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The fabrication and the properties of pretreated corn starch laurate

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ABSTRACT

The pretreated corn starch (PCS) were coagulated from a NaOH/urea/H_2O solution of native corn starch (NCS) using ethanol as the precipitant. NCS laurate (NCSL) and PCS laurate (PCSL) were fabricated by transesterification with methyl laurate under solvent-free conditions. The esterification was characterized by Fourier transform infrared (FT-IR) spectroscopy and Solid carbon nuclear magnetic resonance (^{13}C NMR) studies. Scanning electron microscopy (SEM) showed that the size of most PCS and PCSL were, respectively, about 500 and 50–100 nm. X-ray diffraction revealed that the NaOH/urea pretreatment changed the crystalline pattern and the esterification primarily occurred in amorphous domain. The smaller size and more amorphous domain of PCS improved the degree of substitution (DS) and reaction efficiency (RE) of PCSL. With the increasing of DS, PCSL exhibited the better water resistance, and it was not gelatinized in hot water. PCSL also could produce the oil/water emulsions with excellent stability.

1. Introduction

Starch is cheap, abundantly available and useful in a number of areas, such as thickeners, coatings, detergents and emulsion stabilizers (Shogren & Biresaw, 2007). However, the hydrophilic feature of starch seriously limits the development of starch-based materials. Therefore, chemical derivations such as etherification, esterification, oxidation, grafted and crosslinked reaction, have been studied to expand the application of starch.

The esterification of starch is an effective method to introduce different side groups into the starch molecule. However, the starch esters are generally prepared by reacting starch with fatty acid chlorides in organic solvents such as pyridine, toluene, or dimethylacetamide (Aburto, Alric, Thiebaud, & Borredon, 1999a; Grote & Heinze, 2005; Neumann, Wiege, & Warwel, 2002). The fatty acid chloride is relatively expensive and corrosive. Recently, starch laurate and starch stearate are prepared by reacting the starch with vinyl laurate or vinyl stearate in the presence of alkali catalysts in DMSO (Junistia, Sugih, Manurung, & Picchioni, 2008). Despite the high DS of starch in the above organic solvents, the utilization of toxic reagents should be especially prohibited in the food application. Aburto, Alric, and Borredon (1999b) and Aburto, Hamaili, and Mouysset-Baziard (1999c) gelatinize starch with formic acid, and then react with fatty acid chlorides in the absence of organic solvent, however, the obtained mixture of formate–fatty acid ester of starch is hard to treat and the fatty acid ester degrades rapidly in an acid medium. An improved method is the transesterification with lauric acid methyl ester rather than toxic acyl chloride involving thermal pretreatment and using potassium laurate as catalyst without any solvent (Aburto, Alric, & Borredon, 2005), but the catalyst is hard to remove and DS is low.

Due to the special semi-crystalline structure of starch granules, the reagents cannot readily penetrate into the interior of the granules. As a consequence, reactions often take place only on the surface of the starch granules, and the reaction efficiency of native starch is usually low (Huang, Xie, & Chen, 2008). Therefore, there is great interest in methods to modify the structure in the crystalline region, or decrease the size of crystalline regions (Huang, Lu, Li, & Tong, 2007), which generally include physical processes such as ball-milling treatment (Huang et al., 2008), heat–moisture treatment (Pukkahuta & Varavinit, 2007), radioactive degradation (Yu & Wang, 2007), microwave degradation (Luo, He, & Fu, 2006), ultrasonic degradation (Huang, Li, & Fu, 2007) and chemical processes such as enzymatic degradation (Shariffa, Karim, & Fazilah, 2009), acid hydrolysis (Gunaratne & Corke, 2007) and alkaline hydrolysis (Karim, Nadiha, & Chen, 2008).

Several studies have been carried out on the alkali gelatinization of starch. As a good solvent, strong aqueous alkali is used to dissolve starch and prevent molecular aggregation of starch molecules (Kim & Huber, 2007). And NaOH/urea aqueous solution is an economical and environmentally friendly solvent of cellulose. It has been reported that cellulose could be rapidly dissolved in 7 wt.% NaOH/12 wt.% urea aqueous solution pre-cooled to −12 °C without derivatization (Cai & Zhang, 2006). And the cellulose samples with viscosity-average molecular weight below

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10.0×10^4 exhibit good solubility in aqueous NaOH/urea pre-cooled to -12.6 °C. Moreover, the solubility of the cellulose could be enhanced by decreasing the crystallinity of cellulose (Qi, Chang, & Zhang, 2008).

