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Preparation and characterization of cationic corn starch with a high degree of substitution in dioxane–THF–water media

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ABSTRACT

Cationic corn starch derivatives with a high degree of substitution are prepared in alkaline solution or in mixed media of organic solvent and water with different levels of the cationic reagent, 2,3-epoxypropyltrimethylammonium chloride. The starch cationization yield is investigated, and the results indicate that the degree of substitution (DS) of the samples depends on the reaction conditions and reaction media. The maximum DS values are up to 1.37 in 1,4-dioxane alkaline–aqueous solution. Meanwhile, the structures of the cationic starch derivatives are characterized by elemental analyses, FTIR spectroscopy, X-ray diffraction, and ^{13}C NMR spectroscopy, as well as by SEM techniques.

1. Introduction

The industrial utilization of native starches is limited because of their inherit nature, such as water insolubility and their tendancy to form unstable pastes and gels. Therefore, starch is usually modified physically or chemically to achieve a particular property and cater to the requirements for tailor-made products.[1]

Etherification is a very important aspect of chemical modification. Cationic starch is any starch whose free hydroxyls have been commonly altered by using the cationic monomer 2,3-epoxypropyltrimethylammonium chloride (ETA) or 3-chloro-2-hydroxypropyltrimethyl ammonium chloride (CTA) under wet or dry processes.[2,3] Such modified starches generally have physicochemical properties that are significantly different from those of the parent starches, such as good solubility and more functional groups, thereby increasing their usefulness in the paper, textile, oilfield drilling, wastewater treatment, or cosmetic industries.[4–7] Comprehensive investigations show that cationic starch derivatives of a low degree of substitution (DS 0.03–0.2) are available in many commercial areas.[8–10] High-DS cationic starches have received much more attention in recent years owing to their preferable properties and potential applications.[11–13]

Usually, the high-DS cationic starch is prepared by an aqueous procedure, as water favors the diffusing of the cationic agent into the starch granule. However, hydrolysis or other side reactions may compete for the etherification of starch in the presence of water. Thus, it is necessary to choose appropriate media in which water is partially replaced in the reaction mixture by an active solvent. Han and Sosulski[14] reported that the starch was effectively cationized in an aqueous alcoholic solvent. Ayoub and coworkers[15,16] described a series of cationic starches with low DS (0.05) and high reaction efficiency that were prepared by a reactive extrusion process with ETA as the cationization reagent and sodium hydroxide as the catalyst. Kweon et al.[17] observed that the addition of water-miscible organic solvents to the alkaline aqueous media could achieve high-DS cationic starches, and ethanol was a more effective solvent than methanol or 2-propanol. A further investigation by Heinze et al.[18] described high-DS cationic derivatives that were prepared in aqueous–alkaline solutions, homogeneously with dimethyl sulfoxide (DMSO), and heterogeneously with ethanol–water. The results indicated that the reactivity depended on the reaction media, but compared with the other process, the modification of starch in heterogeneous ethanol–water was least effective.

In this work, the influence of varied solvent media on the DS of cationic starch was evaluated, and then the cationic starches with high DS were prepared in dioxane–THF–water medium by a one-step method. Based on these works, the structures of starch derivatives thus obtained were characterized by elemental analysis, FTIR spectroscopy, X-ray crystallography, and ^{13}C NMR spectroscopy as well as by SEM.

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2. Results and discussion

2.1. Effect of sodium hydroxide concentration on the DS in aqueous–alkaline solutions

In this paper, the degree of substitution of modified starch is a clear function of the varying levels of NaOH (Fig. 1). As observed, the initial increase in the amount of NaOH favorably increased the DS of the prepared cationic starches and reaction efficiency (RE). However, a further increase in NaOH leads to a decrease in both DS and RE. The DS of samples and RE are optimum when the concentration of NaOH is 1 wt %. This phenomenon can be explained in that under basic conditions the hydroxy functional groups of the anhydroglucose units of starch may react in a nucleophilic reaction with the etherification agent,[19] as in the well-known Williamson ether synthesis. But at high alkali concentration, the cationization agent undergoes a hydrolysis reaction, which effects an epoxide ring-opening to form the diol product. Obviously, the hydrolysis of the reagent should be as low as possible to minimize these side reactions. A similar trend was also reported by Lawal et al.[20] on carboxymethyl cocoyam starch.

