



# Homogenous carboxymethylation of starch using 1-butyl-3-methylimidazolium chloride ionic liquid medium as a solvent

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## ABSTRACT

An ionic liquid, namely 1-butyl-3-methylimidazolium chloride (BMIMCl), was employed as a reaction medium for homogenous carboxymethylation of corn starch. The process variables affecting the carboxymethylation reaction such as amount of sodium hydroxide (NaOH) and sodium monochloroacetate (SMCA), reaction time and reaction temperature were investigated regarding the degree of substitution (DS) for the carboxymethyl starch. The highest DS of 0.76 was obtained at molar ratios of NaOH and SMCA to anhydroglucose unit (AGU) of 1.2 and 1.0, respectively, and at 90 °C for 3 h of reaction. Results from FT-IR and <sup>13</sup>C NMR spectra indicated that the hydroxyl groups of starches were substituted by carboxymethyl groups. SEM and XRD studies showed that the morphology and crystallinity of starch was disrupted after the carboxymethylation reaction.

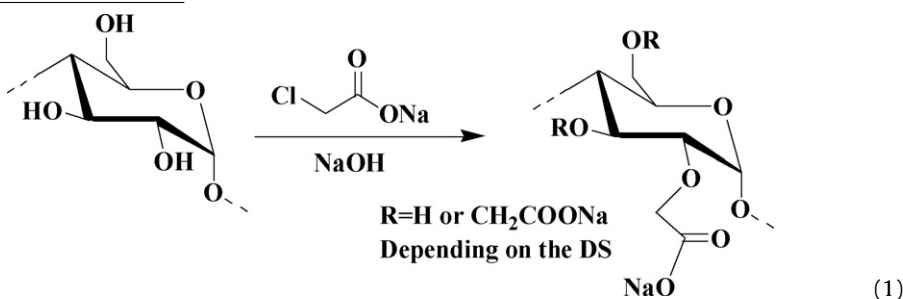
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## 1. Introduction

Starch is one of the most abundant naturally occurring biopolymers and is in the form of granules that exist in the plant cells. Because starch is cheaper than most other biomaterial resources, it has diverse applications in food, pharmaceuticals, textile, paper, plastics as well as in biomedical engineering industries. Unfortunately, the utilization of starch in its native form is often limited by some undesirable characteristics such as poor solubility, low mechanical properties, and instability at high temperature and pH during processing. The chemical modification of starch can overcome these shortcomings by derivatization reactions such as esterification and etherification, to improve significantly the functional properties of starch. In general, starch modification

involves the reaction of the hydroxyl groups on the anhydroglucose unit (AGU) with the formation of starch derivatives. Among the starch derivatives, carboxymethyl starches have attracted considerable attention chiefly owing to their industrial applications in many fields, for example, a sizing and printing agent in the textile industry and as an excipient in the pharmaceutical industry (Lawal, Lechner, Hartmann, & Kulicke, 2007).

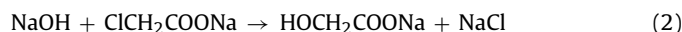
Carboxymethyl starch (CMS) is usually obtained by the reaction of starch with monochloroacetic acid or its sodium salt in the presence of an alkali. A schematic representation of the reaction of starch with sodium monochloroacetate (SMCA) is provided in Eq. (1). Apparently, the extent of variation in the physico-chemical properties of the starch derivative after modification is associated with the degree of substitution of the starch.



Although the reaction is usually carried out in the presence of strong bases to increase the nucleophilicity of the hydroxyl group, an undesired side reaction could also occur with sodium hydroxide, producing sodium glycolate as a by-product from SMCA according

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to Eq. (2).



