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研究论文

离子液体/水体系中制备不同低分子量玉米淀粉

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摘要　提出了一种基于离子液体/水溶液中玉米淀粉的可控水解方法. 该方法环境友好、操作简便，可制得低分子量的无定形淀粉. X射线衍射(XRD)结果表明，离子液体通过破坏分子间及分子内氢键，显著削弱了天然淀粉的结晶结构. 水解处理后，淀粉形貌由原始颗粒状转变为不规则的碎片状，且其分子量可通过水解时间进行有效调控. 随着水解时间的延长，淀粉的热稳定性能呈下降趋势. 本文研究结果为天然淀粉的功能化改性及应用开发提供了新途径.

关键词　玉米淀粉；离子液体；水解；分子量
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Aqueous Ionic Liquid Mediated Hydrolysis of Native Corn Starch to Obtain Different Low Molecular Weight Starch

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Abstract　In this work, we proposed a strategy for the hydrolysis of native corn starch after the treatment of corn starch in an ionic liquid aqueous solution, and it is an awfully "green" and simple means to obtain starch with low molecular weight and amorphous state. X-ray diffraction results revealed that the natural starch crystalline region was largely disrupted by ionic liquid owing to the broken intermolecular and intramolecular hydrogen bonds. After hydrolysis, the morphology of starch changed from particles of native corn starch into little pieces, and their molecular weight could be effectively regulated during the hydrolysis process, and also the hydrolyzed starch samples exhibited decreased thermal stability with the extension of hydrolysis time. This work would counsel as a powerful tool for the development of native starch in realistic applications.

Keywords　Native corn starch; Ionic liquid; Hydrolysis; Molecular weight

1　Introduction

As one of the most abundant biopolymers and natural renewable materials without any contamination, starch plays an important role in the human diet, animal feed and other industrial applications[1—8].

Native starch occurs naturally within the type of insoluble granules, which is a kind of branched polymers made up of two polysaccharides, linear amylose and highly branched amylopectin[9], and these two

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components render it to form a semicrystalline structure with strong hydrogen bond networks between the molecular chains. The ordered structures are primarily composed of two types of helical structures from the side chains of amylopectin, and the ordered arrangement of those helical structures forms its crystalline structure[10]. According to the origin of starch, the granules have a distinct degree of crystallinity ranging about 15%—45%, so that they are varied in shape, size, structure, chemical composition and applications[11].

Owing to the presence of crystalline regions with compact arrangements of molecules, native starch is highly insoluble in most traditional solvents and sometimes cannot be used directly in many industries. To overcome these inherent defects and achieve innovation in starch, up to now, there are many methods introduced for the modifications of starch, such as chemical, physical, enzymatic and genetic modifications. The oldest but still commonly used chemical modification method is acid hydrolysis. Based on the susceptibility differences of semi-crystalline and amorphous starch granules to acid, acid hydrolysis has been used to improve the performance of starch from insoluble granules to 'soluble starch'. However, the crystalline lamellae of starch are more resistant to acid than amorphous lamellae, leading to the initial preferential acid hydrolysis of the amorphous regions, followed by erosion of the crystalline regions.

Ionic liquids (ILs) are generally defined as organic salts with many superiorities beyond some conventional organic solvents, such as almost no vapor pressure, wider liquid range and electrochemical window, better ionic and thermal conductivity, noncombustibility, stronger designability and better solubility for many compounds, *etc*. In recent years, ILs have solved the problem of dissolution for many compounds and are used as a "green solvent", especially for starch[12—14]. ILs disrupt the intermolecular and intramolecular hydrogen bond networks between the hydroxyl groups of the starch biopolymer[15]. In our previous work, we investigated the dissolution of starch in various imidazolium-based ionic liquids and found that the ionic liquid was a kind of non-derivative solvent for starch[16—19]. It demonstrated that when starch granules are dispersed in ionic liquid, it firstly destroys the outer layer of the granules and then penetrates into the granule cores, leading the granules to burst into fragments, which is beneficial to the modification and hydrolysis of starch at the molecular level.