2.2. Effect of reaction temperature and duration of reaction on the DS in aqueous–alkaline solutions

Cationic starch is synthesized by reaction of corn starch with ETA at different temperatures and at various durations of time in aqueous–alkaline solutions (Fig. 2). Results clearly indicate that a reaction time of 6 h is the optimum for all samples, and the highest DS obtained is 0.89 at 60 °C. It can be concluded that the formation of cationization products prevails over the secondary reactions within the studied range. The DS of samples was nearly constant with increase in reaction time when the reaction temperature was low (50 °C). However, upon exceeding this temperature (60 and 70 °C), there was an increase in the deetherification reaction that caused the DS to decrease.

2.3. Comparison of different organic media

The influences of different solvents on the DS of cationic starches prepared in organic solvent–sodium hydroxide–water are investigated in our work, and the results are summarized in Table 1. Compared to the results in aqueous media, the samples prepared in organic media have not shown any evidence of gelatinization when samples are again dissolved.

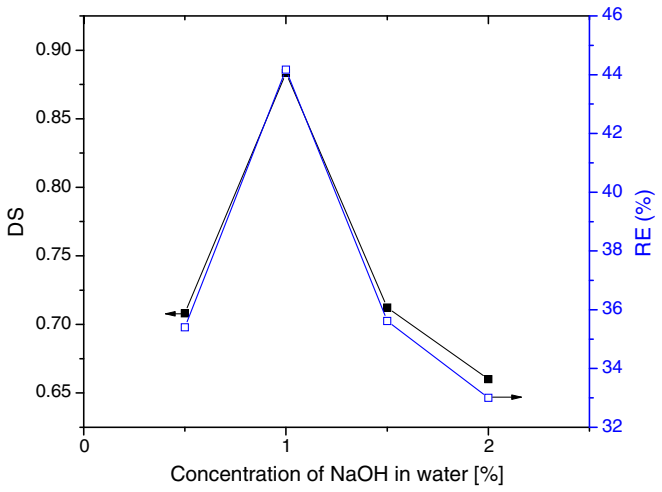

Figure 1. DS of cationic corn starch depending on the amount of NaOH (ETA/AGU = 2:1 mol/mol, 60 °C, 6 h).

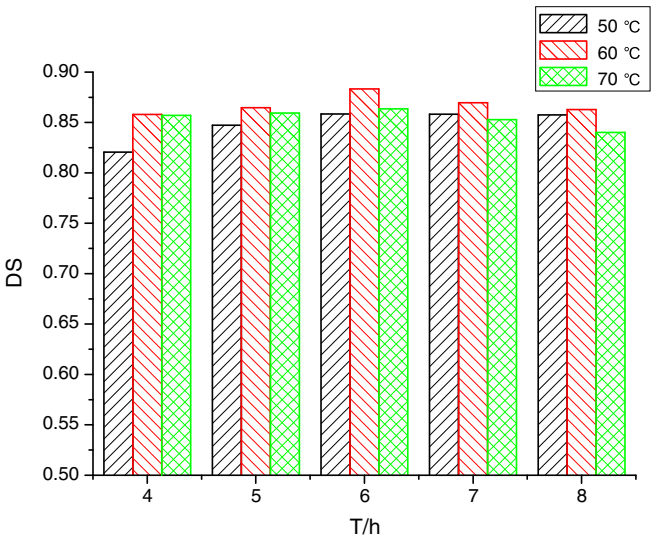

Figure 2. DS of cationic starches prepared at different reaction temperatures and duration of reaction (NaOH concentration 1.0%; ETA/AGU = 2:1 mol/mol).

