion can affect the degree of toxicity (**Fig. 4a**).[50-54] While many ILs are classified as "readily biodegradable",[53] some ILs are relatively stable in the environment due to their resistant to photodegradation[55] and small degree biodegradation[56]. Structural modification-based approaches, which yield nontoxic and biodegradable ILs can be followed to design "greener" ILs (**Fig. 4b**). In the future, the design and synthesis of environmentally benign ILs from the green chemistry point of view, as well as research on the development of techniques for the removal of ILs, should be focused on for the development of starch-based products with ILs.

(a)

(b)
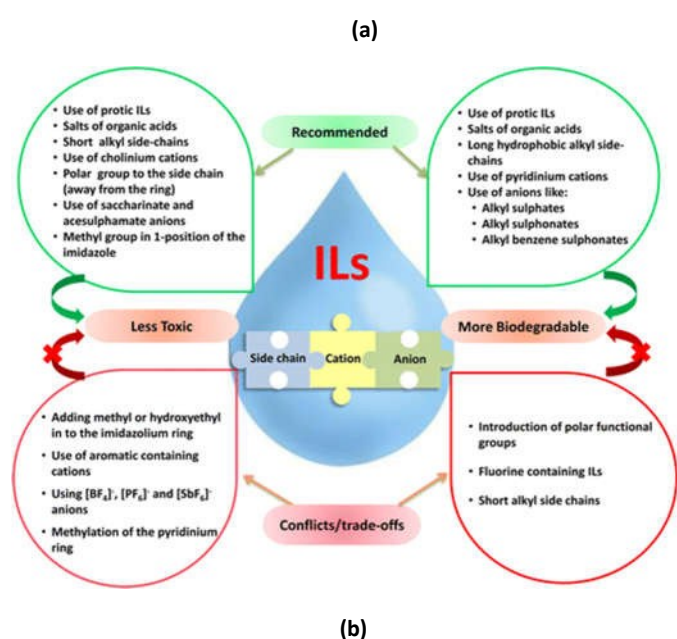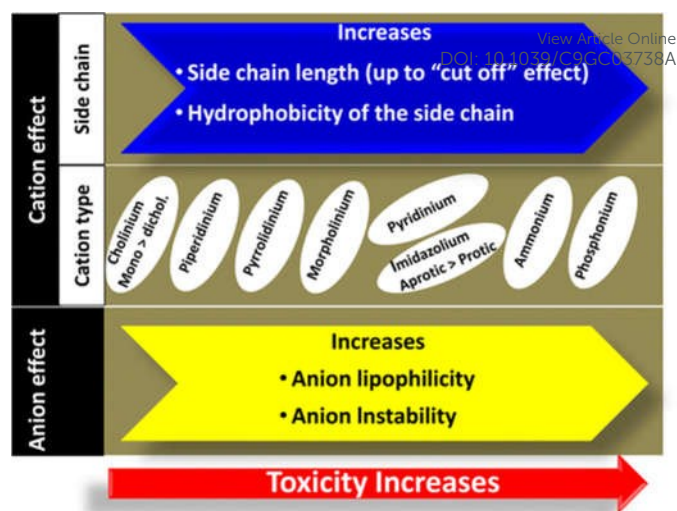
Fig. 4. (a) Effects of structural modification on the toxicity of ILs; (b) Some important routes to the synthesis of less toxic and more biodegradable ILs. Reproduced from Ref. [53] with permission from the American Chemical Society (2015).

3 Starch structure, functionality and industrial application

Biomass such as plant fibers and biopolymers produced from natural resources or microorganisms has been explored for industrial applications.[57-59] Among different biomass feedstocks, starch as a natural biopolymer has been used in various industries (**Fig. 5**) due to its renewability, biodegradability, abundance and low cost. Recently, the sustainable or 'green' engineering of starch has been trending, which requires the minimal use of hazardous substances and the reduction of energy consumption.[3]

Green Chemistry
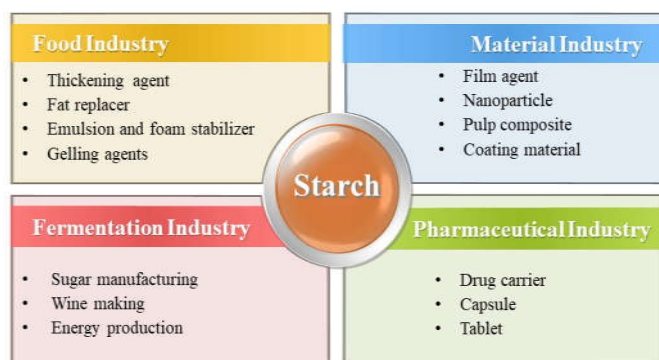
Fig. 5. Summary of various industrial applications of starch.

Native starch granules are formed in heterotrophic plastids by coordinated interactions of multiple biosynthetic enzymes and stored in storage organs as semi-crystalline granules with a complicated structure and unique properties for each plant.[60] Native starch consists mainly of two polysaccharides: lightly branched amylose (AM) and highly branched amylopectin (AP). Amylose is essentially linear and contains approximately 99% α-(1,4) bond and 1% α-(1,6) bond, whereas amylopectin has 95% α-(1,4) bond and 5% α-(1,6) bond linking D-glucose.[61-63] Starch is constructed mainly by alternating semi-crystalline and amorphous growth rings surrounding a central amorphous region, with a degree of crystallinity ranging from 20 to 45%.[64] Starches are generally divided into three main polymorphs (A-, B-, and C-type crystallites), which have distinct functional properties.[65-67] Native starch granules are characterized on structural scales ranging from nano- to micrometer, including granule, growth ring, blocklet, lamellae, and double-helix.[63, 68] The multiscale structures of the starch granule plays a key role in determining functionality and suitability for different applications of starch (**Fig. 6**).

Fig. 6. Starch structures and functional properties. (a) Native pea starch granules as viewed by scanning electron microscopy (SEM); (b) growth rings as observed by SEM; (c) blocklet structures as revealed by atomic force microscope (AFM); (d-h) representations of super helix, lamellar, double-helical structures and amylopectin and amylose molecules, respectively. Adapted from Ref. [63] with permission from Wiley (2015).

4 Dissolution of starch in ILs solvent systems

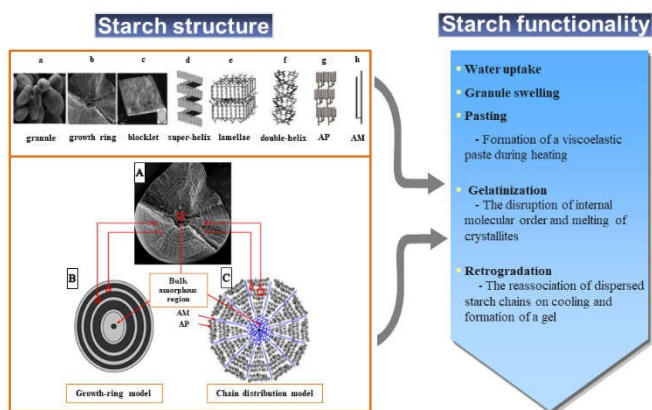Native starch is in the form of granules with a supramolecular semi-crystalline structure and inherent strong intra-/intermolecular hydrogen bonding. The dissolution of starch requires the disruption of these inherent strong hydrogen bonds. In many cases, water is often used to dissolve starch with the aid of heat. Under common heating conditions (below 100 °C), starch cannot be fully dissolved in water, leading to the formation of undissolved ghost structure.[69, 70] Over the past fifty years, great efforts have been focused on other solvents that can completely dissolve starch, such as DMSO,[71-75] strong inorganic alkali solutions (e.g., KOH and NaOH),[76, 77] NaOH/urea,[78] zinc chloride aqueous solution (ZnCl$_2$),[79, 80] *N*-methylmorpholine-*N*-oxide (NMMO),[81, 82] and molten imidazole.[83, 84] However, these solvents may also have their drawbacks including narrow reaction windows (e.g., limited applicable ranges of temperature or starch concentration), undesirable side reactions, the tendency to cause starch degradation, difficulty in solvent separation or recovery, health hazardousness, environmental unfriendliness, and high energy consumption.

Recent studies have shown that ILs could effectively dissolve polysaccharides including starch.[6, 25, 30, 85, 86] Although some ILs are toxic, there are still many ILs that can be synthesized via chemistry and considered as "green" solvents for biopolymers. For example, [Emim][OAc] has desirable properties, e.g., low toxicity (LD50 > 2000 mg·kg^{-1}), low corrosiveness, low melting point (< −20 °C), low viscosity (10 mPa·s at 80 °C), and favorable biodegradability.[17] In the following sections, we will discuss research progress on the dissolution of starch in ILs and the related mechanisms.

4.1. Dissolution of starch in pure ILs

ILs that consist of an imidazolium (less often pyridinium, ammonium, or phosphonium) cation and a strongly basic, hydrogen bond accepting anion (e.g., carboxylates or halides) have the ability to fully or partially disrupt the intermolecular hydrogen bonds present in biopolymeric networks, and to dissolve biopolymers such as starch.[6, 25, 30, 85, 87]

Table 2 provides a summary of typical studies on starch dissolution using pure ILs. It should be noted that the concentrations of starch listed are not necessarily the maximum solubility. The solubility can be measured by adding the solute into the IL at intervals until the solution became unclear.[88] Nevertheless, this process could be tedious.

