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Ionic liquids as solvents for dissolution of corn starch and homogeneous synthesis of fatty-acid starch esters without catalysts

Jing Gao[a,b], Zhi-Gang Luo[a,*], Fa-Xing Luo[a]

[a] Carbohydrate Lab, College of Light Industry and Food Science, South China University of Technology, Guangzhou, Guangdong 510640, PR China
[b] School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, Guangdong 510640, PR China

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ABSTRACT

Ionic liquids (ILs) utilized for dispersing cellulose have gained increasing attention in recent years, but the number of the reports using ILs for starch is still limited. In this study, 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) and 1-ethyl-3-methlyimidazolium acetate ([EMIM]AC) were used to dispersing corn starch. Dimethyl sulfoxide (DMSO), a traditional organic solvent for starch, was added into [BMIM]Cl, and the mixture of [BMIM]Cl/DMSO was utilized for dispersing corn starch as well. Results showed that the starch granules dispersed in ILs was much smaller than native starch granules, and large starch aggregates were partially formed. Starch granules dispersed in [BMIM]Cl at 100 °C for 60 min remained less crystallinity than native starch granules, while it was disappeared when starch granules were dispersed in [EMIM]AC at 100 °C for 60 min. Homogenous synthesis of fatty-acid starch esters without catalysts in these ILs was also studied. The degree of substitution (DS) value of starch laurate was reached to 0.053, 0.068 and 0.100 in [BMIM]Cl, [EMIM]AC and the mixture of [BMIM]Cl/DMSO, respectively, at the reaction conditions of lauric acid/AGU molar ratio 1:5, temperature 120 °C at a reaction time of 3 h.

1. Introduction

Starch is an abundant, inexpensive, renewable, and fully biodegradable natural material with a long and well-established technological base. Although composed simply of glucose polymer, the starch granule is a complex, semicrystalline structure. Much has been written over the last century concerning starch structure (Gallant, Bouchet, & Baldwin, 1997; Hoover, 2001; Tester, Karkalas, & Qi, 2004). Starch granules consist of alpha-glucan, amylase and amylopectin, which form linear polymer chains and hydrogen-bonded supramolecular structures. Starch is insoluble in water and in most common organic liquids. Thus, traditional modification to starch took place in heterogeneous system, including the preparation of fatty-acid starch esters (Aburto, Alric, & Borredon, 1999). Heterogeneous modifications of starches, in which starches are mostly in granular state, have many drawbacks including: instability in processing and a low degree of functionalization. In order to increase a degree of substitution, the starch esters were prepared in organic solvents, and catalysts were sometimes added to these synthesis systems (Junistia et al., 2008; Mathew & Abraham, 2007; Thiebaud et al., 1997). However, these organic solvents are volatile, not recyclable and have strong polarity, which cause serious degradation of the starch. Furthermore, catalysts such as pyridine were toxic and not recyclable. These disadvantages limited the development of starch modifications and their applications.

Homogeneous system was reported to be beneficial to carbohydrate modification (Fang, Fowler, Tomkinson, & Hill, 2002; Heinze & Liebert, 2011; Heinze, Talaba, & Heinze, 2000; McCormick & Lichatowich, 1979; Petzold, Koschella, Klemm, & Heublein, 2003). Recently, homogeneous reactions in green solvents have received a growing awareness. Molten salts with low melting temperature (<100 °C) are referred to as ionic liquids (ILs). In contrast to traditional volatile organic solvents, ILs have many attractive properties, such as chemical and thermal stability, non-flammability and immeasurable low vapor pressure. Many studies have reported that some hydrophilic ionic liquids could be used to dissolve cellulose and modify cellulose as a medium (Pinkert, Marsh, Pang, & Staiger, 2009; Swatloski, Spear, Holbrey, & Rogers, 2002; Zhu et al., 2006). However, only a few authors have investigated the dissolution of starch with ILs. Biswas and his group (Stevenson, Biswas, Jane, & Inglett, 2007) studied changes in structure and properties of four starches dispersed in1-butyl-3-methyl-imidazolium chloride ([BMIM]Cl). They also reported the use of ILs as reaction media for starch (Biswas, Shogren, Stevenson, Willett, & Bhowmik, 2006). The solution of starch in 1-butyl-3-methyl-imidazolium chloride ([BMIM]Cl) was found to acetylated with anhydrides in presence of pyridine to give acetylated starch with various DS. Wang and

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* Corresponding author. Tel.: +86 20 87113845, fax: +86 20 87113848.
E-mail address: zhgluo@scut.edu.cn (Z.-G. Luo).

