Synthesis of Starch Esters in Ionic Liquids

Wenlei Xie, Li Shao, Yawei Liu

School of Chemistry and Chemical Engineering, Henan University of Technology, Zhengzhou 450052, People's Republic of China

ABSTRACT: Chemical modification of corn starches with succinic anhydride or acetic anhydride was carried out using 1-butyl-3-methylimidazolium chloride (BMIMCl) as a reaction medium. The reaction progress was followed in terms of the degree of substitution (DS) for the starch derivatives. The results showed that the homogeneous esterification of starch at 5 : 1 molar ratio of anhydride/anhydroglucose units at 100°C led to formation of acetates with DS ranging from 0.37 to 2.35 and succinates with DS ranging from 0.03 to 0.93. Moreover, the reaction media applied could be easily recycled and reused. Further, the formation of starch esters was confirmed by the presence of the carbonyl signal in the FTIR and NMR spectra. It was shown that the starch granules were mostly converted from their crystalline structure into amorphous state in the ionic liquid system under the given reaction conditions. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 116: 218–224, 2010

Key words: synthesis; polysaccharides; esterification; functionalization of polymers; ionic liquid

INTRODUCTION

The efficient utilization of biomass is increasingly gaining importance mostly because of diminishing resources of fossil oils. As one of the most abundant naturally occurring biopolymers, starches have attracted much attention on account of their non-toxic, renewable, biodegradable, and modifiable.[1,2] Chemical modification of starch is one of the common methods for the production of value-added products. It is based on reactions of free hydroxyl groups in the anhydroglucose units (AGU) with the formation of starch derivatives. The modified starches generally have physicochemical properties that differ significantly from those of the parent starches, and thereby increasing their functionalities.[3,4] Owing to the lack of solubility of native starch in most common organic solvent, the starch heterogeneous modification was conventionally used in the starch research. However, the heterogeneous reactions have drawbacks including the instability in processing and low degree of functionalization.[5,6] Recently, there has been increased interest in homogeneous modification of starch because more uniform and stable products could be obtained by this method. For example, several authors have reported the preparation of modified starches to higher degrees of substitution (DS), relying on the use of sophisticated experimental techniques and solvents, to ultimately achieve homogeneous modification of starches.[7–10]

In recent years, the application of ionic liquids (ILs) as alternative solvent and reaction media for a wide variety of synthetic processes has received significant attention owing to their fascinating and intriguing properties, such as low melting points, wide liquid ranges, and lack of vapor pressure.[11–13] However, there have been limited studies investigating the potential of using ILs as solvents to modify polysaccharides and mostly focused on cellulose.[12] In ILs, namely 1-butyll-3-methylimidazolium chloride (BMIMCl), the acetylation of cellulose has been successfully accomplished in a homogeneous manner and the DS could reach 2.5.[14] Besides, it was found that starch could dissolve in BMIMCl up to 15% (w/w) concentration at 80°C because of the strong hydrogen-bond contacts between the ILs and starch.[15] By using BMIMCl as a reaction media, the graft polymerization of ε-caprolactone onto starch was performed smoothly and the grafting efficiency could reach 24.4%.[16] Moreover, the preliminary results of starch acetylation in this ILs were also reported.[17] In this work, the chemical modification of corn starches with succinic anhydride or acetic anhydride was investigated using BMIMCl as reaction medium and pyridine as a catalyst to improve the method for preparation of starch esters by increasing reaction efficiency. The extent of esterification was measured by the DS of starch esters. The major factors affecting the esterification, such as the molar ratio of anhydride/AGU in starch, reaction duration, and reaction temperature, were also

studied. Furthermore, the modified starches were characterized by fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), X-ray diffraction (XRD), and NMR techniques.

