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Research Article

Homogeneous synthesis and characterization of starch acetates in ionic liquid without catalysts

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Homogeneous modification of corn starch with acetic anhydride was performed in ionic liquids 1-butyl-3-methylimidazolium chloride (BMIMCl) without catalysts. The results indicated that the pretreatment of starch, which starch was dissolved in BMIMCl at 105°C for 2 h before reaction, provided feasible reaction environment for starch functionalization. Optimum modification conditions for maximum degree of substitute (DS 2.11) were shown as following: acetic anhydride/anhydroglucose units (AGU) molar ratio 5:1, reaction temperature 105°C and reaction time 2 h. The pretence of acetyl groups in starch products was confirmed by FTIR and ^{1}H NMR spectroscopy. SEM and XRD data showed that the crystalline structure of native starch was disrupted and new structure was formed during the dissolution and modification processes. The higher DS due to acetylation had a beneficial effect on the thermal stability of samples.

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1 Introduction

In recent years, there has been an increasing trend toward the efficient utilization of biomass for various industrial products mostly because of diminishing resources of fossil fuel [1]. Starch, the storage polysaccharide of many plants, is an important natural, renewable, and biodegradable substance and widely used as a raw material in numerous industrial applications [2]. However, native starches have limitations such as poor processability and solubility which limit their industrial use. To extend their applications, chemical modification, introducing functional groups into the macromolecules to substitute the free hydroxyl groups in heterogeneous phase or homogeneous phase, is often used to alter physicochemical properties of starch. Acetylation is a type of esterification at the hydroxyl groups of the starch. Depending on its degree of substitution (DS), the acetylated starch is classified into low and high DS. The acetylated starches with a low DS (0.01–0.2) have been applied in many areas, such as film forming, binding, adhesion, thickening, stabilizing, and texturing [3–5]. Recently, starch acetates with high DS (>1.0) were suggested for use of biodegradable materials in packing of foods and diverse pharmaceutical applications for their thermo plasticity [5–7]. Preparation of highly acetylated starch usually involved pretreatment and use of sodium hydroxide solution or pyridine as catalysts [8]. High conversion efficiencies were obtained when starch was pretreated with DMSO or hot water. However, the high cost, difficult recovery, and toxicity, as well as the inconvenience of pretreatment, limited commercial development of this technology.

Room-temperature ionic liquids (ILs) have become more and more important as desirable green solvents and reaction media for a wide variety of processes due to their biodegradability and low toxicity [9, 10]. Moreover, ILs have the advantages of melting points around and less than 100°C, wide liquid range, electrochemical stability,

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Abbreviations: AGU, acetic anhydride/anhydroglucose units; **BMIMCl,** 1-butyl-3-methylimidazolium chloride; **DS,** degree of substitution; **ILs,** ionic liquids

Colour online: See the article online to view Fig. 1 in colour.

and lack of vapor pressure [11, 12]. ILs can be used and recycled by removing volatile organic compounds. There have been lots of published articles focusing on the use of ILs as solvent for cellulose [13–15]. However, only a few authors have investigated the application of ILs as solvent in starch [16–20]. In 2006, the use of ILs as reaction media for starch was first reported by Biswas et al. [16]. The authors found the solution of starch in 1-butyl-3-methylimidazolium chloride (BMIMCl) was acetylated with anhydrides in presence of pyridine to give acetylated starch with various DS. Without pyridine the acetylation reaction did not proceed. Xie et al. [17] also reported that chemical modification of corn starches with succinic anhydride or acetic anhydride in BMIMCl was carried out using pyridine as a catalyst. In this IL without pyridine at a temperature of 100°C, the starch esters with a DS in the range of 0.01–0.18 were obtained by varying the substrate ratio and reaction time [17]. However, this reaction system reported by these authors still caused environmental pollution because of the toxicity and volatility of pyridine. Lehmann and Volkert [21] recently reported that high-AM starch acetate was produced in BMIMCl without pyridine. However, the reaction conditions were drastic.

The aim of the present work was to study homogeneous synthesis and mild reaction conditions of starch acetates in IL without catalysts. For this aim, starch dispersion in BMIMCl was first studied at different temperature for different time with optical microscope. Modification conditions of starch with acetic anhydride in BMIMCl, including the molar ratio of acetic anhydride/anhydroglucose units (AGU) in starch, reaction time and temperature, were investigated. Starch acetates were also characterized by FTIR, ^{1}H NMR spectroscopy, SEM, XRD, and thermal stability analysis.