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Xie (2010), Xie, Shao, and Liu (2011) and Xie and Wang (2011) investigated synthesis of starch esters in an ionic liquid using pyridine as a catalyst. However, this reaction system reported by these authors caused environmental pollution because of the toxicity and volatility of pyridine. Maltodextrin stearates with different DS were prepared in ionic liquid, 1-butyl-3-methylimidazolium dicyanamide (bmim[dca]) without the use of any catalysts (Biswas, Shogren, & Willett, 2009; Shogren, Biswas, & Willett, 2010). Ionic liquid could simultaneously act as a solvent and catalyst. Our research group has also reported the homogeneous synthesis of a high degree of substitution of starch acetates in ionic liquid without any catalysts (Luo & Zhou, 2012).

The aim of the present work was to study the structure changes of corn starch dispersed in IL [BMIM]Cl, [EMIM]AC, and the mixture of [BMIM]Cl/DMSO respectively, comparing with native corn starch and the starch dispersed in DMSO and DMF. Then the homogeneous synthesis of fatty-acid starch esters without catalysts in these solvents was also studied.

2. Materials and methods

2.1. Materials

Corn starch (approximately 25% amylase and 75% amylopectin) was obtained from DaCheng Corn Products, China. 1-Butyl-3-methylimidazolium chloride ([BMIM]Cl), 1-ethyl-3-methlyimidazolium acetate ([EMIM]AC) and 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF_6) were purchased from Centre for Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics, China. Lauric acid, palmitic acid and stearic acid were purchased from a local chemical company. All other chemicals were of analytical grade and used as received without purification.

2.2. Dissolution and precipitation of starch

To prepare a 10 wt% of starch solution, 1.0 g of corn starch was placed in a glass vial in an oil bath, and 10 g of ionic liquid was added, and then the system was stirred at desired conditions. The starch was precipitated from the IL solution by the addition of absolute ethanol. The dissolving processes were observed at 100× between crossed polarizer using an Olympus-BH-2 microscope.

2.3. Characterization of precipitated starch

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

X-ray diffraction (XRD) patterns were obtained with a RU200R X-ray diffractometer (Rigaku, Tokyo, Japan) with a chart speed of 20 mm min^{-1}. The starch powder was scanned through the 2θ range of 4–60°. Traces were obtained using a Cu-Kα radiation detector with a nickel filter and scintillation counter operating under the following conditions: 40 kV, 50 mA, 1°/1° divergence slit/scattering slit, 0.30 mm receiving slit, 1 s time constant, and scanning rate of 3°/min.

2.4. Preparation of fatty-acid starch esters in ILs

Dried corn starch was added into IL at a concentration of 10% (w/w) in a three-neck round flask fitted with a magnetic stirrer, which was continuously purged with gaseous N_2, and then heated in an oil bath and stirred thoroughly at 100 °C until a clear, colorless, viscous solution was obtained. Weighted lauric acid, palmitic acid and stearic acid were added, respectively. The mixture was stirred and heated at the desired temperatures. Upon completion of the reaction, the reaction mixture was cooled to room temperature and the starch esters were subsequently precipitated by addition of absolute ethanol under vigorous centrifugation. The precipitate was rewashed further several times to eliminate the residual IL, untreated reagents and byproducts. Finally, the solid was filtered and oven-dried at 40 °C in a vacuum for 48 h.

2.5. Determination of DS

Degree of substitution value of starch esters was determined according to the reported titration method (Varavinit, Chaokasem, & Shobsngob, 2001). A sample of 1 g dry fatty acid starch ester was accurately weighed and dispersed in 30 mL water containing 15 mL of 0.5 mol/L NaOH solution followed by vigorously stirring at room temperature for 4 h. Excess NaOH was then titrated to pH 7 with 0.1 mol/L HCl solution. Each sample was measured in triplicate. The DS value of starch ester was calculated by using the following equation:

$$\text{DS} = \frac{162 \quad \text{M}(V_0 - V)}{1000 \quad \text{W}} \tag{1}$$

where V_0 is the volume in milliliters of 0.1 mol L^{-1} HCl solution used for tirating the blank, V is the volume in milliliters of 0.1 mol L^{-1} HCl solution used for titrating the sample, M is the exact molarity of the used HCl solution, and W is the smaple weight in grams as a dry substance. 162 is the MW of the anhydroglucose unit.