EXPERIMENTAL

Materials

Corn starch consisting of 25% amylose and 75% amylopectin was obtained from a local starch factory (Zhengzhou,China). The acetic anhydride, succinic anhydride, pyridine, and 1-methylimidazole were obtained from a local chemical company and Aldrich chemical company (Milwaukee, WI). All other chemicals were of analytical grade and used as received.

Preparation of ionic liquid BMIMCl

BMIMCl was prepared according to published procedures.[18] Equal molar amounts of chlorobutane and 1-methylimidazole were added to a round-bottomed flask and refluxed for 48–72 h at 70°C under stirring until two phases were formed. After cooling, 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. The ethyl acetate was then decanted followed by the addition of fresh ethyl acetate, and this process was repeated twice. Washing with ethyl acetate should be sufficient to remove any unreacted material from the bottom phase. 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 product, BMIMCl, was slightly yellow and may be crystalline at room temperature.[18]

Esterification of corn starch

Starch esters were prepared by reactions of corn starch with anhydrides such as acetic anhydride or succinic anhydride in BMIMCl. In a 50 mL three-neck round flask equipped with magnetic stirrer, 1.5 g of corn starch was added to 30 g of BMIMCl under constant stirring and heated to 100°C until the starch was completely dissolved. Then, the anhydrides and pyridine were added to this solution with a 1 : 5 : 3 molar ratio of AGU/anhydride/pyridine, and the homogeneous reaction mixture was stirred at a temperature of 100°C for the required time. Upon completion of the reaction, the resulting reaction mixture was left to cool to room temperature, and the soluble starch esters were isolated by precipitation with absolute ethanol with stirring. The obtained product that separated from the solution was filtered and washed thoroughly with ethanol to eliminate ILs, unreacted anhydride, and by-products. Finally, the product was first air-dried and then further dried at 35°C in vacuum oven for 48 h.

In this work, pyridine was used as a catalyst and base. The base-catalyzed reaction of pyridine with starch is considered to be a nucleophilic substitution reaction.[19] In the substitution reaction, pyridine severs to activate the starch granules initially and works as a catalyst by the formation of the succinyl–pyridinum or acetyl–pyridinum intermediate.[20] Besides, other authors have also reported that pyridine could be used as catalysts for the esterification of starch.[4,7,21]

Measurement of DS

The DS for a starch derivative is defined as the number of hydroxyl groups substituted per D-glucopyranosyl structure unit of the starch. The DS of the acetylated starch was determined by the published titration method.[22] The starch acetate of 1 g was accurately weighed and added into the aqueous solution of ethanol (75%) and then the resulting slurry was kept in the water bath (50°C) for 30 min. After the slurry was cooled down, 30 mL of 0.5M KOH solution was added followed by stirring for 72 h at room temperature. Subsequently, the excess KOH was back-titrated with 0.5M HCl solution using phenolaphtalen as an indicator. Reference sample and duplicate sample were treated in the similar way. Acetyl content (%A) was calculated according to following eq. (1).

$$\%A = [(V_0 - V_n) \times N \times 0.043 \times 100]/M \qquad (1)$$

Where V_0 is the volume of 0.5M HCl used to titrate blank (mL), V_n is the volume of 0.5M HCl used to titrate sample (mL), N is the normality of used HCl solution, M is the sample amount as dry substance (g), 43 is the weight of acetyl group.

Acetyl content (%A) was used to calculate the DS, according to following eq. (2)

$$DS = 162 \times \%A/[4300 - (42 \times \%A)] \qquad (2)$$

The method described in the literature was used to measure the DS of succinylated starch.[23] A known weight of succinylated starch was added to a 2.5M HCl/isopropyl alcohol solution followed by stirring for 30 min. Then, the residue was recovered by filtration and washed with isopropyl alcohol. Next, the starch residue was redispersed in deionized water and the resultant dispersion was heated in a boiling water bath for 10 min. The solution was readily titrated with 0.1M NaOH solution, and the DS value was determined from the following eq. (3).

$$DS = \frac{0.16 \times (A \times N)/W}{1 - [0.101 \times (A \times N)/W]} \qquad (3)$$

Where A, N, and W represent the titration volume (mL) of the NaOH solution, normality of the NaOH solution, and weight (g) of the succinylated starch, respectively.

