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Effect of acetylation on the properties of corn starch

Hui Chi [a], Kun Xu [b], Xiuli Wu [a], Qiang Chen [b], Donghua Xue [a], Chunlei Song [b], Wende Zhang [b], Pixin Wang [b,*]

[a] School of Biological Engineering, Changchun University of Technology, Changchun, Jilin 130012, PR China
[b] Polymer Engineering Laboratory, Changchun Institute of Applied Chemistry, Changchun, Jilin 130012, PR China

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Abstract

Acetylated corn starches with different degrees of substitution (DS 0.85, DS 1.78, DS 2.89) were synthesized by the reaction of corn starch with acetic anhydride in the presence of acetic acid under varying reaction temperatures. The product was characterized by FTIR spectroscopy, ^{1}H NMR, X-ray diffraction and contact angle measurement. Acid-base titration and ^{1}H NMR methods were employed to determine the degree of substitution of product. FTIR spectroscopic analysis showed that the characteristic absorption intensities of esterified starch increased with increase in the degree of substitution, and the characterized peak of hydroxyl group almost disappeared in the spectrum of DS 2.89 acetylated starch. The detailed chemical microstructure of native starch and acetylated starch was confirmed by ^{1}H NMR, ^{13}C NMR and ^{13}C–^{1}H COSY spectra. Analysis of ^{1}H NMR spectra of acetylated starches was assigned accurately. Strong peaks in X-ray diffraction of acetylated starch revealed that new crystalline regions were formed. Compared with native starch, the hydrophobic performance of acetylated starch esters was increased. The contact angle of acetylated starch with DS 2.89 was 68.2°.

Keywords: Corn starch; Acetylated starch; High degree of substitute; Structure

1. Introduction

Starch is an abundant, inexpensive, naturally renewable polysaccharide, which finds wide application in diverse areas of polymer science. Starch has been used successfully as a polymer in the packaging industry. It readily biodegrades in soil. However, native starch has several disadvantages such as poor processability and solubility in common organic solvents which limit its wide applications. Therefore, modification of starch, physically or chemically, has been extensively studied.

Chemical modifications of starch including esterification are efficacious methods to improve the properties of starch. Acetylated starch is a starch ester that has been extensively studied over the last two decades (Jatowenko, 1986; Lammers, Tiitola, & Vuorenpaa, 1998; Reinisch, Radics, & Roatsch, 1995; Wang & Wang, 2002; Wolff, Olds, & Hilbert, 1951). In modified starch, part of hydroxyl groups in anhydroglucose units have been converted to acetyl groups. A low degree of substitution (DS) with 0.01–0.2 acetylated starch has been applied in many areas, such as film forming, binding, adhesion, thickening, stabilizing and texturing (Boutboul, Giampaoli, Feigenbaum, & Ducruet, 2002; Matti et al., 2004). Acetylated starch with low DS is commonly obtained by esterification of native starch with acetic anhydride in an aqueous medium in the presence of an alkaline catalyst. However, high DS acetylated starches have received much attention in recent years for their solubility in acetone and chloroform and for their thermoplasticity. Also, high DS acetylated starches can have very different properties such as hydrophobicity, melt processibility and a number of non-food applications such as tablet binders, hot melt adhesives, coating, cigarette filters, biodegradable packaging materials and pharmaceutical aspects have been suggested

* Corresponding author. Tel./fax: +86 431 85262629.
E-mail address: pxwang@ciac.jl.cn (P. Wang).

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(Aburto, Alric, Thiebaud, Borredon, Bikiaris, Prinos, & Panayiotou (1999a); Aburto et al., 1999b; Derradji-Serghat et al., 1999; Fang et al., 2002; Mark and Mehltretter, 1972; Shogren, 2003). Shogren (2003) prepared a series of starch esters, such as acetylated starches by high temperature and pressure reaction. Mehltretter and Mark (1974) prepared highly acetylated starch by reaction with excess acetic anhydride and using sodium hydroxide as the catalyst (Mehltretter & Mark, 1974). However, at present, there are few reports available on the structural characterization of acetylated starch. Laignel, Bliaed, Massiot, and Nuzillard (1997), and Matti et al. (2004) have carried out some work on ^{1}H NMR assignments of high DS acetylated starches, but there is no research on ^{1}H NMR assignments of low DS acetylated starches.