2 Materials and methods

2.1 Materials

Normal corn starch was obtained from ChangChun DaCheng Corn Products Co. (Changchun, China). BMIMCl (>99%) was provided from Lanzhou Institute of Chemical Physics (Lanzhou, China). Acetic anhydride was purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China). Other chemicals and solvents were of analytical grade.

2.2 Starch dispersion in ionic liquid

Starch (100 mg) was dispersed in 2 g IL BMIMCl. Then the slurries were heated at 85, 95, and 105°C, respectively, with stirring throughout. The samples were taken at 30 min intervals to analyze optical microscopic observations with a model BX51 optical microscope. The mixture was precipitated with sufficient anhydrous ethanol and centrifuged at 4500 rpm for 10 min. Pellet was washed with deionized water then precipitated again using anhydrous ethanol to eliminate IL. Finally, starch was filtered and dried in vacuum at 40°C for 48 h. The starch sample prepared by dissolving at 105°C for 2 h was characterized by SEM and XRD.

2.3 Homogeneous synthesis of starch acetates in BMIMCl

One gram corn starch was added to 20 g BMIMCl in a 100 mL three-necked flask, which was continuously purged with gaseous N_2. The mixture was stirred for 5 min for homogeneous mixing, and heated in an oil bath at 105°C for 2 h to dissolve starch. Acetic anhydride was added to the solution with the molar ratio of acetic anhydride/AGU in starch at 2:1, 3:1, 4:1, 5:1, and 6:1, respectively. The mixture was stirred and heated at the desired temperatures of 75, 85, 95, 105, and 115°C for 1, 2, 3, 4, and 5 h, respectively. The resulting reaction mixture was precipitated with anhydrous ethanol then centrifuged at 4500 rpm for 10 min. The volume ratio of ethanol/reaction mixture was maintained at about 3:1. The precipitate was washed thoroughly with sufficient anhydrous ethanol to eliminate IL, unreacted anhydride and byproduct. Finally, the solid was filtered and dried in vacuum at 40°C for 48 h.

2.4 Determination of DS

The acetylation percentage (% acetyl) and DS of modified starches were determined titrimetrically following the method of Wurzburg [22]. The starch acetates of 1.0 g was accurately weighed and added into the aqueous solution of ethanol (75%), then the slurry was kept in the water bath (50°C) for 30 min. After the slurry was cooled down, an exact amount of aqueous solution of potassium hydroxide (0.5 mol/L, 30 mL) was added and the solution was stirred for 72 h at room temperature. The excess alkali was back-titrated with 0.5 mol/L HCl using phenolphthalein as an indicator. The reference samples and duplicates were treated in a similar way. The acetyl content (*A*%) was calculated according to the following equation:

$$A\% = \frac{(V_0 - V_n) \times N \times 43 \times 10^{-3}}{M} \times 100\% \qquad (1)$$

where V_0 (mL) is the volume of 0.5 mol/L HCl used to titrate the blank, V_n (mL) the volume of 0.5 mol/L HCl used to titrate the sample, *N* the normality of the HCl used, *M* (g) the amount of dry starch acetate sample, factor 43 is the formular weight of acetyl groups. The acetyl content (*A*%) was used to calculate the DS, according to the following equation:

$$\mathrm{DS} = \frac{162 \times A}{43 \times 100 - (43 - 1) \times A} \qquad (2)$$

where 162 is the MW of anhydroglucose unit, 43 is the formular weight of acetyl groups, and 1 is the atomic mass of hydrogen.

2.5 FTIR spectra of starch acetates

The FTIR spectra of native and modified starches was recorded on a Nicolet 510 spectrophotometer (Thermo Electron Corporation, Waltham, USA) using potassium bromide (KBr) disks prepared from powdered samples mixed with dry KBr in a ratio of 1:30. Thirty-two scans were taken of each sample recorded from 4000 to 400 cm^{-1} at a resolution of 2 cm^{-1} in the transmission mode.