Characterization of starch esters

FTIR spectra of native and modified starch were recorded on a Shimadzu IR-Prestige-21 spectrometer (Shimadzu Corporation, Kyoto, Japan) using a potassium bromide (KBr) disc technique. The spectra were acquired at a resolution of 4 cm^{-1} in the range of 400–4000 cm^{-1}.

The ^{1}H NMR measurements were performed with a Bruker AVANCE DRX 500 spectrometer (Fallanden, Switzerland) operating at 500.13 MHz in CDCl$_3$ using tetramethylsilane as internal standard. The chemical shifts were expressed in ppm.

SEM were obtained on an AMRAY-1000B scanning electron microscope (Amray Corporation, Bedford, Massachusetts). The accelerating voltage was 20 kV.

X-ray diffraction measurements were conducted on a Philips X, Pert Pro MPD X-ray diffractometer (Philips Corporation, Eindhoven, Netherlands) using a radiation source of Cu Kα ($\lambda = 0.154$ nm) at 40 kV and 80 mA. Data were collected over a 2θ range of 5°–50° with a step size of 0.02° at a scanning speed of 5° min^{-1}.

RESULTS AND DISCUSSION

Factors affecting the esterification

As the anhydride, starch, and the resulting starch esters could be all dissolved in BMIMCl, a homogeneous esterification reaction could be achieved in this ILs. The reaction solution remained clear throughout the reaction by using BMIMCl as a solvent, indicating homogeneous reaction of the esterification. In this ILs 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. However, in the presence of pyridine in the range of AGU/pyridine molar ratio from 1 : 1 to 1 : 3, the DS value ranged from 0.7 to 2.35 for starch acetate and from 0.46 to 0.91 for starch succinate, respectively, when the esterification reactions were carried out at AGU/anhydride molar ratio of 5 : 1 for 3 h. The AGU/pyridine molar ratio of 1 : 3 was found to be necessary for the esterification reaction to be carried out smoothly. The further increase in the pyridine amount had no significant effect on the DS value. In addition, the corn starch could not be dissolved suf-
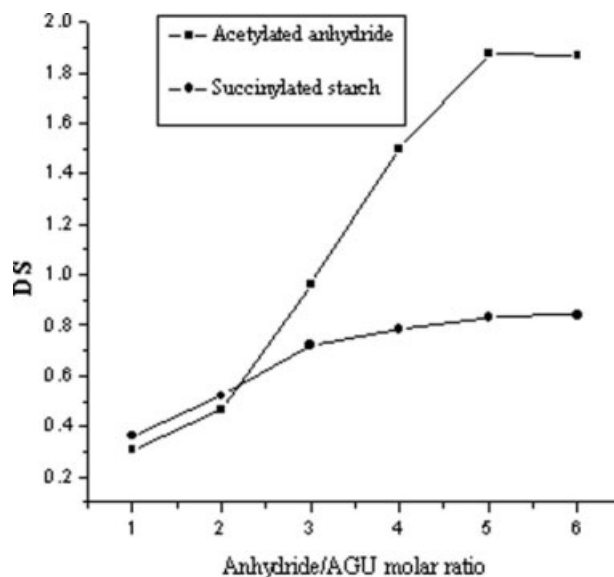

Figure 1 Effects of anhydride/AGU molar ratio on the esterification reaction. Reaction conditions: reaction time 2 h, reaction temperature 100°C.

ficiently in neat pyridine even after stirring overnight at 100°C, and thus, without BMIMCl the esterification of starches in slurry of pyridine leads to a heterogeneous reaction. In this BMIMCl/pyridine system, the uniform substitution of reaction can be carried out by ensuring accessibility of the reagent, and the pyridine acts not only as an esterifying catalyst but also as a reaction medium. Accordingly, the AGU/pyridine molar ratio of 1 : 3 was chosen in the subsequent study for optimization of reaction conditions.