In the previous literature, many kinds of starch, such as corn starch (Bhattacharyya, Singhal, & Kulkarni, 1995), potato starch (Tijssen, Kolk, Stamhuis, & Beenackers, 2001), cocoyam starch (Lawal et al., 2007), water yam starch (Lawal, Lechner, & Kulicke, 2008a), cassava starch (Sangseethong, Ketsilp, & Sriroth, 2005), have been used as materials for the carboxymethylation reaction of starches. Several solvent systems such as water (Hebeish, Khalil, & Hashem, 1990; Ragheb, ElSaiyad, & Hebeish, 1997), water-miscible organic solvent (Bhattacharyya et al., 1995; Tijssen et al., 2001; Tijssen, Scherpenkate, Stamhuis, & Beenackers, 1999) and dimethyl sulphoxide (Heinze, Heinze, Grote, Kötze, & Lazik, 2001; Heinze, Liebert, Heinze, & Schwikal, 2004; Heinze, Pfeiffer, Liebert, & Heinze, 1999) are applied for the synthesis of carboxymethyl starch. A major drawback of the synthetic methodology for carboxymethyl starch is the use of organic solvents, which have a negative environmental impact and may limit further application in industry.

The properties of modified starch are varied significantly after modification depending largely on the nature of the substituent groups and the DS value. The reactions on starches for preparation of the derivatives with a high DS value are not easy, mainly owing to the lack of solubility of starch in most common organic solvents. Nevertheless, the homogeneous modifications of starch, in particular in green solvents, have received much attention because the reactions proceed efficiently and uniformly in a homogeneous manner.

Ionic liquids (ILs) which are considered as desirable green solvents, have been used to replace the traditional organic solvents due to their advantages such as width of liquid range, excellent dissolution ability, freedom from the effect of vapor pressure, and ease of recycling (Sheldon, 2001; Welton, 1999). Recently, ILs have found a wide application in the dissolution of carbohydrates such as cellulose (Swatloski, Spear, Holbrey, & Rogers, 2002; Wu et al., 2004) and starch (Biswas, Shogren, Stevenson, Willett, & Bhowmik, 2006). Studies showed that starch could be solubilized by 1-butyl-3-methylimidazolium chloride (BMIMCl) (Stevenson, Biswas, Jane, & Inglett, 2007) or 1-butyl-3-methylimidazolium dicyanamide (BMIMdca) (Biswas et al., 2006), and could react with acetic anhydride in BMIMdca/pyridine to yield starch acetates. Very recently, Wang and Xie (2010) reported the synthesis of cationic starch with a high DS in BMIMCl. Besides, the acetyl distribution of starch acetates prepared in ionic liquid solvents was studied by Shogren and Biswas (2010). In addition, starch esters prepared from high-amylose starch using ionic liquids as catalysts were also reported (Lehmann & Volkert, 2011). To the best of our knowledge, the carboxymethylation of starch in ionic liquids has not been reported.

In the present investigation, carboxymethyl starches with different degrees of substitution were synthesized under homogeneous reaction conditions using 1-butyl-3-methylimidazolium chloride (BMIMCl) as a reaction medium. The influences of NaOH amount, reactant ratio, reaction time, and reaction temperature on the DS of products were investigated with the aim to find the optimum process conditions. Furthermore, starch derivatives were characterized by FT-IR,  $^{13}\text{C}$  NMR, XRD, SEM and TG-DTG techniques.

## 2. Materials and methods

### 2.1. Materials

Corn starch used in the study, which contained 25% amylose and 75% amylopectin, was obtained from Linghua Company

(Jining, China) and dried at 80 °C for 24 h before use. 1-Butyl-3-methylimidazolium chloride (BMIMCl) was purchased in crystallized form from Centre for Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics, China. All other chemicals were of analytical grade and used as received without further purification.

### 2.2. Carboxymethylation of starch

In a 100 mL three-necked flask fitted with a condenser and a magnetic stirrer, the dried starch was added to the 1-butyl-3-methylimidazolium chloride at a concentration of 10% (w/w) at a temperature of 90 °C. To this mixture sodium hydroxide and sodium monochloroacetate were added under stirring, resulting in a homogeneous transparent solution. Subsequently, the carboxymethylation reaction was allowed to proceed at a set temperature of 90 °C for 3 h. Once the reaction had finished, the formed carboxymethyl starches were precipitated by addition of absolute ethanol. The solid was filtered, washed thoroughly with ethanol and then dried under vacuum at 50 °C for 24 h. The influences of process variables on the carboxymethylation reaction were studied by varying one of the parameters while the others were kept constant.

