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Synthesis of cationic starch with a high degree of substitution in an ionic liquid

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ABSTRACT

Cationic corn starch derivatives containing quaternary ammonium groups with a high degree of substitution were synthesized by reacting corn starch with glycidyltrimethylammonium chloride (GTAC) in a homogeneous manner using 1-butyl-3-methylimidazolium chloride (BMIMCl) as a reaction medium. The influence of reaction time, reaction temperature, the amount of catalyst NaOH and molar ratio of GTAC/anhydroglucose units in starch on the degree of substitution (DS) of products was investigated. The maximum DS value obtained in the optimum reaction condition was up to 0.99. Furthermore, the structure of cationic starch derivatives was characterized by means of Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM), X-ray powder diffraction (XRD), thermal analysis and ^{1}H NMR spectroscopy. The results showed that the ordered crystalline structure of native starch was largely destroyed during the dissolution and functionalization of starch in the ionic liquid BMIMCl, leading to an uniform etherification reaction to be carried out under the homogeneous reaction conditions.

1. Introduction

Starch has attracted much attention for industrial use in recent years because of its relative low price, renewability and biodegradability. However, the utilization of native starch is limited by its physicochemical properties such as water insolubility and its tendency to form unstable pastes and gels. Therefore, starch is usually modified physically or chemically to improve its functionality for industrial applications and thus to extend its usefulness. As one of the chemically modified starches, cationic starches are widely used as additives, for example in the paper, textile, wastewater treatment and related industry. The properties of cationic starch derivatives, such as thermoplasticity and water dissolution, are highly dependent on the preparation method used, the type of cationic groups and the degree of substitution (DS). At present, cationic starches with a high-DS are of increasing interest owing to the promising candidate to replace the synthetic flocculating agents in diverse industrial applications (Bendoraitiene, Klimaviciute, Sableviciene, & Zemaitaitis, 2005; Haack, Heinze, Kulicke, & Oelmeyer, 2002; Krentz et al., 2006).

Conventionally, the high-DS cationic starch can be prepared by the etherifying reaction of starch with the tertiary amino and quaternary ammonium cationizing reagents, such as glycidyltrimethylammonium chloride (GTAC) or 3-chloro-2-hydroxypropyltrimethylammonium chloride (CTAC) in heterogeneous or homogeneous reaction conditions. It was reported that starch was effectively cationized using GTAC or CTAC in an aqueous alcoholic solvent, since the addition of alcohol to the alkaline aqueous media could result in the high-DS cationic starch (Han & Sosulski, 1999; Kweon, Sosulski, & Bhirud, 2006). When starch was modified with CTAC in ethanol/water suspension, the DS value of cationic starch was affected by the substrate ratio and varied between 0.03 and 0.88. Furthermore, the process of the starch modification with GTAC in aqueous sodium hydroxide heterogeneously or in dimethylsulfoxide (DMSO) homogeneously was more effective than in ethanol/water media (Heinze, Haack, & Rensing, 2004). Additionally, Wang and co-workers (Wang et al., 2009) prepared high-DS cationic corn starch in different organic media and obtained the cationic starch with a DS value of 1.37 in dioxane–THF–water media. However, in the aforementioned process a large amount of sodium hydroxide solution or toxic solvent has to be used and serious environmental pollution may be caused.

More recently, room-temperature ionic liquids (ILs), which are considered as desirable green solvents for a wide range of separation and as reaction media, have received significant attention (Welton, 1999). Moreover, the room-temperature ILs having the imidazolium structure have been found to be nonderivatizing solvents for polysaccharides, such as starch (Seoud, Koschella, Fidale, Dorn, & Heinze, 2007). In ILs, namely 1-butyl-3-methylimidazolium chloride (BMIMCl), starch could be dissolved up to 15% (wt/wt) concentration at 80 °C (Stevenson, Biswas, Jane, & Inglett, 2007). By using BMIMCl as a reaction medium, the acetylation of starch could be conducted with a mixture of acetic anhydride and pyridine in a homogeneous manner, yielding the starch acetate with 0.3–2.6 DS (Biswas, Shogren, Stevenson, Willett, & Bhowmik,

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2006). Besides, the synthesis of polymer-grafted starch in BMIMCl was also reported in the literature (Xu, Wang, & Liu, 2008).