The present work pretreated corn starch with NaOH/urea solution and further examined the influence of pretreatment on crystal structure. In order to investigate the influence of the pretreatment on chemical reactivity, the esterification was carried out by transesterification with methyl laurate without any solvent. The higher DS and RE values of PCSL indicated that the pretreatment increased the chemical activity. The PCS laurate (PCSL) was characterized by FT-IR, ^{13}C NMR, SEM, X-ray diffractometry. This work also studied the hydrophobicity, pasting properties and emulsion stability of PCSL, which can be act as emulsion stabilizer.

2. Materials and methods

2.1. Materials

Native corn starch (NCS) was obtained from the Langfang Starch Company (Langfang, Hebei, China). Methyl laurate, hydrochloric acid, ethanol, sodium hydroxide and urea (analytical grade) were purchased from Tianjin Chemical Reagent Factory (Tianjin, China).

2.2. The preparation of PCS

The mixture of sodium hydroxide, urea and distilled water was pre-cooled, and then a certain amount of dried starch was immersed immediately in the pre-cooled solvent and stirred until a homogeneous and thick gelatin was obtained. The gelatin was adjusted to pH 7 by adding hydrochloric acid. Ethanol was then added dropwise into it. Starch was precipitated and washed for several times with ethanol/H_2O, then oven-dried at 50 °C under vacuum for 12 h. The dried PCS was used for testing.

2.3. The preparation of NCSL and PCSL

Methyl laurate (2.31, 4.62, 6.93, 9.24, 13.86 g) was dissolved in 20 ml of ethanol. Then 7 g of dried starch (NCS and PCS, molar ratios of methyl laurate/D-glucose unit = 0.25, 0.5, 0.75, 1.0, 1.5) was slowly added to obtain a slurry and thoroughly mixed. The slurry was heated in vacuum ovens at about 2 mm Hg and 50 °C for 6 h to remove ethanol. The obtained mixture was ground and heated in an oven at 130 °C for various times at (30, 35, 40, 45 h). When the reaction was completed, hot ethanol (50 ml) was added to remove unreacted methyl laurate and precipitated starch laurate (NCSL and PCSL) was filtered by suction with washing twice with 50 ml hot ethanol, and dried at 50 °C in vacuum for 24 h. The dried NCSL and PCSL were used for testing.

2.4. Determination of DS

DS is the number of laurate per anhydroglucose unit (AGU) of starch. DS was determined using the method of Kshirsagar and Singhal (2007) with minor modification. Approximately 1.0 g of dry starch ester was accurately weighed and placed into a 50 ml conical flask. Then 10 ml water and 5 ml 0.5 M NaOH was added, and the conical flask was agitated with a magnetic stirrer at room temperature (30 ± 2 °C) overnight. The excess alkali was back-titrated with a standard 0.1 N HCl and retitrated 2 h later to account for any further alkali that may have leached from the starch. Each sample was measured in triplicate.

The DS of starch laurate (NCSL and PCSL) was calculated according to the Eq. (1).

$$W = \frac{(\text{Blank-Sample}) \times M \times N \times 100}{\text{Weight of the sample,g} \times 1000}$$
$$\text{DS} = \frac{162 \times W}{100 \times M - (M-1) \times W} \tag{1}$$

where W (%) is the mass fraction of methyl laurate; Blank is the volume (ml) of HCl required for blank titration; Sample is the volume (ml) of HCl required for sample titration; N is 0.1N, the concentration of HCl solution; M is 214, molecular weight of methyl laurate.

The reaction efficiency (RE) was calculated by the reaction (2).

$$\text{RE} = \frac{\text{Actual DS}}{\text{Theoretical DS}} \times 100\% \tag{2}$$

The theoretical DS was calculated assuming that all of the added methyl laurate reacted with starch to form the starch laurate.

2.5. Fourier transform infrared (FT-IR) spectroscopy

NCS, NCSL, PCS and PCSL powders were measured with a BIO-RAD FTS3000 IR Spectrum Scanner.

