



Short communication

A method for improving dispersion of starch nanocrystals in water through crosslinking modification with sodium hexametaphosphate

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ABSTRACT

To improve disperibility in water starch nanocrystals (SNC) obtained from the acid hydrolysis of waxy maize starch were modified through crosslinking by using sodium hexametaphosphate (SHMP) in water at temperatures below the gelatinization temperature of starch. Fourier transform infrared spectroscopy, swelling degree and X-ray diffraction were used to characterize the crosslinking modification of SNC. It was found that the crystalline structure of SNC was preserved after the crosslinking. The modification significantly improved the dispersion of SNC in water so that stable and uniform SNC aqueous suspension could be formed.

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1. Introduction

Starch is an abundant, biodegradable, naturally renewable and inexpensive nature polymer. Considerable interest has been focused on finding new applications for this biopolymer. One of these applications has been the use of starch nanocrystals (SNC) to prepare nanocomposites (Dufresne, 2010; Le Corre, Bras, & Dufresne, 2010; Lin, Huang, Chang, Anderson, & Yu, 2011). By submitting native starch to acid hydrolysis at temperature below the gelatinization temperature of starch, the amorphous regions in starch granules are hydrolyzed allowing the separation of nanoscale crystalline residues (Angellier, Choinsard, Molina-Boisseau, Dole, & Dufresne, 2004; Putaux, Molina-Boisseau, Momauro, & Dufresne, 2003). Because of its unique properties such as the nanoscale platelet morphology, intrinsic rigidity, high crystallinity and low permeability, SNC has been used as reinforcement to prepare nanocomposites with matrices of natural polymers and biodegradable polymers (Angellier, Molina-Boisseau, Dole, & Dufresne, 2006; Carcia, Ribbal, Dufresne, Aranguren, & Goyanes, 2009; Kristo & Biliaderis, 2007; Mélé, Angellier, Molina-Boisseau, & Dufresne, 2011; Zheng, Ai, Chang, Huang, & Dufresne, 2009). However, SNC tends to aggregate and settle in water. This behavior affects preparation and properties of SNC reinforced nanocomposites with matrices of thermoplastic starch, chitosan, polyvinyl alcohol and natural rubber, etc., because a procedure of mixing SNC

aqueous suspension with matrix solution is needed in the casting-fabrication of the nanocomposites. Therefore, it is desirable to modify SNC to improve its dispersion in water.

SNC possesses a reactive surface which bears hydroxyl groups and provides the possibility of modification via a chemical reaction strategy. In this paper, we report an easy method to modify SNC through crosslinking in water medium by using sodium hexametaphosphate (SHMP) as crosslinker aiming at improving dispersion of SNC in water.

2. Experimental

2.1. Materials

Waxy maize starch was supplied by Changchun Jincheng Corn Development Co. Ltd., Da Cheng Group (China). Sulfuric acid ($\geq 95\%$) and sodium hexametaphosphate (SHMP) were obtained from Beijing Chemicals Factory (China). All these materials were used as received without further purification.

2.2. Preparations of SNC and cross-linked SNC

SNC was prepared by acid hydrolysis of waxy maize starch granules according to the optimum conditions determined by Angellier et al. (2004). One gram SNC was added into 100 ml of deionized water and dispersed using ultrasound generated from an ultrasonic cleaner (KQ-600KDE NC, Kunshan, China) with full power (600 W) as well as continuously stirring for 30 min at 40 °C to obtain SNC suspension. Then, 1 g NaCl and different amounts of SHMP (4 wt%,

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6 wt% and 8 wt% of SNC) were added into the SNC suspension, the pH of the suspension was adjusted to 10.0 with sodium hydroxide aqueous solution (0.1 mol/L), the reaction was allowed to last 4 h under continuously stirring at 40 °C. Upon completion of the reaction, the pH of the suspension was adjusted to 6.8 with hydrochloric acid aqueous solution (0.1 mol/L), and the product was dried at 40 °C after five washings with water.