2.6. Statistical analysis

All determinations were replicated three times and the mean values and their standard deviations were reported. Analyses of variance (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. Dispersion of starch in ionic liquid

Starch is composed of a mixture of amylose and amylopectin macromolecules consisting of (1 → 6)-α-D-glucopyranose repeating units. While amylose is essentially linear, amylopectin is highly branched via additional (1 → 6)-α linkages, with a cluster type structure (Manners, 1989; Souza & Andrade, 2002). When observed under polarized light, the starch granules show birefringence, which indicates a certain degree of molecular organization. Birefringence results form a directional ordering of the molecules on a scale at least as large as the wavelength of visible light such that the refractive indicates are difference in the *x*, *y* directions (Shogren et al., 2010).

Formulas of [BMIM]Cl, [BMIM]PF6, [EMIM]AC, DMSO and DMF are presented in Fig. 1. Polarizing micrographs of starch dissolved in [BMIM]PF_6, [BMIM]Cl, [EMIM]AC and DMSO at 100 °C and 120 °C for 30 min, respectively, are shown in Fig. 2. During the processes of dissolution, the structure of starch was changed in varying degrees. When heated at 100 °C for 30 min, starch granules dispersed in [BMIM]Cl, [BMIM]PF_6 and [EMIM]AC exhibited a well-defined birefringence pattern with a Maltese cross. When heated at 120 °C for 30 min, nearly all starch granules dispersed in [BMIM]PF_6 still assumed the clear Maltese cross, and partial starch granules dispersed in [BMIM]Cl remained Maltese cross. But, the birefringence of starch granules dispersed in [EMIM]AC at 120 °C for 30 min

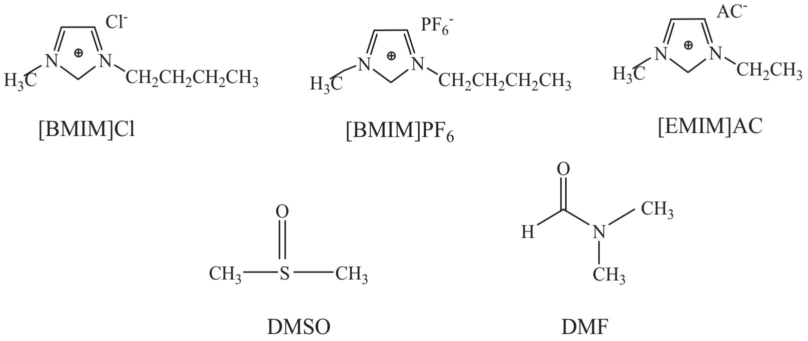

Fig. 1. Formulas of [BMIM]Cl, [BMIM]PF_6, [EMIM]AC, DMSO and DMF.