The effects of the molar ratio of anhydride/AGU on the esterification of corn starches were examined, and the results are illustrated in Figure 1. As can be seen, the DS value for both the starch esters increased steadily in the range of anhydride/AGU molar ratio from 1 : 1 to 5 : 1. This result could be tentatively interpreted by the greater availability of anhydride molecules in the vicinity of starch molecules at the higher concentration of anhydride. Similar result was also reported by Jeon et al., who investigated the modification of starch with dodecyl succinic anhydride, decadecenyl succinic anhydride, and octadecenyl succinic anhydride.[24] However, as the anhydride/AGU molar ratio was raised higher than 5 : 1, the DS value for both acetylated starch and succinylated starch more or less remained an almost constant value, representative of near completion of the reaction under the given reaction conditions. It seems very likely that the excess anhydride had no significant effect on the esterification of starch in the ILs. The maximum DS values, of 1.87 for acetylated starch and 0.84 for succinylated starch, were obtained at the molar ratio of 5 : 1 under the
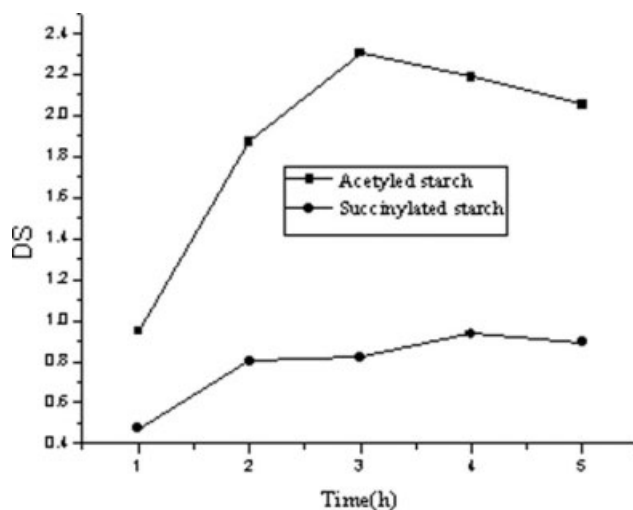
Figure 2 Effects of reaction time on the esterification reaction. Reaction conditions: anhydride/AGU molar ratio 5 : 1, reaction temperature 100°C.
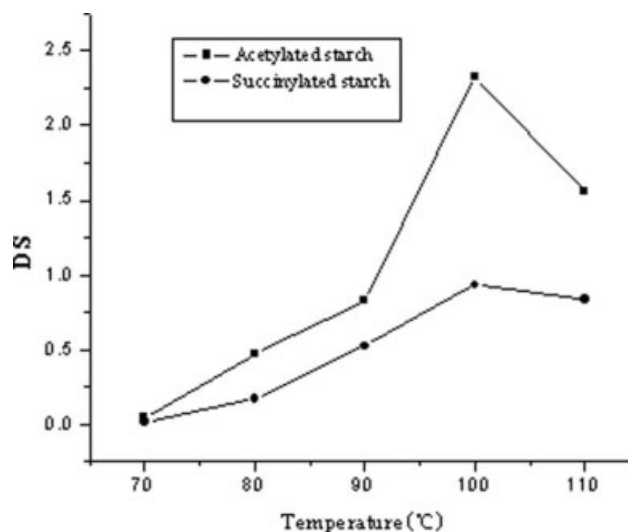

Figure 3 Effects of reaction temperature on the esterification reaction. Reaction conditions: anhydride/AGU molar ratio 5 : 1, reaction time 3 h for acetylated starch and 4 h for succinylated starch.

reaction conditions used, respectively. Therefore, the anhydride/AGU molar ratio of 5 : 1 was preferred for the preparation of starch esters. Additionally, because of steric hindrance resulting in a lower reactivity of succinic anhydride, the DS value of starch succinate was lower than that of starch acetate under the identical reactions.