Currently, starch is primarily utilized in relatively crude forms, such as native starch and its derivatives. However, starches of different molecular weights may exhibit distinct properties and functionalities. In this work, we developed a starch hydrolysis method, with the help of ionic liquid, corn starch was hydrolyzed pretty fast, and its crystalline region could be broken easily, then the low molecular weight starch was obtained, and the molecular weight of the prepared starch can be controllably regulated by changing the treatment time in aqueous ILs with acid. The treatment effects on morphology, molecular weight, and physicochemical properties of starch were also investigated. This work is to achieve the controlled preparation of low-molecular-weight starch, thereby establishing a robust foundation for the precise utilization of starch in the future.

2 Experimental

2.1 Reagents

Corn starch (Aladdin, China, Reagent grade) was dried under vacuum for 48 h at 60 ℃ before use. *N*-methylimidazole (Aladdin, China, Reagent grade) was dried with calcium hydride under stirring and distilled under reduced pressure before use. Dimethyl phosphite (Aladdin, China, Reagent grade) was distilled under reduced pressure before use. Other reagents such as dimethyl sulfoxide (DMSO), THF, anhydrous ethanol, anhydrous methanol, HCl and $NaHCO_3$ were purchased from Beijing Chemical Plant and used as received.

2.2 Preparation of 1,3-Dimethylimidazolium Methyl Phosphonate

1,3-Dimethylimdazolium methyl phosphonate ([MMIM][(MeO)HPO_2]) was synthesized according to the previous literature[17]. Under the protection of N_2, dimethyl phosphite (1.01 mol) was added to a THF solution containing *N*-methylimidazole (1.00 mol) by a drip funnel, and the reactants were stirred at 80 ℃ for 48 h. Then THF was removed by rotary evaporation, and the remaining liquid was extracted with ethyl acetate three times to remove the residual raw material. The ionic liquid was obtained by vacuum drying at 70 ℃ for 48 h. The structure of ionic liquid was shown in Fig.1. ^{1}H NMR (400 MHz, $CDCl_3$): δ: 3.6 (2H, d), 4.0 (6H, s), 6.9 (1H, d), 7.5 (2H, s), 10.6 (1H, s).

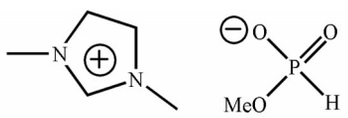


Fig. 1 Chemical structure of [MMIM][(MeO)HPO_2]

2.3 Preparation of Treated Starch in Aqueous Ionic Liquid

Starch was suspended in 90% (mass fraction) aqueous ionic liquid, then the reaction was started by adding 1 mol/L of HCl solution and allowed to proceed for certain temperature and time. After the mixture was cooled in an ice bath for 5 min, the mixture was exposed to air and dropped into excessive deionized water. The precipitate was filtered, washed several times with methanol and dried in a vacuum at 40 ℃. The ionic liquid can be recovered by rotary evaporation of the filtered solution. The yield was calculated by the mass of the recovered starch divided by the initial mass of dry starch.

As compared, the starch treated in 90% (mass fraction) aqueous ethanol was also prepared. Starch was suspended in aqueous ethanol, then the reaction was started by adding a fixed concentration (1 mol/L) of HCl and allowed to proceed at a certain temperature (100 ℃) for different time (0.5, 1.0, 2.0, 3.0, 4.0, 5.0 h). The reaction was stopped by adding a corresponding amount of 1 mol/L $NaHCO_3$. The solution was cooled in ice bath for 5 min, and centrifuged at 5000 r/min for 5 min. The precipitate was washed four times with 50% ethanol (mass fraction) and dried at 40 ℃ under vacuum. The samples were labeled as S-IL-0.5, S-IL-1.0, S-IL-2.0, S-IL-3.0, S-IL-4.0, S-IL-5.0, repectively. The yield was calculated by the mass of the recovered starch divided by the initial mass of dry starch.

2.4 Characterization

Nuclear magnetic resonance (NMR) spectra were obtained on a JEOL JNM-ECZL Series 400 MHz NMR spectrometer with DMSO-*d6* as solvent. Powder X-ray diffraction (XRD) patterns were recorded on a Panatypical B.V. XPERT-PROMPD diffractometer using Cu as an anode material. Fourier transform infrared (FTIR) spectra were obtained by a Shimadzu Affinity-1 Fourier transform infrared spectrometer with the KBr method. The molecular weight of starch was determined by Static Light Scattering (SLS) measurement. It was performed with a Brookhaven BI-200SM instrument at different scattering angles at 25 ℃. Scanning electron microscopy (SEM) observations were performed using a Hitachi S-4800 SEM at an acceleration voltage of 10 kV. Samples were prepared by dropping the micelle solutions onto silicon wafers, air-drying, and coating them with gold. Differential scanning calorimetry (DSC) was performed on a Mettler-Toledo DSC 1 instrument with a heating rate of 10 ℃/min from 0 ℃ to 200 ℃ after eliminating thermal history. Thermogravimetric analysis (TGA) was performed on a Netzsch STA449-F5 analyzer with a heating rate of 10 ℃/min from 25 ℃ to 600 ℃ under N_2.