Table 2 Summary of starch dissolution in pure ILs.

Starch	IL	Conditions	Concentration	Ref.
Maize	[Bmim][Cl]	80 °C, 40 min	15%, w/w (max.)	[87]
Maize, potato, rice, wheat	[Bmim][Cl]	100 °C, 1 h	2%, w/w	[89]

Starch	IL	Conditions	Concentration	Ref.
Wheat, barley, potato, waxy maize, regular maize, rice	[Bmim][Cl]	100 °C, up to 30 min with oil bath; 80 °C, up to 10 min with microwave	5%, w/w	[90]
Potato	[Amim][Cl]	80 °C, 60 min	5%, w/w	[91]
Regular maize	[Emim][Cl]	100 °C, 60 min	10%, w/w	[92]
Barley	[Bmim][Br]	80 °C, 3.5 h, with microwave (20–30 W)	10%, w/w	[93]
	[Hexmim][HCOO], with catalyst p-TsOH at 3%	80 °C, 5 h, with microwave (20–30 W)	10%, w/w	
	[Hmim][HCOO] with catalyst p-TsOH at 3%	80 °C, 4 h, with microwave (20–30 W)	10%, w/w	
	[NH$_3$CH$_2$CH$_2$OH][HCOO] with catalyst p-TsOH at 3%	80 °C, 5 h, with microwave (20–30 W)	10%, w/w	
	[Emim][Me$_2$PO$_4$]	80 °C, 3.5 h, with microwave (20–30 W)	10%, w/w	
Maize	[Mmim][(MeO)HPO$_2$]	80 °C, 50 min	10%, w/w	[94]

As seen from **Table 2**, the dissolution of starch in pure ILs requires aggressive conditions (higher temperatures and/or

microwave treatment), which always lead to the molecular degradation of starch.[89, 90, 93] Stevenson et al.[89] studied the structural changes of starch in 1-butyl-3-methylimidazolium chloride ([Bmim][Cl]), which showed that heat-dispersion of starch in this IL degrades amylopectin to lower-molecular-mass molecules, and that maize, rice and wheat starches degraded more considerably than potato starch. Similar results were also observed in another study,[90] where both amylopectin and amylose degrade during heating in [Bmim][Cl]. It is proposed that the hygroscopic nature of [Bmim][Cl] may result in the formation of HCl, which catalyzes the depolymerization of starch.[90] Lappalainen et al.[93] studied the dissolution and depolymerization of barley starch in various ILs using benzene sulfonic acid (p-TsOH) as a catalyst under controlled microwave heating. The results showed that starch in dialkylimidazolium halide ILs is depolymerized substantially to produce 79–100% water-soluble starch oligomers with the average molecular weight of 1000–2000 Da.[93] In contrast, 1-ethyl-3-methylimidazolium dimethylphosphate ([Emim][Me$_2$PO$_4$]) and 2-hydroxyethylammonium formate ([NH$_3$CH$_2$CH$_2$OH][HCOO]) caused the lowest degree of depolymerization of starch among the tested ILs. [93]

The efficiency of starch dissolution was found to be highly dependent on the cation and anion of the IL used.[93] A larger cation in 1-hexyl-3-methylimidazolium chloride ([Hexmim][Cl]) compared to the cation in [Amim][Cl] or [Bmim][Cl] led to a slightly longer time for starch dissolution.[93] The more nucleophilic anion in [Bmim][Br] and [Hexmim][Br] compared to that in [Bmim][Cl] and [Hexmim][Cl], respectively, resulted in faster dissolution. ILs with [HCOO]$^-$ or [Me$_2$PO$_4$]$^-$ as an anion dissolved starch more slowly than ILs with a halide anion. These results well correspond to a previous finding by Papanyan et al.[95] that there is a linear relationship between the –OH stretch frequencies measured by infrared spectroscopy and the solubility of the salt solutions. In other words, the redshift of the vibrational bands of the polymer in the –OH stretch region can be correlated with the higher solubility of the polymer. They suggested that the solubility capacities of the anions in the salt solutions follow the well-known Hofmeister series, which accounts for the disruption power of the anions and the specific size ratio of the anion/cation combinations.[95]

There were few studies dealing with the dissolution mechanism of starch in ILs. Nevertheless, the mechanism for cellulose dissolution in ILs has been widely reported.[17, 96-98] It has been suggested that basic IL anions (chloride,[96, 99, 100] hydroxide,[101] and formate[102]), acting as proton acceptors, would efficiently promote cellulose dissolution by forming hydrogen bonds with cellulose hydroxyl groups (**Fig. 7**). Both starch and cellulose are polysaccharides consisting of D-glucose units, referred to as homoglucan or glucopyranose. The main difference between the two biopolymers is that the units of starch are mostly linked by α-(1,4)-glycosidic bonds, while those of cellulose are connected by β-(1,4)-glycosidic bonds. Therefore, the dissolution of starch in ILs should also be considered to be due to the basicity of IL anions. When starch granules are dispersed in [Emim][OAc], the IL is able to disrupt the intermolecular and intramolecular hydrogen bonding network between the hydroxyl groups of starch biopolymer.[103]
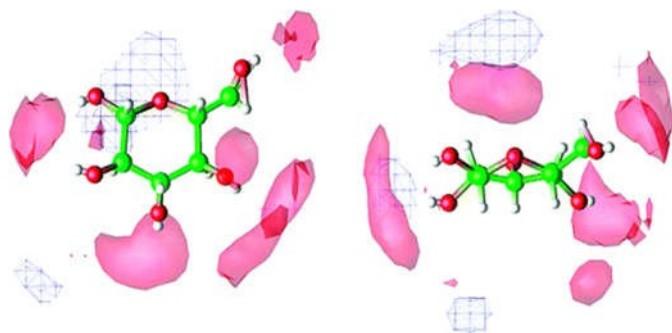
Fig. 7. The three-dimensional distribution of [Bmim][Cl] around the glucose molecule in the chair conformation. Left: the top face of the molecule. Right: looking down onto the ring oxygen. The anion is in the red area and the cation is in the white grid area. Reproduced from Ref. [100] with permission from the American Chemical Society (2007).

4.2 Dissolution of starch in aqueous ILs

In an early study by Zdanowicz and Spychaj,[91] heating starch with low water content (5 wt %) in [Amim][Cl] at 80 °C for 60 min could result in the formation of a clear and amber gel, whereas heating starch with high water content (14 wt%) could generate a clear and amber liquid.[91] Liu and Budtova[104] studied the dissolution of starch in [Emim][OAc]/water mixtures, which showed that the extent of starch dissolution in pure [Emim][OAc] increases with increasing temperature, and the presence of water promotes the dissolution of starch in IL. Compared with pure ILs, the aqueous ILs have many advantages such as low viscosity, low dissolution temperature, low energy consumption, simple processing of starch and ILs (the drying process of ILs is no longer needed before dissolution) and low cost. These features make the aqueous IL solvents promising in the dissolution and pre-treatment of starch.

Xie and coworkers[103] have, for the first time, revealed that starch dissolves most effectively during heating when the [Emim][OAc]/water ratio is 1:7.2 (mol./mol.).[103] Their further research has indicated that the dissolution of starch with this aqueous IL occurs at ambient conditions within 40 min.[105] Soluble starch molecules in aqueous ILs could form a boundary film on hydrophobic surfaces, which is potential for lubrication applications.[106] The mechanism regarding the efficient reaction of this aqueous IL has not been fully elaborated. Conceivably, there are complex interactions among IL, water and starch, which may influence the bulkiness of water and the viscosity of the solution as well.[103, 104] Kim et al. [107] have interrogated the role of hydrogen bonding in water-mediated glucose solubility in 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([Emim][TfO]), which may provide us with a basis for further investigating how the starch-water-IL ternary system works. Based on molecular dynamics (MD) simulations, they have reached the following conclusions[107]:

a) The interaction among glucose molecules tends to be stronger involving more hydrogen bonding in the pure IL than in the water-mediated IL.

b) Water acts as a solubility enhancer, which disrupts glucose–glucose interactions and enhances glucose–

solvent (water and [TfO]⁻) interactions, resulting in higher glucose solubility.

c) Water molecules initially located around glucose molecules are later taken up by [TfO]⁻, leaving glucose molecules surrounded mainly by [TfO]⁻ at equilibrium. Thus, the solubility of glucose in water-mediated IL system may be controlled by the strength of water–anion interaction.

d) In water-mediated IL, all the components have higher diffusivity, which could lead to a higher reaction rate.