The objective of the present study was to prepare low and high DS acetylated starch using acetic anhydride as the esterification reagent, methanesulphonic acid as catalyst and to measure and analyse the structure of native starch and acetylated starches by FTIR, ^{1}H NMR, ^{13}C NMR, ^{13}C–^{1}H COSY NMR, X-ray diffraction and contact angle measurement.

2. Materials and methods

2.1. Materials

Corn starch was obtained from Changchun Dacheng Industrial Group Co., Ltd. (Changchun, China). Glacial acetic acid and acetic anhydride was purchased from Bei Hua Fine Chemicals Co., Ltd. (Beijing, China). Methanesulphonic acid (MSA) was purchased from Hui Shi Biochemical Reagent Co., Ltd. (Shanghai, China). All chemicals used in the study were of analytical grade.

2.2. Preparation of acetylated starch

The starch was dried at 50 °C for 24 h before reaction to avoid the interference of moisture. Ten grams corn starch (0.06 mol anhydroglucose unit) and 0.36 mol glacial acetic acid were placed in a 250 mL three-neck flask. After stirring for 5 min, 0.32 mol cooled acetic anhydride was added to the mixture. After 15 min, 0.0035 mol of methanesulphonic acid was subsequently added to the reactor. The reaction was stirred for 3 h at 200 rpm/min. By changing the reaction temperature at 50 °C, 65 °C, 75 °C, it was possible to prepare esters with three different DS. The reaction was terminated by pouring into distilled water. The mixture was washed with excess distilled water. The solid was dried at 50 °C for 12 h in vacuum oven (Linpin Isotemp 202–00 A, Linpin Scientific, Shanghai, China).

2.3. Characterizations

2.3.1. FTIR analysis

The FTIR analysis was performed using a Bruker Vertex 70 FTIR spectrometer (Rheinstetten, Germany). The native and acetylated starch samples were collected using the KBr pellet method. FTIR spectra were recorded at a resolution of 4 cm^{-1} and with a total of 32 scans, and wave number range between 400 and 4000 cm^{-1}. The native and acetylated starches were equilibrated at 50 °C for 24 h prior to FTIR analysis.

2.3.2. NMR analysis

The NMR spectra were recorded using a Bruker AV400 spectrometer (Ettlingen, Germany) operating at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR, respectively. One-and-two-dimensional NMR measurements were conducted to obtain the detailed information on the structure of native starch. Native as well as acetylated starches were dissolved in dimethyl sulphoxide (DMSO) -d6 at 75 °C to obtain clear solutions. The analysis for starch and acetylated starch was carried out at 25 °C.

2.3.3. X-ray diffraction

The X-ray diffraction was obtained from a D/max 2500 X-ray diffractometer (Tokyo, Japan), a conventional copper target X-ray tube set to 40 kV and 200 mA. The X-ray source was Cu Kα radiation. Data were collected from 2θ of 5.00 to 35.00° (θ being the angle of diffraction) with a step width of 0.02° and step time of 0.4 s, scanning speed of 8°/min, divergence slit width of 0.2 mm, scatter slit width of 0.6 mm, receiving slit width of 0.2 mm at room temperature. Native and acetylated starch samples were dried at 50 °C to a constant moisture (10%) in a vacuum oven, then 50 mg samples were added into the slide for packing prior to X-ray scanning. The native starch and acetylated starches were equilibrated at 50 °C to a constant moisture (10%) prior to analysis.

2.3.4. Contact angle measurements

The contact angle is the angle between a liquid droplet and the surface over which it spreads. The measurement of the contact angle gives an indication of nature of the surface. Contact angle determination was by direct observation of a liquid drop on smooth, horizontal, solid surfaces mounted on a microscope slide. Contact angles were measured at room temperature using a Drop Shape Analysis System G 10/DSA 10 (Kruess, Germany). Water droplets were dropped carefully onto the films. The average contact angle value was obtained by measuring at ten different positions of the same sample.

The native and acetylated starches (0.01 mg/L) for contact angle measurement were heated at 75 °C in dimethyl sulphoxide (DMSO) to obtain clear solution, and cooling at room temperature then casting onto silicon slice dropwise and dried at 80 °C for 2 h in vacuum oven (Linpin Isotemp 202–00A, Linpin Scientific, Shanghai, China).