A plot of the DS value versus reaction duration is shown in Figure 2. It can be observed that the DS value increased first at the reaction time between 1 and 3 h for acetylated starch and between 1 and 4 h for succinylated starch. However, as the reaction time was increased further, the decreased DS value for both the modified starch was observed. This phenomenon could be probably due to the starch ester hydrolysis occurred at longer reaction time as the water (from the starch) was not properly taken out from the reactor. Therefore, a reaction time of 3 h for acetylated starch and 4 h for succinylated starch was considered as most appropriate for preparation of the modified starch under the reaction conditions.

The data in Figure 3 showed that the reaction temperature had an important effect on the reaction efficiency. As shown in Figure 3, an increase of reaction temperature from 70 to 100°C led to an increment in the DS of the products from 0.043 to 2.34 for acetylated starch and from 0.02 to 0.93 for succinylated starch, respectively. However, further increase in the reaction temperature higher than 100°C caused the decreased DS value for the two modified starch. A similar trend of varying the DS value with increasing reaction temperature was also reported by other authors.[5,25] Thus, we concluded that 100°C was the appropriate reaction temperature for the starch esterification in the IL system.

From the viewpoint of environment concern and economic of the process, recycling of the solvent ILs is absolutely required. In this work, upon completion of the esterification reaction, the starch ester was precipitated with absolute ethanol. Afterward, the residual ILs in the filtrate were recovered by a simple process of distillization under reduced pressure to remove volatile compounds such as ethanol. The recovered IL was further used for the next esterification reaction and the recycle test results are presented in Figure 4. As illustrated in this figure, the lower DS value of both the starch derivatives was observed under the same reaction conditions when the recovered IL was used for the subsequent cycles. However, the change in the DS value was not
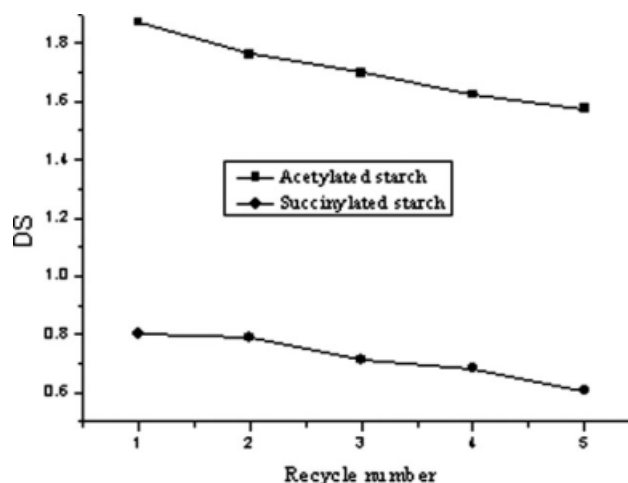

Figure 4 Results of the ionic liquid recycle test. Reaction conditions: anhydride/AGU molar ratio 5 : 1, reaction time 2 h, and reaction temperature 100°C.
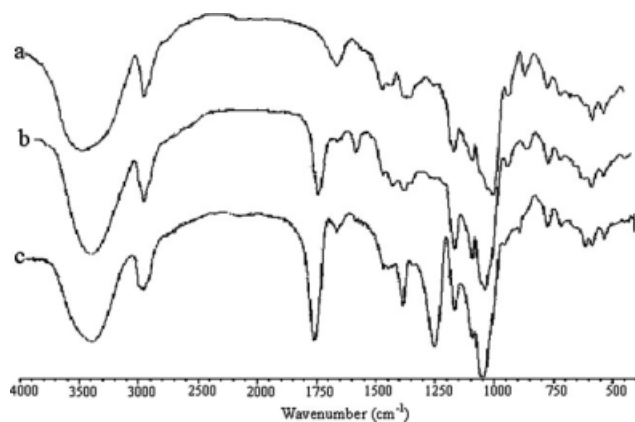
Figure 5 FTIR spectra of native corn starch (a), succinylated corn starch (b), and acetylated corn starch (c).

significant even after five recycles, indicating that the IL could be recovered and recycled. Alternatively, other methods, such as nanofiltration and reverse osmosis, can also be used for the recycling of ILs and may be more practical.