Table 1
The effect of the reaction of starch with ETA in different media on the DS

Sample no.	Media	ETA/AGU molar ratio	DS
1	Ethanol/water	1	0.27
2	Ethanol/water	2	0.54
3	Ethanol/water	4	0.65
4	Dioxane/water	2	0.98
5	Dioxane/water	4	1.26
6	Dioxane/water	6	1.35
7	Dioxane/water	8	1.37
8	THF/water	2	0.93
9	THF/water	4	1.19

The data in Table 1 show an obvious relationship between the DS and the kind of organic solvent. When the molar ratio of ETA/AGU is 4, the highest DS values are 1.26, 1.19, and 0.65 for the reaction in dioxane, THF, and ethanol, respectively. It is evident that dioxane and THF appear to enhance good selectivity for the reaction that favors starch cationization. In comparison with other works, Jie et al.[21] reported that organic solvents obviously had an effect on reaction efficiency, and 2-propanol and *tert*-butanol were better solvents than methanol and ethanol for the carboxymethylation process of cassava starch. However, the reaction efficiency in this part of work cannot be measured because the level of ETA is far more than the normal level (when the molar ratio of ETA/AGU exceeds 3, the reaction efficiency cannot be measured).

Generally, a good organic solvent for the reaction should be one having high miscibility with water to avoid phase separation, as well as the ability to dissolve the etherifying agents and offer stabilization to the process. In addition, water also plays a significant role in aiding the diffusion and adsorption of etherifying agents as well as facilitating the swelling of the starch during the cationization process. At the same time, water also can affect the distribution of the various components between the bulk liquid phase and the starch particles. A prior investigation[22] has shown that NaOH precipitates in a mixture of ETA and NaOH that has a shortage of water. Thus, it is necessary that a particular quantity of water be used for NaOH hydration in the reaction mixture. Typically, in our work the ratio of water to organic solvent is 1:1 (v/v).

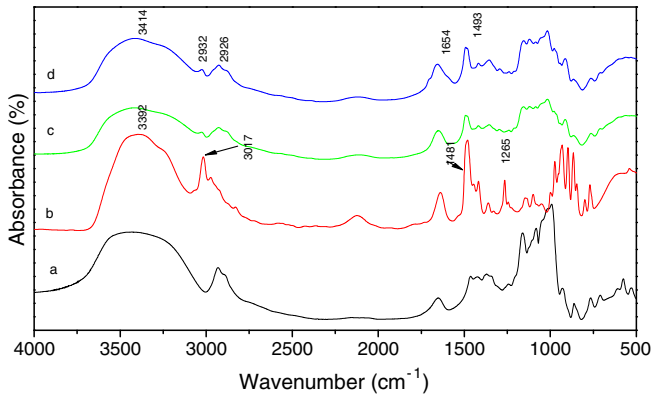

Figure 3. (a) FTIR spectra of native starch (b) ETA and cationic starch with a DS of (c) 0.89, and (d) 1.35.

2.4. FTIR spectroscopy of cationic starches

To determine the structure of cationic starches, FTIR spectra are measured. Spectra of native starch, ETA, and cationic starches are shown in Figure 3.

In the spectrum of native starch (Fig. 3a), the characteristic absorptions that appear at 1154, 1121, and 1017 cm^{-1} are attributed to the C–O bond-stretching vibration of the anhydroglucose units.[23] The band at 2926 cm^{-1} is characteristic of the C–H stretching vibration. Meanwhile, an extremely broad band resulting from vibration of the hydroxyl groups (O–H) appears at 3414 cm^{-1}.

In the case of ETA (Fig. 3b), the broad band at 3392 cm^{-1} is for the O–H stretching vibration of water molecules that remain after drying. The bands at 3016 and 1481 cm^{-1} are assigned to the C–H and C–N stretching vibrations, respectively. A strong band at 1265 cm^{-1} is due to the epoxy ether.