2.4. Determination of degree of substitution (DS)

Degree of substitution is the average number of hydroxyl groups substituted per anhydroglucose unit. The maxi-

mum possible DS was 3.0. Determination of DS of acetylated starch by titration involved complete basic hydrolysis of the ester linkages and titration of the excess alkali. Native and acetylated starches (0.50 g) were weighted accurately and added into the sodium hydroxide solution (25 mL, 0.5 N). The mixture was stirred for 72 h at 50 rpm/min, at room temperature. After indicator (3 to 5 drops of 1% thymolphthalein) was added the solution was immediately titrated with 0.5 N hydrochloric acid to the thymolphthalein endpoint. Reference sample was treated in a similar way.

Acetyl content (ω) was calculated according to the following equation:

$$\omega = \frac{(v_2 - v_1) \times 10^{-3} \times N \times 43}{m} \times 100\% \quad (1)$$

Acetyl content (ω) was used to calculate the degree of substitution, according to following equation:

$$\mathrm{DS} = \frac{162\omega}{43 - 42\omega} \quad (2)$$

Where: v_1 the volume of 0.5 N HCl in mL used for titration of 0.50 g native starch; v_2 the volume of 0.5 N HCl in mL used for titration of 0.50 g sample; N the normality of HCl solution; m the weight of the sample; 43 the molecular weight of the acetyl group; 162 the molecular weight of anhydroglucose unit.

On the other hand, ^{1}H NMR could be used to determine the DS of acetylated starches. Due to the shift of protons to lower magnetic field by acetylation, the calculation of DS of acetylated starch with various DS was different. Based on the report (Teramoto & Shibata, 2006), the DS of acetylated starch with low DS (DS $\leqslant$ 2.5) could be calculated by the following Eq. (3), derived from the equation: $A/3x = B/\{1 + (3 - x)\}$, where x equals $\mathrm{DS_{low}}$. However, based on the report (Matti et al., 2004), the DS of acetylated starch with high DS (DS $\geqslant$ 2.5) could be calculated by the following Eq. (4), derived from the equation: $A/3x = C/7$, where x equals $\mathrm{DS_{high}}$.

$$\mathrm{DS_{low}} = 4A/(3B + A) \quad (3)$$

$$\mathrm{DS_{high}} = 7A/3C \quad (4)$$

Where A the sum of areas of methyl protons at 2.01–2.08 ppm; B the sum of areas of OH and H-1 protons for anhydroglucose unit moiety observed at higher than 4.5 ppm; C the sum of areas of seven protons in anhydroglucose unit observed at higher than 3.95 ppm.

2.5. Statistics

All measurements were carried out in triplicate. Analysis of variance (ANOVA) was performed using the Duncan's multiple range tests to compare treatments means. Significance was defined at $P < 0.05$.

3. Results and discussion

3.1. Degree of substitution (DS)

Acetylated starch was synthesized by the reaction of starch with acetic anhydride in the presence of MSA in acetic acid. The DS of acetylated starches determined by hydrolysis and ^{1}H NMR are summarized in Table 1. The different DS of acetylated starches were prepared by varying with reaction temperature from 50 °C to 75 °C. The results indicated that accuracy of the hydrolysis and ^{1}H NMR method, the values of DS by these two methods were very similar. The slightly high DS determined by ^{1}H NMR were attributed to the end units in starch molecular chain having four acetyl groups (Matti et al., 2004).

3.2. FTIR of acetylated starches

To detect the structure of acetylated starches, FTIR spectra are recorded, and the spectra of the starch, DS 0.85, 1.78, 2.89 acetylated starches are shown in Fig. 1.

In the spectra of native starch (Fig. 1a), there are several discernible absorbancies at 1159, 1082, 1014 cm^{-1}, which were attributed to C–O bond stretching (Goheen & Wool, 1991). Additional characteristic absorption bands appeared at 992, 929, 861, 765, 575 cm^{-1} due to the entire anhydroglucose ring stretching vibrations. An extremely broad band due to hydrogen bonded hydroxyl groups appeared at 3421 cm^{-1} (Fang, Fowler, Sayers, & Williams, 2004).

