



Effects of concurrent ball milling and octenyl succinylation on structure and physicochemical properties of starch

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ABSTRACT

This work concerns the effects of concurrent ball milling (BM) and octenyl succinic anhydride (OSA) modification on the starch microstructure and physicochemical properties (swelling, emulsifying, and rheological). Unlike normal OSA-modified starches, the BM/OSA-modified starch displayed new features such as reduced viscosity and rigidity but increased paste stability during shearing, heating and cooling, regardless of the substitution degree. More interestingly, while the physicochemical properties could be regulated by simply altering the BM treatment time, BM/OSA was more efficient and effective at modulating starch properties during the initial period (approx. 10 h), as seen by the rapid evolutions in starch structural disruption and OSA esterification. Thus, the BM/OSA modification can serve as a viable and cost-effective approach for producing octenyl succinate starches where low viscosity (at relatively high concentrations) and high paste stability are desired.

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1. Introduction

As a traditional food ingredient providing energy for humans, starch has attracted intense interest as a resource for functional foods (Fuentes-Zaragoza et al., 2011). Starch has also extensively studied as bioactive carrier materials (Pu et al., 2011) and biomaterials (Situ, Li, Liu, & Chen, 2015), due to its renewability, biocompatibility and biodegradability (Xie, Halley, & Avérous, 2012; Zhang, Chen, Li, Li, & Zhang, 2015; Zhang, Chen, Xie et al., 2015). Starch contains two glucan biopolymers, *i.e.* amylose, mostly

a linear 1,4- α -D-glucan with several long branches, and amylopectin, a 1,4- α -D-glucan with a large number of 1,6- α linkages at the branch points (Jiang, Gao, Li, & Zhang, 2011; Liu, Halley, & Gilbert, 2010). Despite its great potentials, the application of native starch is often hindered by its undesirable features resulting from the supramolecular and molecular structures, including poor solubility, weak heat and shear resistance, uncontrolled paste consistency, high tendency to retrogradation, and low paste freeze-thaw stability (Lawal, 2009). For improving these physicochemical properties, chemical, physical and enzymatic modifications have been used to modulate the starch structural characteristics relating to the granule, crystallites and molecular chains (Bemiller, 1997; Copeland, Blazek, Salman, & Tang, 2009; Zhang, Chen, Li et al., 2015).

Among different modification methods for starch, the esterification with octenyl succinic anhydride (OSA) endows starch with amphiphilicity, which is instrumental to stabilizing water-in-oil and oil-in-water emulsions for foods, cosmetics and pharmaceu-

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tics (Sweedman, Tizzotti, Schäfer, & Gilbert, 2013). The resultant octenyl succinate starches have better emulsion performance, freeze-thaw stability, and filming properties, which have widened industrial applications (Bhosale & Singhal, 2007; Sweedman et al., 2013). Currently, octenyl succinylation is commonly realized by using specific reactions in an aqueous or organic medium under alkaline conditions (Xu et al., 2012), in which case a high reaction efficiency could be achieved. However, the generation of chemical wastes during OSA modification using solution chemistry could lead to the pollution to the environment. As “green processing” becomes increasingly important in food and non-food industries, there has been intense interest in the design and application of innovative technologies for the production of octenyl succinate starches.

Emerging techniques, especially those based on physical approaches for dry forms, have attracted considerable attention, as it can largely reduce the wastes from the processing and can produce high-safety products. Ball milling (BM), as a cost-effective and eco-friendly physical technique, has been confirmed capable of regulating starch properties (solubility, digestibility, pasting, etc.) (Liu, Ma, Yu, Shi, & Xue, 2011; Tan, Zhang, Chen, Li, Li, & Xie, 2015). The combinatorial effects of friction, collision, impingement and shear in BM can change the starch properties through altering the starch structural features, e.g., granule morphology, crystallinity and molecular weight, (Huang, Xie, Chen, Lu, & Tong, 2008; Kim, Suzuki, Hagiwara, Yamaji, & Takai, 2001; Liu et al., 2011; Tan et al., 2015). In particular, by inducing granule breakage and amorphization, BM may enhance the chemical reactivity of starch, and therefore promote starch modifications such as esterification. Our very recent findings (Chen, Yin, Chen, Xiong, & Zhao, 2014; Zhang, Zhao, & Xiong, 2013) confirmed that the concurrent BM treatment with OSA modification could result in products with varied molecular chain characteristics and thermal behaviors. Moreover, the additional BM treatment could induce starch structural changes (e.g., molecular degradation) that are different to those by only OSA modification. However, it has been unclear of how the BM/OSA modification modulates the key physicochemical properties of starch such as rheological behaviors especially from a structural point of view. The lack of this understanding prevents us from exploring the underlying structure-properties mechanism and rationally designing BM/OSA-modified starches with desired properties for specific applications.