3 Results and Discussion

3.1 Structure and Morphology Characterization

After IL hydrolysis of corn starch, ^{13}C NMR (Fig.2) was used to study the chemical structure change of

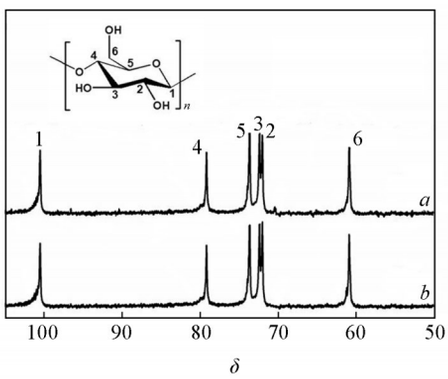


Fig. 2 ^{13}C NMR spectra of corn starch before(a) and after(b) hydrolysis in aqueous IL for 2 h

Solvent: DMSO-*d6*; number of scans: 12000.

Inset: Starch structure formula.

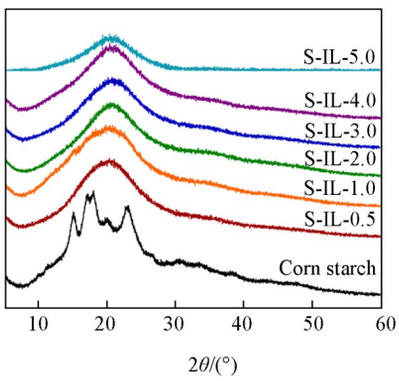


Fig. 3 XRD patterns of corn starch before and after acid hydrolysis in aqueous IL

starch after hydrolysis in [MMIM][(MeO) HPO_2] for 5 h. Six signals of the treated starch appeared at δ: 100.6(C-1), 79.3(C-4), 73.5(C-5), 72.5(C-3), 72.0(C-2), and 60.9(C-6), respectively. It was thus concluded that the anhydroglucose unit was not modified when starch was dissolved in [MMIM][(MeO)·HPO_2]. In other words, this IL was a non-derivative solvent for starch. XRD patterns of corn starch before and after hydrolysis are shown in Fig. 3. The native starch showed four diffraction peaks of 2θ=15.1°, 17.0°, 17.9° and 23.0°. After hydrolysis in [MMIM][(MeO)HPO_2] for 0.5—5.0 h, these four diffraction peaks disappeared, indicating that the degradation of amylopectin was observed immediately after dispersing starch in the aqueous ionic liquid. It is postulated that [MMIM][(MeO)HPO_2] penetrated corn starch granules, thereby disrupting both inter- and intramolecular hydrogen bonds. This interaction substantially disintegrated the native crystalline architecture, which facilitated the depolymerization of amylopectin and ultimately induced a transition of the starch granules into an amorphous state. These changes in the structure of corn starch might be beneficial to the dissolution and modification of the starch in different solvent systems. Different from the acid hydrolysis in aqueous ILs, the higher intensity of diffraction peaks after acid hydrolysis in ethanol reflected the improvement of the crystallinity of starch [Fig.S1, see the Supporting Information of this paper], which was consistent with the reported results[20]. This further reflected that the structural changes of starch after treatment in ILs were caused by the effects of ILs rather than that of acid.

