



Short communication

## Hydrophobization of starch nanocrystals through esterification in green media

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## ABSTRACT

Starch nanocrystals (SNC) were successfully modified through esterification by using dodecyl succinic anhydride (DDSA), 2-octen-1-ylsuccinic anhydride (OSA) and acetic anhydride (AA) in green media. The chemical modifications were confirmed using FT-IR. The esterification extent of the modified SNC was evaluated by degree of substitution (DS). The modifications imparted hydrophobic character to SNC so that the modified SNC could be dispersed in non-polar solvents such as chloroform, dichloromethane and toluene. It was found that the dispersibility of the modified SNC in non-polar solvents increased with increasing of DS and hydrophobicity of the group replacing the hydroxyl groups in starch. XRD analysis showed that the crystalline structure of SNC was preserved after the modifications.

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## 1. Introduction

Starch nanocrystals (SNC), isolated from starch granules by mild acid hydrolysis or enzymatic hydrolysis, have attracted significant interest over the past years (Le Corre et al., 2010; Lin et al., 2012). The unique characteristics, such as biodegradability, impressive mechanical properties, low density, and low permeability make SNC ideal candidate as reinforcement for fabrication of polymer nanocomposites to meet increasing demand for products made from renewable resources (Angellier et al., 2005a, 2006; García et al., 2009; Kristo and Biliaderis, 2007). However, the polar surface and hydrophilicity of SNC result in their poor dispersibility in non-polar solvents and poor compatibility with hydrophobic polymers, which limit processing of SNC reinforced nanocomposites and the function of mechanical reinforcement from SNC. Therefore, one of the main challenges with SNC application in nanocomposites is related to their homogeneous dispersion within polymeric matrix.

Over the past decade, much effort has been devoted to modify SNC for nanocomposite applications. Modifications of SNC have been carried out via grafting polymers (Labet et al., 2007; Namazi and Dadkhah, 2008; Song et al., 2008; Thielemans et al., 2006) and reacting with various reagents (Namazi and Dadkhah, 2010;

Valodkar and Thakore, 2010). Esterification modifications of SNC with alkenyl succinic anhydrides (ASAs) and acetic anhydride (AA) were reported (Angellier et al., 2005b; Xu et al., 2010). However, most of these modifications used toxic and expensive solvents as reaction medium and required prolonged reaction time.

The objective of this work was to modify SNC more environmentally friendly and efficiently through esterification using ASAs and AA in green media to improve dispersibility of SNC in non-polar solvents or hydrophobic polymers so that the application range of SNC as reinforcements in nanocomposites could be broadened.

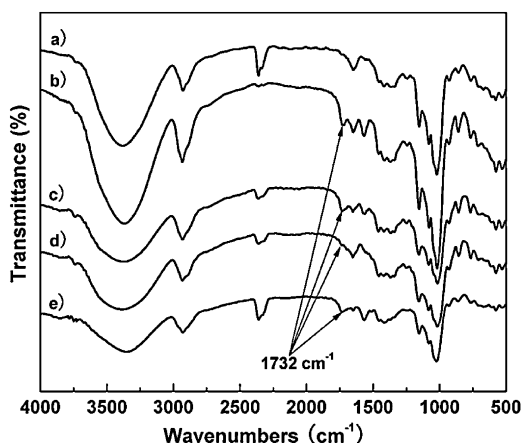
## 2. Experimental

Waxy maize starch was supplied by Changchun Jincheng Corn Development Co. Ltd., Da Cheng Group (China). Dodecyl succinic anhydride (DDSA) and 2-octen-1-ylsuccinic anhydride (OSA) were purchased from Sigma-Aldrich (St. Louis, USA). Acetic anhydride (AA) and other chemicals were obtained from Beijing Beihua Fine Chemicals Co. Ltd. (China). All of these chemicals were used as received.

One gram of SNC, prepared by acid hydrolysis of waxy maize starch according to the optimum condition determined by Angellier et al. (2004), was dispersed in 30 mL reaction medium (water, ethanol or water/ethanol mixture) using ultrasound and stirring for 30 min to obtain SNC suspension. After pH of the suspension was adjusted with NaOH aqueous solution (0.1 mol L<sup>-1</sup>), one gram of DDSA or OSA (diluted five times with ethanol, v/v) was added over 5 min. The reaction was allowed to last 1 h under stirring at

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**Fig. 1.** FT-IR spectra of unmodified SNC (a), DDSA modified SNC in water (pH 8.0–8.5) (b), in water/ethanol mixture (pH 8.0–8.5) (c) and in ethanol (pH 8.0–8.5) (d), OSA modified SNC in water/ethanol mixture (pH 8.5–9.0) (e).

35 °C and selected pH maintained by adding NaOH aqueous solution. Upon completion of the reaction, pH was neutralized to 7 with HCl aqueous solution (0.1 mol L<sup>-1</sup>). For the AA modification, the reaction medium was 36 wt% acetic acid aqueous solution, and 10 mL mixture of H<sub>2</sub>SO<sub>4</sub> and acetic acid (10/90, v/v) was used as catalyst. After a certain amount of AA was added, the reaction was allowed to last 3 h under stirring at different temperatures. All the products were first washed by centrifugation thrice with 70% (v/v) ethanol aqueous solution (for the DDSA and OSA modifications) or water (for the AA modification), then thrice with ethanol to remove all traces of residual reagents and dried at room temperature.