In the present investigation, cationic corn starches with a high-DS were prepared homogeneously by the reaction of native corn starch with GTAC in BMIMCl reaction medium. The major factors affecting the cationization reaction, such as the molar ratio of GTAC/anhydroglucose units (AGU) in starch, reaction time, the amount of catalyst NaOH and reaction temperature were investigated. Further, starch derivatives obtained were characterized by Fourier transform infrared (FT-IR) spectroscopy, X-ray diffractrometry (XRD), scanning electron microscopy (SEM), thermal analysis and ^{1}H NMR spectroscopy.

2. Materials and methods

2.1. Materials

Corn starch, which contained 25% amylose and 75% amylopectin, was obtained from Linghua Company (Jining, China) and dried at 80 °C for 24 h before use. The cationic etherifying agent, glycidyltrimethylammonium chloride (GTAC) was synthesized according to the literature (Yang & Guo, 2007). 1-Methylimidazole and 1-chlorobutane were obtained from Aldrich Chemical Company. All other chemicals were of analytical grade and used as received without further purification.

2.2. Preparation of ionic liquid BMIMCl

Ionic liquid BMIMCl was synthesized according to the procedures described elsewhere (Huddleston et al., 2001). Equal molar amounts of chlorobutane and 1-methylimidazole were added into a three-necked flask fitted with a reflux condenser and a mechanical stirrer. The reaction was carried out at 70 °C for 24–72 h under stirring until two phases were formed. The top phase, containing unreacted starting material, was decanted and ethyl acetate (a volume approximately equal to half of that of the bottom phase) was added with thorough mixing. Subsequently, the ethyl acetate was decanted followed by the addition of fresh ethyl acetate and this procedure was repeated twice. After the third decanting of ethyl acetate, any remaining ethyl acetate was removed by heating the bottom phase to 70 °C under reduced pressure. The obtained product, BMIMCl, was a slightly yellow viscous ionic liquid and may be crystalline at room temperature. Mp: 66–67 °C. The ^{1}H NMR (D_2O, ppm) spectrum of BMIMCl shows the following peak locations: δ 0.92 (3H,t), 1.35 (2H,m), 1.78 (2H,quintent), 3.71 (3H,s), 4.08 (2H,t), 7.06 (1H,s), 7.18 (1H,s) and 7.63 (1H,s). The C NMR spectrum (ppm) contains peaks at: δ 15.21, 33.561, 35.73, 38.12, 51.86, 121.34, 127.29 and 143.54. The H/C NMR spectra were consistent with the results reported by Huddleston et al. (2001).

2.3. Synthesis of cationic corn starches

In a three-neck round flask equipped with a magnetic stirrer, dried corn starch was added to the prepared BMIMCl at a concentration of 10% (w/w). The mixture solution was stirred thoroughly at 80 °C until the starch was dissolved completely. To this mixture, the cationization reagent GTAC and the requisite amount of aqueous NaOH solution were added at a certain temperature, respectively. After stirring for the required time, the reaction mixture was cooled to room temperature and then isolated by precipitation in absolute ethanol with stirring. The obtained precipitate was collected and washed thoroughly with ethanol to eliminate BMIMCl, unreacted GTAC and by-products. Finally, the product was dried at 50 °C in vacuum oven for 48 h.

The nitrogen content of cationic starches was determined by the Kjeldahl method using a KDN-08C Kjeldahl instrument (Shanghai Hongji Corporation, China). The samples were analyzed in triplicates and the degree of substitution (DS) was calculated according to the following equation (Kavaliauskaite, Klimaviciute, & Zemaitaitis, 2008).

$$DS = 162N/(1400 - 151.5 \times N)$$

where N is nitrogen content determined by the Kjeldahl method, %, 162 is the molecular weight of AGU, and 151.5 is the molecular weight of GTAC.