Starch ester characterizations

The esterification of starch could lead to the substitution of hydroxyl groups in starch with carbonyl groups, which can be confirmed by FTIR spectra. The FTIR spectra of native, succinylated, and acetylated starches are indicated in Figure 5. In the IR spectra of native starch, there are several discernible peaks at 1155, 1080, 1021 and 930 cm^{-1}, which were attributed to the characteristic absorption of starch backbone.[4] The peaks at 1080 and 1021 cm^{-1} were ascribed to C—O bond stretching of C—O—C group in the anhydrous glucose ring, and the characteristic peak at 1155 and 930 cm^{-1} was due to the stretching of the C—OH bond in AGU and the whole glucose ring stretching vibrations, respectively.[5,9] Besides, a peak at 1646 cm^{-1} was principally assigned to tightly bound water present in the starch.[26] The 2933 cm^{-1} peak was characteristic of the CH$_2$ group of starch. In addition, an extremely broad band at 3390 cm^{-1} was originated from the vibration of the hydroxyl groups (O—H) of starch.[6]

FTIR spectra of acetylated starches showed some new absorption peaks at 1754, 1378, and 1248 cm^{-1}, respectively, besides the characteristic absorption peaks of starch. The peak at 1754 cm^{-1} was attributed to carbonyl C=O vibrations, and the absorption bands at 1378 and 1248 cm^{-1} were associated with CH$_3$ symmetry deformation vibration and C—O stretching vibration, respectively. This observation is indicative of absorption of acetyl group in the starch acetate.[27] Thus, the acetylated starch was formed during the esterification process. Compared with native starch, the succinylated starch exhibited a

new IR absorption peak at 1724 cm^{-1}, which could be ascribed to the stretching vibration of ester carbonyl group, as a result of the esterification of succinic anhydride with the corn starch.[4,6]

Figure 6 shows the ^{1}H NMR spectra of native corn starch, succinylated, and acetylated corn starches. The lines of the ^{1}H NMR spectra are broad due to overlap of signals from slightly different chemical environments and also due to the viscosity of the samples.[28] In a ^{1}H NMR spectrum of native starch, signals for AGU protons were found in the region 3.85–5.5 ppm.[28,29] The ^{1}H NMR spectra of starch acetate showed, in addition to the characteristic signals of starch, a peak at 1.93 ppm, which could be resulted from an acetyl moiety in the product, indicating that the acetyl groups were introduced into the starch molecules and the acetylation reaction occurred.[28] Similarly, for the succinylated starch, the proton signal at 1.83 ppm was attributed to the methylene group that was associated with succinic anhydride, as an evidence for the succinylation of starch.

Scanning electron photomicrographs of native starch, starch acetate, and starch succinate are presented in Figure 7. As shown in Figure 7, native corn starches consisted of polygonal or irregular granules and their size varied from 5 to 25 μm in diameter. However, as can be seen from Figure 7, the modified starch exhibited clumping of small particles without well-defined edges. Obviously, the crystallinity of succinylated and acetylated starch was lower than the original starch. These results imply that, in the esterification process, the ILs rapidly broke intermolecular and intramolecular hydrogen bonds and disrupted the original structure of starch. The microscopy observations were in good agreement with the results obtained by XRD analyses.