### 2.3. Determination of DS

The DS is an indication of the amount of carboxymethyl group formed on the starch molecule. Technically, the DS of a starch derivative is defined as the average number of hydroxyl groups substituted per D-glucopyranosyl unit of the starch polymer.

The DS value of a modified starch was routinely determined according to the acid–base back titration method described in literatures (Stojanović, Jeremić, Jovanović, & Lechner, 2005). A weighed sample of Na–CMS was first treated in acetone with 5 mol dm<sup>−3</sup> HCl to obtain the acid form of CMS (H–CMS). The dispersion was then neutralized by washing with 80% (v/v) methanol–water mixture for several times, followed by washing with acetone and filtration. The filtrate was dried in an oven at 105 °C for about 5 h. A known weight of the acid from sample (approximately 0.5 g) was dissolved in 20 mL of 0.2 mol dm<sup>−3</sup> NaOH solution and 50 mL of bidistilled water was also added. The excess alkali was then back-titrated with standard 0.05 mol dm<sup>−3</sup> HCl solution using phenolphthalein as an indicator. Each sample was measured in triplicate, and the average value of the HCl volume was used for the calculations. A blank titration was also carried out in parallel. The DS value was calculated by Eq. (3):

$$\text{DS} = \frac{162 \times n_{\text{COOH}}}{m_{\text{ds}} - 58 \times n_{\text{COOH}}} \quad (3)$$

where 162 g/mol is the molar mass of an AGU, 58 g/mol is the net increase in the mass of an AGU for each carboxymethyl substituted,  $m_{\text{ds}}$  (in g) is the mass of dry CMS sample,  $n_{\text{COOH}}$  (in mol) is the amount of COOH calculated from the obtained value of the equivalent volume of known molarity HCl according to Eq. (4).

$$n_{\text{COOH}} = (V_{\text{b}} - V)C_{\text{HCl}} \times 4 \quad (4)$$

where  $V_{\text{b}}$  and  $V$  are the volume of HCl (in mL) consumed for titration of blank and the sample, respectively.  $C_{\text{HCl}}$  (in mol dm<sup>−3</sup>) is the concentration of hydrochloric acid and the number 4 is the ratio of the total volume of the solution (100 mL) to the volume taken for titration (25 mL).

### 2.4. Characterizations of carboxymethyl starch

FT-IR spectra of native and carboxymethyl starch were recorded on a Shimadzu IR-Prestige-21 spectrometer (Shimadzu

**Table 1**

Reaction conditions and results of the reaction of starch with SMCA and SMCA in the BMIMCl ionic liquid.

NaOH/AGU (molar ratio)	SMCA/AGU (molar ratio)	Reaction time (h)	Reaction temperature (°C)	DS value
0.4	1.0	2	80	0.31
0.8	1.0	2	80	0.60
1.2	1.0	2	80	0.71
1.6	1.0	2	80	0.64
2.0	1.0	2	80	0.47
1.2	0.4	2	80	0.38
1.2	0.7	2	80	0.53
1.2	1.0	2	80	0.71
1.2	1.3	2	80	0.74
1.2	1.6	2	80	0.76
1.2	1.0	1	80	0.62
1.2	1.0	2	80	0.71
1.2	1.0	3	80	0.73
1.2	1.0	4	80	0.75
1.2	1.0	5	80	0.76
1.2	1.0	3	70	0.66
1.2	1.0	3	80	0.73
1.2	1.0	3	90	0.76
1.2	1.0	3	100	0.68
1.2	1.0	3	110	0.54

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  $4\text{ cm}^{-1}$  between a wave number range of 400 and  $4000\text{ cm}^{-1}$ .

$^{13}\text{C}$  NMR spectra were obtained on an Avance 400 MHz spectrometer (Bruker Corporation, American) in  $\text{D}_2\text{O}$  with TMS (3-(trimethylsilyl)propionic-2,2,3,3- $d_4$  acid, sodium salt) as internal standard. Prior to the measurements, the samples were degraded by ultrasonic degradation (Lawal, Lechner, & Kulicke, 2008b) with a sonifier W-250 ultrasonic degradation device. The chemical shifts are given in ppm.