2.4. Characterizations of cationic starch

FT-IR spectra of native and cationic starch were recorded on a Shimadzu IR-Prestige-21 spectrometer (Shimadzu Corporation, Japan) using KBr disc technique. For FT-IR measurement, the samples were mixed with anhydrous KBr and were then compressed into thin disk-shaped pellets. The spectra were obtained with a resolution of 4 cm^{-1} between a wave number range of 400 and 4000 cm^{-1}.

X-ray powder diffraction measurements were conducted on a D8 FOCUS X-ray diffractometer (Bruker AXS Corporation, Germany) operating at 35 mA and 40 kV. The X-ray source was Cu $K\alpha$ filtered radiation (λ = 0.15418 nm). The scattering angle (2θ) was varied from 5° to 40° with a step width of 0.02°.

SEM images were obtained with a JSM-6700F scanning electron microscope (JEOL). The samples were mounted on an aluminum stub with a double sticky tape, followed coating with the gold in a vacuum before examination.

The thermal analysis of native starch and cationic starch was carried out using NETZSCH STA409PC thermal analyzer. TG and DTG analyses were performed with a heating rate of 10 °C/min between temperature ranges of room temperature to 600 °C in an atmosphere of flowing dry nitrogen.

^{1}H NMR spectra were acquired on a Bruker AV 300 MHz spectrometer (Bruker Corporation, Switzerland) operating at 500.13 MHz. Samples were dissolved in DMSO-d6 using tetramethylsilane as internal standard. The chemical shifts were expressed in ppm.

3. Results and discussion

3.1. Influence of the reaction parameters

In general, the limited solubility of biopolymers restricts the nature of reagents that could have been used to modify these biopolymers. In this investigation, corn starches were cationically modified using GTAC in BMIMCl. BMIMCl can efficiently dissolve starches and provide feasible reaction environments for the functionalization and therefore a homogeneous etherification reaction could be achieved in this IL. The homogeneous modification of starch relies upon the destructurisation of the semi-crystalline starch granules and the effective dispersion of starch, allowing starch hydroxyl groups more accessible to electrophilic reactants. During the modification of starch in this study, several factors could influence the extent of the starch cationization. These factors include the sodium hydroxide concentration, GTAC/AGU molar ratio, reaction time and reaction temperature. The optimization of cationization process was performed by varying the reaction parameter while other parameters were kept constant.

The influence of various molar ratios of NaOH to starch (AGU) on the DS value is presented in Fig. 1. As observed, without addition of NaOH in the reaction mixture, the product obtained had a DS value of 0.021, and the initial increase in the molar ratio of NaOH/AGU favorably increased the DS value until the DS value

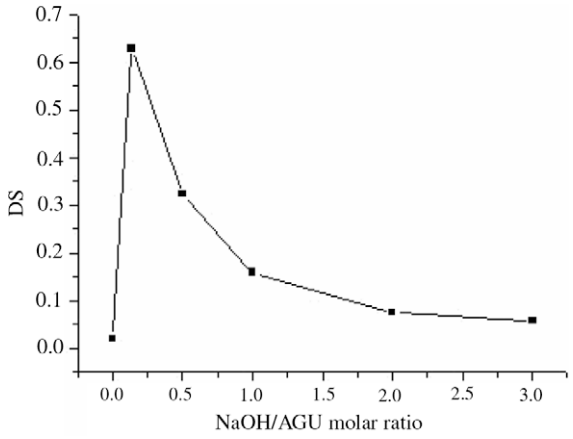

Fig. 1. Effects of NaOH concentration on the cationization reaction. Reaction conditions: AGU/GTAC molar ratio = 1:1, reaction temperature 80 °C, reaction time 2 h.