Table 1
Degree of substitution of corn starch at different temperatures

Reaction temperature (°C)	Degree of substitution (DS)	
	Hydrolysis	^{1}H NMR
50	0.81	0.85
65	1.70	1.78
75	2.83	2.89

Conditions: 0.43 mol glacial acetic acid, 0.06 mol anhydroglucose unit, 0.32 mol acetic anhydride, 0.0035 mol of methanesulphonic acid.

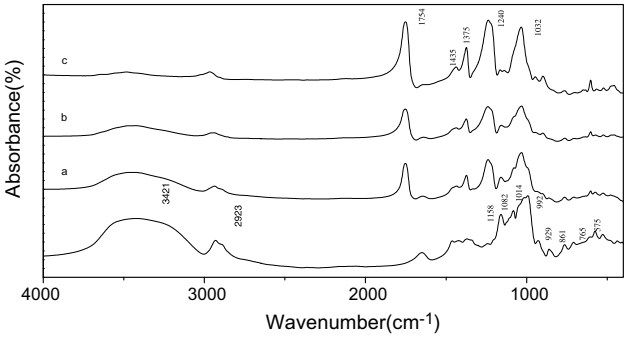

Fig. 1. FTIR spectra for native starch and acetylated starches at DS 0.85 (a), DS 1.78 (b), DS 2.89 (c).

FTIR spectra of different DS of acetylated starches showed some new absorption bands at 1754, 1435, 1375, 1240 cm^{-1} assigned to carbonyl C=O, CH_3 antisymmetry deformation vibration, and CH_3 symmetry deformation vibration and carbonyl C–O stretch vibration, respectively. These new absorptions suggest that the acetylated starch products were formed during the esterification process. In addition, the spectra of acetylated starch showed that the anhydroglucose unit moved towards a high wave number. With DS increasing, the intensities of peaks at 3421, 1082, 1014 cm^{-1} were gradually weakened and almost disappeared when DS reached to 2.89, indicating hydroxyl groups were just about to participate in the reaction.

3.3. NMR of native starch and acetylated starches

Native starch is analyzed by ^1H NMR and ^{13}C NMR and ^{13}C–^1H COSY, and the assignments of ^1H-shifts and ^{13}C-shifts are summarized in Table 2. Based on the reports of peak assignment for proton and carbon species in amylose, amylopectin, starch (Choi, Kim, & Park, 1999; Friebolin, Keilich, & Siefert, 1969; Heins, Kulicke, Kauper, & Thielking, 1998; Mclntyre, Ho, & Vogel, 1990; Peng & Perlin, 1987), we assigned the carbon signals of native starch by ^{13}C NMR, partly proton signals by ^1H NMR, but there are some confusion existed in the assignments of ^1H-shifts of starch at 3.24–3.66 ppm. The ^{13}C–^1H COSY spectra could enable us to assign the correction peak of each carbon and its directly attached proton. Therefore, we further used the ^{13}C–^1H COSY spectrum assign the signals of native starch accurately.

Based on the reports (Choi et al., 1999; Friebolin et al., 1969; Heins et al., 1998; Mclntyre et al., 1990; Peng & Perlin, 1987), we assigned the peaks at 78.72, 73.21, 71.93, 71.56, 69.92, 60.82, 60.45 ppm, respectively, to C-4, C-3, C-2, C-5, C-4 (end group) and C-6 carbons in the anhydroglucose of native starch and analysis of our COSY spectra, we assigned ^1H- chemical shifts of the protons at 3.07–3.66 ppm connecting to proton at 3.35 ppm to H-4, 3.67 ppm to H-3, 3.30 ppm to H-2, 3.59 ppm to H-5, 3.07 ppm to H-4 (end group), 3.64 and 3.46 ppm to H-6,6′, respectively. The chemical shifts of H-1, OH-2, 3, 6 were 5.10, 5.40, 5.50, 4.59 ppm, respectively.