The X-ray diffraction patterns were recorded with D8 FOCUS X-ray diffractometer (Bruker AXS Corporation, Germany) operating at 35 mA and 40 kV. The X-ray source was Cu  $\text{K}\alpha$  filtered radiation ( $\lambda$  0.154 nm). The diffractograms were registered at Bragg angles ( $2\theta$ ) of  $5\text{--}60^\circ$  with a step width of  $0.02^\circ$ .

SEM images were examined 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.

TG and DTG measurements were conducted with NETZSCH STA449C Thermal Analyzer Instrument. The measurement was recorded in an atmosphere of flowing dry nitrogen. The sample was heated from room temperature to  $600^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$ .

### 3. Results and discussion

#### 3.1. Influence of process variables

Starch is composed of linear amylose and branched amylopectin. The branched amylopectin is responsible for the crystalline region, while the amylose is associated with the amorphous region. Owing to the crystalline structure of starch, the reagents cannot readily penetrate into the granules. The heterogeneous modification, in which starches are usually kept in granular state, is prone to result in lower DS value than a homogeneous one. As the corn starch, NaOH, SMAC and CMS were soluble in the BMIMCl, the carboxymethylation reaction solution remained clear throughout the reaction and thus a homogeneous modification could be achieved in this IL. In this investigation, BMIMCl acted as a reaction medium, relying on the deconstructurisation of the

crystalline granules of starch. As a result, the uniform substitution of carboxymethylation reaction could be carried out by ensuring the hydroxyl group of starch are more accessible to the reagents. The extent of starch modification can be affected by several reaction parameters, such as NaOH amount, SMCA/AGU ratio, reaction time and reaction temperature. For the optimization of the carboxymethylation process, different experiments were performed by varying the reaction parameters.

Table 1 summarizes the reaction conditions and the results of the carboxymethylation reaction of starch with SMCA and NaOH in the BMIMCl ionic liquid. As a catalyst, sodium hydroxide was considered capable of enhancing the SMAC reaction with the hydroxyl groups of starch. As can be seen from Table 1, the DS was increased as the molar ratio of NaOH to AGU increased from 0.4 to 1.2. This can be explained due to the more reactive starch alkoxide formed when the NaOH amount increased, leading to the higher reaction probability of starch with SMAC. However, a further increase in the NaOH amount from 1.2 to 2 resulted in a reduction in the DS values. It is reasonable that higher amount of NaOH enhances the reaction of sodium hydroxide with sodium monochloroacetate to form sodium glycolate (Eq. (2)), thus causing the decreased DS values. This observation is consistent with previous reports on carboxymethyl corn and amaranth starch (Bhattacharyya et al., 1995). Therefore, the optimum molar ratio of NaOH to AGU for the carboxymethylation reaction was approximately 1.2.

The influence of molar ratio of SMCA to AGU on the DS value is shown in Table 1, in which different amounts of SMCA were used. When the molar ratio of SMCA to AGU increased from 0.4 to 1.0, noticeable increase in the DS value of CMS was observed. However, with further increase in the molar ratio of SMCA to AGU from 1.0 to 1.6, a slight increase in the DS value is observed in Table 1. The increase in DS values as the amount of SMCA increased, could be reasonably attributed to increased contact between the starch molecules and the etherifying agent. Similar observation was reported on carboxymethylation of cocoyam starch (Lawal et al., 2007) and kudzu root starch (Wang, Pan, Hu, Miao, & Xu, 2010). Therefore, the molar ratio of SMCA to AGU of 1.0 was considered as the most appropriate for preparation of carboxymethyl starch under the reaction conditions.

The effect of reaction duration on the carboxymethylation reaction was investigated at a reaction temperature of  $90^\circ\text{C}$  for different reaction time from 1 to 5 h, with the NaOH/AGU molar ratio of 1.2 and SMCA/AGU molar ratio of 1.0. Results displayed in Table 1 showed that the DS value was increased from 0.62 to 0.73 as the

reaction time rose from 1 to 3 h. The increase in the DS value with reaction duration was probably owing to the enhanced contact period of starch molecules with the reagents. However, no remarkable further increment was observed in DS values after 3 h of reaction, representative of near completion of the reaction. From the results, the maximum DS value is achieved after 3 h of reaction time.