2.6. ^{13}C solid state nuclear magnetic resonance (solid state ^{13}C NMR) spectra

The Solid state ^{13}C NMR spectra were recorded on Infinity Plus 300 MHz spectrometer. ^{13}C NMR of PCSL (DS = 0.3543): δ15.1 (C18), 19.2 (C9–17), 31.2 (C8), 60.6 (C6), 72.7 (C2, 3, 5), 82.1 (C4), 103.1 (C1), 175.0 ppm (C=O).

2.7. Scanning electron microscopy (SEM)

Samples of NCS, PCS and PCSL were prepared from a drop of a dilute suspension, which was deposited and let dry on a formvar grid, and examined using a Nanosem 430 Scanning Electron Microscope.

2.8. X-ray diffraction

X-ray diffraction patterns were recorded in the reflection mode in the angular range 10–30° (2θ) at ambient temperature by a BDX3300 diffractometer, operated at the Cu $K\alpha$ wavelength of 1.542 Å. Radiation from the anode, operated at 36 kV and 20 mA, monochromized with a 15 μm nickel foil. The diffractometer was equipped with 1° divergence slit, a 16 mm beam bask, a 0.2 mm receiving slit, and a 1° scatter slit. Radiation was detected with a proportional detector.

2.9. Water absorption measurement

Samples were stored in a desiccator containing saturated sodium chloride to provide a constant RH of 75% at 25 °C. When the samples were stored for a period of time, water contents were calculated on the basis of original weight w_0, current weight w and α_0. Water content α is calculated with Eq. (3).

$$\alpha = \frac{w}{w_0}(1 + \alpha_0) - 1 \tag{3}$$

2.10. Pasting properties

The pasting properties were determined on a Rapid Visco Analyser (Newport Scientific, Sydney, Australia) according to AACC method 76–21 (Angellier, Choisnard, & Molina-Boisseau, 2004). 2.5 g NCS, PCS and PCSL particles were dispersed into 25 ml of distilled water. The starch slurry was kept at 50 °C for 1 min, then heated to 95 °C at 12.2 °C/min and held at 95 °C for 2.5 min. It was then cooled to 50 °C (cooling rate of 11.8 °C/min) and kept at 50 °C for 2 min. The paddle speed was 960 rpm for 10 s and then decreased to 160 rpm for the remainder of the experiment.

2.11. Emulsification assay

The method was adapted from Shogren and Biresaw (2007). Emulsions were prepared by blending 10 ml soybean oil, 90 ml water and 0.5 g emulsifier in a shear homogenizer at 5000 rpm for 3 min. Emulsions were then poured into 150 ml graduated cylinders and volumes of separated oil and cream phases after 1 min, 1 h and 24 h were measured.

2.12. Statistical methods

DS, water absorption and emulsification were replicated three times and the mean values were calculated.

3. Results and discussion

3.1. Preparation of NCSL and PCSL

3.1.1. Effect of the pretreatment on the chemical activity of starch

The DS and RE of NCSL prepared at 130 °C for 35 h with the molar ratio (mole of methyl laurate/mole of D-glucose unit) of 0.5 are both zero, while the DS and RE of PCSL prepared at the same experimental condition was 0.3543% and 70.86%. The results indicated that the NaOH/urea pretreatment increased the chemical activity of starch.

3.1.2. Effect of reaction time and molar ratio of methyl laurate/D-glucose unit on esterificaton of PCS

The effect of reaction time and molar ratio of methyl laurate/D-glucose unit on DS and RE is shown in Table 1. With the increasing of the reaction time from 30 to 35 h, DS and RE were increased. When the reaction time was beyond 35 h, DS and RE decreased. In the reaction, the methyl laurate was gradually depleted and the PCSL was decomposed at higher temperature, thus the optimum reaction time was 35 h at the molar ratio 0.5 of methyl laurate/D-glucose unit. When the molar ratio increased from 0.25 to 1.5, the DS increased, the RE reached a maximum value of 88.89% at the molar ratio of 0.5.