Figure 3c and d shows the FTIR spectra of cationic starches of different DS values. Cationic starch and native starch have similar profiles. Besides the characteristic starch backbone peaks, additional adsorption bands for the quaternary ammonium groups appear at 2932 cm^{-1} (C–H) and 1493 cm^{-1} (C–N). In addition, with an increasing DS (Fig. 3c and d), the intensity of peaks at 1493 cm^{-1} is gradually strengthened, which is clear evidence for the incorporation of a cationic moiety onto the backbone of the starch. These results are similar to those reported earlier.[6]

2.5. ^{13}C NMR spectroscopy of cationic starch

The ^{13}C NMR spectrum of native starch in Figure 4a shows the correlation peak of each carbon of the anhydroglucose unit. Gong et al. reported the assignment of the ^{13}C shifts of the glycopyranan units of the native starch.[24] In cationic starch (Fig. 4b), the prominent peak for C-10 at 53.9 ppm is attributed to the $–CH_3$ carbon of the cationic group. The peaks at 99.1 and 96.0 ppm are assigned to C-1. As observed, two peaks appear here because of the cationization status of C-2. In this sense, two different environments could occur for C-1, depending on whether or not there is cationization substitution at C-2. The result here suggests that cationization substitution at C-2 causes a split of C-1. Unsubstituted and substituted C-2, C-3, and C-5 appear between 70.6 and 76.0 ppm. The signal at 79.9 ppm is assigned to C-4, while C-6 appears at 60.0 ppm. The signals at 72.4 , 67.6, and 64.8 ppm are believed to belong to the carbons of C-7, C-9, and C-8, respectively. The peak assignments for the CH_2 groups at C-6, C-7, and C-9 have negative intensities and can be easily distinguished from the CH groups by a DEPT-135 experiment, a fact that has been verified by Heinze et al.[18]

2.6. Morphology of native starch and cationic starch

Scanning electron microscopy (SEM) is used to study the changes in morphology of the native and modified starch granules. The native corn starch granules (Fig. 5a) are round and polygonal in shape with well-defined integrity, whereas the cationization process considerably changes the starch granule morphology. When the DS of cationic starch is low, the cationic reagent penetrates the interior of the starch molecule, and the starch granules are markedly enlarged and begin to disintegrate (Fig. 5b). With a further increase in DS, the surfaces of the starch granules completely disintegrate, and their edges drastically lose

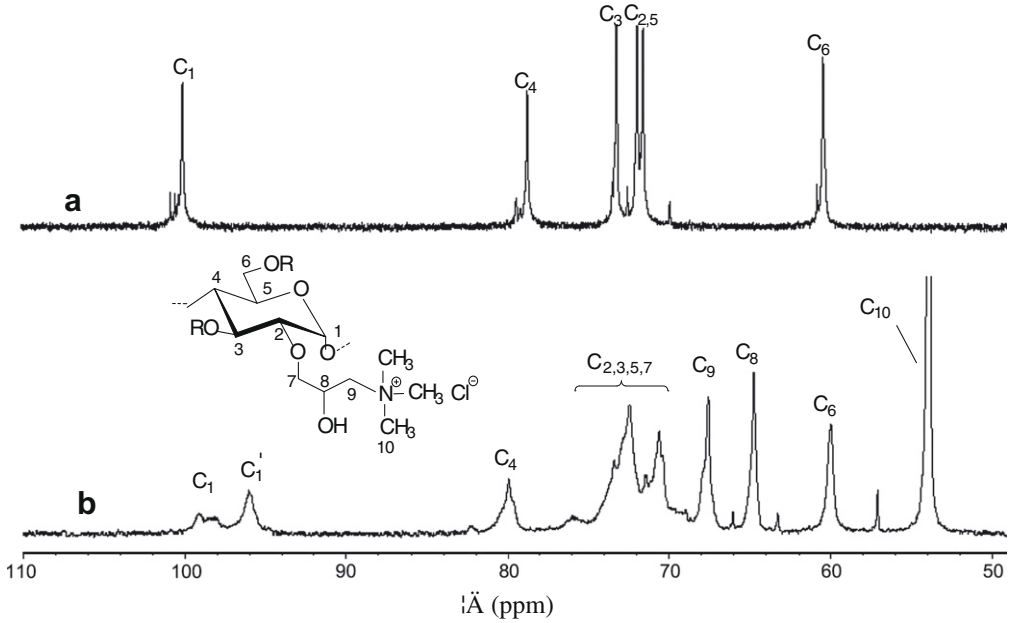

Figure 4. ^{13}C NMR spectra of (a) native starch and (b) cationic starch of DS 0.89 (R = H or cationic group according to DS).