The DS value as a function of reaction temperature is also illustrated in Table 1. As observed from Table 1, there was an increase in the DS with increasing the reaction temperature from 70 to 90 °C. This increase may be due to the fact that higher temperature increases the solubility and diffusion of the etherifying reagents. When the reaction temperature increased from 90 to 110 °C, the decrease of the DS value was observed. This phenomenon could be probably attributed to the side reaction, which preferentially occurred at high temperature and long reaction duration. Based on the results, we concluded that the reaction temperature of 90 °C was appropriate for the carboxymethylation reaction.

The recyclability of the BMIMCl was investigated by recovering and reusing the IL. The same reaction conditions were applied for these experiments. Prior to reuse of the IL, it was recovered by separating the product and distilling under reduced pressure to remove volatile compounds. The recycle test was conducted in five consecutive runs at 90 °C for 3 h. When the recycle number was 1, 2, 3, 4 and 5, the obtained product had a DS value of 0.75, 0.74, 0.71, 0.69 and 0.66, respectively. Clearly, the DS value was decreased gradually as the increase in recycle times of the IL. It seems likely that some by-products and salt existing in the recycled IL influenced the character of the IL. However, the products still had a correspondingly high DS value even after the IL had been recycled for five times, showing that the IL can be recycled and reused without significant drop in DS values.

### 3.2. Carboxymethyl starch characterizations

The FT-IR spectrum of the carboxymethyl starch is presented in Fig. 1. For comparison, a spectrum of native corn starch is also included. In the IR spectrum of native corn starch, the extremely broad band at 3390 cm<sup>-1</sup> and the band at 2927 cm<sup>-1</sup> were attributed to the O–H stretching and the C–H stretching vibrations, respectively. Besides, the bands at 1189, 1075 and 990 cm<sup>-1</sup> were characteristic of the C–O stretching vibrations of AGU. The absorption band at 1641 cm<sup>-1</sup> was principally ascribed to bound

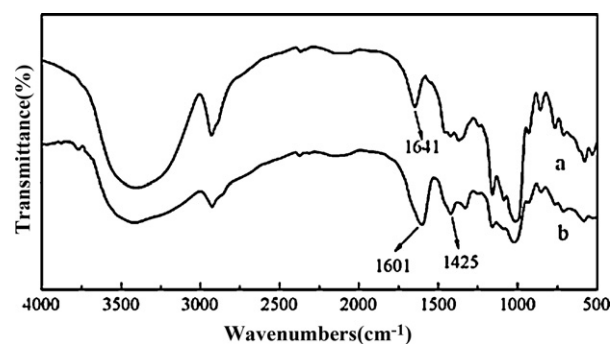


Fig. 1. Infrared spectra of native starch (a) and carboxymethylated starch (b).

water present in the starch. In the IR spectrum of the carboxymethyl starch, besides the characteristic peaks of starch backbone, additional absorption bands appeared at 1601 and 1425 cm<sup>-1</sup>, which were assigned to the carboxymethyl moieties (Bhattacharyya et al., 1995). These new absorption bands were not present in unmodified starch and thus could be considered as the convincing evidence for the starch carboxymethylation.

The typical <sup>13</sup>C NMR spectrum and peak assignments of carboxymethyl corn starch are shown in Fig. 2. The poorly resolved NMR spectrum was probably due to the overlap of signals from slightly different chemical environments and also due to the viscosity of the samples. The peak at 177.90 ppm was ascribed to the carbonyl carbon (C-8) of the carboxymethyl group. Besides, there are two resolved peaks at 99.67 and 96.39 ppm, which were assigned to the anomeric carbon (C-1). Two peaks appeared here because of two different environments of C-1, relying upon whether the carboxymethylation reactions occurred at the neighboring C-2 or not and causing a split of the peak at C-1. As shown in Fig. 2, a similar phenomenon also occurred on C-2, C-3 and C-6. The NMR signals of substituted and unsubstituted C-2, C-3 and C-6 were observed at different positions. Additionally, the peak of 79.94 ppm was believed to correspond to C-4, while the signal at 73.38 ppm was assigned to C-5. Furthermore, the three peaks at 70.78, 70.26, 70.02 ppm could be attributed to methylene carbon atoms of the carboxymethyl group (C-7), owing to the carboxymethyl reactions occurred in three different positions (C-2, C-3 or C-6) (Lawal et al., 2008b). Thus, the <sup>13</sup>C NMR results confirmed the presence of carboxymethyl groups in the products.