reached 0.63. However, further increase in the amount of NaOH led to the decreased DS of the product. Generally, the cationization reaction is carried out in the presence of strong base to increase the nucleophilicity of hydroxyl groups in starch. However, at a high NaOH dosage, a side reaction of GTAC with sodium hydroxide could also occur, forming the diol product by the hydrolysis of the epoxide in GTAC, and mostly due to this, the DS value was decreased as the amount of NaOH was further increased beyond 0.135. The similar trend was also observed by Heinze et al. who studied the modification of starch with GTAC and CTAC in homogeneous or heterogeneous process (Heinze et al., 2004). By drawing the results, a certain NaOH loading is necessary for the etherification reaction and the optimal NaOH/AGU molar ratio was 0.135:1.

Fig. 2 shows the effect of GTAC/AGU molar ratio on the DS value of cationic starch. It was observed that at the first stage the DS value of cationic starch increased gradually with an increase in the GTAC/AGU molar ratio, and was up to the highest value of 0.99 when the GTAC/AGU molar ratio was 3:1. However, by increasing the molar ratio of GTAC/AGU beyond 3:1, the DS value of product was feckly invariable. Therefore, in the solvent IL, the effect of the excess amount of GTAC on the cationization reaction was not significant under the given reaction conditions. Given the results, it can be inferred that the optimum GTAC/AGU molar ratio for the reaction was 3:1.

The effect of reaction duration on the cationization reaction was investigated at a reaction temperature of 80 °C, with the molar ratio AGU:GTAC:NaOH of 1:3:0.135. It was shown that the DS value of cationic starch increased sharply from 0.23 to 0.99 when the reaction duration rose from 1 to 2 h. As the reaction time was prolonged from 2 to 8 h, the DS remained an almost constant value of 0.99, representative of near completion of the etherification reaction, which could be due to the depleted GTAC after 2 h as the reaction progressed. Therefore, we can conclude that 2 h was the most appropriate reaction time for the synthesis of cationic starch in the IL solvent.

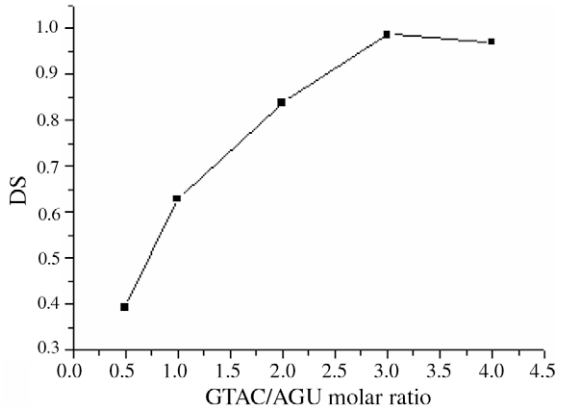

Fig. 2. Effects of GTAC/AGU molar ratio on the cationization reaction. Reaction conditions: AGU/NaOH molar ratio = 1:0.135, reaction temperature 80 °C, reaction time 2 h.

Native corn starch was modified by reaction mixtures with a constant molar ratio AGU:GTAC:NaOH of 1:3:0.135, at different temperatures from 70 to 110 °C for 2 h. It was indicated that the reaction temperature had an important influence on the DS value of cationic starch. With an increase in reaction temperature from 70 to 80 °C, the DS value was observed to increase rapidly from 0.19 to 0.99. However, an increasing temperature from 80 to 110 °C caused the decrease of the DS value to 0.56. This phenomenon could be probably attributed to the side reaction, such as the deetherification reaction and the decomposition of GTAC, which preferentially occurred at high temperature and long reaction duration (Zhang, Ju, Zhang, Ma, & Yang, 2007). Thus, the reaction temperature of 80 °C was optimal for the etherification reaction.