The dissolution efficiency of aqueous ILs is still linked to the cation and anion of IL as already discussed for the case of pure ILs. Sciarini et al.[108] found that [Emim][OAc] and cholinium acetate ([Ch][OAc]) have their respective amounts of water (3:7 water/[Emim][OAc] and 2:8 water/[Ch][OAc], wt./wt.) to allow most efficient destruction of starch granules. As these concentrations, destruction (depolymerization and dissolution) starts at temperatures as low as 36 °C and 68 °C, respectively.[108] This suggests that specific starch chain breaking reactions occur depending on the cation present in the IL, which can be linked to the theory of Papanyan et al.[95]

Recently, a mixture of [Emim][OAc]:water (mole ratio 0.15:1) was reported to dissolve normal maize starch at 28 °C,[105] although in another study, waxy maize starch was not dissolved completely in aqueous [Amim][Cl] at 25 °C.[109] We must highlight that the mechanism of starch dissolved in aqueous ILs under ambient condition is different from the mechanism during heating due to the interaction between starch and water are negligible at ambient temperature. The dissolution behavior of maize starch in the mixtures of water and alkylmethylimidazolium chloride at ambient temperature (22–23 °C) was studied by Ren et al.[110] At water:IL ratios of 10:1 and 5:1 (mol./mol.), the extent of disruption of the starch structure followed the order: [Bmim][Cl] > [Pmim][Cl] > [Emim][Cl]. At lower water:IL ratio (2:1, mol./mol.), the complete disruption of starch granule morphology and ordered structures in aqueous [Pmim][Cl] and aqueous [Emim][Cl] mixtures indicates these mixtures were more effective in dissolving starch than aqueous [Bmim][Cl] mixture. They have concluded that both the alkyl chain length of cations and water:IL ratio play key roles in the dissolution of starch, predominantly by affecting the interaction between ILs and water and the viscosity of aqueous ILs.[110] Their further research[111] has indicated that at high water/IL molar ratios, the hydrogen bonding capacity of the IL anions play a major role in starch dissolution, whereas the viscosity of the water/IL mixtures dominates starch dissolution at low water/IL ratio. Although maize starch was dissolved in an aqueous [Emim][OAc] of IL:water (6:4, wt./wt.) at ambient temperature, potato starch was not dissolved completely, which were attributed to structural differences of the granule surfaces.[67]

While the maximum solubility of starch in ILs has been found when there is a certain content of water mixed with the IL, this is not the case for cellulose, another polysaccharide with the same glucose repeat structure but different glycosidic bonds. For cellulose, the dissolution efficiency of ILs will significantly decrease with increasing water content in the system,[88] which makes the dissolution mechanism of polysaccharides by aqueous ILs more mysterious. Nonetheless, Taheri et al.[112] reported that for the dissolution of

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cellulose, chitosan, and chitin using an acidic IL 1-(carboxymethyl)pyridinium chloride ([CMPy][Cl]), the 6/4 (wt./wt.) [CMPy]Cl/water mixture outperformed others. Xu et al. [113] found that lignin was efficiently dissolved by aqueous choline carboxylate solutions at 25 °C. Therefore, more research is demanded to understand the interactions among IL, water and polysaccharides.

4.3 Dissolution of starch in mixtures of ILs and other solvents

Research has shown that the addition of DMSO into ILs such as [Bmim][Cl] could facilitate the dissolution and breakage of the original structure of starch.[92] Similarly, [Bmim][OAc]/DMSO,[114-116] [Bmim][OAc]/DMF[117] and [Emim][OAc]/DMF[118, 119] have been found to be better solvents for cellulose with the absence of significant aggregation of the dissolved chains. According to Radhi et al.,[40] DMSO, at a low mole fraction (< 0.4), can weakly associate with the cation and in doing so disrupts the strong ion–ion association that exists in the pure IL. As a result, the anomalous diffusion (bulky cation moving faster than anion in pure [Emim][OAc]) is reduced with the addition of DMSO, and above 0.6 mole fraction of DMSO, the anion diffuses in a "normal" way, that is, faster than the cation.[40] This could explain why DMSO can assist the dissolution of either starch or cellulose in ILs (**Fig. 8**).
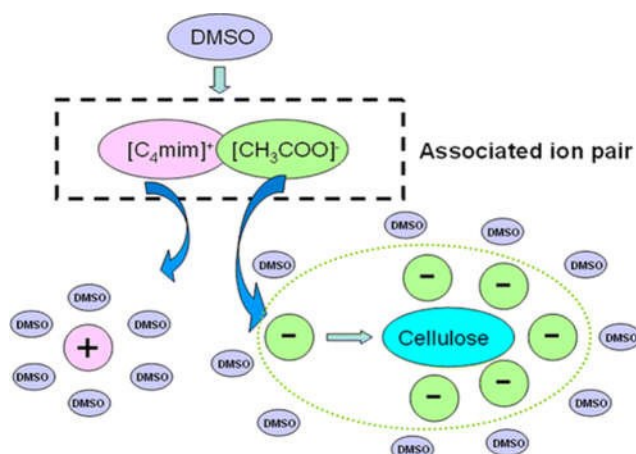

Fig. 8. Co-solvent effect of DMSO. Reproduced from Ref. [115] with permission from the American Chemical Society (2013).

Shen et al.[94] found that the presence of an appropriate amount of water can accelerate the dissolution while the methanol is just the opposite. Their results showed that methanol can promote the dissolution of starch in the 8:2:3 (wt./wt./wt.) mixture of [Mmim][(MeO)HPO$_2$]/water/methanol as methanol can penetrate into the starch granules and swell the outer layer of the granules.[94] They demonstrated that this ternary mixture is as good as the 7:3 (wt./wt.) [Mmim][(MeO)HPO$_2$]/water mixture to dissolve maize starch at a lower temperature.[94]

Some deep eutectic solvents (DESs) that include IL components have been found to be excellent solvents for polysaccharides such as starch as well.[84, 120-123] For example, a 20 wt.% potato starch (30% amylose content) solution can be prepared in 3:7 (wt./wt.) choline chloride ([Ch][Cl])/imidazole mixture after heating to 100 °C for 1 h.[84] Dai et al.[122] found that many plant-abundant primary metabolites changed their state from solid to liquid when they were mixed in

proper ratio, which has led to their discovery of many natural deep eutectic solvents (NDESs) from nature such as mixtures of [Ch][Cl] with lactic acid, maleic acid, citric acid, aconitic acid, glycol, glycerol, xylitol, sorbose, sucrose, or maltose. These NDESs showed clear hydrogen bonding and high viscosity. Their viscosity decreased significantly with the addition of small amounts of water but preserving their characteristics. The NDESs, due to their supramolecular structure and broad polarity range, proved to be excellent solvents for a wide range of metabolites of low to medium polarity that is non-soluble or poorly soluble in water, such as DNA, proteins and polysaccharides (including starch).[122] Ramesh et al.[124, 125] showed that a DES of 1:2 (wt./wt.) [Ch][Cl]/urea could effectively suppress the crystallinity of maize starch. It has been shown that the addition of urea to [Emim][OAc] could facilitate the dissolution of cellulose (with less time).[126] So far, the work on the effects of IL mixtures with other co-solvents on starch is still quite limited and more research is worth to be undertaken in this area.

5 Phase transition of starch in mixtures of ILs and water

Starch often undergoes gelatinization in the presence of water upon heating. Although the starch structure is disrupted during gelatinization, the granule remnants may still be present.[70] The incomplete disruption of starch represents an issue when trying to obtain homogeneous amorphous materials. Recently, the mixtures of ILs and water have been used as an effective solvent for starch dissolution and plasticization,[6] facilitating the development of biopolymer-based materials. For developing promising biodegradable starch-based materials, it is crucial to understand the phase transition mechanism of starch in water and IL mixtures.

5.1 Phase transition process of starch in water/IL mixtures

The phase transition process of starch in mixtures of water and IL was commonly studied using DSC. The most frequently used transition parameters are: the onset temperature (T_o, the intersection point of tangents to the thermogram before maximum heat flow), the peak temperature (T_p, the temperature of maximum heat flow), the conclusion temperature (T_c, the intersection point of tangents to the trace at the upslope after T_p and an estimate of the baseline); and the heat input enthalpy change (ΔH, the area under the line drawn from the start temperature to the end temperature).[69]

Fig. 9 shows the DSC thermograms of native waxy maize starch in water:[Amim][Cl] mixtures.[127] During DSC heating, a single well-defined gelatinization endotherm was observed for the native starch in pure water. With decreasing water/IL ratio, the phase transition was changed from only a single endothermic event to endothermic plus exothermic transitions, then to only a single exothermic event. Specifically, as the water/IL ratio was decreased to 10:1 (mol./mol.), the single endothermic transition shifted to a higher temperature. Further decreases in water/IL ratio resulted in a shift of the gelatinization endotherm to lower temperatures, which was still higher than that of the starch-water mixture. At a water/IL ratio of 3:1 (mol./mol.), a small exothermic transition was followed by an obvious endothermic transition. As the ratios of water/IL further decreased, there was only a well-defined exothermic transition. Interestingly, an exothermic transition of starch in water/IL mixture

of 2:1 and 1.5:1 (mol./mol.) occurred at a lower temperature than in pure water and pure IL, indicating water favoring the starch disruption in aqueous ILs with low cost and energy consumption. Over the past few years, these similar results concerning the starch phase transition in other aqueous ILs ([Emim][OAc],[103, 108, 128] [Amim][Cl],[129] [Ch][OAc][108]), aqueous NMMO,[81] and aqueous DMSO[130] have been reported.
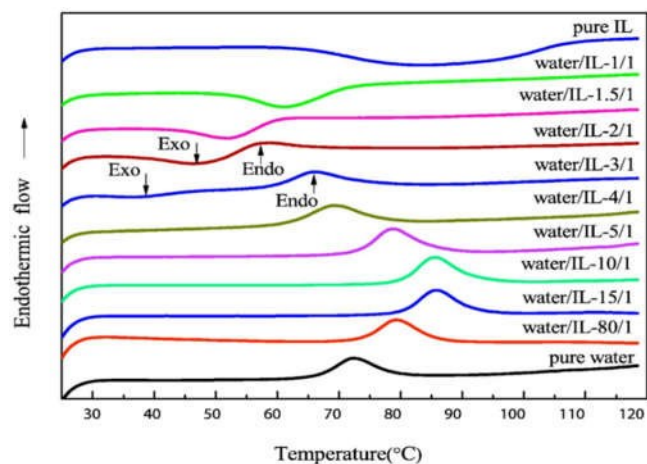

Fig. 9. DSC thermograms of waxy maize starch in water/IL mixtures. The numbers above the curves indicate the mole ratios of water/IL. Reproduced from Ref. [127] with permission from Elsevier Ltd. (2018).