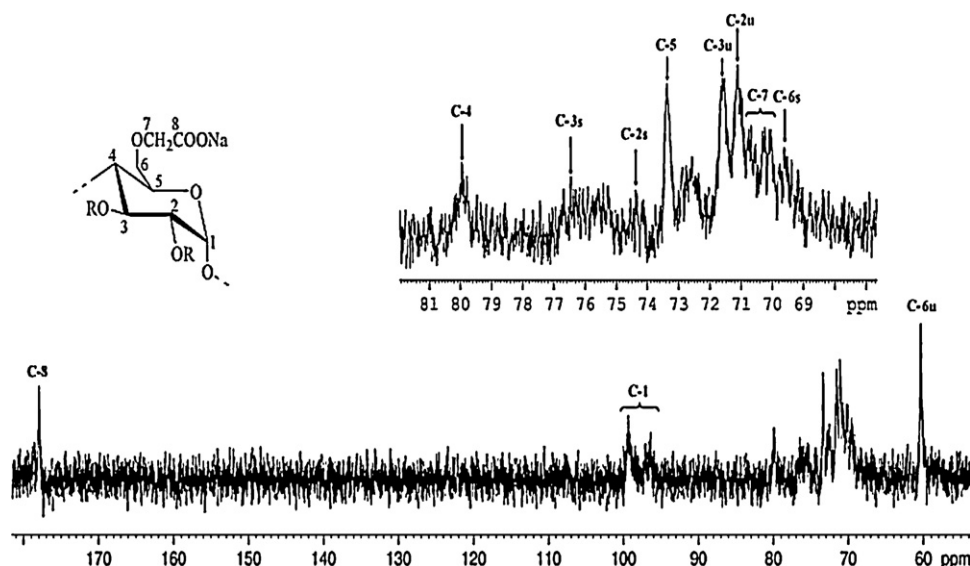


Fig. 2. <sup>13</sup>C NMR spectra and peak assignments of carboxymethylated starch. S = carbon with carboxymethyl substituent; U = carbon without carboxymethyl substituent.