Table 2
Chemical shift assignments for ^1H- and ^{13}C species of native starch

^1H assignment	Chemical shift (ppm)	^{13}C assignment	Chemical shift (ppm)
H-1	5.10	C-1	100.04
H-2	3.30	C-2	71.93
H-3	3.67	C-3	73.21
H-4	3.35	C-4	78.72
H-4 (end group)	3.07	C-4 (end group)	69.92
H-5	3.59	C-5	71.56
H-6,6′ (1–4)	3.64	C-6,6′ (1–4)	60.45
H-6,6′ (1–6)	3.46	C-6,6′ (1–6)	60.82.
OH-2	5.40	–	–
OH-3	5.50	–	–
OH-6	4.59	–	–

With esterification process, acetyl groups were introduced into starch, proton resonances of anhydroglucose unit showed some changes compared with that of native starch, the ^1H NMR spectra of acetylated starches are presented in Fig. 2 and the assignments of ^1H-shifts are summarized in Table 3. As can be seen in the spectra of DS 0.85 and DS 1.78 acetylated starches, we could still observe the characteristic peaks of anhydroglucose unit owing to the

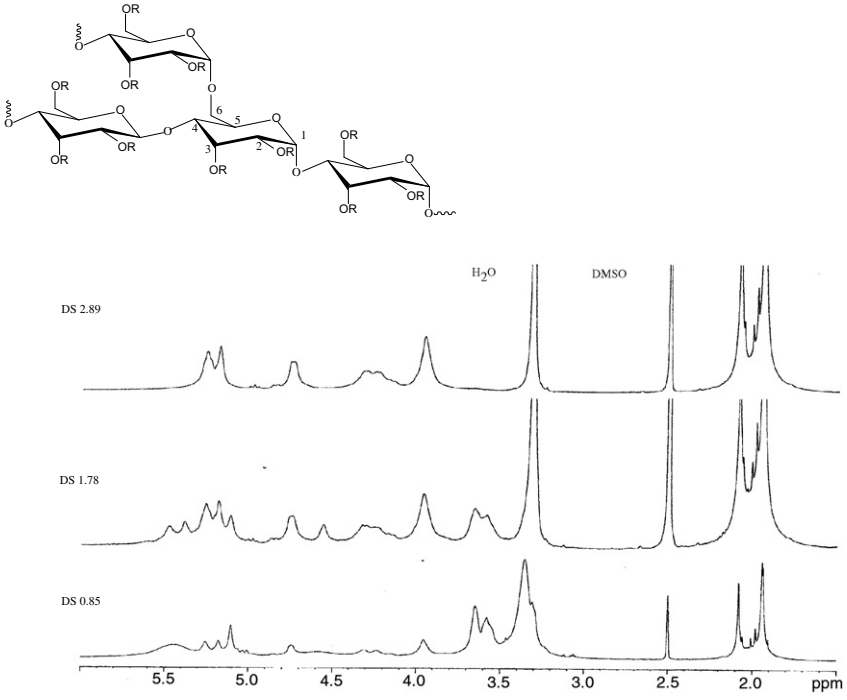

Fig. 2. ^1H NMR spectra of acetylated starches at different degree of substitution.

Table 3
Chemical shift assignments for ^{1}H species of acetylated starches

^{1}H assignment	Chemical shift (ppm)		
	DS 0.85	DS 1.78	DS 2.89
H-1[a]	5.18	5.18	5.18
H-2[a]	4.74	4.74	4.74
H-3[a]	5.25	5.26	5.26
H-4,5[a]	3.96	3.96	3.96
H-6,6′[a]	4.32–4.25	4.32–4.25	4.32–4.25
OH-3[b]	5.44	5.38	–
OH-2[b]		5.44	–
OH-6[b]	4.58	4.56	–
-CH_3 (acetyl group)	2.08–2.01		

Designation "a" and "b" refer to proton signals attributed to participate reaction and original protons of anhydroglucose unit.

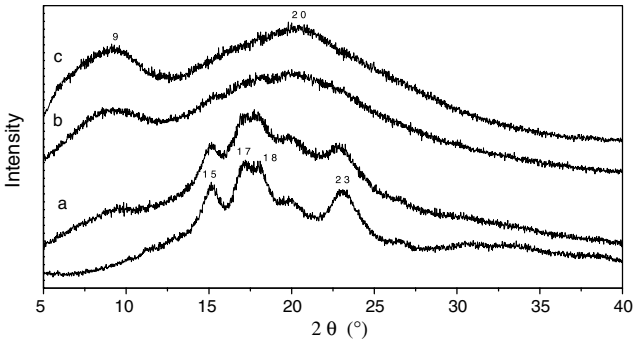

Fig. 3. X-ray diffraction patterns of native starch and acetylated starches at DS 0.85 (a), DS 1.78 (b), DS 2.89 (c).