Undoubtedly, the endothermic transition process of starch can be ascribed to the starch gelatinization at high water/IL ratios. However, there has been no consensus over whether the exothermic transition of starch in water/IL mixtures at a low water/IL ratio is dissolution or gelatinization. Most researchers have suggested that the exothermic transition is due to starch dissolution considering the only exothermic transition of starch in pure ILs,[103, 129] during which significant starch depolymerization occurs[108, 130]. However, there has been a different opinion suggesting that the exothermic transition should still be associated with the starch gelatinization process,[127] which is based on the definition of starch gelatinization (viz. "disruption of molecular orders within the starch granule manifested in irreversible changes in properties such as crystallite melting, unwinding of double helices, loss of birefringence, and starch solubilization").[69] Hence, the definition of the phase transition of starch in aqueous ILs needs to be further clarified.

5.2 Structural changes of starch during phase transition in water/IL mixtures

The structure of starch determines its functional properties, and the starch structural changes during heating provided a better understanding of the phase transition mechanism of starch in water/IL mixtures. Hence, the structural changes of starch in water/IL mixtures during phase transition has gained wide attention.

Microscopy is a simple yet reliable method to study the morphology (under normal light) and crystalline structure (under polarized light) of starch. Many researchers[103, 104, 108, 129] have reported a similar observation of morphological changes of starch in water/IL mixtures during heating using normal and polarized light microscopy. Before heating, the normal starch showed a well-defined granule structure and clear birefringent "Maltese cross"

patterns. Then, whether being heated in pure water or water/IL mixtures at a high water/IL ratio, most of the granules were tremendously swollen and deformed with less remaining birefringence at T_p; and finally, the swollen granules showed no birefringence at T_c. It is noteworthy that at T_p of the exotherm in the water:IL mixture at a low water/IL ratio, most granules were still intact and showed birefringence, although no granule remnants and birefringence were observed at T_c.

Zhang et al.[128] studied the changes of crystalline and lamellar structures in maize starch heated in [Emim][OAc]:water mixtures using synchrotron X-ray scattering analysis *in situ*. Firstly, a preferable increase in the thickness of the crystalline lamellae rather than that of the amorphous lamellae causes an overall increase in the thickness of the semi-crystalline lamellae; then, the amorphous lamellae starts to decrease probably due to the diffusion of starch molecules from them; this forms fractal gel on a larger scale (than the lamellae) which gradually decreases to a stable value as the temperature increases further (**Fig. 10**). This hints to the future work that using certain aqueous ILs for disrupting the starch semi-crystalline structure is the key to realize green processes to obtain homogeneous amorphous materials.
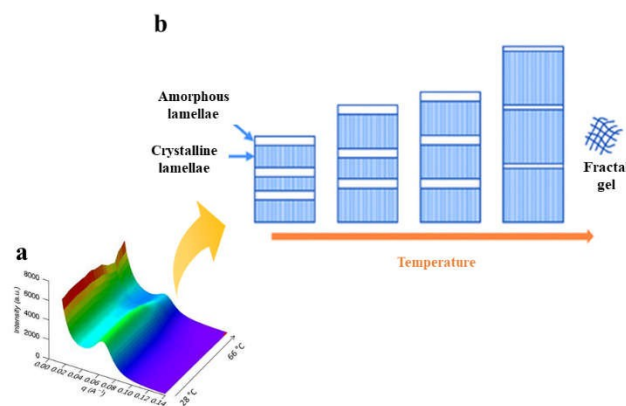
Fig. 10. (a) Temperature-resolved SAXS surface for the starch in 90.8:1 mol/mol water:[Emim][OAc] solution. The brighter color indicates stronger SAXS intensity. (b) Changes of starch semi-crystalline lamellar structure in water-[Emim][OAc] mixtures. Adapted from Ref. [128] with permission from the Royal Society of Chemistry (2015).

Xiang et al.[127] studied the multi-scale structural changes of waxy maize starch heated in water/[Amim][Cl] mixtures. They found whether being heated in pure water or water:IL mixtures, no obvious structural disruption of ordered structures in starch was evident at T_o of the phase transition, whereas at T_c of the thermal transitions, the starch samples were completely disrupted. In particular, no apparent crystalline structural changes of starch as heated to the peak temperature of the exothermic peak before the endothermic peak at water/IL ratios of 3:1 and 2:1 (mol./mol.). Hence, they proposed that the exothermic transition followed by the gelatinization endotherm observed at water/IL 3:1 and 2:1 (mol./mol.) could be attributed to the interaction of ILs and amorphous regions in starch.

The depolymerization of starch molecules in ILs was elucidated by characterizing the molecular mass distribution changes of starch

using high-performance size-exclusion chromatography (HPSEC)[89, 93] and high-performance liquid chromatography (HPLC)[90]. Sciarini et al.[108] found that addition of rather small quantities of water (20%) could significantly reduce the depolymerization of starch caused by [Emim][OAc] and [Ch][OAc] during heating. While its depolymerization should be avoided, the water/IL mixtures can be considered as suitable solvents for starch modifications. Additionally, although these ILs did not completely avoid starch depolymerization, the reductions in molecular mass were 1–3 orders of magnitude lower than those resulting from the use of halide-based imidazolium ILs.[108]

5.3 Phase transition mechanism of starch in water/IL mixtures

Over the past few years, the nature of the phase transitions of starch in water/IL mixtures has been the subject of extensive research, leading to several assumptions.

The phase transitions of starch in water and IL mixtures are mainly determined by water/IL ratio, which has been proposed by many researchers.[103, 104, 108, 128-130] At a high water/IL ratio, the interaction between starch and water dominates, resulting in an endothermic transition of starch; at a low water/IL, the interaction between starch and IL prevails, leading to an exothermic transition of starch. This agrees with the study by Xie and coworkers,[128] which has shown that when the water content is high, there is enough water to both solvate starch and interact with ILs; consequently, IL has little chance to interact with the starch molecules. Contrarily, when the amount of water is low, the IL-water interaction decreases and the IL is still able to interact with the starch.

Researchers[103, 104, 108, 127-130] have assumed that the phase transition behavior of starch in water/IL mixtures is affected by the viscosity of the water/IL mixtures and the interactions between ILs and water. At a high water/IL ratio, with increasing IL content, the endotherm of starch shifted to a higher temperature. The hydrogen-bonding interaction between water and IL (the kosmotropic effect) could reduce the availability of water, leading to the delay of starch gelatinization.[108, 128] At a low water/IL, the exotherm of starch occurred at a lower temperature than the phase transition temperature of the starch-water system or the starch-IL system.[103, 108, 127] According for this observation, two reasons have been proposed[104]: (a) Water, being much less bulky than [Emim][OAc], penetrates the granule first, swells the outer layer and facilitates IL penetration and starch disruption; and (b) The viscosity of 75% [Emim][OAc]–25% water is much lower than that of pure [Emim][OAc], leading to a higher polymer diffusion coefficient, more rapid homogenization of the whole system, and thus a more expeditious phase transition. This finding could lead to the fabrication of starch materials with low energy consumption. For example, Zhang et al.[11] prepared starch-based electro-conductive films with [Emim][OAc] and water mixtures at 55 °C and 65 °C, much lower than those commonly used in biopolymer melt processing (typically over 150 °C).

Recently, Xiang et al.[127] systematically elucidated the mechanisms underlying the endotherm and exotherm of starch in water/[Amim][Cl] mixtures. In pure water, starch interacts with free water during DSC heating, leading to the disruption of hydrogen bonding between starch molecules. As a small amount of the IL is introduced (water/IL ratios of 80:1 to 10:1, mol./mol.), a small

proportion of water molecules interact with the IL to form an HOH⋯IL⋯HOH network,[44] resulting in reduced water availability for starch gelatinization, higher transition temperatures, and a greater enthalpy change. With decreasing amounts of water (water/IL ratio from 5:1 to 2:1, mol./mol.), the IL interacts strongly not only with water molecules but also with starch molecules during DSC heating, weakening the hydrogen bonding between starch molecules, leading to lower gelatinization temperatures and a reduced enthalpy change. At a low water content, the IL interacts with water to form of IL⋯HOH⋯IL,[44] which makes more IL ions interact with starch molecules, leading to a heat release during the starch phase transition (an exothermic event). In the presence of pure IL, starch molecules can interact strongly with the IL and release a greater amount of heat, leading to the formation of new hydrogen bonds between the hydroxyl groups of starch and the IL ions. Due to viscosity effects, the diffusion of IL into starch granules is increasingly retarded with decreasing water/IL ratios, thus leading to increased gelatinization temperatures and a greater enthalpy change. So far, the study on the phase transition of starch in water/IL mixtures especially the role of structures of IL cations and anions is still quite limited. Furthermore, the mechanisms of interactions among starch, water and ILs during the phase transition are mainly based on assumptions. Hence, more research is worth to be undertaken in this area.

