



Dual modification of starch nanocrystals via crosslinking and esterification for enhancing their hydrophobicity



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ABSTRACT

The aim of this study was to enhance the hydrophobicity of starch nanocrystals (SNCs) and improve their dispersibility in non-polar solvents through dual modifications. The dual modifications were carried out by crosslinking first and then followed esterification. The results of characterizations showed that the dual modifications resulted in a higher degree of substitution of SNCs than single esterification modification. The SNCs with the dual modifications possessed lower polarity and showed stronger hydrophobicity than the SNCs with single crosslinking or esterification modification and therefore could be dispersed in non-polar solvents such as chloroform, dichloromethane and toluene. In addition, the crosslinking protected the crystalline structure of SNCs being disrupted in the followed esterifications. The modified SNCs can be used as reinforcements for nanocomposites with hydrophobic polymer matrices or emulsion stabilizers and rheology modifiers.

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1. Introduction

Starch is major carbohydrate in plant tubes and seed endosperm, where it is found as granules. Starch nanocrystals (SNCs) originated from starch granules have been extensively studied in their preparation and utilization for many years (Dufresne, 2014; Kim, Park, and Lim, 2015; Le Corre and Angellier-Coussy, 2014; Lin, Huang, and Dufresne, 2012). The nanoscale morphology, nontoxicity, biocompatibility and biodegradability of SNCs make them suitable to be used as reinforcements to fabricate nanocomposite materials for food packaging (Lin, Huang, Chang, Anderson, and Yu, 2011) and emulsifiers to prepare Pickering emulsions which have applications in foods, beverages, cosmetics and pharmaceuticals (Kim et al., 2015; Li, Sun, and Yang, 2012). SNCs reinforced nanocomposites can be produced from blends of SNCs and polymers via three general techniques, casting, extruding, and compression molding (Moon, Martini, Nairn, Simonsen, and Youngblood, 2011). The casting method was suggested as a better choice than other thermal methods for the preparation of SNCs reinforced nanocomposites (Kim et al., 2015; Le Corre and Angellier-Coussy, 2014).

However, due to polar surface of SNCs or their hydrophilicity, dispersibility of SNCs in non-polar solvents and compatibility of SNCs with hydrophobic matrices are very poor. In a soy protein isolate matrix,

the number and the size of SNCs domains simultaneously increased with an increase in SNCs content (>2 wt%) due to a strong self-aggregation tendency of SNCs, which resulted in a gradual decrease of strength and Young's modulus (Zheng, Ai, Chang, Huang, and Dufresne, 2009). In the carboxymethyl chitosan matrix, SNCs aggregated and the phase separation between aggregates and matrix occurred when SNCs content was higher than 30 wt%, and thus tensile strength of the composite films decreased (Duan, Sun, Wang, and Yang, 2011). A considerable decrease in tensile strength with increasing of SNCs content was also observed in SNCs reinforced thermoplastic starch due to an increased tendency of SNCs aggregation at high contents (Angellier, Molina-Boisseau, Dole, and Dufresne, 2006; Gonzalez, Retegi, Gonzalez, Eceiza, and Gabilondo, 2015; Kristo and Biliaderis, 2007; Li et al., 2015). In the case of waterborne polyurethane as matrix, as the SNCs loading increased, the self-aggregation of SNCs caused size expansion of nano-phase along with increase of nano-phase number, and hence they decreased the mechanical performances (Chen, Wei, Chen, Huang, Dufresne, & Chang, 2008). Only a very little improvement of strength and strain at break (10% at best) was observed for poly(vinyl alcohol) filled with SNCs (<10 wt%), which was also attributed to the poor compatibility of the filler and the matrix (Chen, Cao, Chang, & Huneault, 2008). The poor dispersibility of SNCs in dichloromethane was thought the source of the poor mechanical properties and thermal stability of the SNCs reinforced polycaprolactone nanocomposites (Habibi and Dufresne, 2008). Therefore, it is necessary to lower the polarity or enhance the hydrophobicity of SNCs to improve their dispersibility in hydrophobic matrices and non-polar solvents.