The morphology changes of corn starch granules during acid hydrolysis in aqueous ILs were characterized by SEM. Native corn starch granules showed irregular polygonal shapes and smooth surfaces with a diameter of around 5—20 μm(Fig.S2 in the Supporting Information of this paper). Aqueous ILs hydrolysis induced progressive disintegration of native corn starch granules, with substantial fragmentation occurring within 0.5 h [Fig.4(A)]. The markedly diminished conductivity of the hydrolyzed samples presumably reflects their amorphous state character. However, when corn starch was treated with ethanol for 1.0 h, the great majority of the starch granules still maintained their original polygonal shapes [Fig.4(B)], but some starch granules presented slight fractures on the surface; when the treatment was up to 2.0—5.0 h, the starch showed distorted and wrinkled surfaces with some rupture to the granules[Fig.4(C)—(F), Fig.S3 in the Supporting Information of this paper]. With the combination of the structural changes of starch in XRD as shown in Fig.2, it can be concluded that the morphology changes of hydrolyzed corn starch were probably related to the crystallinity, amylose/amylopectin ratio, and granule structures etc., after acid hydrolysis by aqueous ILs.

The hydrolyzed starches were also characterized by FTIR as shown in Fig.5. The peaks in the range of 2800—3000 cm^{-1} were the characteristic of the CH_2 group of starch, and the peak at 1638 cm^{-1} was attributed

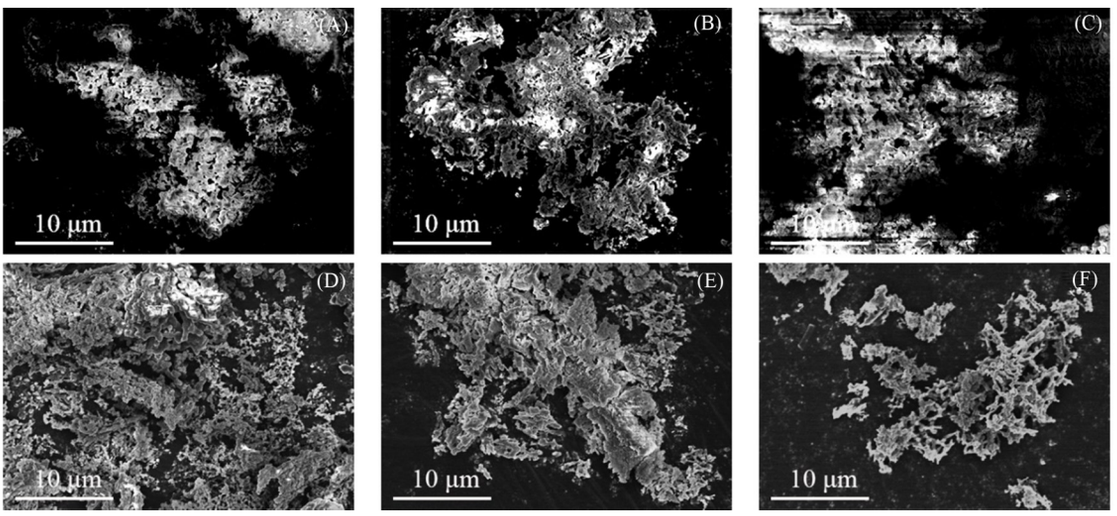


Fig. 4 SEM images of IL-hydrolyzed starches after hydrolysis for 0. 5(A), 1. 0(B), 2. 0(C), 3. 0(D), 4. 0(E) and 5. 0 h(F), respectively

to the CH_3 symmetry deformation vibration. The bands that appeared at 1600 and 1636 cm^{-1} had been considered to be related to the vibration of the water molecules in the non-crystalline region of starch. The bands that appeared at 926, 862, 769, and 572 cm^{-1} were assigned to the C—O and C—C stretching vibrations of the anhydroglucose ring in starch. An extremely broad band between 3000—3700 cm^{-1} originated from the vibration of the hydroxyl groups (O—H) of starch. The spectral region of 950—1200 cm^{-1} (red line box highlighted) corresponded to the "saccharide band" arising from C—O—C stretching vibrations in glycosidic linkages and glucose rings, which is sensitive to polymer conformation and hydration[21]. Notably, aqueous ILs treatment attenuated the splitting and broadening of this band—a change absent in corn starch treated with 90%(mass fraction) ethanol (Fig.S4 in the Supporting Information of this paper)—thereby revealing sub-stantial disruption of the hydrogen bond networks and conformational transformation of the starch chains[22].