To study the effect of the modification on the crystalline structure of starch, the native and modified starches were examined by powder X-ray diffraction. As indicated in Figure 8, the native corn starch had a typical A-type pattern structure, with the sharp diffraction peaks at 15°, 17°, 18°, and 23°.[5,30] For succinylated and acetylated starch, even though the similar type of diffraction pattern was observed, the X-ray diffraction spectra had dispersive broad peaks and
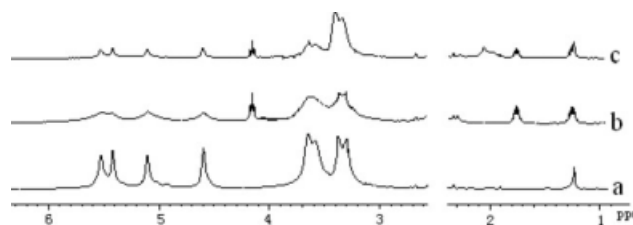

Figure 6 H^1 NMR spectra of native corn starch (a), succinylated corn starch (b), and acetylated corn starch (c).
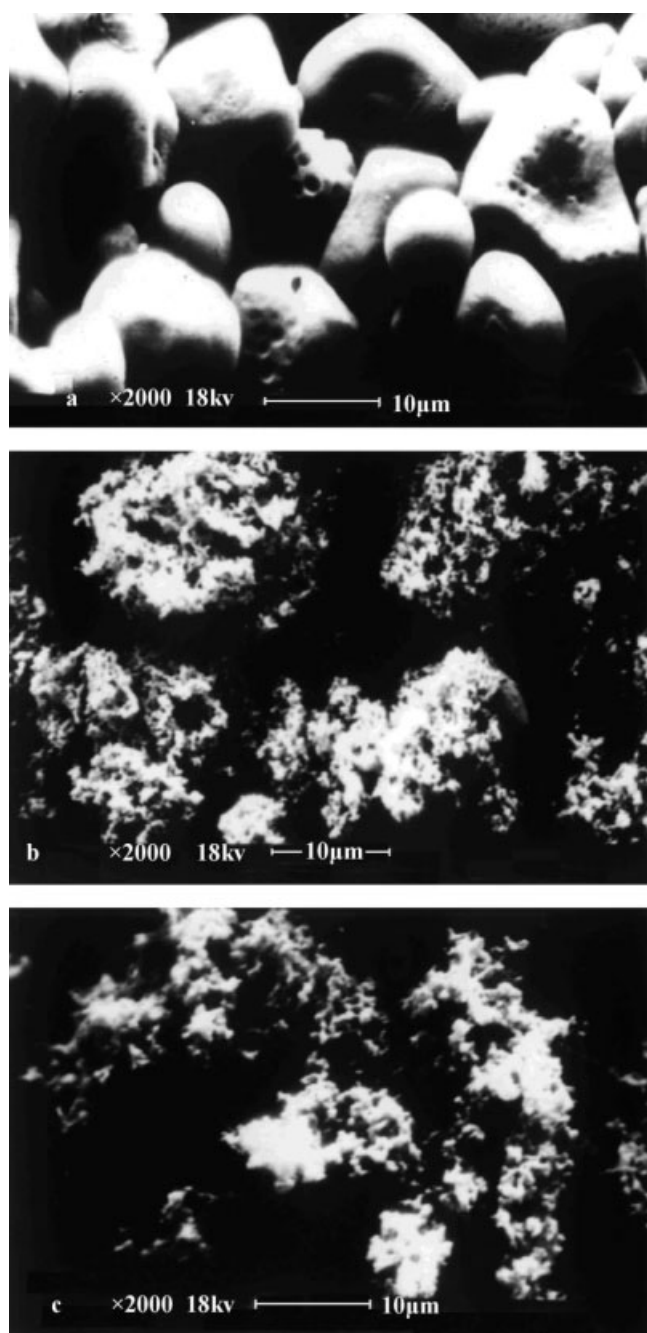
Figure 7 SEM images of native corn starch (a), succinylated corn starch (b), and acetylated corn starch (c).

the intensity of the diffraction peaks reduced significantly, which suggests that most of crystalline structure of the starch was probably converted into the amorphous shape, and thus increasing its accessibility. As a result, the esterification reaction primarily occurred in the amorphous regions and the high DS value of starch esters was therefore achieved. This result showed that the ordered crystalline structure of native starch was destroyed in the esterification process, as also suggested by SEM results.