3.2. Properties of PCSL

3.2.1. Fourier transform infrared (FT-IR) spectroscopy

The FT-IR spectra of NCS, NCSL, PCS and PCSL powders are shown in Fig. 1. Compared to NCS, NCSL exhibited no new peak, which indicated that NCS was not esterified at 130 °C for 35 h when the molar ratio was 0.5. At the same experimental conditions, PCS could react with methyl laurate. A new peak at 1730 cm^{-1} was ascribed to the characteristic peak of ester groups. It indicated that chemical reactivity of PCS was higher than NCS due to the decrease of starch crystallinity, the smaller granular size and the increase of the surface area. The peak at about 1010 cm^{-1} was attributed to C–O bond stretching of the C–O–C group in the anhydroglucose ring, which, respectively, appeared at 1010, 1020 and 1030 cm^{-1} for NCS, PCS and PCSL. It has been reported that if C–O bond stretching was shifted red, the hydrogen-bond interaction could weaken (Huang, Yu, & Ma, 2004). When NCS was pretreated with NaOH/urea, the hydrogen-bond interaction was weakened in PCS, which was propitious to the esterification between PCS and methyl laurate. After being esterified, the hydrogen-bond interaction was further weakened in PCSL.

Table 1
The effect of reaction time and methyl laurate/PCS molar ratio on DS and RE of PCSL at 130 °C.

Time(h)	Methyl laurate/PCS molar ratio	DS	RE (%)
30	0.5	0.3153	63.06
35	0.25	0.165	66
35	0.5	0.3543	70.86
35	0.75	0.6667	88.89
35	1	0.6776	67.76
35	1.5	0.7034	46.89
40	0.5	0.3	60
45	0.5	0.2673	53.46

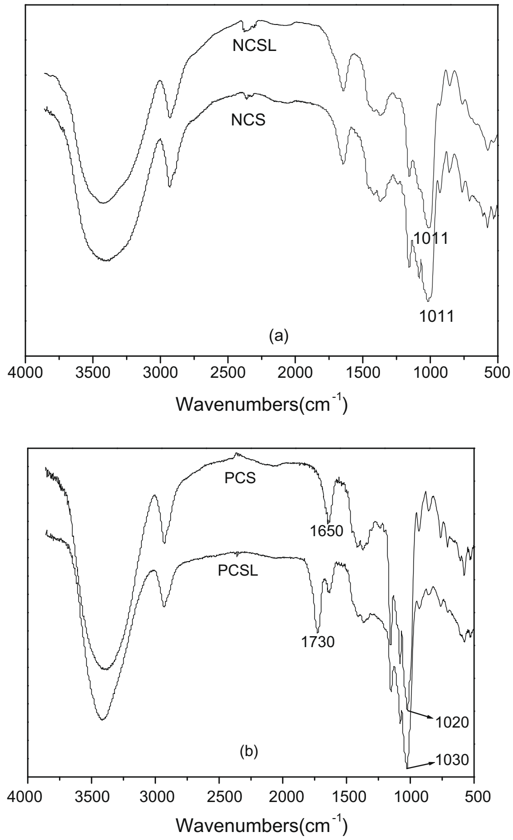

Fig. 1. FT-IR spectrum of NCS, NCSL, PCS and PCSL$_{(DS=0.3543)}$.

3.2.2. Solid state ^{13}C NMR spectra

Typical ^{13}C NMR spectra of PCS and PCSL (DS = 0.3543) are given in Fig. 2. Clearly visible are the carbon resonances of the fatty ester chains (δ10–35 ppm) and the C atom of the ester group (δ170–175 ppm). The presence of peaks arising from the fatty ester chains clearly indicated that the esterification of PCS with methyl laurate was successful.

3.2.3. Scanning electron microscopy (SEM)

Scanning electron photomicrographs of NCS, PCS and PCSL particles are presented in Fig. 3. SEM investigations showed that the NaOH/urea pretreatment caused some changes in the granularity of starch as compared with native starch. The PCS showed no pores or cracks but the granularity became smaller (about 500 nm). When starch was immersed in the pre-cooled NaOH/urea solution, the hydrogen bond between the starch macromolecules and the solvent molecules was formed, bringing starch into the aqueous solution and formed a starch gelatin (Qi et al., 2008). The addition of ethanol by dropwise into the gelatin resulted in the precipitation of the nanoparticles. It was known that the stability of the nano-