6 Chemical modification of starch in ILs

Native starch is limited for industrial applications due to several drawbacks such as insolubility in cold water and tendency to retrogradation and syneresis.[131] Therefore, it is necessary to improve the physicochemical and functional properties of starch for enhanced and broadened applications. Among the most widespread starch derivatives, esterified and etherified starches have attracted the most attention. These two modified starches are generally synthesized by traditional technologies using conventional solvents such as aqueous phase,[132, 133] pyridine,[134-136] DMSO,[137] and DMAc/LiCl.[138] Over the few years, ILs have been considered as possible green substitutes for these toxic organic solvents and reaction media for the etherification and esterification of carbohydrates including starch.[5, 54] Some recent advances in etherification and esterification of starch in ILs over the past decade are listed in **Table 3**.

There have been limited reports on starch etherification in ILs. Xie et al.[139,140] synthesized a maize starch ether with a high DS of 0.021–0.99 by reacting maize starch with different reactants in a homogeneous manner using [Bmim][Cl] as a reaction medium. Similarly, Bakouri et al.[141] reported a homogeneously modified maize starch synthesized with sodium monochloroacetic acid in [Bmim][Cl]. A high degree of etherification (DS of 0.79) could be achieved within a short time in [Bmim][Cl], which is conceivably due to the excellent dissolving capacity and catalytic effect of IL.[141]

In contrast, the esterification of starch in ILs have been more widely studied. Several kinds of starch esters, such as starch laurate,[92, 142, 143] starch palmitate,[92, 144] starch stearate,[92, 143] starch succinate,[145] starch acetate,[142, 145-148] and starch vernolate[149, 150] have been chemically synthesized using pure ILs or IL/other solvent mixtures as reaction media. Examples of ILs solvents studied in this

regard include [Bmim][Cl],[140, 141, 143, 145, 148, 150, 151] [Emim][OAc],[144, 147] [Bmim][Dca],[147] [Bmim][BF$_4$][144, 152] and [Bmim][PF$_6$][149]. Among them, [Bmim][Cl] is the most widely used IL for the esterification of native starch.

In these studies, the reaction media was a mixture of ILs/DMSO or IL/IL in addition to pure IL. Lehmann et al.[92] described homogeneous esterification of maize starch with different chain length fatty acids (lauric acid, palmitic acid, and stearic acid) using [Bmim][Cl], [Emim][OAc] and a [Bmim][Cl]/DMSO mixture, respectively, without catalysts. The DS of starch laureate was the highest and reached 0.10 when the mixture of [Bmim][Cl]/DMSO was the reaction media, which was more efficient than pure ILs.[92] Lu et al.[144] reported the lipase-catalyzed synthesis of starch palmitate in IL mixtures consisting of [Bmim][OAc] and [Bmim][BF$_4$]. The maximum DS of 0.144 was obtained for a [Bmim][BF$_4$]/[Bmim][OAc] mass ratio of 19:5 at 60 °C during 3 h with a reactant/AGU ratio of 3:1.[144]

Starch esterification was also conducted in ILs using biocatalysts. Lu et al.[144] showed that a slightly higher DS of 0.153 could be reached by increasing the lipase (*Candida rugosa lipase*) dosage from 0.1 g to 0.2 g. However, the excess amount of enzyme was suggested to have no apparent influence on the reaction.[144] Their further work concerned the same enzymatic synthesis of starch laurates in [Bmim][BF$_4$] and [Bmim][Cl] starting from high-amylose maize starch and lauric acid.[152] In this work, they used a two-step method consisting, first, the pre-gelatinization of the starch in [Bmim][Cl] in order to destroy its granule structure and, then, adding the dried pregelatinized starch to [Bmim][BF$_4$] for lipase esterification.[152] These conditions led to a maximum DS of 0.171.[152] Recently, Li et al.[153] and Desalegn et al.[149] have used the same enzyme (*Novozyme 435 lipase*) to catalyze the synthesis of starch esters. Li et al.[153] reported that the biosynthesis of octenyl succinic anhydride (OSA) starch (DS of 0.0006–0.013) using 1-octyl-3-methylimidazolium nitrate ([Omim][NO$_3$]) as the reaction medium. Desalegn et al.[149] synthesized epoxy fatty acid esters (DS of 0.95) of cassava starch by reacting the starch with vernonia acid methyl ester using [Bmim][PF$_6$] as a reaction medium and DMSO as a co-solvent. Zarski et al.[151] conducted the esterification of potato starch with oleic acid in [Bmim][Cl] using immobilized lipase from *Thermomyces lanuginosus* as the catalyst. The product with the highest DS (0.22) was obtained at 60 °C for 4 h, but a higher temperature or a longer reaction time led to a decrease in the DS due to the formation of water as a by-product that could favor hydrolytic reactions.[151] These previous studies have shown that ILs can be used as a convenient, homogeneous reaction medium and/or catalysts for the esterification or etherification of starch with defined substitution patterns, expanding their applications (**Fig. 11**). In comparison with native starch, etherified starch shows desirable physico-chemical properties such as thermal stability, ion activity, higher reaction efficiency, and thixotropy. Starch ethers can be applied in many areas such as coating, flocculants, drug delivery and food additives.[154] Starch ester possesses higher viscosity, glueyness and transparency, so it can be used as an adhesive, thickener, stabilizer or drug bulking agent. Moreover, amphiphilic polymer esters have a wide range of industrial applications, particularly for emulsification, encapsulation, films and coatings, and gel production.[131, 155, 156] While IL residues in the regenerated starch after treatment with ILs could not be detectable,[105] they may still pose potential biological toxicity risk.

Thus, more research is demanded to detect IL residuals and to develop methods for the removal of ILs.
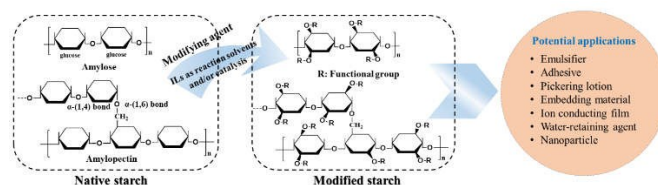
Fig. 11. Reaction scheme of esterified and etherified starch in ILs and their potential applications.

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Table 3 Etherification and esterification of starch in ionic liquids.

Starch	ILs	Product	Reactant	Reactant/AGU (mol./mol.)	Catalyst	Process parameters	DS	Ref.
Maize starch	[Bmim][Cl]	Starch ether	Glycidyltrimethyl ammonium chloride	0.5-4	NaOH	70-110 °C 1-8h	0.021-0.99	[139]
Maize starch	[Bmim][Cl]	Starch ether	Sodium monochloroacetate	0.4-1.6	NaOH	70-110 °C 1-5h	0.31-0.76	[140]
Maize starch	[Bmim][Cl]	Starch ether	Sodium monochloroacetic acid	1	NaOH	90 °C 3h	0.79	[141]
Maize starch	Imidazole derivative	Starch esters	Acid anhydrides / acyl chlorides	2.25/0.5, 4.5/0.5	Imidazole derivative	95-115 °C 1.5h	0.79-3	[142]
Maize starch	[Bmim][Cl], [Bmim][PF$_6$], [Emim][OAc]	Starch esters	Lauric acid (L), palmitic acid (P)or stearic acid (S)	1	-	100-140 °C 3h	0.023-0.105 (L) 0.032-0.098 (P) 0.038-0.092 (S)	[92]
Maize starch	[Bmim][Cl]	Starch esters	Methyl laurate (ML) or methyl stearate (MS)	1-4	Pyridine	100-140 °C 1-6h	0.15-0.37 (ML) 0.12-0.28 (MS)	[143]
High-amylose maize starch	[Bmim][BF$_4$]/[Bmim][OAc]	Starch palmitate	Methyl palmitate	1-4	*Candida rugosa lipase*	50-80 °C 1-4h	0.034-0.153	[144]