Obviously, the DS value of the cationic starch derivatives can be controlled in range from 0.05 to 0.99 by adjusting the cationization reaction conditions employed. The DS value of 0.99 as an upper limit was achieved even though the GTAC/AGU molar ratio of 3:1 for the reaction was used. It is thus evident that a smaller proportion of GTAC reacts with the corn starch to produce the cationic starch in the reaction. A similar result was also reported in the literature (Haack et al., 2002; Heinze et al., 2004). Starch cationization consists of substituting the hydroxyl groups of the glycosyl units by one of the cationic groups. If all three hydroxyls on each of the anhydroglucose units were cationized, the DS value is maximum and is equal to 3. However, the lower reactivity of two secondary alcoholic OH groups on the anhydroglucose unit and some side reactions could lower the cationization reaction efficiency, and therefore in the present work an upper limit for DS value was 0.99.

To determine the reusability of IL, a recycling experiment was conducted under comparable reaction conditions. In this work, at the end of the etherification reaction, the cationic starch was precipitated with absolute ethanol, and subsequently, the residual filtrate including BMIMCl and ethanol was neutralized to pH 7 using 0.1 M HCl. Afterwards, the filtrate was filtered again and then distilled under reduced pressure to eliminate water and ethanol. Then the recovered IL was used in the next cationization reaction under the same reaction conditions. The recycle experiment was conducted at 80 °C for 2 h with the molar ratio AGU:GTAC:NaOH of 1:3:0.135. When the recycle number was 1, 2, 3, 4 and 5, the obtained cationic starch had a DS value of 0.98, 0.93, 0.86, 0.82 and 0.67, respectively. During the cationization reaction, some by-products resulted from undesired side reactions of GTAC, such as *N*-(2,3-dihydroxy)propyl-*N*,*N*,*N*-trimethylammonium chloride and dimer of GTAC, may be formed in the reaction mixture, depending on the reaction conditions (Kavaliauskaite et al., 2008). These impurities could be dissolved in ILs and could not be removed completely even if the IL mixture was filtered and distilled, and had an influence on the character of IL. As a result, the DS value decreased gradually as the increase in recycle times of the IL. However, the cationic starch still had a correspondingly high-DS value even after the IL had been recycled for four times, suggesting that the IL can be recycled and reused.

3.2. Cationic starch characterizations

The FT-IR spectra of native corn starch, GTAC and cationic corn starch are depicted in Fig. 3. In the IR spectrum of native corn

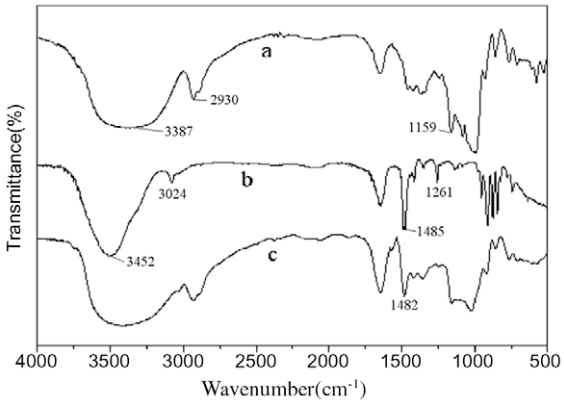

Fig. 3. FT-IR spectra of native corn starch (a), GTAC (b) and cationic starch (c).

starch (Fig. 3a), the extremely broad band at 3387 cm^{-1} and the band at 2930 cm^{-1} were attributed to the O–H stretching and the C–H stretching vibrations, respectively. Meanwhile, the bands at 1159, 1084 and 993 cm^{-1} were characteristic of the C–O stretching vibrations of AGU (Pal, Mal, & Singh, 2005). In the case of GTAC (Fig. 3b), the broad band at 3452 cm^{-1} was assigned to the O–H stretching vibration of water that remained after drying. A strong band at 1485 cm^{-1} recorded in the IR spectrum of GTAC was associated with the C–N stretching vibration. Besides, the bands at 3024 and 1261 cm^{-1} were originated from the C–H and the epoxy ether vibrations, respectively.