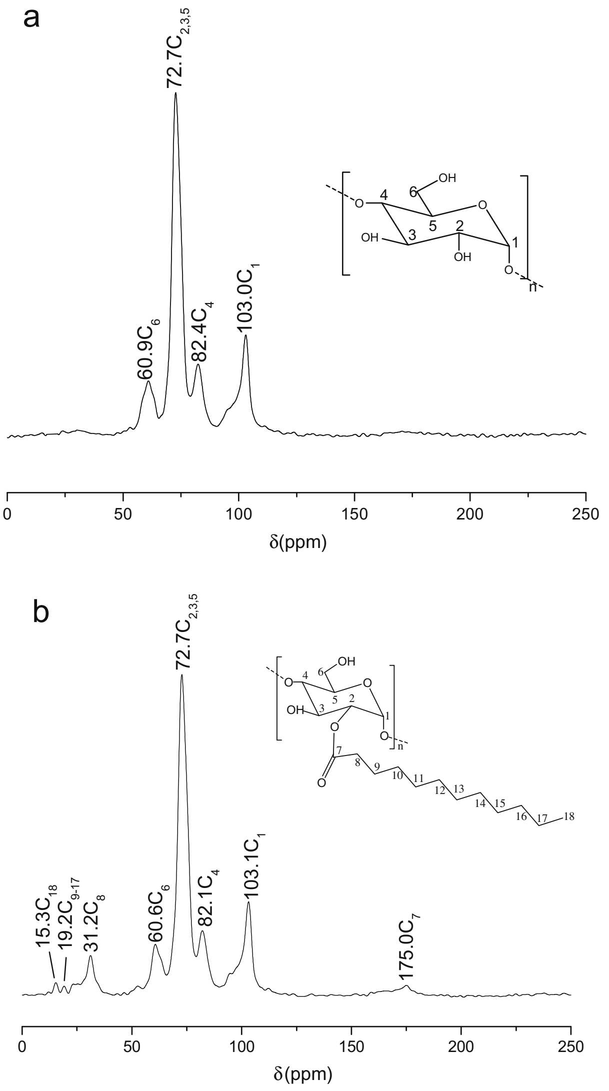

Fig. 2. Solid state ^{13}C NMR spectra of NCS (a) and PCSL (b) $_{(DS=0.3543)}$.