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Starch	ILs	Product	Reactant	Reactant/AGU (mol./mol.)	Catalyst	Process parameters	DS	Ref.
Maize starch	[Bmim][Cl]	Starch esters	Acetic anhydride (AA) or succinic anhydride (SA)	1-6	Pyridine	70-110 °C 1-5h	0.04-2.35 (AA) 0.02-0.93 (SA)	145
Maize starch	Reactant	Starch esters	Acetic anhydride (AA) or propionic anhydride (PA)	1.5-4.5	ILs, mainly [Bmim][Cl]	110-150 °C 1-4h	0.05-2.89 (AA) 0.77-2.86 (PA)	146
Maize maltodextrin	[Bmim][Dca], [Bmim[NO$_3$], [Bmim][Cl], [Bmim][OAc]	Starch acetate	Vinyl acetate	1 or 3	-	40 °C 70h	0.008-1.8	147
Maize starch	[Bmim][Cl]	Starch acetate	Acetic anhydride	2-6	-	70-115 °C 0.5-2.5h	0.1-2.11	148
Cassava starch	[Bmim][PF$_6$]/DMSO	Starch vernolate	Vernolic acid methyl ester	3	Novozyme 435 lipase	40°C 72h	0.95	149
Cassava starch	[Bmim][Cl]	Starch vernolate	Vernolic acid methyl ester	3	Pyridine	110°C 24h	1.03	150
Potato starch	[Bmim][Cl]	Starch oleate	Oleic acid	3	Thermomyces lanuginosus lipase	60-80°C 4-8h	0.09-0.22	151
High-amylose maize starch	[Bmim][BF$_4$]	Starch laurate	Lauric acid	1-4	Candida rugosa lipase	50-80°C 3-11h	0.048-0.171	152
Waxy maize starch - not defined	[Omim][NO$_3$]	Starch esters	Octenyl succinic anhydride	0.023	Novozyme 435 lipase	40-70°C 1-7h	0.0006-0.013	153

7 Plasticization of starch in ILs

Starch can be considered as a crystalline material. It can be thermomechanically processed by industrial techniques such as extrusion or injection molding.[157] Water is the most basic processing aid for starch. When mixed with a limited amount of water and subjected to heat and shear treatments, starch undergoes spontaneous destructuration, leading to a homogeneous material known as thermoplastic starch (TPS).[158] Unfortunately, water is highly volatile and easy to lose during processing. Since the 1990s, polyols (in particular, glycerol) have emerged as the most widely used compounds for starch plasticization. However, compared with water, polyols are less capable of inducing the phase transition of starch during processing.[159] Moreover, small molecules such as glycerol are likely to diffuse out of polymer materials after some time, causing changes in the material properties. Recently, ILs (especially imidazolium-based IL) have been studied as new plasticizers for starch, which are summarized in **Table 4**.

Table 4 Plasticization of starch in ionic liquids.

Starch	ILs	Plasticizer	Process parameters	Ref.
Maize starch	[Bmim][Cl]	Glycerol and [Bmim][Cl]	110 °C, 5 min	8
Maize starch	[Amim][Cl]	Glycerol/[Amim][Cl]	75 °C, 30 min	10
Maize starch	[Amim][Cl]	[Amim][Cl]/water	80 °C, 30 min	160
Maize starch	[Amim][Cl]	[Amim][Cl]	75 °C, 30 min	161
Maize starch	[Amim][Cl]	[Amim][Cl]	80 °C	162
Potato starch	[Bmim][Cl]	[Bmim][Cl]	100 °C, 24 h	9
Maize starch	[Bmim][Cl]	Glycerol and [Bmim][Cl]	110 °C, 5 min	163
Maize starch	[Emim][OAc]	Glycerol and [Emim][OAc]	160 °C, 10 min	164
Gelose 80 maize starch	[Emim][OAc]	Glycerol and [Emim][OAc]	160 °C, 10 min	165
Acetylated di-starch phosphate	[Bmim][Cl]	Glycerol and [Bmim][Cl]	80 °C, 72 h / 140 °C, 14 min	166
Tapioca starch	[Emim][OAc]	[Emim][OAc]/water	50 °C	167
Tapioca starch	[Emim][OAc]	[Emim][OAc]	90 °C	168
Potato, corn, wheat starch		[Emim][OAc]/water	96 °C, 40 min	169
High-amylose maize starch	[Emim][OAc]	Glycerol and [Emim][OAc]/water	160 °C, 10 min	170
Maize starch	[Emim][OAc]	[Emim][OAc]/water	55 or 65 °C, 30 min	11

Sankri et al.[8] reported that during starch extrusion, [Bmim][Cl] resulted in a greater decrease in molecular mass and a smaller average molecular mass than did glycerol, although [Bmim][Cl]-plasticized starch showed lower hydrophilicity. Wang et al.[10] observed that the anion (Cl⁻) can interact locally with the hydrogen atom of the starch hydroxyl group, while the cation ([Amim]⁺) interacts weakly with the oxygen atom of the hydroxyl group. In this case, the two hydroxyl groups are still capable of forming hydrogen bonds with other hydroxyl groups of starch or water molecules. Therefore, the plasticized starch prepared with [Amim][Cl] is more hydrophilic than the glycerin plasticized starch.[10] However, this difference was not seen for the starch plasticized with [Bmim][Cl].[8]

Unlike traditional solvents, ILs can provide a plasticization effect to a variety of biopolymers and can be used as important media for plasticizing composite materials.[160, 161] Wu et al.[162] prepared a series of biobased composite films based on cellulose, starch and lignin using [Amim][Cl] by coagulating in a non-solvent condition. They found that the composite films have excellent thermal stability and high gas barrier capacity, and the $CO_2:O_2$ permeability was close to 1.[162] Among these composites, starch was found to contribute to film flexibility.[162] Leroy et al.[163] reported that the use of [Bmim][Cl] improved the plasticization efficiency of starch and zein and the compatibility of the blend compared the use of glycerol. Kadokawa et al.[9] prepared a homogenous mixture of cellulose 10% and starch 5% (mass fraction) in [Bmim][Cl] for several days at room temperature. They demonstrated that this mixture could then be used to fabricate a composite gel, or a composite fiber through regeneration (100–200 μm in diameter) (**Fig. 12**).
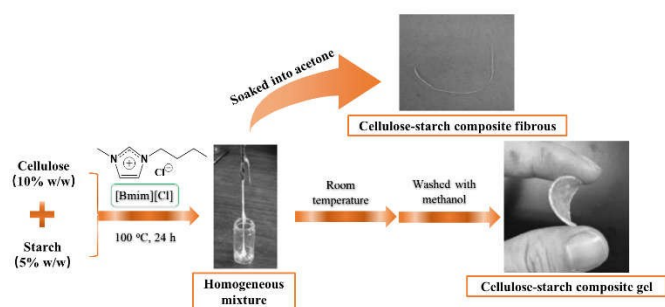
Fig. 12. Cellulose-starch composite gel and fiber by the plasticization of cellulose and starch in [Bmim][Cl]. Adapted from Ref. [9] with permission from Elsevier Ltd. (2009).

Xie et al.[164] compared [Emim][OAc] and glycerol for the preparation of starch-based films. They found that [Emim][OAc] is more conducive to the plasticization of starch and can inhibit the destruction of starch-based materials by bacteria.[164] They also found that amylose content was not a significant factor determining the material properties when starch was plasticized by [Emim][OAc], which was opposite to the cases with the use of other plasticizers.[165] Liu et al.[166] obtained a polybutylene succinate (PBS)/starch blend using [Bmim][Cl] as a plasticizer, as compared to that plasticized by glycerol. They found that ILs had a stronger plasticizing effect on starch than glycerol, which allowed the starch to be more finely dispersed in the PBS matrix, improving the mechanical properties of the blend.[166] Ismail et al.[167] found that 1:4 (wt./wt.) [Emim][OAc]/water at 70% total content as a plasticizer could destroy the A-type crystal structure, resulting in a V_H-type crystalline structure and improving the mobility of amorphous starch. In addition, this [Emim][OAc]/water mixture could also transform starch into TPS under mild conditions (90 °C).[168] Zhang et al.[170] reported that starch-based films plasticized by [Emim][OAc] had better uniformity than those plasticized by glycerol. When [Emim][OAc] was used as a plasticizer, the interactions between starch chains were much weaker and the starch-[Emim][OAc] interactions became stronger, resulting in decreased strength and stiffness but increased flexibility of the films.[170] Moreover, [Emim][OAc] has been shown to effectively retard the retrogradation of starch-based films.[170]

Additionally, ILs can act simultaneously as a plasticizer and conductive agent.[10, 160, 161, 169, 171] Recently, Zhang et al.[11] found that starch could be straightforwardly processed into optically transparent electro-conductive films by compression molding in aqueous [Emim][OAc] at a relatively mild temperature (55 or 65 °C), much lower than those commonly used in biopolymer melt processing (typically over 150 °C) (**Fig. 13**). This finding could guide the evolution of material processing techniques for reducing energy consumption as well as enhancing processing versatility to incorporate heat-sensitive ingredients. Although ILs have many advantages and characteristics as plasticizers, these still have potential risks of biological toxicity. Therefore, for practical applications, more attention should be paid to the development of nontoxic or biodegradable ILs in starch plasticization.
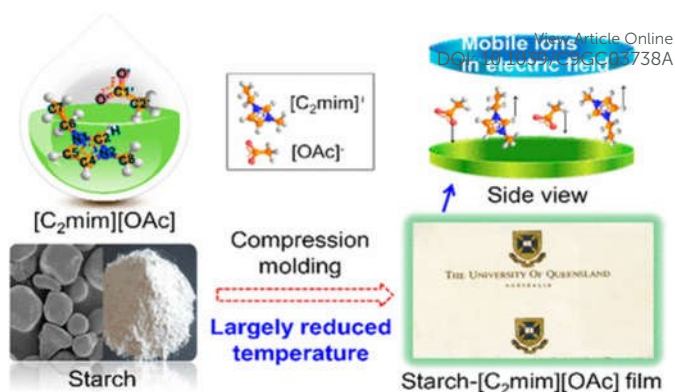

Fig. 13. Schematic of simple preparation of electro-conductive starch films in a mixture of [Emim][OAc] and water at mild temperature. Reproduced from Ref. [11] with permission from the American Chemical Society (2017).