The modified SNCs were characterized with FT-IR (IRAffinity-1 spectrophotometer, Shimadzu, Japan). The specimen was prepared by grinding SNC sample together with KBr and then pressed into a disk. The resolution was 4 cm<sup>-1</sup> and the total scans were 32.

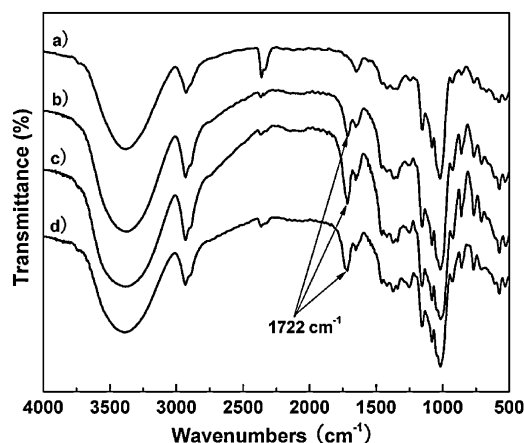
Degree of substitution (DS) refers to the average number of the hydroxyl groups substituted per D-anhydroglucose unit in starch, the maximum possible DS is 3.0. DS of the ASA (DDSA or OSA) modified SNCs was determined using the method of Jeon et al. (1999). DS of the AA modified SNC was determined by saponifying acetate groups (Miladinov and Hanna, 2001).

Wettability test was used to assess surface polarity of SNCs. 5 mg of sample was mixed with two immiscible solvents (5 mL each) having different polarities and densities in a vial to observe the wettability of the sample with the solvents.

Crystalline structure of SNCs was characterized by using a Rigaku D/max-2500 X-ray diffractometer (Rigaku Corporation, Tokyo, Japan) with Cu-Kα radiation ( $\lambda = 1.542 \text{ \AA}$ ) at 40 kV and 250 mA. The X-ray diffraction patterns were recorded over the  $2\theta$  range of 3–35° at a speed of 1°/min. Relative crystallinity was determined from the ratio of the areas of the diffraction peaks to the area of the whole diffraction pattern subtracted amorphous background patterns.

### 3. Results and discussion

Figs. 1 and 2 showed FT-IR spectra of the ASA and AA modified SNCs. Comparing with the spectrum of the unmodified SNC, there was a clear new peak which was located at 1732 cm<sup>-1</sup> in the spectra of the ASA modified SNCs or located at 1722 cm<sup>-1</sup> in the spectra of the AA modified SNCs. Since this peak is associated with carbonyl stretching from esters (Biswas et al., 2008) and the modified SNCs were thoroughly washed to remove the unbound anhydrides, this ester carbonyl bands peak is the evidence that esterification modification of SNC with ASA or AA occurred.



**Fig. 2.** FTIR spectra of unmodified SNC (a), AA modified SNC (AA/SNC = 10/1, mL/g) at 30 °C (b), AA modified SNC (AA/SNC = 30/1, mL/g) at 30 °C (c), and AA modified SNC (AA/SNC = 30/1, mL/g) at 50 °C (d).

DS value was used to evaluate esterification extent of modified SNCs. As presented in Table 1, the modification with DDSA in the water/ethanol mixture (when pH > 8.0) yielded higher DS than that in water or ethanol, meaning there are synergistic interactions between water and ethanol which increase DS. It is known that SNC swell in water and water can increase mobility of starch molecules, while ethanol can dilute DDSA and help it diffuse into SNC. The water/ethanol mixture brought these factors together and therefore increased probability of the reactive moieties combining and resulted in higher esterification extent of SNC. Data in Table 1 also showed that DS of the DDSA modified SNC increased with increasing of pH in the reaction system and attained the maximum value when the pH ranged in 8.5–9.0. The results could be explained by the fact that higher pH values (>9.0) favor anhydride hydrolysis whereas lower pH values (<8.5) are not sufficiently to activate the hydroxyl groups in starch for nucleophilic attack of the anhydride moieties.

Generally, DS and length of the alkenyl group determine the hydrophobicity of ASA modified SNC. In place of DDSA (C<sub>12</sub>), OSA (C<sub>8</sub>) was used to modify SNC. It was found that, reacted in the water/ethanol mixture with pH of 8.5–9.0 and temperature of 35 °C for 1 h (weight ratio of OSA/SNC was 1), the DS of the OSA modified SNC was 0.034 which was higher than the DDSA modified one (0.021), indicating that modification of SNC with ASA having shorter chain of alkenyl group was more easily to yield a high DS. This is because, with decrease of the length of the alkenyl group, diffusion capability of ASA toward SNC increases and space baffle effect which can interrupt the reactive moieties combining decreases.

Table 2 listed DS values of the AA modified SNCs with different amounts of AA at various reaction temperatures. The increase of AA amount from 10 to 30 (in proportion to SNC, mL/g) gave rise to a significant increase in DS. An increase of reaction temperature (below gelatinization temperature of starch) resulted in increased

**Table 1**

DS of the modified SNCs using DDSA in different media with various pH at 35 °C for 1 h.

pH	Water	Ethanol	Water/ethanol (50/50, in volume)
7.5–8.0	0.004	0.005	0.005
8.0–8.5	0.013	0.012	0.017
8.5–9.0	0.017	0.016	0.021
9.0–9.5	0.015	0.014	0.019

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