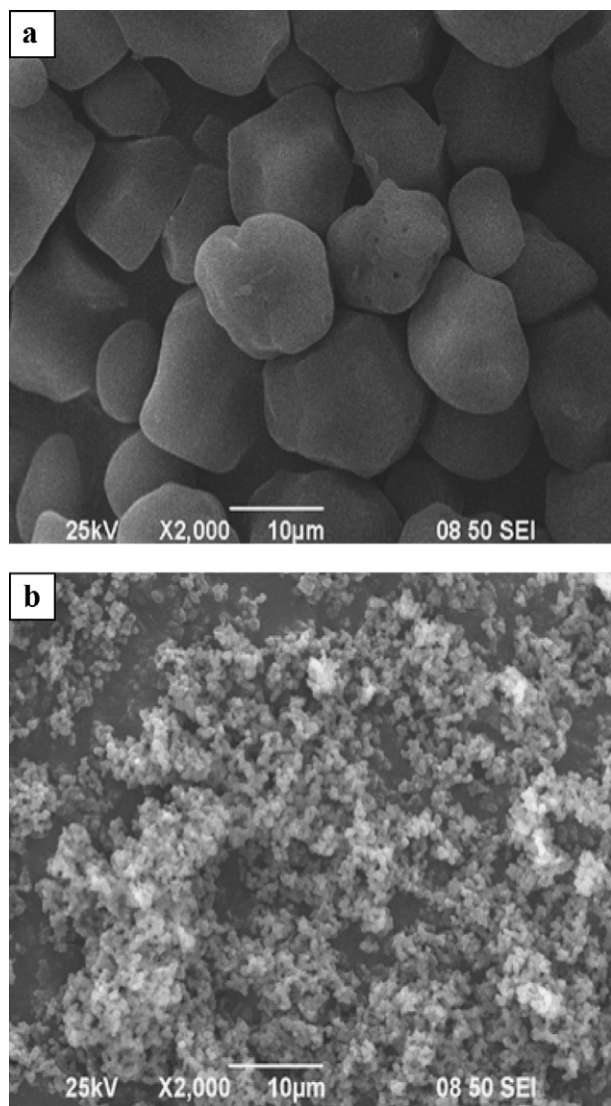


Fig. 3. Scanning electron micrographs of native corn starch (a) and carboxymethylated starch (b).

Scanning electron microscopy was used to investigate the granule morphology of the native starch as well as the CMS. As shown in Fig. 3a, granules of corn starch were round and polygonal in shape with various sizes. However, pictures of the carboxymethylated products showed remarkable difference in appearance compared to native starch, and the granular structure was lost after starch carboxymethylation (Fig. 3b). Apparently, the reaction medium of IL was responsible for the clear change in the granular structure of CMS. It seems mostly reasonable that during the carboxymethylation 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. Such results were also reported in the previous literature (Biswas et al., 2006; Wang & Xie, 2010).

The X-ray powder diffraction patterns obtained for native starch and a representative carboxymethylated derivative are presented in Fig. 4. The diffractogram of native corn starch exhibited a typical A-type crystallinity pattern, giving two peaks at  $2\theta$  of  $15^\circ$  and  $23^\circ$ , and an doublet at  $2\theta$  of  $17^\circ$  and  $18^\circ$  (Kuo & Lai, 2007). After carboxymethylation, the product showed no crystalline pattern, indicating its amorphous character. Clearly, the loss of crystallinity could be attributed to the effect of IL during the dissolution pro-

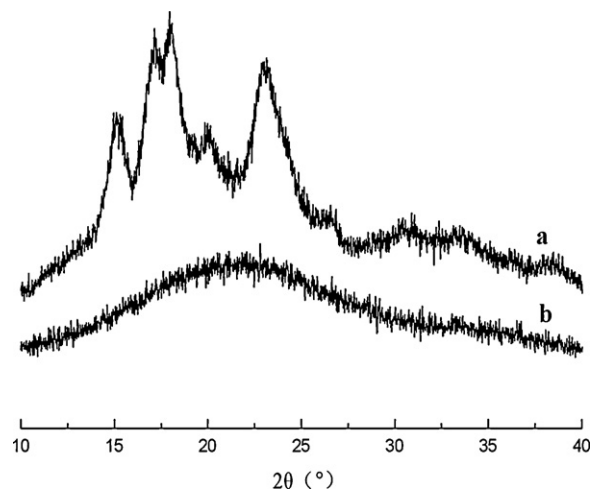


Fig. 4. X-ray diffraction patterns of native starch (a) and carboxymethylated starch (b).

cesses and thus allowing the reagents to have more access to the starch molecules for the carboxymethylation processes. This observation was in good agreement with the SEM results.

The thermal stability of the carboxymethylated starch has been investigated using DTG and TGA techniques. As illustrated in Fig. 5, it can be seen that the TGA and DTG profiles of CMS were similar to those of native starch. On the TGA curves, the mass loss process occurred in two steps. The first range between  $40$  and  $240^\circ\text{C}$

