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Dissolution of starch in urea/NaOH aqueous solutions

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ABSTRACT: Dissolution of starch in urea/NaOH aqueous solutions was studied by using polarizing microscope and viscometry. The experimental results revealed that starch could dissolve in urea (2–20 wt %) and NaOH (10–1 wt %) aqueous solutions at temperature ranging from −12 to 25 °C, where the optimized dissolution condition was in the aqueous solution of mixed urea 14% and NaOH 4% at 0 °C for 30 min or above. Under the conditions, the starch solubility could be 99.0 and 92.1% as the starch weight percent was 1 and 10%, respectively. Measurements for the molecular weight and amylose content of the starch before and after the dissolution indicated that there was no serious degradation during the process. The results from determinations of X-ray diffraction, Fourier transform infrared, and rapid visco analysis revealed that the recovered starch from the starch solutions was an amorphous solid with a part of V-type pattern (single-helix). The urea/NaOH aqueous solvent may have potential significance for starch processing and modification. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43390.

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INTRODUCTION

Starch is the reserve substance of plants from sunlight, one of the most abundant natural polymeric materials in the world. It is composed of amylose and amylopectin. Amylose is a linear glucan with glucopyranose units linked through α-D-(1–4) glycosidic linkages, while the amylopectin is formed by linear amylose chains with side chains branched on the C-6 position.[1] Native starch has a semicrystalline structure with varying levels of crystallinity, depending on the biological sources.[2] As the major polysaccharide in plants, starch contributes 50–70% caloric intake in our diets,[3,4] which provides a direct source for glucose needed by human body. In addition to being a major food item, starch is receiving increasing attentions in industries, because of its cheapness, well cost-effect, renewability, and biodegradability. Starch has been used as various industrial products such as thickener, water retention agent, gelling agent, adhesive, and colloidal stabilizer.[5] Also, starch is often modified to improve its end-use properties.[6] However, the application or the modification of starch is greatly restrained by its poor solubility. Because of the high molecular weight, strong hydrogen bonding between molecules and compact granule structures, starch can hardly dissolve in common solvents and cold water.[7]

In the past decades, efforts have been made to develop starch solvents. Dimethyl sulfoxide (DMSO) was first used in 1959 to dissolve starch,[8] and has been the most common and best known organic solvent for starch[9–11] up to now. The dissolution of starch in DMSO is a very slow process that may take several days, and heating can speed the dissolution. The dissolving capacity of DMSO for starch depends on the crystallinity of the starch granules, amylose/amylopectin ratio, and DMSO content in the aqueous solution. When the weight ratio of DMSO and water is 9/1, starch has a maximum solubility.[10,12,13] DMSO as the starch solvent has been extensively used in determinations of molecular weight, amylose content of starch, and so on.

Strong alkaline solutions of alkali metal hydroxides (such as NaOH and KOH) are solvents for amylose[14] and have been frequently used for gelatinization and structural analysis of starch.[3,15,16]

The real dissolution of starch is a process in which each the starch molecule is surrounded by solvents. Driving forces of the dissolution may be from stronger affinities between solvent and starch molecules than the intramolecular interaction of starch itself. The affinity can be hydrogen bodings for protonic solvent (water) and dipolar aprotic solvent (DMSO) and hydration of ionized hydroxyl of starch in the presence of NaOH. The latter introduces electrostatic forces between starch molecules, which can give a positive influence to dissolution of starch as well as to the stability of the starch solution.

More than 30 years ago, a report[17] disclosed *N*-methyl morpholine *N*-oxide (N-MMO) as a solvent for starch, and recently,

Koganti's group[18,19] has focused in research of behavior and structure of starch dissolving in N-MMO. Lately, Jordan *et al.*[20] first reported molten imidazole as a new solvent for starch, where a clear 20 wt % starch solution with some starch degradation was observed. In the last decade, ionic liquids have gained a lot of attention as a new kind of solvents for polysaccharides.[21–23] Biswas *et al.*[24] used ionic liquids as solvents for chemical modifications of starch. From then on, more and more studies on ionic liquids used as solvents for starch were reported.[25–27] However, the facts that the solubility depends on structure of ionic liquids, together with high temperature needed and high cost, greatly restrain their applications in starch industry.