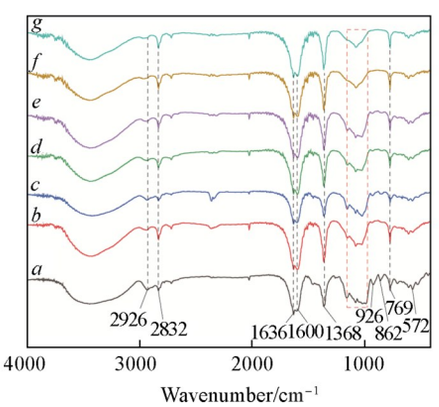


Fig. 5 FTIR spectra of corn starch hydrolyzed in aqueous IL for 0(*a*), 0. 5(*b*), 1. 0(*c*), 2. 0(*d*), 3. 0(*e*), 4. 0(*f*) and 5. 0 h(*g*)

3.2 Molecular Weight and Solubility of the Treated Starch

The absolute heavy average molecular weight of the substance can be obtained by fitting a Berry or Zimm plot after static light scattering tests. However, since starch contains a large number of branched chains and is not a linear polymer, if the Zimm plots are used for fitting, they may not show good linearity, which may lead to difficulties in extrapolating the data, so the experimental results were calculated using Berry plots. Fig.S5 (see the Supporting Information of this paper) shows the Berry plots of native corn starch at different angles and concentrations, and the fitted calculated heavy average molecular weight is about 1.4×10^8 g/mol.

Table 1 shows the molecular weight and yield of the starch after aqueous ILs hydrolysis. It was clear that the native corn starch hydrolyzed faster in the first 2 h, and a significant molecular weight value decrease had been obtained, the molecular weight of corn starch sharply decreased from 1.4×10^8 g/mol to 1.03×10^5 g/mol at 0. 5 h, and then slowed down to 4.50×10^3 g/mol at 3. 0 h, until 2.50×10^3 g/mol at 5. 0 h. These results revealed that with the hydrolysis of corn starch in aqueous ILs, the depolymerization of native corn

starch occurred quickly, and then preferred to prepare low molecular weight starch. In addition, a lower molecular weight was obtained as compared with 90% ethanol (Table S1 in the Supporting Information of this paper and Fig.6), revealing that the hydrolysis degree of starch in aqueous ILs occupied a competitive advantage over that of 90% ethanol [Fig.6(A) and (B)]. Accounting for the recoverability of starch in ionic liquid, which fully rivals the other solvent systems, getting hydrolyzed granules with a small enough molecular weight from native starch in ionic liquid satisfies the requirement of green chemistry and will have a good application prospect in industry. Furthermore, we changed the concentration of acid and the temperature of hydrolysis, and the results after hydrolysis at different time were presented in Table S1. These results show that the preparation of starch with different molecular weights can be controlled by changing the conditions.

Table 1 Molecular weight and yield of starches after treatment in 90%(mass fraction) aqueous ILs

Sample[a]	Hydrolysis medium	Hydrolysis time/h	Yield[b](%)	Molecular weight[c]/(g·mol^{-1})
S-IL-0.5	Aqueous ILs	0.5	91	1.03×10^5
S-IL-1.0	Aqueous ILs	1.0	91	7.49×10^4
S-IL-2.0	Aqueous ILs	2.0	92	1.33×10^4
S-IL-3.0	Aqueous ILs	3.0	89	4.50×10^3
S-IL-4.0	Aqueous ILs	4.0	90	2.90×10^3
S-IL-5.0	Aqueous ILs	5.0	88	2.50×10^3

a. 1 mol/L HCl at 100 ℃; *b*. (mass of starch after treatment)/(mass of starch before treatment)×100%; *c*. obtained from static light scattering.

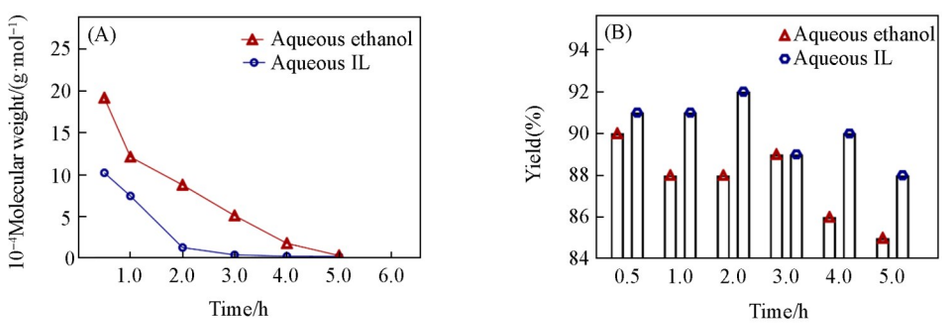


Fig. 6 Correlations of molecular weight(A) and yield(B) with hydrolysis time of starches after treament in aqueous ethanol and aqueous ILs