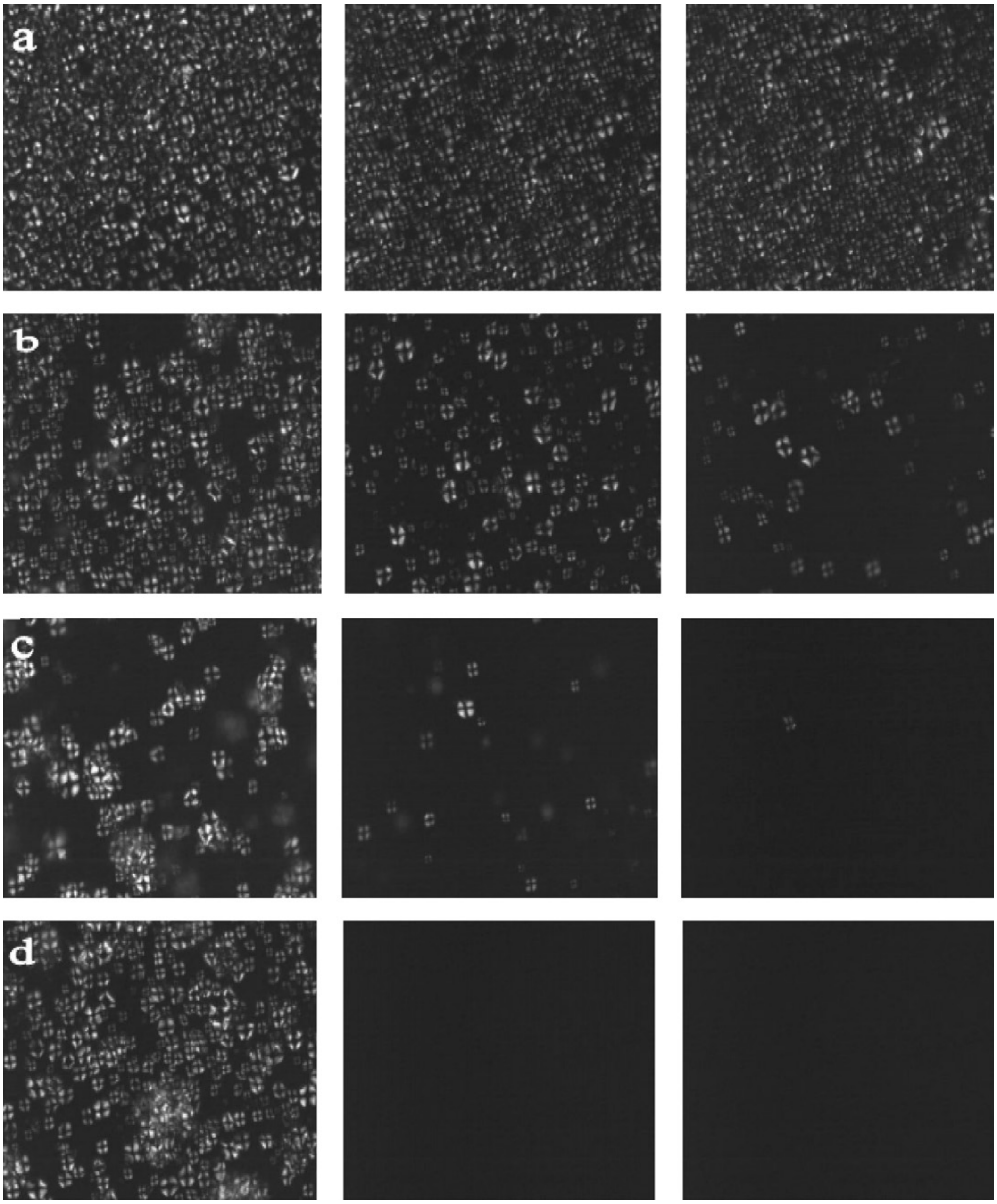

Fig. 2. Polarizing micrographs of starch dissolved in [BMIM]PF_6 (a), [BMIM]Cl (b), [EMIM]AC (c) and DMSO (d) at 100 °C for 0 min (left), 30 min (middle) and at 120 °C for 30 min (right).

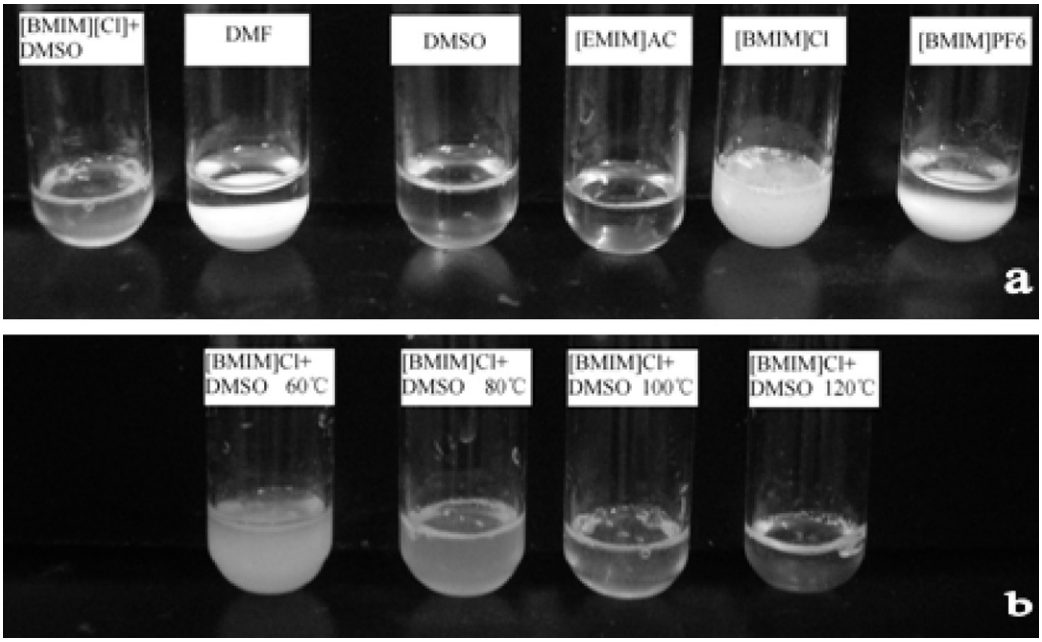

Fig. 3. Photos of starch dissolved in different solvents at 100 °C for 30 min (a) and in mixture of [BMIM]Cl and DMSO (1:1, w/w) at 60, 80, 100 and 120 °C for 30 min (b).