2.6 ^{1}H NMR spectra

^{1}H NMR spectra were recorded on a Bruker DRX-300 spectrometer (Bruker Corporation, Fallanden, Switzerland) at the frequency of 300.13 MHz. Starch samples (0.015 g) were dissolved in 1 mL of deuterated DMSO (DMSO-d_6) for more than 4 h with stirring. The solution was centrifuged at 10,000 *g* for 5 min. The supernatant was measured using tetramethylsilane as internal standard.

2.7 SEM

The surface structure of the starch granules was observed by SEM. Starch samples were mounted on circular aluminum stubs with double sticky tape and then coated with 20 nm of gold and examined and photographed in a model 1530 VP scanning electron microscope (LEO, Oberkochen, Germany) at an accelerating potential of 20 kV.

2.8 XRD

XRD was conducted with a RU200R X-ray diffractometer (Rigaku, Tokyo, Japan) with Cu Kα radiation at 35 kV and 20 mA, a theta-compensating slit, and a diffracted beam monochromator. The moisture content of all samples was adjusted to about 20% in a sealed dessicator at room temperature before analysis. The diffractograms were recorded between 5 and 60° (2θ).

2.9 Thermal stability analysis

Thermogravimetric analyses (TGA) were done with a Diamond TG-DTA thermogravimetric analyzer (PerkinElmer Co., Waltham, USA). The apparatus was continually flushed with nitrogen. About 10 mg samples were heated from 60 to 650°C with a heating rate of 20°C/min. The moisture content of native starch, starch acetates with DS 1.04 and 2.11 was 10.8, 7.5, and 5.1%, respectively.

2.10 Statistical analysis

All determinations were replicated three times and mean values and SDs were reported. ANOVA were performed and the mean separations were performed by Tukey's HSD test ($p < 0.05$) using SigmaStat Version 2.0 (Jandel Scientific/SPSS Science, Chicago, IL, USA).

3 Results and discussion

3.1 Starch dispersion in ionic liquid

To obtain highly substituted starch acetates, starch should be completely dissolved in IL, which is beneficial to homogeneous modification. Dissolution temperature had an effect on complete dissolution. The complete dissolution time decreased with the increase of incubation temperature. To get a complete dissolution, the incubation time was 12, 4, and 2 h, respectively, when starch was heated in IL at 85, 95 and 105°C. The dispersion of corn starch in BMIMCl at 105°C for 2 h are showed in Fig. 1. The number of starch granules decreased with the extension of incubation time. There was no starch granule with birefringence in the optical photos when starch slurry was heated in IL for 2 h, which indicated starch dissolve completely. Hence, the hydroxyl groups of starch had full access to react in a homogeneous manner. XRD pattern of starch dissolved in ILs at 105°C for 2 h showed the diffusion peaks at 15, 17, 18, and 23° (2θ) disappeared and only a dispersive wide peak appeared (Fig. 6), suggesting that the crystallinity of native starch was damaged completely during the dissolution process. The effect of dissolution time on the DS of starch acetate is presented in Fig. 2. It was found that at the first stage the DS value increased rapidly with the increase of dissolution time. As the dissolution time increased from 0 to 2 h, the DS value increased from 0.1 to 1.04. After 2 h, the DS value remained constant. These data indicate that starch homogeneous dispersion in IL had positive effect on the DS of starch acetate. It can be concluded that BMIMCl can efficiently dissolve starches and provides suitable reaction environment for starch functionalization.

3.2 Influence of the reaction parameters

Prior to modification, dissolution of starch in BMIMCl at 105°C for 2 h resulted in starch homogeneous dispersion.