2.3. Characterization

The intact and cross-linked SNC were characterized with FT-IR (IRAffinity-1 spectrophotometer, Shimadzu, Japan). The specimens were prepared by grinding samples together with KBr and then pressed into a disc. The resolution was 4 cm⁻¹ and the total number of scans was 32.

The structures of waxy maize starch, intact and cross-linked SNC were characterized by using a Rigaku D/max-2500 X-ray diffractometer (Rigaku Corporation, Tokyo, Japan) with Cu K α radiation ($\lambda = 1.542 \text{ \AA}$) at 40 kV and 250 mA. The X-ray diffraction patterns were recorded at room temperature over the 2θ range of 3–35° at a speed of 1°/min.

Swelling degree (SD) of the intact and cross-linked SNC was measured. Accurately weighed sample (0.2 g) was put into a 100 ml beaker, and then 20 ml deionized water was added. The sample and water were mixed using ultrasound generated from an ultrasonic cleaner (KQ-600KDE NC, Kunshan, China) with full power (600 W) as well as continuously stirring for 30 min at 40 °C. The obtained suspension was centrifuged at 8000 rpm (4250 $\times g$) for 10 min. To measure the SD, the supernatant was removed and the centrifuge tube with sediment was weighed, and then the sediment was carefully transferred into a Petri dish and dried overnight in a hot air oven at 105 °C. The SD was calculated as:

$$SD = \frac{(W_2 - W_1)}{W_0}$$

where W_0 is the weight of sediment on dry basis, W_1 is the weight of the centrifuge tube, and the W_2 is the weight of the centrifuge tube with swollen sediment. The tests were performed in triplicate for each sample.

3. Result and discussion

3.1. FT-IR analysis

During the crosslinking reaction between starch and SHMP, SHMP reacts with the hydroxyl groups of starch molecules, forming intra and inter ester linkages. Alkaline condition is needed to allow the hydroxyl groups of starch to become oxygen anions and enable the crosslinking reaction. FT-IR was used to find evidence of the reaction, and the FT-IR spectra for intact and cross-linked SNC were presented in Fig. 1. Since the absorbance peak of the P=O vibration, located at 1400–1150 cm⁻¹ (Xu, Sun, Zhao, Zhang, & Zheng, 2007), was too weak, and the absorbance peak of the P–O–C vibration, located at 1050–995 cm⁻¹, overlapped with the absorbance peak of C6–OH vibration of the starch glucose unit (Xu et al., 2007), it is difficult to directly characterize the crosslinking reaction between SNC and SHMP through FTIR. However, it was noted that the peak attributed to stretching of hydroxyl groups at 3381 cm⁻¹ shifted to lower wave numbers, suggesting new interactions formed after modification (Yin, Li, Liu, & Zhong, 2005).

3.2. SD analysis

It is known that crosslinking modification inhibits swelling of starch, with the inhibition being related to the degree of crosslinking (Mao, Wang, Meng, Zhang, & Zheng, 2006), therefore, SD was

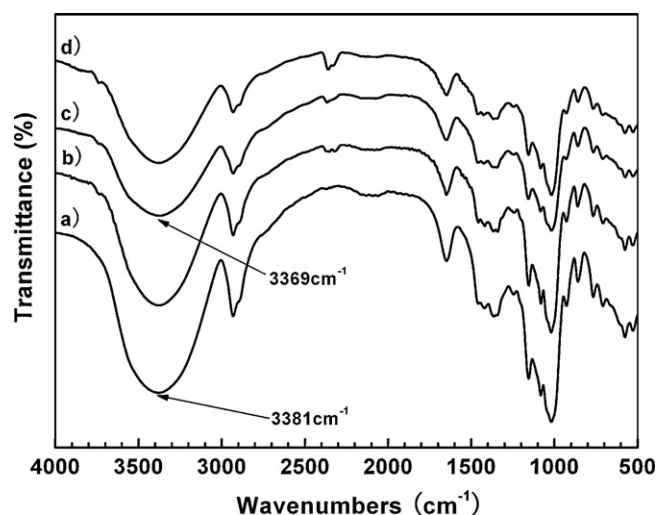


Fig. 1. FTIR spectra for the intact (a) and cross-linked SNC with 4% SHMP (b), 6% SHMP (c) and 8% SHMP (d).

used to characterize crosslinking modification of SNC. Fig. 2 showed the SD for the intact and cross-linked SNC. The measured SD for the intact SNC was 4.91, while the ones for cross-linked SNC with 4%, 6% and 8% SHMP were 3.99, 3.93, and 3.80, respectively. These data indicated that the SD of SNC decreased markedly after the modification, suggesting the crosslinking did occur.