almost disappeared. In addition, the birefringence of all starch granules disappeared in DMSO when heated at 100 °C for 30 min. The results indicate that starch granules were hardly dissolved in [BMIM]PF_6, but [BMIM]Cl and [EMIM]AC were good solvents for starch, and the solubility of [EMIM]AC is better than [BMIM]Cl.

Photo of starch dispersed in different solvents at 100 °C for 30 min (Fig. 3a) shows that the solution of starch dispersed in both [BMIM]AC and DMSO was clear and transparent, and that starch dissolved in the mixture of [BMIM]Cl/DMSO (1: 1w/w) at partial degree, was hardly dissolved in [BMIM]PF_6 and DMF. The addition of a small quantity of DMSO was an effective method to decrease the high viscosity of starch/IL system. The photo of the mixture of [BMIM]Cl/DMSO (1:1, w/w) dissolving starch at 60, 80, 100 and 120 °C for 30 min is showed in Fig. 3b. It could be seen that the solution of starch and the mixture of the solution was gradually clear when the heating temperature was increased from 60 to 120 °C. Results indicate that the higher temperature will increase the dissolving degree of starch in the mixture whose dissolving ability was between [BMIM]Cl and DMSO.

As shown in Table 1, to disperse starch (10%, w/w) in IL completely, the system of starch/[BMIM]Cl should be heated at 100 °C for 60 min. Starch/[EMIM]AC should be heated at 100 °C for 45 min or at 120 °C for 30 min. Starch/[BMIM]Cl/DMSO should be heated and at 100 °C for 60 min or at 120 °C for 30 min.

Table 1
Dissolution of starch (10%, w/w) in ionic liquids and organic solvents.

Solvent	Time (min) (at 100 °C)						Temperature (°C) (for 30 min)			
	0	15	30	45	60	120	60	80	100	120
[BMIM]Cl	–	–	±	±	+	+	–	–	±	±
[EMIM]AC	–	±	±	+	+	+	–	–	±	+
[BMIM]PF_6	–	–	–	–	–	–	–	–	–	–
DMSO	–	±	+	+	+	+	–	±	±	+
DMF	–	–	–	–	–	–	–	–	–	–
[BMIM]Cl+ DMSO	–	–	±	±	+	+	–	±	±	+

–, starch was not dissolved; ±, starch was not dissolved completely; +, starch was dissolved completely.

For [BMIM]Cl and [BMIM]AC, the dissolution temperature had a notable effect on dissolution. The number of starch granules dissolved in solvent was increased with the increase of heating temperature, while starch was hardly dissolved in [BMIM]PF_6 though the heating temperature was high enough. The solubility of starch in hydroxyl ILs is depended on the polarity of anions and the bulk of cation in hydroxyl ILs. On one hand, the cation [EMIM] is smaller than [BMIM], which makes [EMIM]AC easier to attract with starch granules. On the other hand, the ability of anions of hydrogen bonds which are indispensable for the enhanced, and expanded polarity in these ILs is the following: $PF_6 < Cl < AC$ (Zhang, Qi, Ma, Lu, & Deng, 2010). Solubility is increased when the polarity of the solvents is also increased. The polarity of DMSO is the highest among these solvents, thus the ability to dissolve starch in these solvents is the following: [BMIM]PF_6 < [BMIM]Cl < [EMIM]AC < DMSO. It is important to emphasize that because of the recovery difficulty, volatility and toxicity, the commercial development and application of DMSO is limited.