As shown in Fig.7 and Fig.S6(see the Supporting Information of this paper), compared to low-molecular-weight starch prepared *via* ethanol-mediated hydrolysis, the product obtained using the ionic liquid/water system under equivalent temporal conditions exhibited markedly enhanced water solubility, surpassing that of the ethanol system by >10% at 60 ℃[Fig.7(A)]. Solubility further increased with temperature[Fig.7(B)], reaching >96% for samples hydrolyzed more than 3 h at 90 ℃[Fig.7(C)]. This pronounced solubility is attributed to the substantially reduced molecular weight at this hydrolysis stage, comparable to that of dextrin.

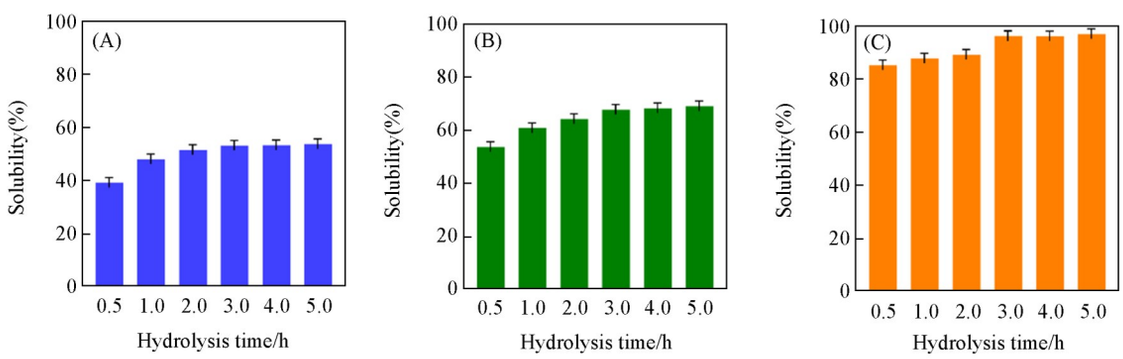


Fig. 7 Solubility of low molecular weight starch at 60(A), 75(B) and 90 ℃(C) after different hydrolysis times in 90%(mass fraction) aqueous ILs

3.3 Thermal Study of the Hydrolyzed Starch

The calorimetric responses of corn starch treated in aqueous ILs as a function of acid hydrolysis time were also examined through DSC analysis, and the diagrams are illustrated in Fig. 8(A). The glass transition temperature(T_g), which generally reveals the interaction between corn starch and molecular weight, exhibited an obvious decrease upon the processing time of native corn starch in aqueous ILs, especially in the range of 2.0—4.0 h, where the T_g dropped dramatically from 92.4 ℃ to 74.3 ℃[Fig.8(B)]. With the molecular weight decreased, the T_g of the treated corn starch also exhibited a gradual decrease as shown in Fig.8(C). These results demonstrated that during corn starch treated in aqueous ILs for different time, the strong interaction between the starch chain and aqueous ILs disrupted the original interchain hydrogen bonding and the crystalline structure of native corn starch, and then broke the long chain of starch into short chains, enabling the molecular weight decline, thus enhanced the mobility of starch molecular chain with high conductivity for thermoplasticity[23].

