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Octenyl succinylation of granular and debranched waxy starches and their application in low-fat salad dressing

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ABSTRACT

The reactions of octenyl succinic anhydride (OSA) at 3% and 15% concentrations (based on weight of starch) with granular and debranched starch forms of waxy rice and waxy potato starches were investigated and compared. Reaction efficiencies of debranched starches with 3% OSA (83.6–87.4%) were significantly higher than those of the granular starches (51.2–56.1%), but their recovery yields were lower (80–85% and 94–98% for debranched and granular starches, respectively). Similar trends were found for the starches modified with 15% OSA but with less reaction efficiencies. Molecular weights of the modified debranched starches were substantially higher than the unmodified ones, presumably due not only to the substituted groups, but also the association of starch chains. Native, debranched, 3% OS granular and 3% OS debranched starches were then evaluated as a fat replacer in a low-fat salad dressing. Viscosities of the dressings incorporated with native and OS granular starches were reduced markedly after storage for 3 d, while the consistency and appearance of the dressings containing debranched starches, either modified or not, were similar to commercial low-fat dressing at up to 90 d storage. Relative calorie values of the dressings containing debranched starches were approximately 50% and 10% less than the reference formula and commercial dressing, respectively.

1. Introduction

Starch is widely used as an ingredient in various food and non-food products. Starch can be modified to develop desirable functional properties, such as solubility, texture, adhesion, dispersion and heat tolerance, in order to be suitable for industrial applications (Wurzburg, 1986). One of the common chemical modifications is to substitute starch with organic acid esters using dicarboxylic acid anhydrides. By substituting with hydrophobic groups, the modified starch molecules containing both hydrophilic and hydrophobic groups are known to possess improved emulsification properties (Kim, Sandhu, Lee, Lim, & Lim, 2010). Among all modifications with dicarboxylic acid anhydride, only starch modified with octenyl succinic anhydride (OSA) is currently permitted in many countries for use in food applications, with a maximum allowable level of added OSA of 3% (Bhosale & Singhal, 2007; Liu et al., 2008). Octenyl succinylated (OS) starch has been used in several products: for example, as an emulsifier in salad dressings and creams, clouding agent in drinks, coating agent for food, encapsulating agent for flavors (Kim et al., 2010; Thomas & Atwell, 1999; Trubiano, 1986), and for forming biodegradable plastics (Jane, Robert, Nidolov, & Roque, 1991). It has also been suggested for use as a fat replacer in emulsified foods such as muffins (Chung, Lee, Han, & Lim, 2010) and mayonnaise (Cho, Lim, Park, Hwang, & Lim, 1999).

OS starches are commonly prepared from the reaction of starch in a granular form with OSA in aqueous alkaline media. OSA has poor water solubility and native starch granules are partially crystalline; thus, the reaction requires a relatively long time, and the efficiency of the reaction is quite low. To enhance the reaction efficiency, alterations of granule structure to be more accessible to OSA have been reported. Size reduction of rice starch granules by

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ball milling (Zhang, Zhao, & Xiong, 2010), increasing the swelling power of starch granules by annealing (Chen, Xiaowei, & Huang, 2014), increasing cavities/channels inside the granules by heat–moisture treatment (Jiranuntakul, Puncha-arnon, & Uttapap, 2014), and increasing the surface area of waxy maize starch granules by creating pinholes (Bai & Shi, 2011) could significantly increase the degree of substitution (DS) and reaction efficiency. Another approach to increase the accessibility of OSA to hydroxyl groups of starch could be to allow OSA to react directly with dispersed/hydrolyzed starch molecules. Only research work conducted by Bai and Shi (2011) has used this approach. They reported that the reaction efficiency of OSA with soluble maltodextrin was greater than that with granular starch, which indicated that maltodextrin had more reaction sites available.

Our previous study on the physicochemical and structural properties of debranched waxy rice, waxy corn and waxy potato starches (Klaochanpong, Puttanlek, Rungsardthong, Puncha-arnon, & Uttapap, 2015) revealed that debranched starch gels are non-sticky, smooth, and have a glossy appearance; therefore, these gels are suggested to be used as gelling agents in food, cosmetics and pharmaceutical products. These debranched starches could function as fat replacers, thickeners, bulking agents and/or binders. At low concentrations, debranched starch can be used as a clouding agent in juices and beverages. However, in food systems consisting of both water and oil phases, substitution of some hydroxyl groups of debranched starch with hydrophobic ligands might make them more effective in stabilizing the components in such foods. To produce OS debranched starch, there are two possible procedures: octenyl succinylation of granular starch and then debranching, and the reverse, debranching the granular starch prior to octenyl succinylation.