Fig. 3c showed the FT-IR spectrum of cationic corn starch. It was shown that the IR profile of cationic starch was similar to that of native starch. Besides the characteristic peaks of starch backbone, an additional band appeared at 1482 cm^{-1} assignable to the C–N stretching vibration. This band was not present in unmodified starch and thus was an evidence for the incorporation of a cationic moiety onto the backbone of starch. Moreover, the absence of the band of epoxy ether at 1261 cm^{-1} further confirmed the cationization reaction of starch with GTAC.

The introduction of cationic groups into native starch can also be evidenced by NMR spectroscopy. The ^1H NMR spectra of native starch and cationic starch were measured in DMSO-d6. In the ^1H NMR spectrum of native starch (Fig. 4a), the signals at 3.3 and 2.5 ppm were assigned to hydrogen atom of the solvent DMSO. As expected, the peaks recorded between 4.5 and 5.5 ppm were ascribed to the hydrogen atoms of starch backbone, and the peak at 3.6 ppm was attributed to O–H group (Heinze et al., 2004). Compared to native starch, the cationic corn starch exhibited an additional peak at nearby 3.1 ppm (Fig. 4b), which was ascribed to the CH_3–N^+ group substituted cationic group. The existence of this signal resulting from the hydrogen atom of the substituent indicated a cationic group was introduced into the backbone of starch and the etherification reaction occurred.

The X-ray powder diffraction patterns of native starch and cationic starch are displayed in Fig. 5. From this figure, it was obvious that native corn starch (Fig. 5a) exhibited a typical A-type X-ray diffraction pattern (Kuo & Lai, 2007). In the XRD pattern of native corn starch, the strong reflections (2θ) were found at about 15° and 23°, and an unresolved doublet was at nearby 17° and 18° (Puchongkavarin, Bergthaller, Shobsngob, & Varavinit, 2003). However, the cationic starch only had a dispersive broad peak and showed no crystal peak of starch (Fig. 5b), which implies that the crystallinity of native starch was damaged completely during the starch modification. This loss in crystallinity could be attributed to the effect of IL during the dissolution processes. The SEM photographs also showed the same result.

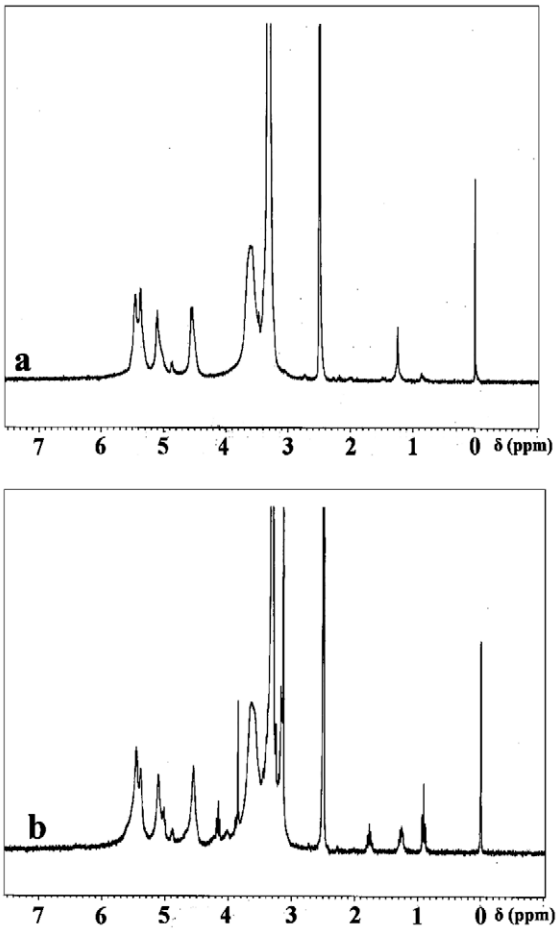

Fig. 4. ^1H NMR spectra of (a) native starch and (b) cationic starch.