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SNCs have reactive surfaces bearing lots of hydroxyl groups suitable for chemical modification and much effort has been devoted over the past years. Angellier et al. (Angellier, Molina-Boisseau, Belgacem, & Dufresne, 2005) reported the chemical modification of SNCs with alkenyl succinic anhydride and phenyl isocyanate in toluene. The modified SNCs migrated toward dichloromethane, indicating a lower polar nature. Namazi and Dadkhah (2010) reported a method to prepare hydrophobic SNCs with octanoic acid, nonanoic acid and decanoic acid by mild esterification using acyl chlorides in aqueous media. The modified SNCs had affinity toward chloroform. Xu et al. (2010) prepared acetylated SNCs in glacial acetic acid, the modified SNCs exhibited much improved solubility in common organic solvents such as *N,N*-dimethylformamide, acetone, carbon tetrachloride and toluene.

Author's previous works showed that the crosslinking modification of SNCs with sodium hexametaphosphate (SHMP) significantly improved dispersion of SNCs in water (Ren, Jiang, Wang, Zhou, and Tong, 2012), and the esterification modifications of SNCs using dodecyl succinic anhydride (DDSA), 2-octen-1-ylsuccinic anhydride (OSA), and acetic anhydride (AA) imparted hydrophobic character to SNCs (Ren, Dong, Jiang, Tong, and Zhou, 2014). The crystalline structure of the SNCs was preserved after the crosslinking modification, but it was partly preserved after the esterification modifications. Because the crosslinking modification gave rise to a stable and uniform SNCs aqueous suspension, this may facilitate esterification modification of SNCs and result in higher esterification extent in SNCs. On the other hand, the preserved crystalline structure of SNCs after the crosslinking modification may keep its integrity in the following esterification modification due to the protection of the crosslinking networks. Therefore, dual modification of SNCs, first crosslinking and then followed by esterification, was carried out. Fourier-transform infrared (FTIR) spectroscopy, degree of substitution (DS), zeta potential, scanning electron microscopy (SEM), wettability test, contact angle, and X-ray diffraction (XRD) were used to characterize the SNCs with the dual modifications and to examine if the dual modifications could give SNCs better performance as reinforcing fillers for nanocomposites.

2. Material and methods

2.1. Materials

Waxy maize starch was supplied by Changchun Jincheng Corn Development Co. Ltd., Da Cheng Group (Changchun, China). The DDSA (dodecyl succinic anhydride, 90% purity) and OSA (2-octen-1-ylsuccinic anhydride, 97% mixture of *cis* and *trans*) were purchased from Sigma-Aldrich (St. Louis, USA). Sulfuric acid ($\geq 95\%$), sodium hexametaphosphate (SHMP), glutaraldehyde (GA), acetic anhydride (AA), sodium hydroxide, hydrochloric acid (36%), ethanol, chloroform, dichloromethane, and toluene were obtained from Beijing Chemical Works (Beijing, China). All these materials were used as received without further purification.

2.2. Preparation and dual modification of SNCs

SNCs were prepared by acid hydrolysis of waxy maize starch according to the optimum conditions determined by Angellier, Choïnard, Molina-Boisseau, Dole, and Dufresne (2004). Then, SNCs were modified via crosslinking first using SHMP and GA, respectively, and followed esterification using DDSA, OSA and AA, respectively.