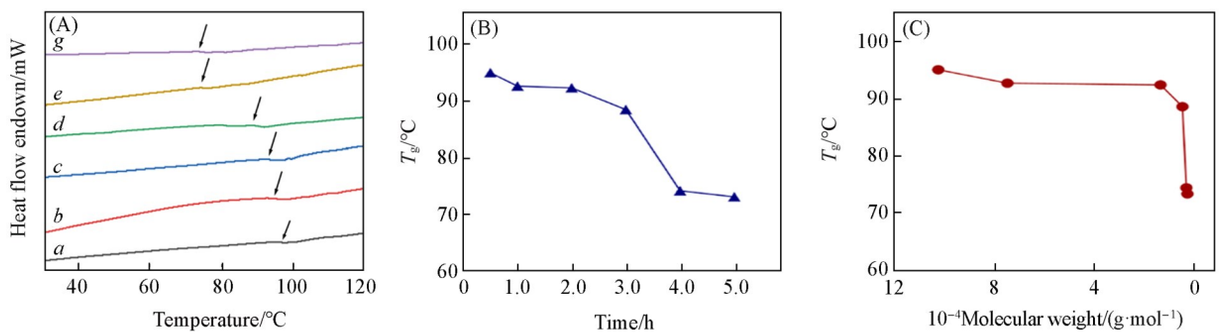


Fig. 8 DSC curves of the corn starch treated in aqueous IL for 0.5(*a*), 1.0(*b*), 2.0(*c*), 3.0(*d*), 4.0(*e*) and 5.0 h(*f*), respectively(A), and the correlation of T_g with treated time in aqueous ILs(B) and molecular weight of hydrolyzed corn starch(C)

The thermal stability of the hydrolyzed starch was evaluated by measuring mass loss by TG. As shown in Fig.9(A) and Table 2, it can be seen that there were two major mass loss stages for all samples with different time treated in aqueous ILs. The first minor stage represented the evaporation/dehydration, the mass loss in

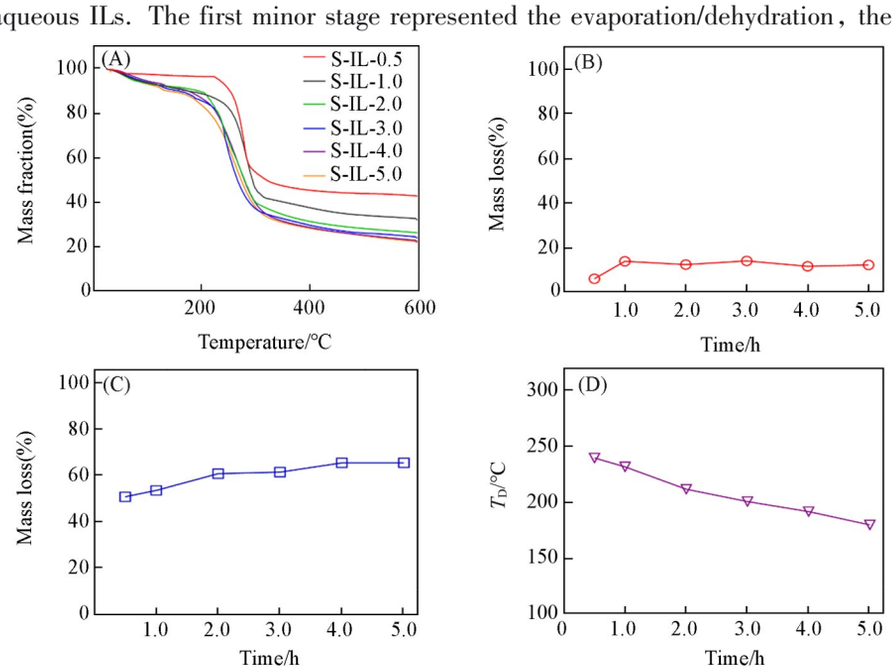


Fig. 9 TGA curves of corn starch hydrolyzed in aqueous IL for 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 h(A), the correlation of the mass loss in the first stage(B) and the second stage(C), as well as the decomposition temperature(T_D) with the hydrolysis time(D)