3.3. XRD analysis

The XRD patterns of waxy maize starch, intact and cross-linked SNC were given in Fig. 3. All the samples showed a similar scattering pattern generally obtained for the A-type with the clear diffraction peaks, a strong peak at 15.1°, a strong double peak at 17.1° and 17.9°, and a strong peak at 23.0° of 2θ . These XRD patterns indicated that the acid hydrolysis did not destroy or transform the starch crystalline structure and the crosslinking modification with SHMP in water medium preserved the integrity of SNC's crystalline structure. Therefore, it is inferred that the crosslinking reaction may only occur on the surface of SNC. This is because the compact structure of SNC hindered the crosslinker from entering the inner of SNC and so the crosslinking reaction simply took place between the adjacent hydroxyl groups on the surface.

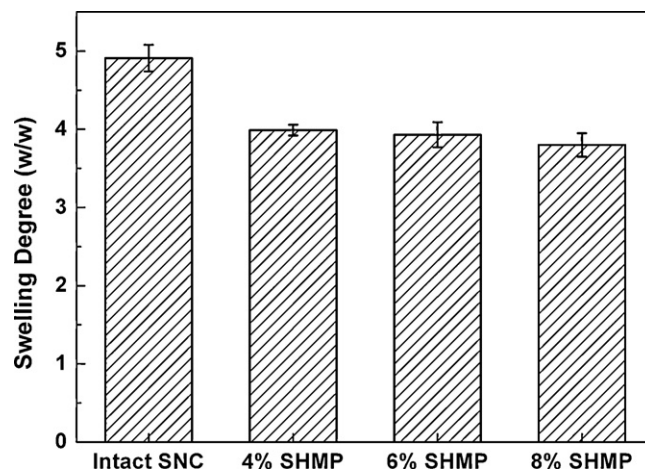


Fig. 2. Comparison of the SD for intact SNC and cross-linked SNC with different SHMP.

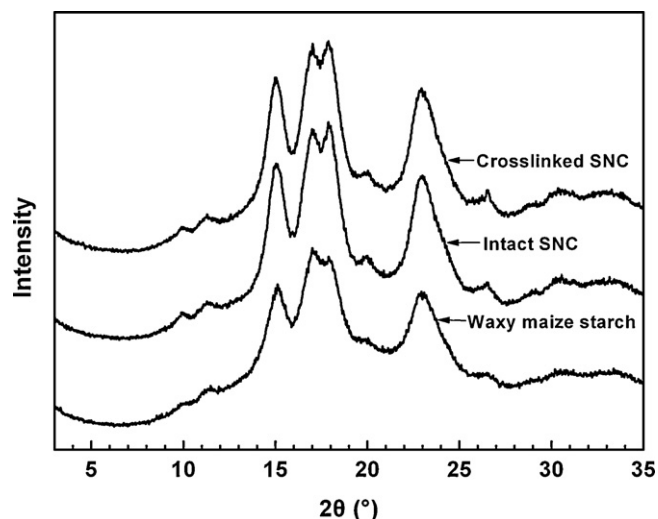


Fig. 3. X-ray diffraction patterns of waxy maize starch, intact SNC and cross-linked SNC with 6% SHMP.



Fig. 4. Dispersion of SNC in water: intact SNC (A); cross-linked SNC with 6% SHMP (B), intact SNC, 0.5 h later (C) and cross-linked SNC with 6% SHMP, 72 h later (D).