3.2. *Microscopic observations of precipitated starch*

Scanning electron micrographs were used to reveal the granule morphology of native corn starch. The starch dispersed in [BMIM]Cl, [EMIM]AC and DMSO, respectively, at 100 °C for 60 min. As shown in Fig. 4a, granules of corn starch were round and polygonal in shape with various sizes. However, pictures of the starch dispersed in ionic liquids and DMSO showed remarkable difference in appearance compared to native starch. The starch granules dispersed in ILs [BMIM]Cl and [EMIM]AC (Fig. 4c and e) still had a clumping structure, but exhibited a much smaller size than the native starch. The granular structure of the starch dispersed in DMSO (Fig. 4g and h) was lost and exhibited small starch scraps.

The process of starch dispersed in ILs was very different from the process of starch dissolved in water. Almost all the granules swelled because of absorbing moisture and broke apart in the water at or before 80 °C, and had aggregates with little partition (Ratnayake & Jackson, 2006; Stevenson et al., 2007). When starch granules were dispersed in ILs, the ILs disrupted the intermolecular and intramolecular hydrogen bonds and sequentially destroyed

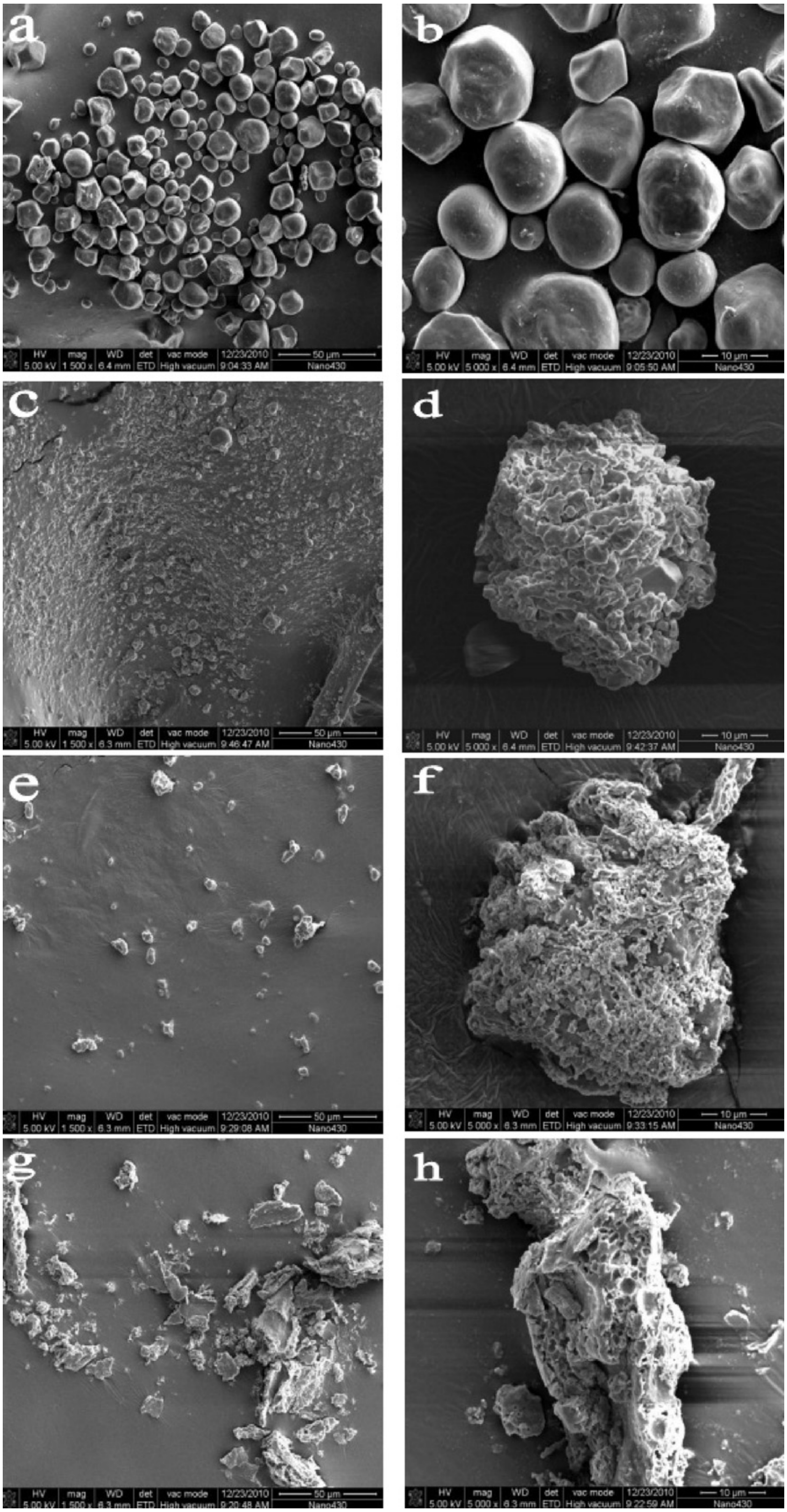

Fig. 4. SEM microphotographs of native maize starch (a and b) dissolved in [BMIM]Cl (c and d), [EMIM]AC (e and f) and DMSO (g and h) at 100 °C for 60 min.