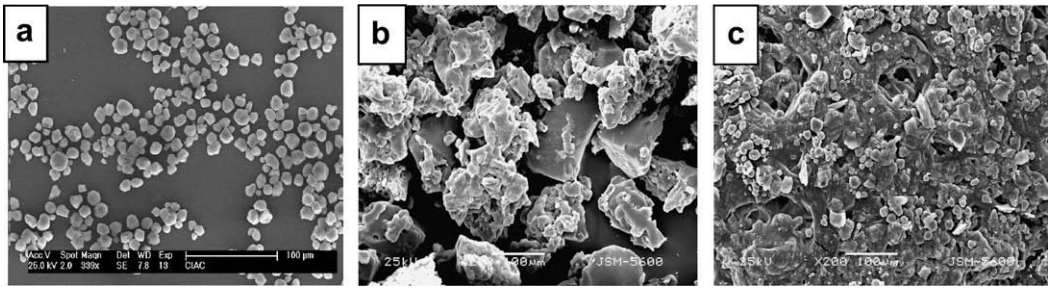

Figure 5. SEM pictures of starch granules: (a) native starch 1000×; (b) DS 0.54 cationic starch 200×; (c) DS 1.35 cationic starch 200×.

definition (Fig. 4c). Apparently, cationization destroys the structure of the corn granule and reduces hydrogen bonding. Combined, these factors facilitate rapid water uptake to the point that even the higher DS cationic starch will dissolve in cold water.

2.7. X-ray diffraction studies

X-ray diffraction measurements are performed to investigate the change of the crystallinity of starch, and the results are presented in Figure 6. Native corn starch exhibits an A-type crystallinity pattern.[25,26] The strong reflections (2θ) are approximate to 15° and 23°, and an unresolved doublet appears at 17° and 18° (Fig. 6a). It is noted that the crystallinity pattern of the starches can be damaged due to gelation, and these characteristic patterns can be partly recovered during the precipitation and drying of samples. However, the damage to the crystallinity pattern of the starches due to cationization can hardly be recovered. In our investigation, after cationization, the A-type crystallinity pattern of the starches is slightly weakened with a DS of 0.27 in ethanol–water (Fig. 6b). This result suggests that the crystallinity pattern of starch is partly damaged. With an increase in DS, the small peaks disappear and merge into a single, broad, rounded peak that indicates the disappearance of the crystallinity pattern (Fig. 6c and d). This loss in crystallinity can be attributed to the effect of the alkaline environment and water during the modification. This opens up a potential utilization of cationic starches as flocculants, because amorphous granules would enhance their ability to form a colloidal or true solution in cold water. These solubility characteristics are very important from a practical point of view, because in wastewater treatment plants flocculants are often dissolved in cold water.

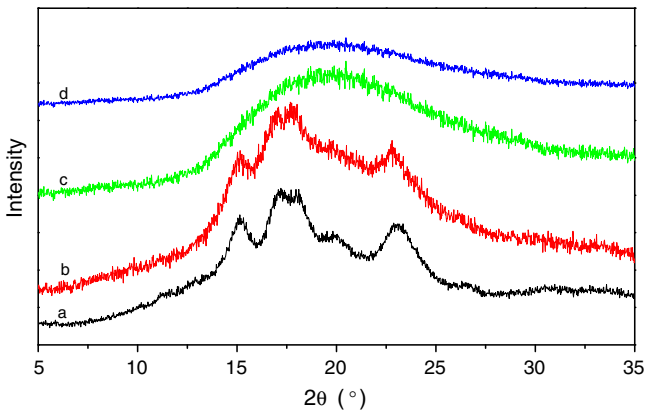

Figure 6. X-ray diffraction patterns of (a) native starch and cationic starch with a DS of (b) 0.27, (c) 0.54, and (d) 0.89.