Although several solvents have been developed to dissolve starch, it is still essential to seek some cheaper and environmental friendly starch solvents both for processing and chemical modification under homogeneous conditions. In view of the good plasticization of urea for starch[28,29] and the good dissolving capacity of NaOH solution to starch,[15,16] urea/NaOH aqueous solutions[30] can be a potential solvent for starch.

In this article, urea/NaOH aqueous solutions were used as solvents for starch, and the dissolving properties and structures of the starch recovered from the aqueous solution are studied as well.

EXPERIMENTAL

Materials

Maize starch was obtained from Xian Guowei Starch (Xian, China). NaOH and urea of analytical grade were supplied by Chengdu KeLong Chemical (Chengdu, China) and used without further purification. All other chemical reagents of analytical grade were purchased from commercial sources in China.

Preparation of Starch Aqueous Solution

Urea and NaOH were dissolved in distilled water to obtain urea/NaOH aqueous solutions and then precooled to 0 °C. The concentrations of urea and NaOH ranged from 2 to 20 wt % and from 1 to 10 wt %, respectively. Starch was suspended in urea/NaOH aqueous solutions for dissolution under stirring for 30 min and then stored at 0 °C for 24 h to ripen and obtain starch solution with weight concentration of 5%.

Viscosity Measurement

Starch solution was diluted to concentration of 0.5% with urea (14%)/NaOH (4%) aqueous solution, and viscosity of the diluted solution was measured at 25 °C with a calibrated Ubbelohde viscometer. Intrinsic viscosity $[\eta]$ was calculated from Huggins and Kraemer plots.

Recovered Starch

To obtain recovered starch, starch solution was first neutralized with a right amount of 1.0 mol/L HCl, then precipitated by adding a large number of ethanol, filtered, washed several times with ethanol, and finally dried in a vacuum oven at 50 °C to a constant weight. The product was crushed and sifted through a 100-mesh sieve for use.

Viscosity-Average Molecular Weight ($\overline{M}$)

Dry native starch or recovered starch sample was dissolved in dimethyl sulfoxide, and the viscosity value was measured at 25 °C by using the Ubbelohde viscometer. The viscosity-average molecular weight ($\overline{M}$) of the sample was calculated from the following equation[31]:

$$[\eta]=2.16\times10^{-3}\overline{M}^{0.67}\ \ (\mathrm{mL/g}). \tag{1}$$

Solubility and Maximum Concentration of the Native Starch

Solubility and maximum concentration of the native starch were measured following the method of Mukerjea *et al.*[7] and Jivan *et al.*[32] with slight modification in an aqueous solution containing urea 14 wt % and NaOH 4 wt %. The aqueous solutions of native starch contents 1 and 10 wt % were prepared separately, according to the procedure in the "preparation of starch aqueous solution" section. After dissolution, the two starch solutions were centrifuged at 1200 × *g* for 20 min, respectively, and each of the supernatant was collected.

The supernatant was neutralized with 1.0 mol/L HCl, precipitated with ethanol, and then centrifuged again. The precipitate was washed with ethanol and filtrated. The filter residue was dried in a vacuum oven at 50 °C to a constant weight. The solubility (S) and maximum concentration (C) of starch were calculated as:

$$S\ (\%)=\frac{W_1}{W_{s1}}\times100 \tag{2}$$

$$C\ (\%)=\frac{W_{10}}{W_{ss10}}\times100, \tag{3}$$

where W is the weight of the dried filter residue, W_s is the weight of starch sample used, W_{ss} is the weight of starch solution, and subscript 1 or 10 refers to the used starch content of 1 or 10 wt % accordingly.

Amylose Content

Amylose content was determined based on the colorimetric measurement of the iodine complexes of starch.[33] Dried starch or recovered starch (0.1 g) was accurately weighed and suspended in 1 mL ethanol in a 100-mL volumetric flask, slowly stirred, and then 10 mL of NaOH (1 mol/L) was added. The starch suspension was heated in a boiling water bath for 15 min. After cooled to room temperature, the solution was then diluted to 100 mL with deionized water. The above solution of 5 mL was accurately taken out of the flask and into another 100-mL volumetric flask, then 50 mL of water was added, together with addition of 1 mL of acetic acid (1 mol/L) and 2 mL solution of iodine in potassium iodide (0.2 g I_2 and 2 g KI in 100 mL water). Finally, the solution was diluted to 100 mL with water. After coloration for 10 min, the absorbance of this solution in a quartz cell was read at 620 nm using a UV/Visible spectrophotometer (Shimadzu UV-3600, Japan) with a blank (without starch). The standard curve of amylose concentration was plotted within amylose weight contents of the solution from 0 to 70% that composed of different ratios of amylose and amylopectin (Sigma, USA).