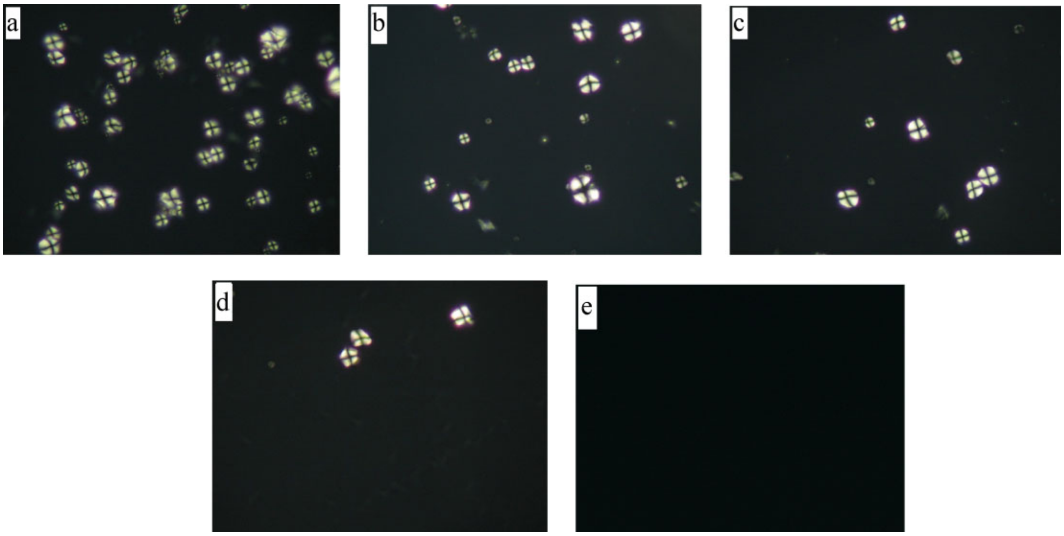

Figure 1. Polarized micrographs of starch dissolved at 105°C at different dissolution time 0 min (a), 30 min (b), 60 min (c), 90 min (d), and 120 min (e).

In this case, the high chloride concentration and its activity in ILs play an important role in effectively breaking the extensive hydrogen-bonding network present in starch [20]. The influence of the molar ratio of AGU in starch on DS is shown in Table 1. The DS of starch acetates gradually increased with an increase in acetic anhydride/AGU molar ratio at the first stage. The molar ratio of acetic anhydride/AGU of 5:1 was found sufficiently to reach maximum DS value. However, the DS value remained at almost constant value if the molar ratio of acetic anhydride/AGU increased beyond 5:1. Hence, the influence of the excess amount of acetic anhydride on reaction was not significant under the given reaction conditions. Xie et al. [17] reported that the DS value for acetylated starch remained constant value as the anhydride/AGU molar ratio was raised higher than 5:1. Similar result was also reported by Billmers and Tessler [23], who studied the modification of intermediate DS starch esters in aqueous solution with sodium hydroxide as catalyst. Acetic anhydride/AGU molar ratio of 5:1 was selected for the following runs.

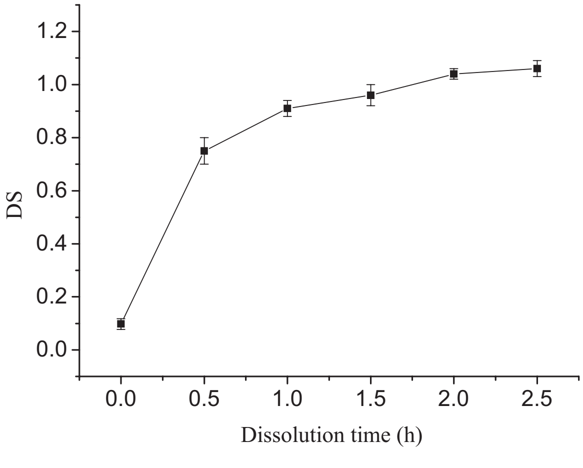

Figure 2. Effect of dissolution time on the DS. Other conditions: dissolution temperature 105°C, acetic anhydride/AGU molar ratio 5:1, reaction temperature 85°C, reaction time 2 h.

As showed in Table 2, it was indicated that the reaction temperature had an important effect on the DS value of

Table 1. Effect of acetic anhydride/AGU molar ratio on the $\text{DS}^{a),b)}$

Acetic anhydride/ AGU molar ratio	2:1	3:1	4:1	5:1	6:1
DS	0.43^{d}	0.67^{c}	0.86^{b}	1.04^{a}	1.06^{a}

a) Other reaction conditions: reaction temperature 85°C, reaction time 2 h.
b) Values in the same row with different superscript letter are significantly different ($p < 0.05$).

Table 2. Effect of reaction temperature on the $\text{DS}^{a),b)}$

Reaction temperature (°C)	75	85	95	105	115
DS	0.75^{e}	1.04^{d}	1.35^{c}	2.11^{a}	1.84^{b}

a) Other reaction conditions: acetic anhydride/AGU molar ratio 5:1, reaction time 2 h.
b) Values in the same row with different superscript letter are significantly different ($p < 0.05$).