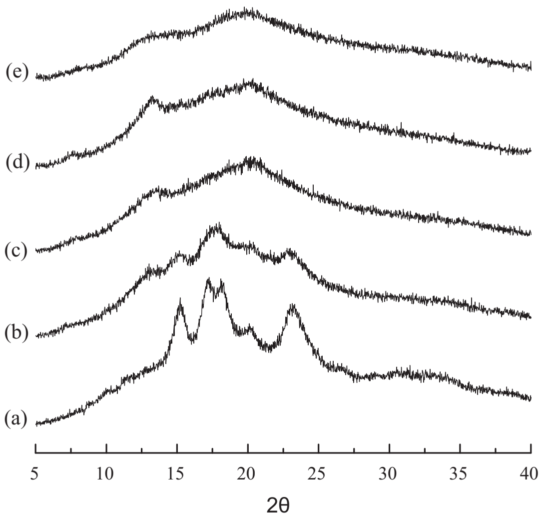

Fig. 5. XRD profile of native maize starch (a) and starch dispersed in [BMIM]Cl (b), DMF (c), DMSO (d) and [EMIM]AC (e) at 100 °C for 60 min.

the crystalline structure of starch granules. Such results were also reported in prior literatures (Biswas et al., 2006; Wang & Xie, 2010). Furthermore, starch granular dispersed in ILs fuse together to form large aggregates (Fig. 4d and f).

3.3. X-ray diffracton of precipitated starch

Both amylase chains and exterior chains of amylopectin in starch granules can form double helices which may in turn associate to form crystalline domains (Tester et al., 2004). XRD measurements were performed to check if solvents altered the crystallinity of starch.

XRD patterns of native starch and starch dispersed in [BMIM]Cl, [EMIM]AC DMF and DMSO, respectively, at 100 °C for 60 min are presented in Fig. 5. It could be found in this figure that native corn starch (Fig. 5a) exhibited a typical A-type X-ray diffraction pattern, giving strong reflections at about 15° and 23°, and unresolved doublet at nearly 17° and 18° (Kuo & Lai, 2007; Puchongkavarin, Bergthaller, Shobsngob, & Varavinit, 2003). However, the starch dispersed in [BMIM]Cl (Fig. 5b) showed much weaker reflections than native starch. The starch dispersed in DMF, DMSO and [EMIM]AC only had a dispersive broad peak and showed no crystal peak of starch (Fig. 5c–e), which implied that the crystallinity of native starch was damaged partially even completely during the dissolution processes. The crystallinity of starch dispersed in ILs varied with dissolution conditions. The starch dispersed in [BMIM]Cl/pyridine system (Xie et al., 2011) overnight at 100 °C still showed noticeable reflections, and they were much weaker than native starch. But the starch dispersed in [BMIM]Cl/methyl laurate and [BMIM]Cl/methyl stearate systems (Xie & Wang, 2011) at 110 °C for 2 h showed a broad peak without a crystal peak. The loss in crystallinity could be attributed to the effect that ILs weakened the inter- and intra-molecular hydrogen bonds. According to Fig. 5b and e, the effect of [EMIM]AC was more notable than [BMIM]Cl on destroying the molecular structure of starch granules. According to the SEM and XRD profiles, the starch granules were decomposed and mostly converted from a crystalline structure into amorphous state during the dissolution processes in ILs. In addition, compared with dissolution picture (Fig. 3a) and XRD (Fig. 5c) of DMF, it could be found that DMF could only dissolve a little starch but destroyed the crystalline structure of starch remarkably.