8 Preparation of starch nanoparticles in ILs

Compared with starch nanocrystals which refer to the crystalline part of starch obtained by hydrolysis, nanoparticles prepared by crosslinking may be amorphous.[172] Several ways of preparing starch nanoparticles have been investigated, such as precipitation, spray drying, solvent evaporation and emulsion-cross-linking.[173] Most of these techniques have disadvantages such as the difficulty in particle size control, the generation of chemical wastes, the requirement of long production time.[174] In comparison, the water-in-oil (W/O) emulsion-crosslinking technique is more advantageous and has been more extensively used for the preparation of starch-based nanometer materials.[175]

Concerning the emulsion-cross-linking technique, ILs can be used to substitute for the water phase or oil phase, or even as surfactants to prepare starch nanoparticles (**Table 5** and **Fig. 14**). ILs, due to their dissolution effect for starch, is capable of creating a favorable environment for the formation of starch nanoparticles. However, the preparation of starch nanoparticles using IL microemulsion systems has been rarely studied so far. Long-chained ILs [$C_n$mim][X] can be used to substitute for surfactants to stabilize W/O microemulsion, of which the mean diameter was 94.3 nm.[14] According to Davis et al.[176], ILs could act as surfactants to facilitate the emulsification of fluoroalkanes with phases. A similar approach was performed by Wang et al.[177], who used [C_{16}mim][Br] and [Omim][OAc] as both the surfactant and polar phase. The generated starch nanoparticles were even smaller (80.5 nm), perhaps because ILs as surfactants could help stabilize the suspended phase. In another study,[15] [C_3OHmim][OAc] was tailor-made as the polar phase with superior solubility, which could be used to prepare spherical OSA starch-based nanoparticles. Starch nanoparticle can be used as a carrier of gene/drug.[178] Hence, the residual ILs in medicine or materials should be considered and minimised for application safety purposes.
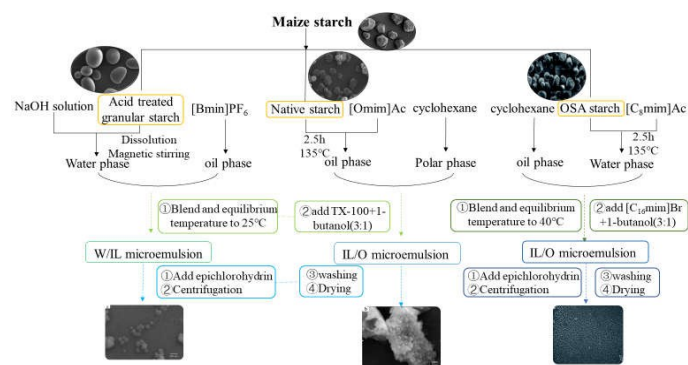
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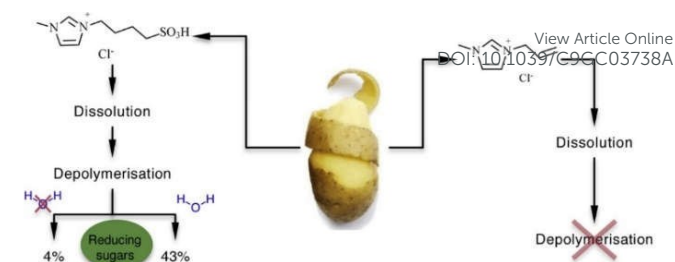Fig. 14. Preparation routes of starch nanoparticles using ILs as reaction media.

Fig. 15. Route for the catalytic conversion of starch-based industrial waste (potato peels) and potato starch into reducing sugars in ILs. Reproduced from ref. [180] with permission from the Elsevier Ltd (2014).

9 Other applications of ILs in starch

The ILs play many important roles in starch chemistry, expanding the industrial applications of ILs in starch, such as the conversion of reducing sugars and hydroxymethylfurfural, the fabrication of electrically conductive materials, and the exploitation of drug carrier (**Table 6**).

The depolymerization of starch into reducing sugars is mainly performed under high temperature or concentrated strong acidic conditions for a long time. Starch depolymerized into water-soluble products during the dissolution of starch in ILs has been widely reported.[89, 90, 93, 108] For example, Lappalainen et al.[93] found that dialkylimidazolium halide ILs dissolve barley starch effectively (microwave heating, 80 °C) and depolymerized it substantially producing 79–100% water-soluble starch oligomers with the average molecular weight of 1000–2000 Da. They also prepared water-soluble starch oligomers of 1500–2000 Da (yield varied from 60 to 99%) by depolymerization of starch in [Amim][Cl] using oil bath (50 °C) or microwave heating (60 °C).[179] Produced starch oligomers could be used in bacterial cultivations as a glucose source.[179] Hernoux-Villière et al.[180] tested the conversion process of potato peels and starch into reducing sugars in two ILs ([Amim][Cl] and 1-(4-sulfobutyl)-3-methylimidazolium chloride [SBmim][Cl]) (**Fig. 15**). Although [Amim][Cl] is more suitable for dissolving potato, the [SBmim][Cl] could dissolve and depolymerize the materials into sugars in an aqueous Brønsted-acidic medium just in one step.[180] Using potato starch and potato peels (20 wt.%) as raw materials to be depolymerized in aqueous ILs over 2 h, a solution containing up to 43% and 98% reducing sugars respectively at low temperature (60 °C) could be obtained.[180]

Hydroxymethylfurfural (HMF) has been called a ''sleeping giant'' because of its high potential versatility in the chemical industry.[181] While the conversion of many carbohydrates and raw plant biomass to HMF in the ILs has been studied extensively,[182-187] few studies focus on the conversion of starch to HMF in IL media. Hu et al.[188] obtained an impressive HMF yield of 47% from starch using $SnCl_4$/[Emim][BF_4]. Stahlberg et al.[189] found that starch could be converted to HMF (yield of 33%) in [Emim][Cl] without metal catalyst. Chun et al.[190] found a simple, direct and cost-effective conversion method of starch into HMF using 1-octyl-3-methylimidazolium chloride ([Omim][Cl]), and $CrCl_2$ catalyst. The highest yields of HMF (73.0 wt%) were obtained in tapioca starch dissolved in 0.5M HCl.[190] Then, they reported a sustainable production method of HMF from starch-rich raw acorn biomass using [Omim][Cl].[191] The highest HMF yield (58.7 wt%) was achieved in the reaction mixture of 40% [Omim][Cl] + 10% ethyl acetate + 50% 0.3M HCl extract containing a $CrBr_3$/CrF_3 mixture.[191] The addition of two halide catalysts combined was more effective in the synthesis of HMF (1.2-fold higher on average) than their single addition.[191] Roy et al.[192] reported that a maximum of 64 wt. % HMF was obtained from waxy corn substrates in the presence of $AlCl_3·6H_2O$ in a water-[Bmim]Cl/MIBK biphasic medium, and high HMF yields were achieved from amylopectin-rich starches.

ILs are electrically conductive and can act as a vehicle for electrically conductive starch-based materials. ILs could contribute to starch-based electrolytes with a reduced glass transition temperature (T_g), wider potential stability and improved electrochemical performance.[193, 194] Upon addition of 50 wt.% of [Bmim][PF_6], the biopolymer electrolytes achieved the highest ionic conductivity of (1.99 ± 0.02) × 10^{-4} S/cm at 80 °C.[194] Wang et al.[10] reported that the conductance of a TPS film with 30 wt% [Amim][Cl] content could reach $10^{-1.6}$ S/cm at 14.5 wt% water content. Their further research[160] showed that a higher conductivity value ($10^{-0.3}$ S/cm) was obtained by adding sodium montmorillonite (9%, wet weight) to the starch plasticized with [Amim][Cl]. Zhang et al.[11] prepared the [C_2mim][OAc]-plasticized electroconductive starch films (highest electrical conductivity was 1.18 × 10^{-2} S/cm) at mild temperature (55 and 65 °C). A lower processing temperature could lead to higher electrical conductivity, whereas either an increase in relative humidity (RH) or [C_2mim][OAc] content could increase the electrical conductivity.[11] Khanmirzae and Ramesh[171] prepared a nanocomposite polymer electrolyte (NCPE) from rice starch, lithium iodide (LiI), 1-methyl-3-propylimidazolium iodide ([Pmim][I]) and titanium dioxide (TiO_2) using solution cast technique. The ionic

conductivity of NCPE (3.63×10^{-4} S/cm) was enhanced compared with polymer electrolyte without IL and TiO_2, favoring the development of solar cell.[171] Then, they prepared a novel polymer electrolyte of higher ionic conductivity (1.20×10^{-3} S/cm) by changing LiI to NaI.[195] The fabricated dye-sensitized solar cells using this electrolyte showed the highest energy conversion efficiency of 2.09%.[195] Recently, Lobregas and Camacho[196] fabricated a dye-sensitized solar cell with a starch-based gel polymer electrolyte (containing cationic starch and 1-glycidyl-3-methylimidazolium chloride [Gmim][Cl]) as the quasi-solid-state electrolyte system which could give 0.514% efficiency. Despite its low performance against the liquid electrolyte control, this cell exhibited stability due to its good filling contact between the electrodes.[196]

The cross-linked starch nanoparticles prepared with ILs are promising carriers in the drug delivery system due to their relatively small size and narrow size distribution.[13-15] Zhou et al.[13] tested the drug loading and release properties of starch nanoparticles which were prepared in [Bmim][PF$_6$]. With mitoxantrone hydrochloride as a drug model, drug loading ascended significantly to 0.7317 mg/g at 1.5 h and then decreased as time extended to 3 h, and 79.95% of mitoxantrone hydrochloride contained in starch nanoparticles was released within 10 h.[13] Similar results have been observed in the methylene blue drug model[14] and the indomethacin drug model[15].