3.4. Dispersion experiments

Both the intact and cross-linked SNC were dispersed in water at a concentration of 4 mg/ml at room temperature. Dispersions of SNC in water were shown in Fig. 4. Although both intact and cross-linked SNC were well dispersed in water after shaking as shown in Fig. 4A and B, the intact SNC started settling in several minutes due to aggregation and completely settled to the bottom of the container in 30 min as shown in Fig. 4C, while the cross-linked SNC was still well dispersed even after 72 h as shown in Fig. 4D. It should be pointed out that there was no observed difference in dispersions of the cross-linked SNC, so only the cross-linked SNC with 6% SHMP was used for comparison with the intact one in Fig. 4.

The observations of the dispersions suggested that the crosslinking modification of SNC by using SHMP changed surface nature of SNC and prevent SNC from aggregation in water. It is supposed that the modification could put negative charge on SNC, which would reduce aggregation.

4. Conclusion

SNC obtained from acid hydrolysis of waxy maize starch was successfully modified through crosslinking with SHMP in water medium at temperature below the gelatinization temperature of starch. The crosslinking modification did not disrupt the crystalline structure of SNC, but significantly improved the dispersion of SNC in water and gave rise to a stable and uniform SNC aqueous suspension.

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References

- Angellier, H., Choinsard, L., Molina-Boisseau, S., Dole, P. & Dufresne, A. (2004). Optimization of the preparation of aqueous suspensions of waxy maize starch nanocrystals using a response surface methodology. *Biomacromolecules*, 5, 1545–1551.
- Angellier, H., Molina-Boisseau, S., Dole, P. & Dufresne, A. (2006). Thermoplastic starch-waxy maize starch nanocrystals nanocomposites. *Biomacromolecules*, 7, 531–539.
- Carcia, N. L., Ribbal, L., Dufresne, A., Aranguren, M. I. & Goyanes, S. (2009). Physico-mechanical properties of biodegradable starch nanocomposites. *Macromolecular Materials and Engineering*, 294, 169–177.
- Dufresne, A. (2010). Processing of polymer nanocomposites reinforced with polysaccharide nanocrystals. *Molecules*, 15, 4111–4128.
- Kristo, E. & Biliaderis, C. G. (2007). Physical properties of starch nanocrystal-reinforced pullulan films. *Carbohydrate Polymers*, 68, 146–158.
- Le Corre, D., Bras, J. & Dufresne, A. (2010). Starch nanoparticles: A review. *Biomacromolecules*, 11, 1139–1153.
- Lin, N., Huang, J., Chang, P. R., Anderson, D. P. & Yu, J. H. (2011). Preparation, modification, and application of starch nanocrystals in nanomaterials: A review. *Journal of Nanomaterials*, 2011, 1–13.
- Mao, G. J., Wang, P., Meng, X. S., Zhang, X. & Zheng, T. (2006). Crosslinking of corn starch with sodium trimetaphosphate in solid state by microwave irradiation. *Journal of Applied Polymer Science*, 102, 5854–5860.
- Mélé, P., Angellier, H., Molina-Boisseau, S. & Dufresne, A. (2011). Reinforcing mechanisms of starch nanocrystals in a nonvulcanized natural rubber matrix. *Macromolecules*, 12, 1487–1493.
- Putaux, J. L., Molina-Boisseau, S., Momaur, T. & Dufresne, A. (2003). Platelet nanocrystals resulting from the disruption of waxy maize starch granules by acid hydrolysis. *Macromolecules*, 4, 1198–1202.
- Xu, H., Sun, L. P., Zhao, D. Q., Zhang, B. & Zheng, G. F. (2007). Preparation and structure characterization of crosslinked potato starch. *Journal of the Chinese Cereals and Oils Association*, 22, 67–72.
- Yin, Y. P., Li, J. F., Liu, Y. C. & Zhong, L. (2005). Starch crosslinked with poly(vinyl alcohol) by boric acid. *Journal of Applied Polymer Science*, 96, 1394–1397.
- Zheng, H., Ai, F. J., Chang, P. R., Huang, J. & Dufresne, A. (2009). Structure and properties of starch nanocrystal-reinforced soy protein plastics. *Polymer Composites*, 30, 474–480.