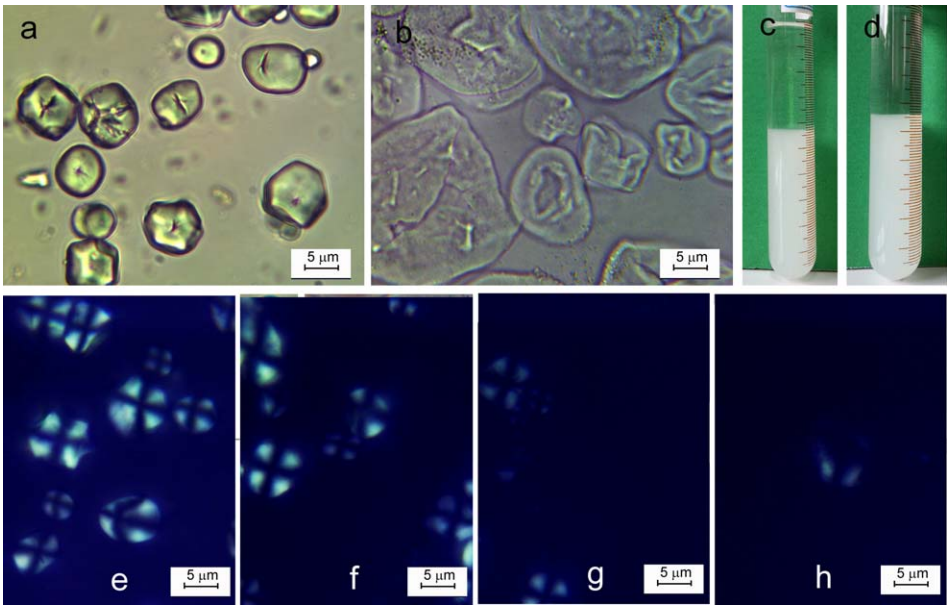

Figure 1. Optical micrographs of native starch in 20% urea aqueous solution (a) at normal temperature, (b and c) at 0 °C for 24 h, and (d) in 10% NaOH aqueous solution with starch concentration of 5 wt %, and polarizing light microscope photos of the starch dissolving in 14% urea/4% NaOH mixed aqueous solution for (e) 0 min, (f) 5 min, (g) 10 min, and (h) 30 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Characterization

X-ray diffraction (XRD) of dry native and recovered starch samples were recorded with a Philips X-ray diffractometer (X'Pert Pro MPD, Philips, The Netherlands), using a scanning speed of 0.5°/min from 4° to 40° of diffraction angle 2θ.

The pasting profile of native and recovered starch samples were analyzed using a Rapid Visco Analyzer (RVA-4, Newport Scientific, Australia). A starch slurry of 28 g containing 3 g of starch (dry weight) was equilibrated at 50 °C for 1 min, heated to 95 °C at a rate of 12 °C/min, and held at 95 °C for 2.5 min. The starch slurry was then cooled to 50 °C at a rate of 12 °C/min and held at 50 °C for 2 min. The RVA paddle speed was 960 rpm for the first 10 s and then 160 rpm for the remainder of the experiment.

Fourier transform infrared (FTIR) spectra of the native and recovered starch granules were recorded on a Brucker FTIR spectrometer (EQUINOX55, Brucker, Germany) using the KBr-technique.

Ordinary and polarized light micrographs of starch were viewed and taken by using a Phenix polarizing microscope (PZ-2, Phenix, China) at 400× magnification.