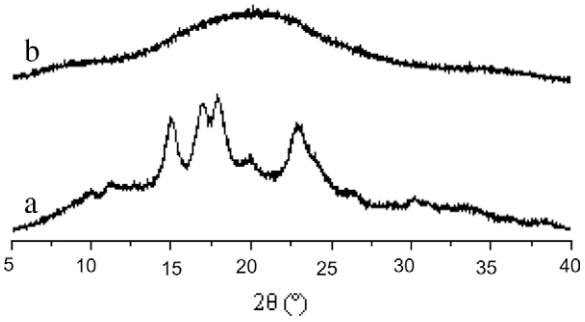

Fig. 5. X-ray powder diffraction patterns of (a) native corn starch and (b) cationic starch.

SEM images of native starch and cationic starch are shown in Fig. 6. The native corn starch (Figs. 6a and b) was composed of granules with round and polygonal shapes and various sizes, whereas the morphology of cationic starch (Figs. 6c and d) was changed markedly during the cationization process. As shown in Figs. 6c and d, the surface of cationic starch granules completely disintegrated and their well-defined edges drastically lost. It could be concluded that during the cationization process the IL disrupted the intermolecular and intramolecular hydrogen bonds and sequentially destroyed the crystalline structure of starch granules, owing to the strong hydrogen-bond contacts between the IL and starch.

The thermal properties of native starch and cationic starch were characterized by TGA and DTG measurements in an N_2 atmo-

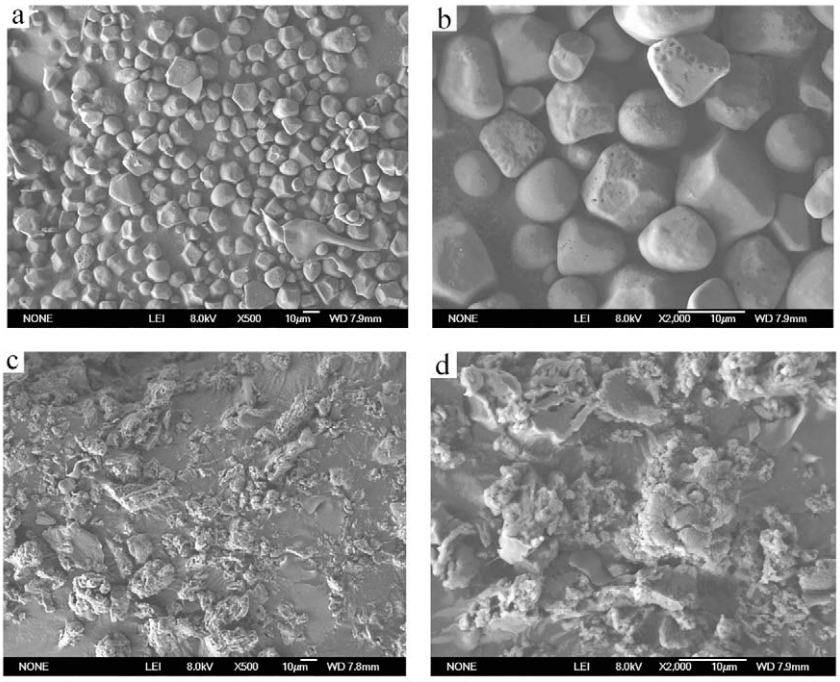

Fig. 6. SEM images of starch granules: (a) native starch × 500; (b) native starch × 2000; (c) cationic starch × 500; (d) cationic starch × 2000.

sphere. The TGA and DTG thermograms of native and cationic starch are shown in Figs. 7 and 8, respectively. As can be seen from the TGA curve (Fig. 7), for the two samples, there was little mass loss until a temperature of 240 °C was reached. On further increase in the temperature there was a sharp mass loss at 305 °C for the native starch and at 275 °C for the cationic starch, respectively, which were resulted from the decomposition of samples. From the DTG plot (Fig. 8), it can be observed that the thermal degradation of native starch was commenced at 270 °C following a significant mass loss with an increase in the temperature to 333 °C. However, the cationic starch was decomposed thermally at a temperature of 247 °C and the rate of mass loss was rapid between 247 and 307 °C, which were lower in comparison to the native starch. Clearly, the cationically modified starches undergo thermal degradation at a lower temperature than in the case of native starch. Besides, since the thermal degradation happens in an N_2 atmosphere, the depolymerization of native starch and cationic starch terminates with the production of carbon. This indicates that the thermal stability of cationic starch is decreased due to the cationization of starch. This result was similar to those described