In this work, waxy rice starch was used as a raw material for preparing BM/OSA-modified starches. We used planetary BM as it is more efficient than other conventional BM techniques. This work explored the effects of BM/OSA modification on the starch structures (granule morphology and polymorph) and physicochemical properties (swelling power, solubility, freeze-thaw stability, emulsification and rheological behaviors). Based on that, we established the structure-property relationship and discussed the underlying mechanism.

2. Materials and methods

2.1. Materials

Waxy rice was purchased from Dong Po Oil Group (Huanggang, China), and its chemical composition was determined as $90.45 \pm 0.62\%$ total starch with $<5\%$ amylose content, $7.83 \pm 0.26\%$ moisture content and $0.15 \pm 0.00\%$ crude protein, according to AACC standard methods (Quinton & Kennedy, 2002). High-purity octenyl succinic anhydride (OSA) (99.9%) was acquired from Dixie Chemicals (No. 7757-96-2, Houston, USA). All other chemicals used were of analytical grade.

2.2. Preparation of octenyl succinate starches

Approximately 2 kg (dry basis) of waxy rice was saturated into 6 kg of 0.4% NaOH solution for 24 h, followed by wet-milling and filtration. The remained slurry was washed with 0.4% NaOH solution (ca. 6 kg) for four times. Then the resulting slurry was adjusted to pH 7.0 using 0.6 M HCl solution and washed using distilled water for five times. The slurry was centrifuged at 4000g for 10 min. The precipitate was dried at 40 °C for 12 h, and the pristine waxy rice starch was obtained.

The pristine starch (ca. 30 g) was mixed with 0.27 g of 4% NaOH solution and 1.2 g of OSA. The mixture was mechanically activated using a QM-1SP2 planetary ball mill (Nanjing Nanda Instrument Plant, China) with four containers containing mixtures of 6 and 10 mm balls. The cylindrical container was tumbled at a rotation speed of 450 rpm (the ratio of rotation and revolution speed, 2:1) for 3, 10, 30 or 50 h, with the temperature kept at around 30 °C. After removing free OSA and NaOH using 70% ethanol solution, the modified starch (octenyl succinate starch) was obtained.

In the following discussion, codes typically as “S-BM/OSA-3” are used, where “S” denotes the starch, “BM3” indicates the time (3 h) of BM treatment, and “OSA” shows the OSA modification. “S-BM-3” is the sample treated by BM with NaOH solution (ca. 0.9% of starch weight) but without OSA. “S-BM-0” represents the pristine waxy rice starch; “S-BM/OSA-0” indicates the starch sample obtained by directly washing the mixture of starch-NaOH-OSA using ethanol solution before the BM treatment.

2.3. Degree of substitution (DS)

The DS for octenyl succinylation, i.e., the average number of hydroxyl groups of each glucose unit substituted by OSA, was determined for the starch samples using a previously-reported method (Bhosale & Singhal, 2006; Li et al., 2012). All results were reported as the averages of three replicates.

2.4. Scanning electron microscopy (SEM)

The granule morphology was observed using a JSM-6390 scanning electron microscope (NTC, Japan), operated at 5 kV. All the samples were coated with a gold thin film before the observations.

2.5. X-ray diffraction (XRD)

The starch samples were placed in the sample holder of a JDX-10P3A X-ray diffractometer (Tokyo, Japan) equipped with the Cu K α X-ray source having a wavelength of 0.1542 nm. XRD patterns were recorded for an angular range (2θ) of 4–40°, with a step size of 0.02° and a step rate of 1 s per step. The radiation parameters were set at 30 kV and 20 mA. The degree (X_c) of crystallinity was calculated with the method of Lopez-Rubio, Flanagan, Gilbert, and Gidley (2008). The PeakFit software (Version 4.12, Systat Software, Inc., San Jose, CA, USA) was used for the deconvolution of the peaks, and the following equation was used for the calculation:

$$X_c = \frac{\sum_{i=1}^n A_{ci}}{A_t} \quad (1)$$

where A_{ci} is the area under each crystalline peak with index i , and A_t is the total area (both the amorphous background and crystalline peaks) under the diffractogram. The measurements were undertaken in triplicate.

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