Table 3. Effect of reaction time on the DS[a),b)]

Reaction time (h)	1	2	3	4	5
DS	1.09^e	2.11^a	1.84^b	1.74^c	1.63^d

a) Other reaction conditions: acetic anhydride/AGU molar ratio 5:1, reaction temperature 105°C.
b) Values in the same row with different superscript letter are significantly different ($p < 0.05$).

products. When the reaction temperature increased from 75 to 105°C, the DS value rapidly increased from 0.75 to 2.11. However, further increase in reaction temperature above 105°C reduced the DS value. Xie et al. [17] reported that an increase of reaction temperature from 70 to 100°C led to an increment in the DS of acetylated starches from 0.043 to 2.34 when starch acetates were performed in IL with pyridine as a catalyst. DS decreased with increasing temperature as reaction temperature was higher than 100°C. It was concluded that reaction temperature had a similar effect on DS values of starch acetates prepared in IL with or without catalyst. From the above analysis, we could draw the conclusion that the optimal temperature was 105°C.

The effect of reaction time on DS is presented in Table 3. The DS increased with an increase in reaction time. However, the decrease in DS was observed with increasing reaction time beyond 2 h. A plausible reason is that the concentration of anhydride was depleted due to esterification reactions with the reaction proceeding. As a result, side reactions such as hydrolysis of starch acetate and/or elimination reactions probably occurred at longer reaction times because water (from the starch and as by-product produced by the esterification reaction) was not properly taken out from the reactor [17, 24, 25].

3.3 FTIR of native and acetylated starches

The introduction of the carbonyl groups can be evidenced by FTIR spectroscopy. The FTIR spectra of native and acetylated starch are given in Fig. 3. In the spectrum of native starch, there are several discernible absorbencies at 1159, 1082, and 1014 cm^{-1}, which are attributed to C–O bond stretching [26]. Additional characteristic absorption bands at 992, 929, 861, 765, and 575 cm^{-1} are due to the entire anhydroglucose ring stretching vibrations. The extremely broad band between 3000–3600 cm^{-1} and the peak at 2,950 cm^{-1} correspond to OH and CH stretchings, respectively, while the peaks at 1647 cm^{-1} corresponds to δ (OH) bending [27]. FTIR spectra of different DS of acetylated starches showed some new absorption at 1736, 1374, and 1251 cm^{-1} assigned to carbonyl C=O, CH_3 symmetry deformation vibration and carbonyl C–O stretch vibration, respectively. These new absorption indicated that the acetylated starches were formed during esterification process. The intensities of peaks at 3414, 1647 cm^{-1} were gradually weakened with the increase of DS and the peak at 1647 cm^{-1} almost disappeared when DS reached to 2.11, which indicated that acetyl groups replaced hydroxyl groups in the starch molecules. This led to the loss of starch granule crystallinity, which was consistent with XRD results (Fig. 6). The similar results were reported by Xu et al. [8] and Zhang et al. [28].

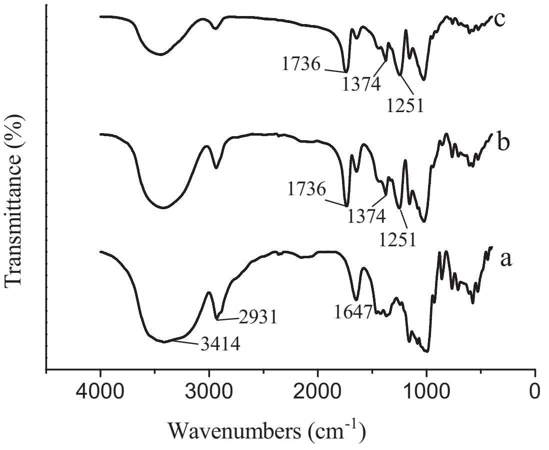

Figure 3. FTIR spectra of native starch (a) and acetylated starches at DS 1.04 (b) and DS 2.11 (c).