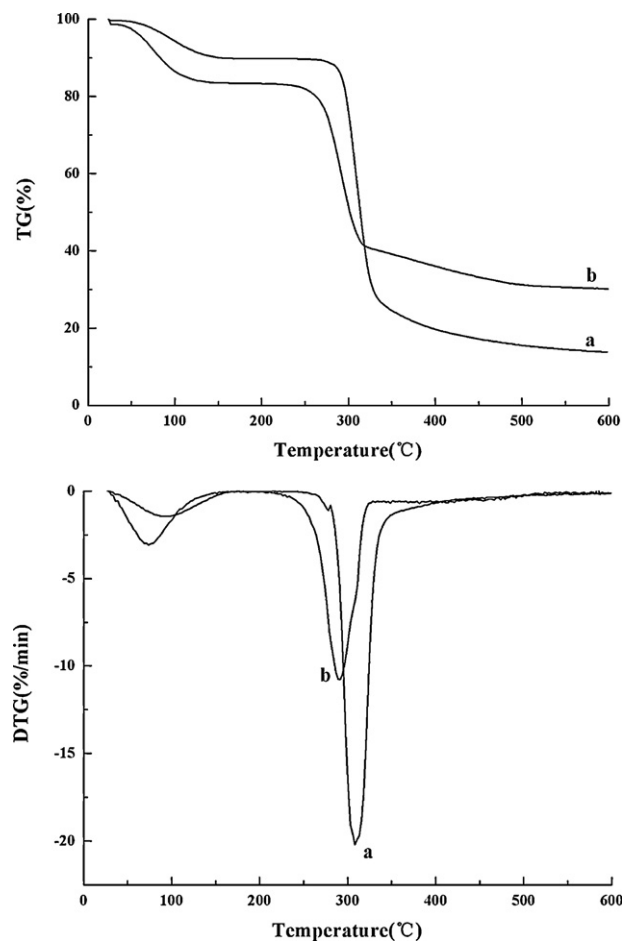


Fig. 5. TG-DTG curves of native starch (a) and carboxymethylated starch (b).

was associated with the loss of water, whereas the second range (261–472 °C) corresponded to the degradation of starch. From the DTG plot, one can see that the thermal degradation of native starch was commenced at 263 °C following a significant mass loss with an increase in the temperature to 372 °C. However, the CMS was decomposed thermally at a temperature of 238 °C and the rate of mass loss was rapid between 252 and 345 °C. Furthermore, it was also instructive that only 47% of the total mass of the CMS was lost in the second range of mass loss temperature where the thermal degradation took place. This value was lower than the 65% that was observed in the unmodified starch in the same range. As a consequence, the starch carboxymethylation resulted in products with enhanced thermal stability. As also observed for modified starch in the literature, this result was probably caused by the reduced amount of remaining hydroxyl groups in starch molecules after the carboxymethylation reactions, because the main thermal degradation of starch is the dehydration reactions between the starch hydroxyls (Lawal et al., 2008a). In comparison with the literature, the thermal properties of CMS prepared in the BMIMCl ionic liquid seem to be similar to those obtained by conventional procedures, and a slight difference was probably owing to the different DS values (Lawal et al., 2008a; Li et al., 2010).

By drawing on the above results, the ionic liquid BMIMCl is a promising media for homogeneous functionalization of starch. Carboxymethyl starch with a range of DS value could be prepared by controlling the reaction conditions. According to the XRD and SEM profiles, no starch granules could be observed in the carboxymethylated starch and the ordered crystalline structure of the original starch was largely destroyed during the carboxymethylation process, resulting in an equal accessibility of the starch hydroxyls to the reagent and a homogeneous substitution reaction to be carried out in the IL. Compared with homogeneous starch derivatization in other solvents, the main advantages using IL as reaction media include short reaction time, simple separation of products and solvents, easy solvent recovery, and products of uniform substitution to be obtained.

#### 4. Conclusions

This study has shown that the carboxymethyl corn starch of a range of DS value can be prepared with an ionic liquid BMIMCl as a solvent. The highest DS of 0.76 was attainable at molar ratios of NaOH and SMCA to AGU of 1.2 and 1.0, respectively, with the reaction time of 3 h and the temperature of 90 °C. The ionic liquids for the reactions can be easily recovered and reused. The FT-IR and <sup>13</sup>C NMR spectrometry revealed that carboxymethyl groups were introduced into the starch molecules and the carboxymethylation reaction occurred under the reaction conditions. SEM and XRD results showed that the granules of starch were mostly destroyed by breaking a large fraction of hydrogen bonds in starch during the carboxymethylation process. It was found that the carboxymethyl starch was more thermally stable than the native starch.

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