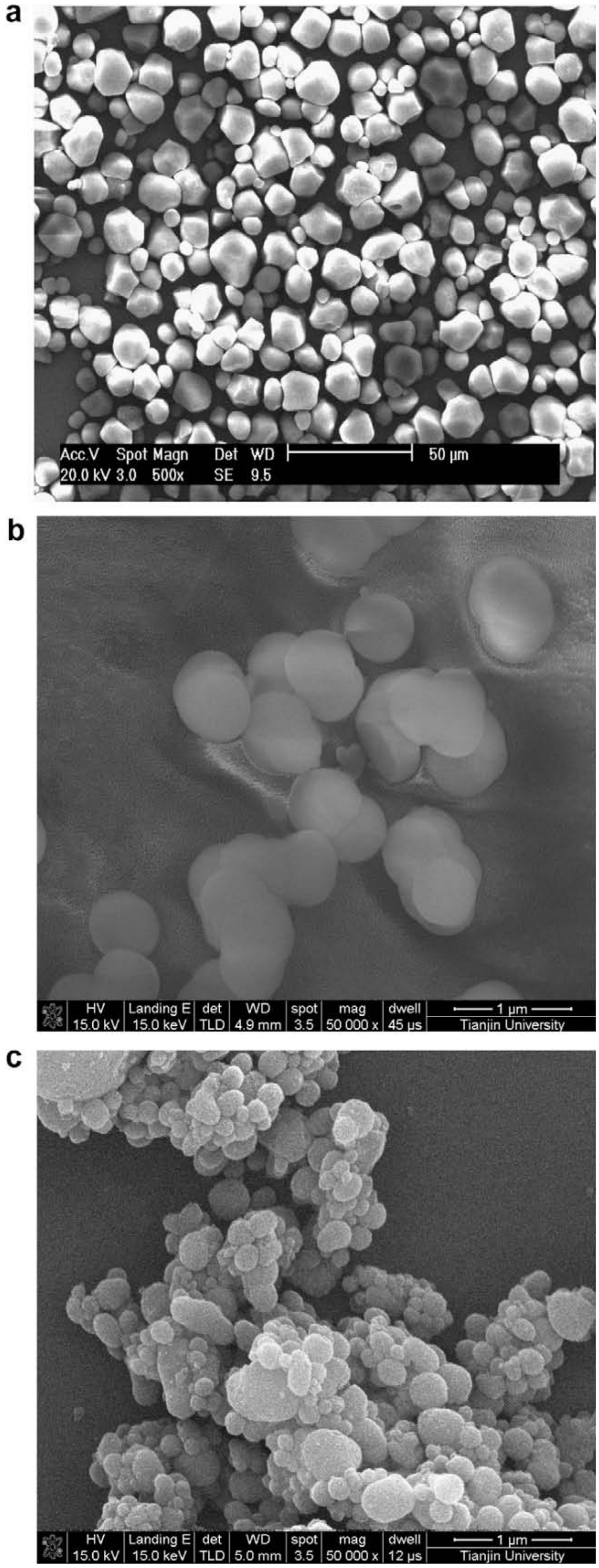

Fig. 3. SEM micrograph of NCS (×500, a), PCS (×50000, b) and PCSL$_{(DS=0.3543)}$ (×50000, c).

particle suspensions was important prerequisites for preparing these nanoparticles. The interaction of hydrogen bond between PCS and starch pasting played the important role on the stability of the precipitated nanoparticles in the suspension (Ma, Jian, & Chang, 2008). The esterification of PCS with methyl laurate seemed not damage the PCS. The PCSL was smooth but the size of most PCSL was about 100 nm. It seemed that the esterification decreased the aggregation of PCS, which was similar to citric acid-modified starch nanoparticles (Ma et al., 2008).

3.2.4. X-ray diffraction

X-ray diffraction is performed to investigate the change of the crystallinity. X-ray diffraction spectra of NCS, PCS and PCSL are presented in Fig. 4. NCS exhibited an A-type crystallinity pattern (Puchongkavarin & Bergthaller, 2003), while the crystallinity degree of PCS decreased and the crystallinity pattern of PCS was converted into V_H style, which could originate from a single-helical structure “inclusion complex” made up of starch molecules and ethanol (Van Soest & Vliegenthart, 1997). When starch was in NaOH/urea solution, the starch granule was gelatinized which led to uncoiling or dissociation of double-helical regions and the breakup of crystalline structure (Chen & Jane, 1994). The neutralization and the addition of ethanol by dropwise enabled the starch molecules to form single-helical complexes with ethanol (V-complex). In Ma’s reports, the starch nanoparticles also exhibited the V_H-style crystallinity (Ma et al., 2008). PCSL and PCS displayed similar X-ray

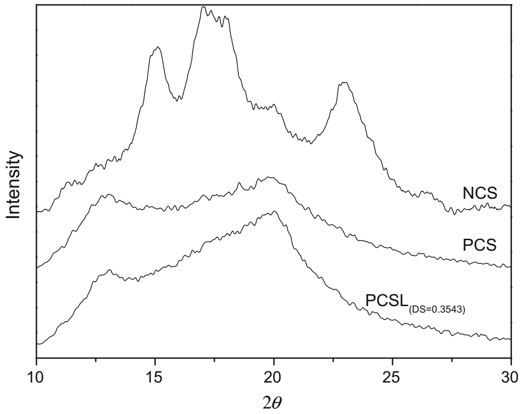

Fig. 4. X-ray diffractograms of NCS, PCS and PCSL$_{(DS=0.3543)}$.

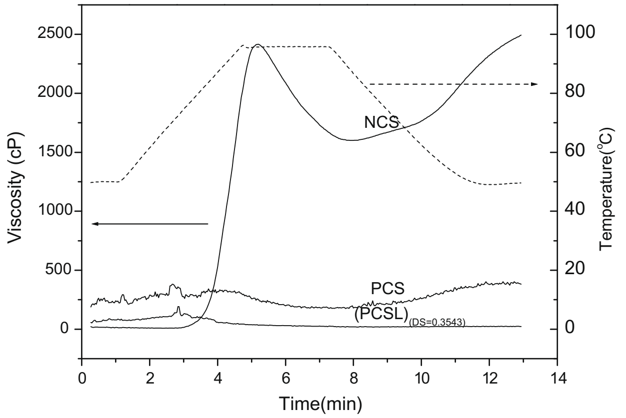

Fig. 6. Pasting curves of NCS, PCS and PCSL$_{(DS=0.3543)}$. The top curve (dash dot line) is the temperature profile.

reflections. This observation showed that esterification mainly occurred primarily in amorphous domain, and did not change the crystalline pattern of PCS.