3.4 ^1H NMR spectra

The esterification process of starch was also studied by ^1H NMR spectroscopy, and the spectra of acetylated

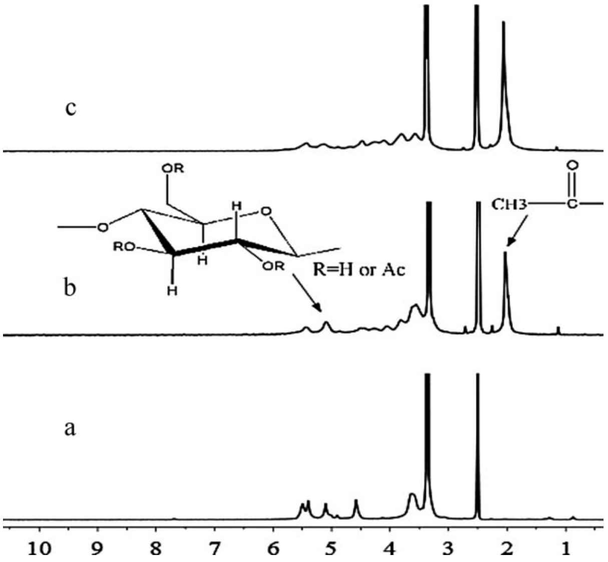

Figure 4. ^1H NMR spectra of native starch (a) and starch acetates at DS 1.04 (b) and DS 2.11 (c).

starches are presented in Fig. 4. With acetyl groups being gradually introduced into starch, proton resonances of anhydroglucose unit showed some changes compared with that of native starch. In most cases, the starch backbone signals at 3.6–5.5 ppm and the methyl protons of acetate at 1.9–2.1 ppm could be assigned [7]. There were also some peaks appearing at 2.5 and 3.3 ppm, respectively, due to protons in DMSO-d_6 and H_2O. In the ^{1}H NMR spectra of starch acetates, there was a peak at 2.05 ppm which indicated that the acetyl groups substituted hydrogen atom of hydroxyl groups. With the increase of DS, the intensities of peak at 2.05 ppm increased.

3.5 SEM

SEM was used to investigate the morphology of native starch, starch recovered from IL solution before acetylation and acetylated starches (Fig. 5). The results showed that native corn starch granules were polygonal or irregular in shape, the starch granules lost their individuality and smoothness in starch recovered from IL solution and starch acetates. The change of granular structure could be attributed to the dissolving pretreatment, which disrupted the original structure of starch granules due to IL breaking the hydrogen bonds of molecules, and modification process.

3.6 XRD patterns

XRD measurements were performed to check if chemical modification altered the crystallinity of starch. The XRD patterns of native and acetylated starches are presented in Fig. 6. The intra- and inter-molecular hydrogen bonds were responsible for the highly ordered crystalline structure [10]. Native corn starch showed the typical A-type X-ray pattern. The diffusion peaks at 15, 17, 18, and 23° (2θ) disappeared in acetylated starch. However, the typical wide peaks of acetylated starches with DS 2.11 at 9 and 20° (2θ) appeared which gave an amorphous pattern. These diffraction peaks may have originated from a new ordered structure with increasing DS [29]. The similar results were reported by Chi et al. [30] and Zhang et al. [28].

3.7 Thermal stability analysis

The changes in thermal stability caused by acetylation were examined using TGA. The TG curves for native starch and starch acetates are shown in Fig. 7. The native corn starch showed a two-stage weight loss below 650°C, with the first minor one corresponding to the loss of water below 100°C and the other one corresponding to the starch decomposition. Water is the main product of decomposition at temperatures below 300°C. Further heating up to 650°C resulted in carbonization and ash formation [31]. For native starch, the second thermal degradation was initiated at 303°C. Starch acetate with DS 1.04 also showed a two-stage weight loss, and the second weight loss occurred at 322°C due to the pyrolytic volatilization of acetylated starch. When DS increased to 2.11, acetylated starch had an initial decomposition temperature of 344°C, 22°C higher than that of DS 1.04. The thermal stability increased with increasing DS. The reason was that in high DS starch acetate there remained a small number of hydroxyl groups after acetylation, which caused slower