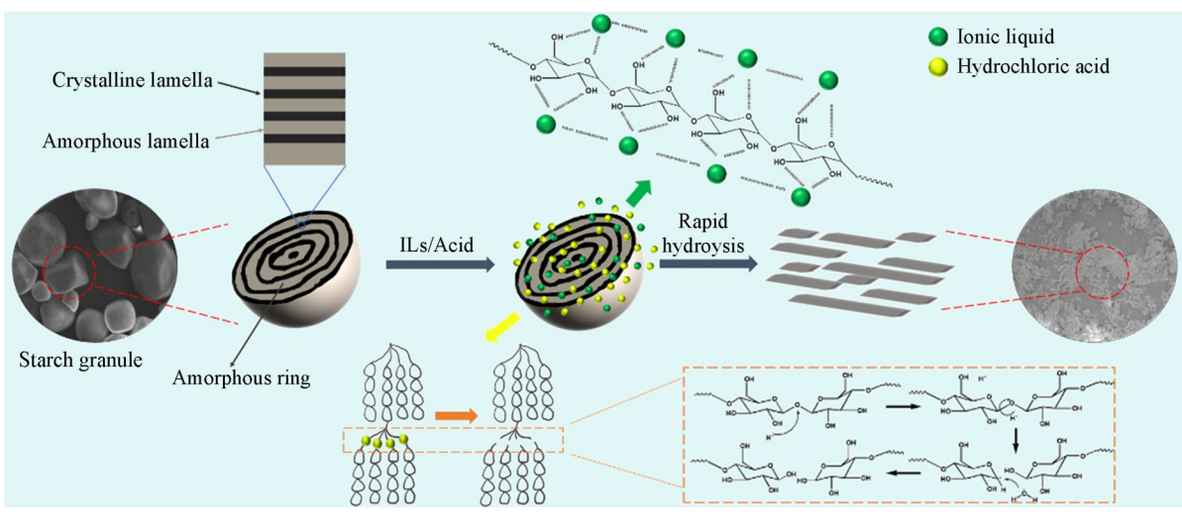
Table 2 TG studies of the corn starch hydrolyzed in aqueous ILs with different time

Sample	The 1st stage	The 2nd stage	
	mass loss(%)	T_D/℃	Mass loss(%)
S-IL-0.5	6.08	240	50.81
S-IL-1.0	13.94	232	53.58
S-IL-2.0	12.52	212	60.80
S-IL-3.0	14.15	201	61.49
S-IL-4.0	11.73	192	65.45
S-IL-5.0	12.34	180	65.43

this step was dependent on the moisture content in the starch samples, there was no obvious mass loss but only a slight water loss observed in the thermogravimetric curves at temperature below 240 ℃ for all the samples, and it also can be seen that the hydrolysis time or degree of hydrolysis had no significant effect on the initial water content[Fig.9(B)]. The mass loss of these samples mainly occurred from 240 ℃ to 320 ℃, and the mass loss in this region can probably be attributed to the decomposition of carboxylic groups along with the elimination of hydroxyl groups in these samples[24]. After the hydrolysis of corn starch, the samples had lower decomposition temperatures and a higher rate of mass loss in the second stage with the hydrolysis time in aqueous ILs as shown in Fig.9(C) and (D). That's to say, the hydrolyzed starch samples became thermally more unstable with the extension of hydrolysis time, which was due to the gradual decline in molecular weight of starch, and the higher amount of hydroxyl groups in the starch molecule after hydrolysis was also responsible for the decreased thermal stability[25].

3.4 Process of Starch Hydrolysis in Ionic Liquid/Water

Considering the above discussion, we propose a possible mechanism process for the acid dissolution of the starch in the ionic liquid dissolution system(Scheme 1). At the early stage of hydrolysis, hydrochloric acid follows the ionic liquid to diffuse rapidly inside the starch granules, and the anion of the ionic liquid, as a proton acceptor, will produce hydrogen bonding with the hydroxyl groups on the starch chains, leading to the orderly crystalline region of starch starting to disintegrate, and all the starch chains are gradually exposed to the whole system, at which time the hydrolysis of starch is very fast, and the acid destroys the amorphous and crystalline regions of starch at the same time, causing deformation and fracture on the granule surface that induce adhesion between the granules until they are completely broken into blocks.



Scheme 1 Hydrolysis mechanism of the corn starch in ionic liquid/water system

4 Conclusions

A series of low-molecular-weight starches was successfully obtained by hydrolysis with aqueous ionic

liquid for different time from native corn starch. With the hydrolysis of native corn starch in ionic liquid, the intermolecular and intramolecular hydrogen bonds of native starch could be broken, then its crystalline region was largely disrupted by ionic liquid, and the morphology of starch was extensively eroded from particles into little pieces. Furthermore, the hydrolysis degree of corn starch can be effectively controlled by hydrolysis time, and its thermal stability showed a significant decrease with the decrease in molecular weight and the increase in the number of hydroxyl groups. We proposed a convenient, green and effective manner to obtain starch with an amorphous state and low-molecular-weight originated from native corn starch, which is of great help for more extensive application of starch in practice.

The Supporting Information of this paper see http://www.cjcu.jlu.edu.cn/CN/10.7503/cjcu20250328.

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