RESULTS AND DISCUSSION

Dissolution of Starch in Urea/NaOH Aqueous Solution

The dissolution of maize starch in urea/NaOH aqueous solutions was investigated. Figure 1 shows the photographs of starch dissolving in different ratio of solvents, observed with the light microscope, naked vision, or polarizing microscope. Starch could not dissolve in a 20 wt % urea aqueous solution at normal temperature as shown in Figure 1(a), but could be swollen by the solution at 0 °C for 24 h [Figure 1(b,c)]. Similarly, the starch could not dissolve in an aqueous solution of 10 wt % NaOH [Figure 1(d)]. However, when the two solvents were combined into one, i.e., a solution containing 20% urea and 10% NaOH, starch could dissolve in it. Figure 1(e–h) shows the gradual change and disappearance of the polarization cross of the starch in the mixed solution under polarized light with dissolving progressing. Furthermore, we found out that starch could dissolve in appropriate concentration ranges of urea/NaOH aqueous solutions with urea from 2 to 20 wt % and NaOH from 1 to 10 wt % in 5 wt % starch concentration with a transparent appearance. This phenomenon means a synergy effect of urea and sodium hydroxide occurred in the solution, thereby causing swelling and gelatinization of starch. The strong solvation effect of the mixed solution on the starch may result from ionization, hydrogen bonding,[28,30] electrostatic force, and their combination.

To seek an optimal ratio of urea and NaOH for starch dissolution, a series of urea/NaOH aqueous solutions were prepared by changing the ratio of urea and NaOH, and the intrinsic viscosity $[\eta]$ of starch in urea/NaOH aqueous solutions was measured. The three-dimensional diagram for relationship of the intrinsic viscosity and concentrations of urea and NaOH is shown in Figure 2. Viscometry is a simple, effective, and sensitive analytical technique to investigate polymer dissolution. It is well known that intermolecular interactions of a polymer in a solution play a key role in the viscosity of the polymer solution. The value of $[\eta]$ reflects the expanded extent of the macromolecular chains. A higher value of $[\eta]$ for a polymer solution

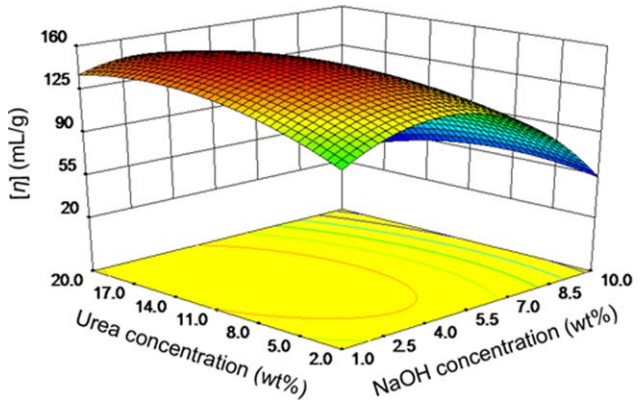

Figure 2. Three-dimensional diagram for intrinsic viscosity [η] of starch aqueous solution versus urea and NaOH concentrations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

indicates better dissolving capacity of the polymer in the solvent. Figure 2 reveals that with the increase of the urea and/or NaOH concentrations the dissolving capacity of starch first increased and then decreased, and reached a maximum in urea (14–16%)/NaOH (3–4%) aqueous solution. Moreover, the starch solution with the optimal urea/NaOH ratio was relatively stable with time of storage, just as shown in Figure 3. The [η], along with the clear and transparent appearance, of the starch aqueous solution with 14 wt % of urea and 4 wt % of NaOH remained almost constant for 18 days at 5 °C. The subtle increase of the [η] on the third day relative to the initial solution could be resulted from the dissolution mature of the starch. After that, the [η] of the starch in the solution experienced a slow decrease process where a slight hydrolysis of the starch could have been happened.

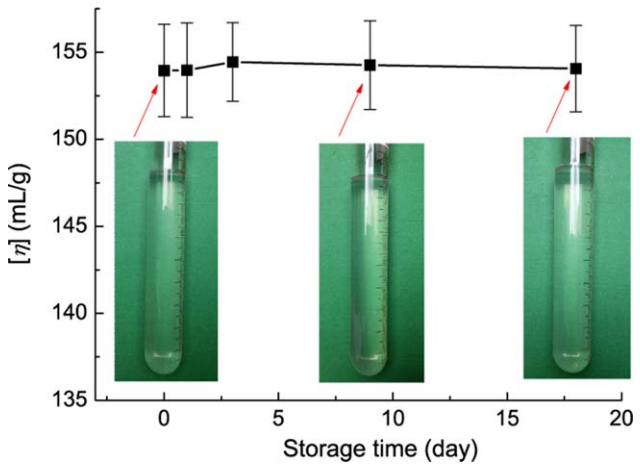

Figure 3. Dependence of [η] and appearance of starch in urea (14%)/NaOH (4%) aqueous solution on storage time at 5 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