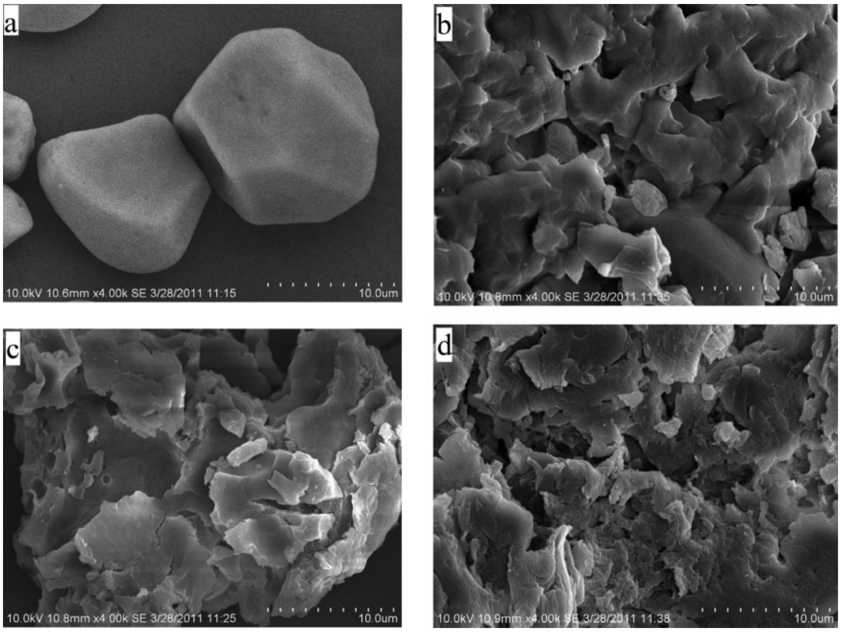

Figure 5. SEM photos of native starch (a), starch dissolved in ILs at 105°C for 2 h (b) and acetylated starches at DS 1.04 (c) and DS 2.11 (d).

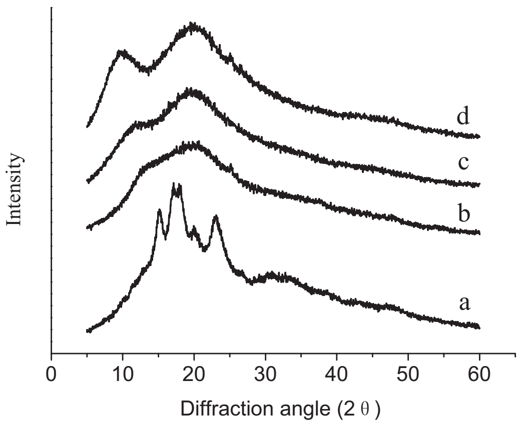

Figure 6. XRD patterns of native starch (a), starch dissolved in ILs at 105°C for 2 h (b) and acetylated starches at DS 1.04 (c) and DS 2.11 (d).

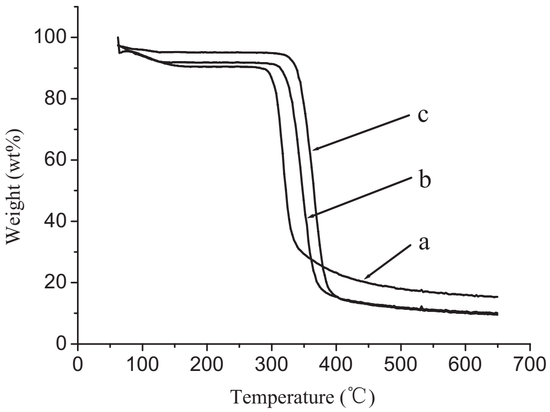

Figure 7. TG curves of native starch (a) and starch acetates at DS 1.04 (b) and DS 2.11 (c).

decomposition reaction. Therefore, the higher DS due to acetylation had a beneficial effect on the thermal stability of products. Similar results were reported by Zhang et al. [28] and Xu et al. [8].

4 Conclusions

In conclusion, the homogeneous reaction of starch acetates with high DS could be successfully achieved in BMIMCl without catalysts. The dissolving pretreatment of starch provided convenient reaction environment for acetylation. The mild reaction conditions of starch acetates were optimized for the molar ratio of AGU in starch, reaction time, and temperature. Moreover, acetyl groups had been introduced into the backbone of starch, which was confirmed by FTIR and ^{1}H NMR spectroscopy. SEM and XRD data indicated that starch was substantially disrupted, the crystallinity was completely converted into amorphous state and new structure was formed during dissolution and modification processes. The thermal stability of starch acetate depended on DS. The great thermal stability was attributed to the small number of hydroxyl groups in starch molecules.

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