fact that only a portion of hydroxyl groups participated in the esterification in 3.24–3.66 ppm range; chemical environments of other protons in anhydroglucose unit did not change in these two products. There were also some new peaks appearing at 5.25, 5.18, 4.74, 4.32–4.25, 3.96 ppm, respectively, due to H-3, H-1, H-2, H-6,6′, H-4, 5 signals belonging to protons of acetylated starch. The protons of acetyl groups appeared at 2.01–2.08 ppm. There were some hydroxyl groups in low DS acetylated starches, so we could observe the chemical shifts of protons of hydroxyl groups at 5.44 and 4.58 ppm, which were similar with the resonances of protons in hydroxyl groups of native starch. In the ^{1}H NMR spectrum of DS 2.89 acetylated starch, which was DS approached the theoretical DS of 3, signal peaks of hydroxyl groups in anhydroglucose units disappeared. Compared to the ^{1}H NMR of native starch, proton chemical environments were all changed, instead of protons characteristic peaks of acetylated starch, 5.25 ppm to H-3, 5.18 ppm to H-1, 4.74 ppm to H-2, 4.32-4.25 ppm to H-6,6′, 3.96 ppm to H-4, 5. The results gave the detailed information of low and high DS acetylated starch, which can help us to analyze the structure of samples.

3.4. X-ray diffraction pattern

X-ray diffraction measurements were performed to check if chemical modification altered the crystallinity of starch. The X-ray diffraction spectra of native starch and acetylated starches are presented in Fig. 3. The native starch had sharp diffraction peaks at 15°, 17°, 18°, 23° (2θ), which indicated typical A pattern of cereal starch (Zobel, 1988). As can be seen in Fig. 3a, DS 0.85 acetylated starch showed a similar profile of native one, but it had a new peak at 9° (2θ), which appeared diffusion peaks of acetylated starch. However, DS 1.78 and DS 2.89 acetylated starches represented typical peaks of acetylated starches, which had wide peaks at 9° and 20° (2θ). The X-ray diffraction indicated that with esterification processing, crystalline structures of native starch were destroyed, and new structure of acetylated starch was formed.

3.5. Contact angle measurements

After esterification, the most prominent feature of the esterified starches was their increased hydrophobicity as determined by contact angle measurement. The reduced hydrophilicity of esters was attributed to the replacement of hydrophilic hydroxyls by the relatively hydrophobic ester groups.

When adding a drop of distilled water, it was quickly spread on the starch surface and gave the lowest contact angle value. Because there are many OH groups on the surface of native starch macromolecule, the hydrogen bond can be formed in water. With acetylation processing, contact angle was higher for modified substance, indicating that chemical treatments induced dramatic changes in surface polarity of starch. Compared with native and DS 2.89 acetylated starch, contact angle was increased from 43.1° to 68.2° indicating that lower wettabilities between two phases. The modified starches improved hydrophobicity performance of starch materials, having good applied prospect.

4. Conclusions

A series of acetylated starches with different degrees of substitution (DS) were synthesized and their structures investigated by FTIR, ^{1}H NMR, ^{13}C NMR and ^{13}C–^{1}H COSY spectra. FTIR spectroscopy showed that the characteristic absorption intensities of esterified starch increasing with DS increasing and hydroxyl groups almost disappearing when the DS of product was 2.89. The ^{13}C NMR and ^{13}C–^{1}H COSY spectra of native starch were assigned proton chemical shifts at 3.07–3.66 ppm accurately. The ^{1}H NMR of acetylated starches revealed that with DS increasing, the proton chemical shifts of hydroxyl at 5.44 and 4.58 ppm gradually disappeared, and the characteristic proton chemical shifts of acetylated starch appeared at 2.01–2.08, 5.25, 5.18, 4.74, 4.25–4.32, 3.96 ppm. Meanwhile, X-ray diffraction confirmed that the crystal structure of the native starch was disappeared and new crystal structure of acetylated starch was formed at 9° and 20° (2θ). Compared with native starch, the hydrophobic perfor-

mance of acetylated starch esters was improved, which the contact angle increased from 43.1° to 68.2°. Therefore, because of the hydrophobicity of acetylated starch, the uses of acetylated starches have increased. It will be further studied of the blend of native and acetylated starch to decrease the cost of acetylated starch and hydrophilicity of starch materials.

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