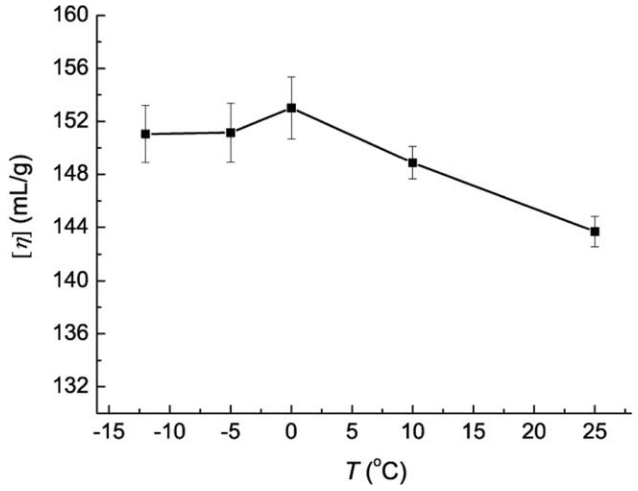

Figure 4. Variation of [η] of starch in urea (14%)/NaOH (4%) aqueous solution with temperature.

Figure 4 shows dependence of [η] of the starch solution containing 14 wt % urea and 4 wt % NaOH on the solution temperature. The curve indicates that the starch could dissolve in the urea/NaOH aqueous solution at temperature ranging from −12 to 25 °C, and the dissolving capacity reached the maximum at 0 °C. Solubility of a native starch in cold water is negligible (~4%).[32] In our experiments, however, the native starch can dissolve in urea (14%)/NaOH (4%) aqueous solution at 0 °C with a solubility $S = 99.0\%$ and a maximum concentration up to $C = 9.21\%$, calculated by eqs. (2) and (3). That is, under the conditions, the starch solubility could be 99.0 and 92.1% as the starch weight percent was 1 and 10%, respectively. The solubility was apparently affected by the starch percent in the solvent. Therefore, in solubility determinations starch content is generally limited to about 1% or less,[7,10] even 0.3% starch content, where the diluted starch molecules are considered as fully solvation.[10] At higher starch percents, almost all of solvent molecules involve in starch solvation, and then there is not enough free solvent molecules for dissolving starch further. As a result, small part of swollen amylopectin with high molecular weight keep their secondary and tertiary structures of starch granules, and dissolved amylose molecules tend to retrogradation.[7,10]

Mukerjea *et al.*[7] found that a maize starch suspension of 1.1% (w/v) concentration can dissolve in water with 75.1% (w/v) solubility at 121 °C autoclaved for 30 min, and the solubility declined to 62.2% (w/v) as the starch percent was doubled. They also found that the starch is soluble in 1 mol/L NaOH at 20 °C stirred for 15 h and in 85 : 15 (v/v) DMSO/H_2O at 20 °C stirred for 8 h. When the starch percent was 11% (w/v) regardless of the moisture content in the starch granules, the solubility is 82.2% and 62.1% (w/v), respectively. Compared roughly with previous studies for dissolving starch, the urea (14%)/NaOH (4%) aqueous solution in our experiment is as good, if not

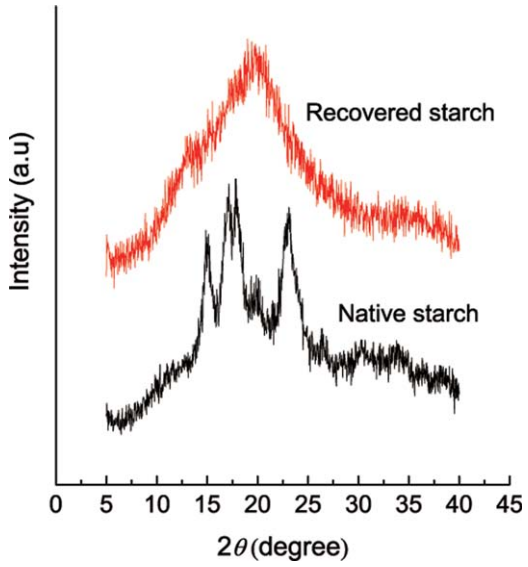

Figure 5. XRD patterns of the native starch and recovered starch. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