The SNCs crosslinked with SHMP (SHMP-SNCs) were prepared according to the procedure described by Ren et al. (2012). One gram SNCs were dispersed into 100 mL of deionized water by using ultrasound generated from an ultrasonic cleaner (KQ-600KDE NC, Kunshan, China) at a power of 600 W and with continuous stirring for 30 min at 40 °C to obtain the SNCs suspension. Next, 1 g NaCl and 0.08 g SHMP (8 wt% of SNCs) were added into the SNCs suspension, the pH of the

suspension was adjusted to 10.0 with sodium hydroxide aqueous solution (0.1 mol L⁻¹), and the reaction was allowed to proceed for 4 h under continuous 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⁻¹). For the preparation of the SNCs crosslinked with GA (GA-SNCs), the pH of the SNCs suspension was adjusted to 2.0 with hydrochloric acid aqueous solution (1.0 mol L⁻¹), and then 0.4 g GA (40 wt% of SNCs) was added to the SNCs suspension. The reaction was allowed to proceed for 4 h under continuous stirring at 40 °C and then stopped by addition of ethanol.

The crosslinked SNCs (SHMP-SNCs or GA-SNCs), dried at 40 °C after five washings with water, were modified through esterification by using DDSA, OSA and AA, respectively, under the optimum condition determined in author's previous work (Ren et al., 2014). One gram crosslinked SNCs were dispersed in 30 mL water/ethanol mixture (50/50, in volume) using ultrasound and stirring for 30 min to obtain SNCs suspension. After pH of the suspension was adjusted to 8.5–9.0 with NaOH aqueous solution (0.1 mol L⁻¹), one gram of DDSA or OSA (diluted five times with ethanol, v/v) was added over 5 min. The reaction was allowed to proceed for 1 h under stirring at 35 °C and selected pH maintained by adding NaOH aqueous solution. Upon completion of the reaction, pH was neutralized to 7 by using HCl aqueous solution (0.1 mol L⁻¹). For the modification with AA, the reaction medium was 36 wt% acetic acid aqueous solution, and 10 mL mixture of H₂SO₄ and acetic acid (10/90, v/v) was used as catalyst. After 50 mL AA was added, the reaction was allowed to proceed for 3 h under stirring at 50 °C. All the products were first washed by centrifugation thrice with 70% (v/v) ethanol aqueous solution (for the modifications using DDSA and OSA) or water (for the modification using AA), then thrice with ethanol to remove all traces of residual reagents and dried at room temperature.

2.3. Characterization

2.3.1. Fourier transform infrared (FT-IR)

The modified SNCs were characterized with FT-IR (IRAffinity-1 spectrophotometer, Shimadzu, Japan). The specimens were prepared by grinding SNCs with KBr and then pressing the samples into a disc. The resolution was 4 cm⁻¹ and the total scans were 32.

2.3.2. Determination of degree of substitution (DS)

DS of the SNCs modified with DDSA or OSA was determined using the method described in literature (Jeon, Viswanathan, and Gross, 1999). Modified SNCs (0.2 g) was dissolved in 10 mL of dimethylsulfoxide by heating (70 °C, 10 min). After cooling to room temperature, 5–6 drops of phenolphthalein indicator were added. This solution was titrated against 0.05 M standard sodium hydroxide aqueous solution until a permanent pale pink color was seen. The DS was calculated by using the following equation:

$$DS = \frac{162 \times V \times M}{1000W - 266 \times V \times M} \quad (1)$$

where, *V* is the volume of sodium hydroxide aqueous solution used during titration, *M* is the molarity of sodium hydroxide aqueous solution, and *W* is the weight of SNCs sample. Tests were performed in triplicate for each sample.

DS of the SNCs modified with AA was determined by saponifying the acetate groups (Miladinov and Hanna, 2001). Modified SNCs (0.2 g) was put into a 100 mL conical flask containing 20 mL of distilled water and dispersed by stirring, 3 drops of phenolphthalein (1% w/v phenolphthalein in ethanol solution pH indicator) were added and this mixture was titrated against 0.1 M standard sodium hydroxide aqueous solution until a permanent pale pink color was not seen. Then 10 mL of 0.5 M sodium hydroxide aqueous solution was added into the flask and the mixture was conditioned for 60 min at room temperature to saponify

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