3.2.5. Water absorption

Water absorptions of PCS and PCSL with different DS are depicted in Fig. 5. PCS and PCSL reached the balance of water absorption when they were stored at the environment of RH 75% for about 24 h. With the increasing of DS, water absorption of PCSL at the balance decreased. Since the hydrophilic hydroxyl groups of starch were partially replaced with hydrophobic ester groups, PCSL with higher DS exhibited the lower water absorption. This was consistent with the research of Kapusniak & Siemion (2007), in which the water binding capacity of starch linoleic acid ester decreased when the degree of esterification increased.

3.2.6. Pasting properties

In the presence of water and heat, starch granules were swollen by absorbing water, the granules began to break down, and the gelation formed during cooling. The RVA pasting curves of NCS, PCS, and PCSL are shown in Fig. 6. NCS exhibited a characteristic pasting curve of native starch with gelatinization temperature (78 °C), peak viscosity (2417 cP), breakdown (817 cP) and final viscosity (2496 cP). PCS revealed a different pasting curve with lower viscosity. Because the NaOH/urea pretreatment degraded the crystalline regions of the starch, PCS in the size of nanometer could completely dissolve into water even at the far lower temperature than gelatinization temperature of NCS. The viscosity of PCS aqueous solution changed less during the heating cycle (Ma et al., 2008). The pasting curve of PCSL was flat with a lower viscosity than PCS. It indicated that PCSL did not gelatinize during the test process. The esterification introduced hydrophobic long-chain fatty acid chain, increased the hydrophobic of starch, and also resisted the starch gelatinization.

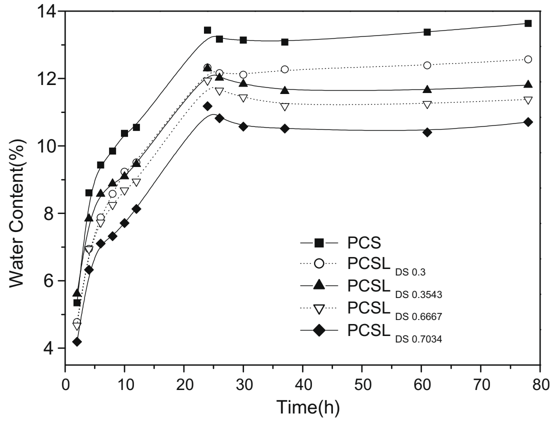

Fig. 5. Water absorption versus time of PCS and PCSL.

3.2.7. Emulsification properties

Emulsification activities for PCSL and Tween 20, a typical synthetic surfactant at 0.5 wt.%, are shown in Table 2. Oil and water separated rapidly for the control test without any surfactant. PCSL with DS of 0.165 displayed considerable emulsifying ability. For the emulsions of the oil/water type, PCSL exhibited high stability, as no oil was separated after the emulsion was stored for 24 h. The emulsion stability could be ascribed to the hydrophilic/hydrophobic balance governed by the type, amount, and distribution of the hydrophobic substituent, the molecular structure and hydrodynamic properties of the surfactants (Rouzes, Durand, & Leonard, 2002). Therefore, the introduction of the hydrophobic long fatty acid chains to the hydrophilic starch chain increased the interactions between the oil phases and the hydrophobic chains, thus led to the increase of emulsion stability of PCSL (Viswanathan, 1999).

4. Conclusions

NCS was pretreated with NaOH/urea solution by adding ethanol dropwise, and the obtained PCS was about 500 nm in size and exhibited V_H type pattern. NaOH/urea pretreatment of NCS could increase the chemical reactivity which probably due to the lower crystallinity, smaller size and larger surface area of PCS. The presence of a hydrophobic group in the PCSL resisted the starch gelatinization and allowed it to emulsify oil phases and produced emulsions of the oil/water type with excellent stability, comparable to the commercial emulsifier Tween 20. It could be used as food emulsifier. The pretreatment methods of starch and the esterifica-

Table 2
Emulsification of soybean oil/water with PCSL$_{(DS=0.165)}$.

	Oil/cream volumes (ml)		
	1 min	1 h	24 h
0[a,b]	7/0	7/7	10/0
PCSL	0/0	0/6	0/6
Tween 20[b]	0/0	1/0	1/10

[a] Control sample (oil, water only).

[b] The data of Shogren (Shogren & Biresaw, 2007).

tion were in full compliance with the principles of green chemistry. It could also be applied to other natural polysaccharides such as cellulose.

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