Table 5 Application of ILs in the preparation of starch nanoparticles.

Materials	ILs	Microemulsion	Methods	Cross-linker	Conditions	size	Ref.
Acid-treated granular starch	[C$_{16}$mim][Br]	W/O	ILs as surfactants	Epichlorohydrin	50 °C, 3 h	94.3 nm	[14]
Acid-treated granular starch	[Bmim][PF$_6$]	W/IL	ILs as the oil phase	Epichlorohydrin	50 °C, 4 h	91.4 nm	[174]
Native maize starch	[Omim][OAc]	IL/O	ILs as the polar phase, TX-100, 1-butanol as surfactant	Epichlorohydrin	50 °C, 3 h	96.9 nm	[12]
OSA starch	[C$_{16}$mim][Br] [Omim][OAc]	IL/O	ILs as surfactants and polar phase	Epichlorohydrin	35 °C, 3 h	80.5 nm	[177]
OSA starch	[C$_3$OHmim][OAc]	IL/O	IL as the polar phase and combining surfactant, cosurfactant 1-butanol	Epichlorohydrin	50 °C, 24 h	86.7 nm	[15]

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Table 6 Industrial application of ILs in starch.

Starch product	Starch	ILs	Conditions	Product quality	Ref.
Reducing sugars	Barley starch	[Rmim][Cl], [Rmim][Br], [Rmim][HCOO]	Microwave heating (80 °C)	Yields: 79-100 %, 1000–2000 Da-sized.	[93]
	Wheat, barley, rice, maize, wax maize, and potato starch	[Amim][Cl]	Oil bath (50 °C) or microwave heating (60 °C), p-TsOH catalyst	Yields: 60-99 %, 1500–2000 Da-sized.	[179]
	Potato peels and starch	[Amim][Cl], [SBmim][Cl]	60–90 °C, 120 min	Yields reached to 43 % and 98 % for potato peels and starch.	[180]
Hydroxymethylfurfural	Starch	[Emim][BF$_4$]	100 °C, 180 min, SnCl$_4$ catalyst	Yields: 47 %.	[188]
	Starch	[Emim][Cl]	120 °C, 180 min, boric acid catalyst	Yields: 33 %.	[189]
	Maize, wheat, rice, potato tuber, sweet potato, tapioca, acorn, and kudzu starch	[Omim][Cl]	120 °C, 30-120 min, CrCl$_2$ catalyst	Yields: 28.3-73.0 wt%.	[190]
	Starch-rich acorn biomass	[Omim][Cl]	120 °C, 30-120 min, CrBr$_3$/CrF$_3$ catalyst	Highest yield: 58.7 wt%.	[191]
	Regular, waxy, and high amylose maize starch	[Bmim][Cl]	140 °C, 180 min, AlCl$_3$·6H$_2$O catalyst	Highest yield: 64 wt%.	[192]
Biopolymer electrolytes	Maize starch	[Bmim] [TfO]	80 °C, LiPF$_6$	Ionic conductivity: 6.00×10^{-4} S/cm	[193]
	Maize starch	[Bmim][PF$_6$]	80 °C, LiPF$_6$	Ionic conductivity: 1.99×10^{-4} S/cm.	[194]
	Maize starch	[Amim][Cl]	75 °C , 30 min	Ionic conductivity: $10^{-1.6}$ S/cm.	[10]
	Native starch	[Amim][Cl]	80 °C, 30 min	Ionic conductivity: $10^{-0.3}$ S/cm.	[160]
	Maize starch	[Emim][OAc]	55 or 65 °C, 30 min	Ionic conductivity: 1.18×10^{-2} S/cm.	[11]
Solar cells	Rice starch	[Pmim][I]	80 °C , 15 min, LiI and TiO$_2$	Ionic conductivity: 3.63×10^{-4} S/cm. Energy conversion efficiency: 0.17 %.	[171]
	Rice starch	[Pmim][I]	80 °C , 15 min, NaI and TiO$_2$	Ionic conductivity: 1.20×10^{-3} S/cm Energy conversion efficiency: 2.09 %.	[195]
	Cationic potato starch	[Gmim][Cl]	70 °C, 30 min, KI/I$_2$	Energy conversion efficiency: 0.514 %.	[196]
Drug carriers	Acid-treated starch	[Bmim][PF$_6$]	Mitoxantrone hydrochloride drug model	Drug loading: 0.5-1.56 mg/g Encapsulation efficiency: 11.54-16.55 % Drug releasing rate of 79.95 % in 10th hour.	[13]
	Acid-treated starch	[C$_{16}$mim][Br]	Methylene blue drug model	Drug loading: 5.18-21.54 mg/g Encapsulation efficiency: 32.50-80.24 % Drug releasing rate of 99.9 % in 8th hour.	[14]
	OSA-maize starch	[C$_3$OHmim][OAc]	Indomethacin drug model	Drug loading: 1.12-3.75 mg/g Encapsulation efficiency: 5.8-12.9 % Drug releasing rate of 48.76 % in 6th hour.	[15]

[Rmim] represented dialkylimidazolium.

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10 Conclusions and perspectives

ILs with desirable properties play important roles in starch chemistry (including starch dissolution, gelatinization, modification and plasticization) as solvents, plasticizers or reaction media. The multiple roles of ILs in starch chemistry have expanded the application of ILs in starch-related application areas such as the synthesis of chemically modified starches of high DS, the development of TPS and starch-based composite films, the conversion of starch into reducing sugars and HMF, the fabrication of biopolymer electrolytes and solar cells, and the fabrication of starch nanoparticles and drug carriers. The processing of starch with ILs is mainly affected by the IL cation and anion structures, ratio of IL and co-solvents, type of co-solvents, and processing conditions.

Despite all of these advantages and applications, the current high costs of ILs could prevent many commercial applications.[5, 49] However, this drawback may be overcome by adding a co-solvent. Not only low costs, but also the mixtures of IL and co-solvent have many other advantages such as low viscosity, low dissolution temperature, low energy consumption, biodegradability, simple processing of starch and ILs (the drying process of starch and ILs is no longer needed before dissolution). These features make the IL co-solvent systems promising in the dissolution and pre-treatment of starch. The other main drawback of ILs is their potential toxicity, limiting the applications of ILs in starch-based foods and starch fermentation. Besides the complete removal of residual ILs after processing, one important way to address this issue is to develop and use of safe ILs likely be synthesized based on proper cations (e.g., cholinium)[197, 198] and anions (e.g., saccharinate/acesulphamate),[199, 200] which have already been widely attempted.

Although significant progress has been made in our understanding of the interactions of starch-ILs, the proposed molecular mechanism is still mostly based on speculation. For example, the dissolution mechanisms of starch in IL solvents are generally deduced from the study of the dissolution of cellulose in ILs. While both starch and cellulose are natural polysaccharides consisting of the glucose unit, many structural differences exist between these two biopolymers (e.g. glycosidic bond, crystalline structure, micromorphology, and molecular weight)[18, 69] that affect the biopolymer-IL interactions, leading to different IL treatment effects. For example, most starches can be more easily treated with ILs than cellulose due to the weaker hydrogen-bonding interaction in starch granules. While [Bmim][Cl] can dissolve cellulose easily, it is difficult to interact with potato starch at the same conditions due to the presence of charged phosphor-monoesters in potato starch.[21, 89] Besides, the physicochemical properties of IL solvent systems also affect the biopolymer-IL interactions. Different from the case of cellulose, the co-solvents (e.g., water, DMSO, DMF, DMAc) interact with starch in IL solvent systems, therefore the related dissolution mechanisms are more complex. Therefore, future research is necessary for understanding the mechanisms of starch changes in IL co-solvent systems.

While there is a growing literature about the use of ILs in the processing of starch for the fabrication of starch-based materials, some underdeveloped fields such as starch-based food, drug/gene delivery and Pickering emulsions demand more attention. In summary, we fully expect great progress in this area because of the tremendous application potentials of ILs in starch processing, but also the significant benefits that ILs can offer to address urgent environmental challenges.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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