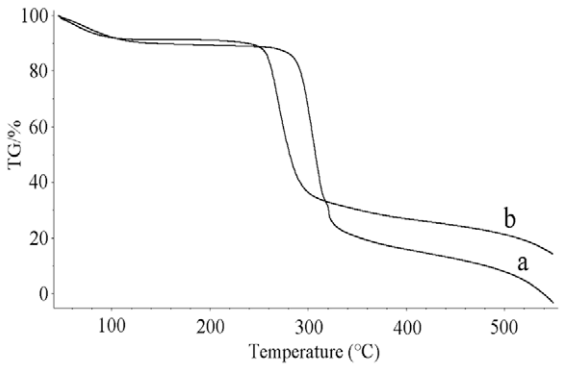

Fig. 7. TGA curves of (a) native starch and (b) cationic starch.

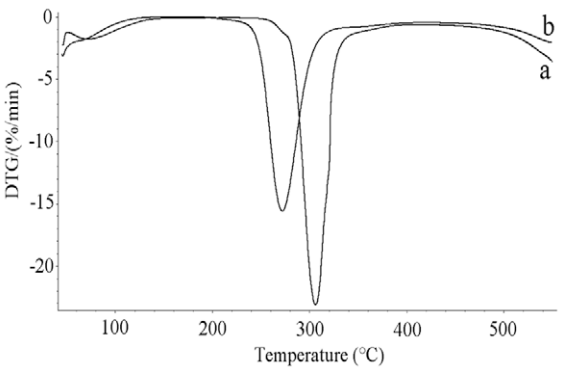

Fig. 8. DTG curves of (a) native starch and (b) cationic starch.

by Aggarwal and Dollimore who studied the effect of chemical modification on starch by using thermal analysis method (Aggarwal & Dollimore, 1998).

The modification of starch is usually carried out in a heterogeneous manner owing to the lack of solubility of native starch in most common organic solvents. The heterogeneous modification, in which starches are kept in granular state, is prone to result in lower DS value than a homogeneous one. As observed in the SEM and XRD profiles, the starch granules, in this study, were mostly converted from their crystalline structure into amorphous shape during the dissolution processes, indicating that an uniform etherification reaction was carried out in a homogeneous manner by ensuring the hydroxyl groups of starch more accessible to the reactant. The loss of ordered crystalline structure in native starch under the homogeneous conditions was required for the efficient modification and the uniform etherification of starch. Therefore, by using BMIMCl as dissolving media, a high cationization degree of starch was achieved in an environmentally benign process.

Based on the above results, BMIMCl is a promising alternative reaction medium for the preparation of cationic starch with a

high-DS and this treatment method seems to be simple and efficient. However, the cost of ionic liquid is the main drawback for its application in a larger scale. Besides, we are inclined to think that the performance of the reusability of the retrieved BMIMCl could be further improved when the reaction is carried out for the industrial use.

4. Conclusions

In this work, cationic starches were prepared homogeneously from the reaction of native corn starch with GTAC in an ionic liquid BMIMCl. The highest DS value of cationic starch obtained was about 0.99, in which a reaction temperature of 80 °C, a molar ratio of AGU:GTAC:NaOH of 1:3:0.135 and a reaction time of 2 h were employed. The DS value of cationic starch can be adjusted by varying the reaction conditions. Further, a cationic group had been incorporated on the backbone of starch, as evidenced by FT-IR and ^{1}H NMR spectroscopy. SEM and XRD results obviously showed that the ordered crystalline structure of native starch was damaged after starch modification and there are no crystals of native starch in the thus prepared cationic starch. It is shown that cationic starches undergo thermal degradation at lower temperature compared to the native starch.

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