3. Conclusions

The synthesis and characterization of cationic derivatives of corn starch are presented in this paper. A cationic starch with high DS can be prepared with ETA in a suspension of starch in water or in a mixture of an organic solvent in an aqueous–alkaline solution. Moreover, various reaction parameters and synthesis conditions were investigated, and the results indicate that the procedure using 1,4-dioxane with an alkaline aqueous solution as co-solvent is preferred. The highest DS obtained was about 1.37, in which a reaction temperature of 60 °C and a reaction time of 6 h are employed. From the above-mentioned experiment, it can be concluded that on the backbone of starch a cationic group is incorporated, as confirmed by FTIR and ^{13}C NMR spectroscopy. SEM and X-ray diffraction patterns obviously show that cationization damages the starch granules and the amount of amorphism increases during the process.

4. Experimental

4.1. Materials

Corn starch was obtained from Changchun Dacheng Industrial Group Co., Ltd (China) and was dried at 100 °C under vacuum. 2,3-Epoxypropyltrimethylammonium chloride (ETA) was purchased from Shandong Guofeng Fine Chemical Co., Ltd (China). Sodium hydroxide, ethanol, 1,4-dioxane, and tetrahydrofuran (THF) used in the study were of analytical grade.

4.2. Preparation of cationic starch

4.2.1. Cationization of starch in aqueous–alkaline solutions

Starch (10.0 g) was suspended in 50 mL of various concentrations of aq NaOH solution with agitation at 60 °C for 1 h. Then, the cationization reagent ETA (70 wt % aq solution) was added dropwise. The ratio of ETA to anhydroglucose unit (AGU) was varied from 1 to 4 (mol/mol) in order to obtain starch derivatives with different DS values. After stirring for 4–8 h at a given temperature, the solution was cooled to room temperature, and the pH was adjusted to 7 using 0.1 M HOAc. The product was isolated by precipitation into EtOH and purified by dialysis against water, followed by freeze drying.

4.2.2. Cationization of starch in an organic solvent–NaOH–water mixture

Starch (10.0 g) was suspended in 50 mL of 1:1 (v/v) organic solvent and aq NaOH solution containing 0.5 g NaOH at 60 °C for 1 h. Subsequently, the cationization agent ETA (ETA/AGU = 1–8 mol/mol) was added dropwise to the suspension, and the mixture was stirred for 6 h at 60 °C. Again, the samples were neutralized, precipitated, purified, and freeze-dried as for the aqueous–alkaline procedure in Section 4.2.1.

4.3. Measurements

FTIR analysis was performed using a Bruker Vertex 70 FTIR spectrometer (Germany). The samples were mixed with KBr. FTIR spectra were recorded with a resolution of 4 cm^{-1} and 32 scans and a wave number range of 400–4000 cm^{-1}.

The ^{13}C NMR spectra were acquired by a Bruker AV 400 MHz Fourier-transform spectrometer (Germany). Samples were dissolved in D_2O at 80 °C, and the analysis was carried out at 25 °C.

X-ray diffraction was obtained from a Philips PW1710 based diffractometer, a conventional copper target X-ray tube set to 40 kV and 30 mA. The X-ray source was Cu Kα filtered radiation. Data were collected in the 2θ range of 5.00–35.00° (θ being the angle of diffraction) with a step width of 0.1°.

Surface morphologies of granular characteristics of starch and derivative particles were analyzed using scanning electronic microscopy (SEM) with a JMS-5600 Electron Microscope (JEOL). The freeze-dried starch and derivative powders were used for SEM analysis. SEM images were collected from gold-sputtered substrate surfaces.

The nitrogen elements of cationic starches were estimated by elemental analysis (Vario EL III, Germany). DS was calculated according to the nitrogen content (*N*%) using the following equation:

$$DS = \frac{162N\%}{1400 - 151.5N\%}.$$

4.4. Statistics

All measurements were made in triplicate. Analysis of variance (ANOVA) was performed using the Duncan's multiple range tests to compare treatments means. Significance was defined at $P < 0.05$.

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