This study aimed to compare the efficiency of octenyl succinylation of waxy starches in granular and debranched forms. Moreover, the OS granular starches were debranched, and the OS debranched starches obtained were analyzed for the degree of substitution and compared with the OS debranched starches derived directly from the reaction of OSA and debranched starches. In order to assess the application potential of these OS starch products in real food, salad dressing was chosen as a representative because it is a simple emulsion system. The OS starches are supposed to provide several functions in salad dressing: mainly as a thickener, an emulsifier and a fat replacer, and also contributing a nutritional starch fraction (slowly digestible or resistant starch).

2. Materials and methods

2.1. Materials

Two types of waxy starch, waxy rice and waxy potato starches, were subjected to the modifications. Waxy rice (RD 12) grains were provided by the Sakon Nakhon Rice Research Center (Sakon Nakhon, Thailand). Waxy potato starch (3.92% amylose content) was acquired from National Starch Food Innovation (Bangkok, Thailand). *Bacillus acidopullulyticus* pullulanase (EC 232-983-9P; $\geq$ 400 U/mL), high-purity octenyl succinic anhydride, maltoheptaose, and two pullulan standards (P6000 and P12000) were purchased from Sigma-Aldrich (St. Louis, MO). A commercial low-fat salad dressing containing 30.0% w/w oil and 1.5% acetylated distarch phosphate was purchased from a local supermarket. All chemicals used in this experiment were analytical grade.

2.2. Waxy rice starch isolation

Starch with amylose content of 0.35% was isolated from waxy rice grains according to the procedures described by Jiranuntakul, Puttanlek, Rungsardthong, Puncha-arnon, and Uttapap (2011). De-hulled waxy rice grains were steeped in distilled water at 4 °C for 24 h. The supernatant was discarded, and the steeped waxy rice grains were ground with a blender and then passed through a 63 μm screen. The slurry was kept at 4 °C for 48 h. The supernatant was removed, and the starch cake was re-suspended in 0.35% sodium hydroxide solution and kept at 4 °C for 48 h. The supernatant was decanted and the starch layer was re-slurried with water. The starch slurry was passed through a 63 μm sieve and kept at 4 °C for 48 h. The steps of washing with water were repeated four times until the pH of the starch slurry reached 7, and then it was stored at 4 °C for 48 h. Finally, the supernatant was removed and the starch cake was dried in an oven at 40 °C for 24 h.

2.3. Preparation of debranched starches

Starch debranching was carried out according to the method of Yotsawimonwat et al. (2008), with a slight modification. Waxy starch was suspended in 0.05 M acetate buffer, pH 5.0 (10%, w/w). The suspension was cooked in a boiling water bath with stirring for 60 min, followed by autoclaving at 121 °C for 60 min to complete gelatinization. The gel solution was cooled to 55 °C and hydrolyzed with pullulanase (45 U/g of starch) at 55 °C in a shaking water bath for 20 h. The enzyme was then deactivated by heating at 100 °C for 30 min. The debranched starch was precipitated with 99% ethanol, filtered with Whatman No. 4 filter paper, washed three times with 95% ethanol, dried in an oven at 50 °C for 18 h, and sifted through a 106 μm sieve. Debranched waxy rice and potato starches obtained were denoted as DWRS and DWPS, respectively.

2.4. Preparation of octenyl succinylated (OS) starches

2.4.1. OS debranched starch

Debranched starch was prepared following the procedure described in Section 2.3 until the step of enzyme deactivation. After this step, the pH of the solution was adjusted to 8.0–8.5 by adding 3% NaOH solution, and temperature was controlled at 40 °C. Then, a weighed quantity of OSA (3% or 15%, based on starch weight) diluted with five times the volume of isopropyl alcohol was slowly added over 15 min. The reaction was continued for 2 h; the pH was then adjusted to 6.5 with 0.325 M HCl. OS debranched starch was recovered using the same procedure as in Section 2.3.

2.4.2. OS granular starch

Waxy starches in granular form were modified with OSA using the same procedure as for the debranched starch. OS granular starch was recovered by washing three times with DI water, filtration with Whatman No. 4 filter paper, drying in an oven at 40 °C for 24 h, and sieving through a 106 μm sieve.

2.4.3. Debranched OS granular starch

The OS granular starch was debranched following the procedure described in Section 2.3.

2.5. Determination of degree of substitution (DS)

DS is the average number of substituted hydroxyl groups per glucose unit. The DS of OSA starch was determined using a titration method (Kweon, Choi, Kim, & Lim, 2001). OS starch (1.0 g) was accurately weighed and dispersed in 25 mL of 2.5 M HCl–isopropyl alcohol solution by stirring for 30 min. A total of 100 mL of 90% (v/v) aqueous isopropyl alcohol solution was added and stirred for an additional 10 min. The suspension was filtered through a glass filter, and the residue was washed with 90% isopropyl alcohol solution until no Cl^- was detected (using 0.1 M $AgNO_3$ solution). The starch

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