The synthesis of starch esters in a homogeneous manner usually involved toxic solvents (for example, dimethyl sulfoxide and dimethylacetmamide) and corrosive reagents such as acid chlorides.[7,21,31–33] Although solvent-free reactions of starch with methyl esters have been reported, these reactions typically require the thermal pretreatment to initially swell the corn starch and yield low DS products.[34] In this study, the BMIMCl can efficiently dissolve the corn starch and provide feasible reaction environments for the esterification reaction. The homogeneous modification of starch relies upon the destructurization of the semicrystalline starch granules allowing starch hydroxyl groups freedom to react and thus resulting in formation of high DS products. According to the SEM and XRD profiles, the starch granules were mostly converted from their crystalline structure into amorphous state during the dissolution processes, which leads to the uniform esterification reaction to be conducted under homogeneous conditions. Moreover, it has been reported that the BMIMCl could efficiently dissolve corn starch and could disrupt a great amount of hydrogen bonds in starch.[15,17] A SEM micrograph of the starch regenerated from its solution in BMIMCl solvent showed a noticeable loss of ordered crystalline structure,[15] an important starch morphology modification required for its efficient functionalization. Therefore, the main benefit of our approach, when compared to heterogeneous esterification method, is the use of ILs as dissolving media that contributes to a high esterification degree.
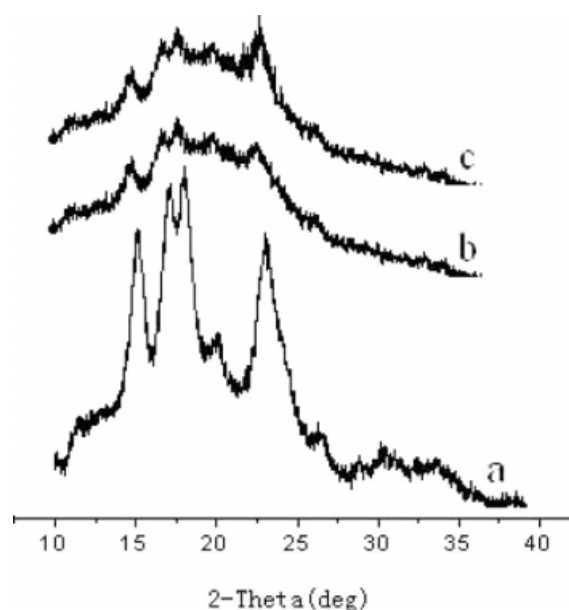

Figure 8 Power X-ray diffraction patterns of native corn starch (a), succinylated corn starch (b), and acetylated corn starch (c).

CONCLUSIONS

The esterification of corn starch with succinic anhydride or acetic anhydride using BMIMCl as reaction media was successfully accomplished in a homogeneous manner. The DS value of starch derivatives ranged from 0.03 to 0.93 for succinylated starch and from 0.37 to 2.35 for acetylated starch, respectively, and increased with the increment of reaction temperature from 70 to 100°C, reaction time from 1 to 4 h, and the molar ratio of anhydride/AGU in starch from 1 : 1 to 5 : 1. FTIR and NMR spectra analysis provided the evidence for the esterification reaction by the occurrence of the carbonyl signal. During the dissolution and functionalization of starch in the ILs, the crystallinity of the corn starch was largely disrupted. The chemical modification of starch in the ILs represents a suitable and effective method for the esterification of starch.

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