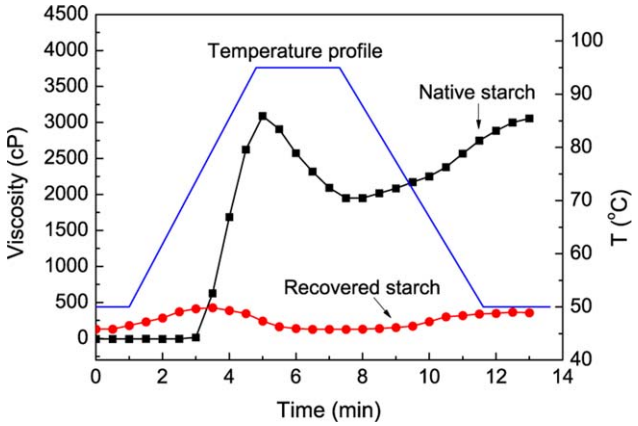

Figure 6. RVA pasting profiles of the native and recovered starch granules. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

better than, as the NaOH and DMSO/H_2O solvents mentioned above. More importantly, the newly developed solvent system can dissolve starch in a simple way without VOC content.

Structure Changes between Native and Recovered Starch Granules

Starch is a semicrystalline polysaccharide, and the crystal morphology of its double helixes can be classified into A, B, and C forms.[34,35] The XRD patterns of the native and recovered starch granules are presented in Figure 5. The native starch shows a typical A-type pattern,[34] with strong diffraction peaks at 2θ about 15° and 23° and an unresolved big doublet at 2θ about 17° and 18°. For the recovered starch, however, the A-type pattern disappeared, and was replaced by a V-type pattern with diffraction peaks at 2θ 13.0° and 19.9°, a typical feature of single helix.[34] This indicates that granular structures of the native starch destroyed and the double helixes changed into single helix after dissolving and recovery. In addition, the crystallinity of starch decreased greatly from 30.2 to 11.8%, calculated by use of analysis software MDI Jade 5.0 (Materials Data Ltd., USA). In the NaOH/urea aqueous solution the —OH groups of starch could be deprotonated by the strong caustic and turned into negative charges, followed by a strong solvation of water and urea.[28] The deprotonation of NaOH and solvation of urea had doubtlessly a synergistic effect for dissolving starch. Starch granules swelled, as a result, and the double-helical structure of starch was dissociated along with destruction of the crystallites of starch.[36] After neutralization of the starch solution and being precipitated by ethanol, most of starch aggregates presented an amorphous pattern, and a small number of starches formed a single-helical structure (V-type pattern).

In addition, the recovered starch granule can dissolve in cold water in our experiment, which can also confirm the amorphous pattern of the recovered starch.[37] RVA was used to determine the pasting behavior of the native and recovered starch granules. The pasting profiles and corresponding data are presented in Figure 6 and Table I. The pasting temperature of native starch is 74.4 °C and that of the recovered starch significantly decreases to 50.3 °C. Higher pasting RVA viscosities of native starch were caused by its bigger hydrodynamic diameters of highly swollen granule.[38] After the dissolving process in our experiment, the original crystal structure of native starch was completely destroyed according to Figure 5, and the lower crystallinity of V-type crystal was reconstructed in the recovered starch during the recovery process. Therefore, the recovered starch granules with decreased crystallinity and looser structure swelled at a faster rate when heated, which led to a lower pasting temperature.[39]

On the other hand, the pasting viscosity of the recovered starch greatly decreased when compared with the native starch. The mechanism behind the phenomenon can be complex. According to a conceptual model proposed by Ziegler and coworkers[40] for behavior of starch in excess water on heating, swollen network

Table I. Pasting Characteristics of the Native Starch and Recovered Starch

Sample	Peak viscosity (cP)	Trough viscosity (cP)	Final viscosity (cP)	Breakdown viscosity (cP)	Setback viscosity (cP)	Pasting temperature (°C)
Native starch	3096	1928	3057	1168	1129	74.4
Recovered starch	452	121	350	331	229	50.3

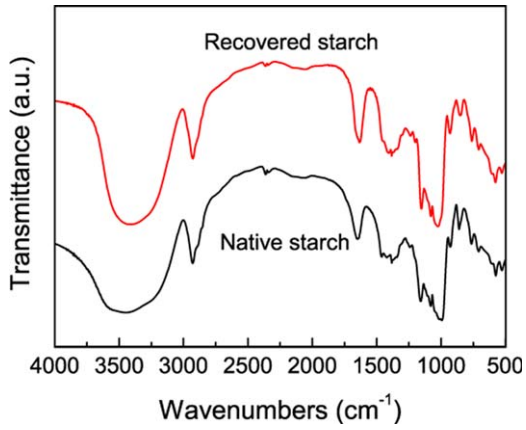

Figure 7. FTIR spectra of native and recovered starch granules. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

entanglements of double helices have much higher viscosity than the system of nematic liquid crystals composed of single helices corresponding to our recovered starch. In addition, differences in molecular weight and amylopectin content might be other reasons for the reduction of pasting viscosities.