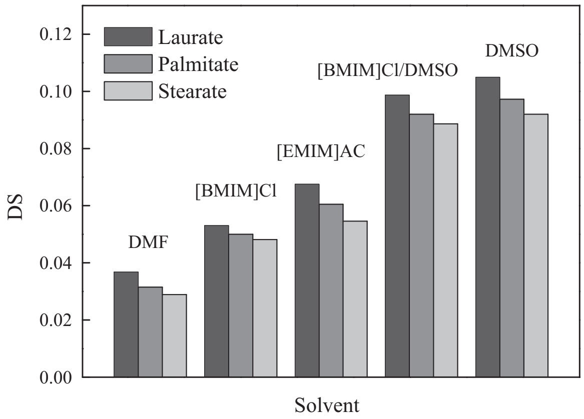

Fig. 6. Effects of fatty acid on DS in different solvents. Reaction conditions: fatty acid/AGU molar ratio 1:1, temperature 120 °C and reaction time 3 h.

3.4. Synthesis of fatty-acid starch esters

The destructurization of the semicrystalline starch granules could allow more starch hydroxyl groups to react with reagents in homogeneous modification system, thus this result in formation of high DS products even though they are without catalysts. According to the previous study, the starch was dissolved completely in [BMIM]Cl, [EMIM]AC and the mixture of [BMIM]Cl/DMSO at 100 °C for 60 min.

The influence of solvent on DS values of fatty-acid starch esters is shown in Fig. 6. [EMIM]AC was found to reach a higher DS value than [BMIM]Cl as a reaction medium. The DS value was increased in the mixture of [BMIM]Cl/DMSO, because the destructurization of starch granules is enhanced and the viscosity of the reaction system is decreased by the addition of DMSO. The lower viscosity increases the fluidity of reagents in the reaction system. Thus, the addition of DMSO in [BMIM]Cl played an important role in reaction processes. Furthermore, it could be observed that the DS value of starch laurate was the highest and DS value of starch stearate was the lowest, which is in accordance with their relative molecular weight.

The influence of reaction temperature on the DS values of fatty-acid starch esters is presented in Fig. 7. The DS value of starch laurate was increased from 100 °C to 120 °C. However, it was decreased when the reaction temperature was increased to 140 °C. The reason for this result could be due to the degradation of starch at a higher temperature. A similar tendency was also reported in other literature (Grote & Heinze, 2005; Xie & Wang, 2011).

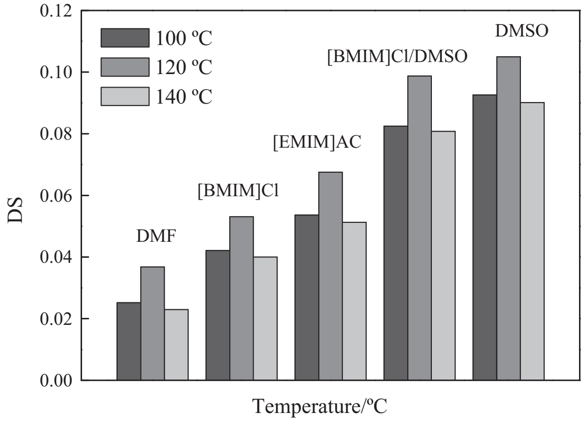

Fig. 7. Effects of temperature on DS values in different solvents. Reaction conditions: lauric acid/AGU molar ratio, 1:5; [BMIM]Cl/DMSO ratio, 3:1; temperature 120 °C; and reaction time 3 h.

4. Conclusion

Corn starch was completely dissolved in [BMIM]Cl and [EMIM]AC at 100 °C for 60 min. [EMIM]AC was a better solvent for starch than [BMIM]Cl. The size of starch granules dispersed in ILs was smaller than native starch, but some large starch aggregates was formed during the dispersed processes. The starch granules dispersed in [BMIM]Cl at 100 °C for 60 min showed less crystallinity than native starch granules. The crystallinity disappeared when the starch granules was dispersed in [EMIM]AC, DMSO and DMF. Furthermore, the addition of DMSO could increase the dissolubility of ILs, but too much DMSO could seriously destroy the structure of starch granules, which hinders the application of these starch products in industry.

The esterification of corn starch with lauric acid, palmitic acid and stearic acid using [BMIM]Cl, [EMIM]AC and the mixture of [BMIM]Cl/DMSO, respectively, were successfully accomplished in a homogeneous system without catalysts. The DS value of starch laurate was the highest, and reached to 0.053, 0.068 and 0.10 when [BMIM]Cl, [EMIM]AC and the mixture of [BMIM]Cl/DMSO were the reaction medium, respectively, and the reaction condition is lauric acid/AGU molar ratio 1:5, temperature 120 °C at a reaction time of 3 h.

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