The FTIR spectra of native and recovered starch granules are illustrated in Figure 7. In the spectrum of the recovered starch compared with that of the native starch, a narrowed band around 3400 cm^{-1}, corresponding to intermolecular and intramolecular hydrogen bonds of starch,[41] is noticed along with an enhanced peak at 1640 cm^{-1} from bound water in starch, which means that starch granular structure tends to be loosened. In the fingerprint region, the stretching peak of C—O in C—O—H groups shifted from 993 cm^{-1} in the native starch to 1028 cm^{-1} after recovery. The blue shift of recovered starch indicates a weaker hydrogen bonding interaction between starch molecules compared with the native starch.[42] Besides, CH_2 bending peak[43] at 1465 cm^{-1} almost disappeared after recovery, perhaps resulting from self-assembly of the CH_2 into the hydrophobic interior of V-type single helix. This confirms to the analysis of XRD data. There are no additional special peaks in the spectra of recovered starch, which means that the urea/NaOH mixed aqueous solution is a nonderivatizing solvent for starch.

In a strong alkali solution, the majority of —OH groups in starch are ionized, and the crystal structure of starch chains can be destroyed.[44] So, starch can be dissolved in alkali solutions. However, molecular degradation can speed up by alkali in the solution. Han and Lim[3] reported that the molecular weight of amylopectin and amylose decrease by about 47 and 35%, respectively, when a corn starch dissolve in 1 mol/L NaOH under vigorous vortexing (2500 rpm) for 10 min. While in our study the viscosity-average molecular weights of the native and recovered starch were 1.53×10^7 and 1.36×10^7 g/mol calculated by using eq. (1), respectively, and the amylose content increased from 25.00% for the native starch to 25.45% for the recovered one according to the iodine colorimetry. This indicates that the starch was slightly degraded only by 11% after the dissolution and recovery. The reason of the decrease in molecular weight could be from amylopectin more susceptible to shearing-induced depolymerization than amylose,[12] and then the amylose content increased slightly. Little changes in molecular structures of starch occurred in the urea/NaOH aqueous solvent system, together with the fact that there was no obvious degradation while stored at 5 °C for 18 days (see Figure 3). This means that the added urea can help to prevent starch macromolecules from hydrolysis and make the starch solution stable.

CONCLUSIONS AND OUTLOOK

Maize starch could dissolve in aqueous solutions containing urea 2–20 wt % and NaOH 10–1 wt % at temperatures ranging from −12 to 25 °C, preferably under the condition of urea 14 wt %/NaOH 4 wt % at 0 °C. After dissolution and recovery, the average molecular weights slightly decreased from 1.53×10^7 to 1.36×10^7 g/mol, and amylose content increased from 25.00 to 25.45%. The starch had not obviously degraded during the dissolution and recovery process, and the starch solution could keep stable and clear when stored at 5 °C for 18 days. The double-helical structure of the native starch was dissociated and the A-type crystal morphology changed into an amorphous pattern with partly V-type after recovered.

The new solvent system for dissolving starch in a way of simplicity and low cost with zero VOC could be considered as a true "green" solvent. The key points of the aqueous solvent also include lower toxicity, slight degradation of starch during dissolution, and stable viscosity of starch solution. Therefore, the new method with the urea/NaOH aqueous solvent may have extensive applications for processing and chemical modifications of starch. For instance, the new solvent system can be used to prepare starch derivations such as fatty acid starch esters, acting as both solvent and alkaline catalyst during the reaction. The solvent can also be used to make granular cold-water-soluble starch with single-helix structure, which may activate the chemical reactivity of starch. In addition, starch fibers and films can be regenerated from their urea/NaOH aqueous solutions. The pursuit of these potential applications is our next research tasks.

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