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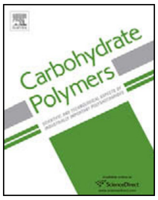

Research Paper

Effects of hydrothermal-alkali and freezing-thawing pre-treatments on modification of corn starch with octenyl succinic anhydride

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ABSTRACT

Pre-treatments by freezing/thawing (F/T) and hydrothermal-alkali (HA) were used in the modification of starch with octenyl succinic anhydride (OSA). In comparison with OSA-modified starch prepared without pre-treatment (degree of substitution, DS = 0.0172; reaction efficiency, RE = 73.9%), HA pre-treatment increased the DS of OSA-starch and RE of subsequent OSA modification (0.0185 and 79.7%, respectively). In contrast, F/T pre-treatment gave the opposite results (0.0152 and 65.5%, respectively). OSA modification markedly increased the viscosities but decreased the gelatinization parameters of native starch. Esterification of starch by OSA was confirmed with Fourier transform infrared and Raman spectroscopy, which indicated markedly decreased short-range molecular orders of native starch. The present study showed that HA pre-treatment before OSA modification is an efficient way to improve the reaction efficiency of OSA with starch and thereby to modify the pasting properties of starch. F/T pre-treatment did not increase the reaction efficiency of starch with OSA.

1. Introduction

Native starch does not always possess properties that meet the requirements for a multitude of industrial applications (BeMiller & Huber, 2015). The functional limitations of native starch can be improved greatly by modifications, of which chemical modification is most intensively studied (Kaur, Ariffin, Bhat, & Karim, 2012; Wang & Copeland, 2015). Octenyl succinic anhydride (OSA), a dicarboxylic acid anhydride, can react with starch to form starch octenylsuccinate containing both hydrophilic and hydrophobic groups (Bhosale & Singhal, 2007; Sweedman, Tizzotti, Schäfer, & Gilbert, 2013). The introduction of hydrophobic groups results in the amphiphilic character of OSA-modified starches (OSA-starch). Amphiphilic polymers have a wide range of industrial applications, particularly for emulsification, encapsulation, films and coatings, and gel production. OSA-starch has attracted much attention in recent years due to its good stabilizing, encapsulating, interfacial, thermal, nutritional and rheological properties (Sweedman et al., 2013). Moreover, OSA-starch has been permitted by the United States Food and Drug Administration as a legal food additive, with a maximum OSA addition level of 3.0% and a degree of substitution (DS) less than 0.02 (Miao et al., 2014).

The synthesis of OSA-starch is performed typically by mixing granular starch and OSA in aqueous medium under mild alkaline conditions. Due to the low solubility of OSA in water, the reaction between granular starch and OSA is heterogeneous, occurring with a mixture of OSA droplets and dissolved OSA (Shogren, Viswanathan, Felker, & Gross, 2000). As a result, the penetration of OSA into the interior of granules is hindered and the DS is low (Wang, He, Fu, Huang, & Zhang, 2016). Several physical and enzymatic pre-treatments are used to increase the susceptibility of granular starch to modification with OSA. Enzymatic pre-treatments create pinholes on the surface of starch granules (Bai & Shi, 2011; Huang et al., 2010), resulting in higher DS and reaction efficiencies (RE, defined as the theoretical DS divided by the actual DS obtained with a specific amount of OSA) (Bai & Shi, 2011), although contradictory results have also been reported (Huang et al., 2010). Hydrothermal pre-treatments of starch were shown to increase DS and RE on subsequent OSA modification (Chen, He, & Huang, 2014; Jiranuntakul, Puncha-arnon, & Uttapap, 2014).

Increasing the roughness of the granule surface increases its relative surface area, which should enhance the RE and DS of OSA with starch. In contrast to intact granules, the decreased size of the damaged starch granules increases the reactive surface area and therefore the reaction efficiency (Sweedman et al., 2013). Freez-

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ing/thawing (F/T) and mild hydrothermal-alkali (HA) treatments are two mild modifications to alter the surface structures of starch granules without significantly altering the internal ordered structures. Mild hydrothermal-alkali treatment has been shown to cause roughening of the surface and slight swelling of starch granules without significantly altering the internal ordered structure of the starch (Wang & Copeland, 2012a; Wang et al., 2014). Szymońska and Wodnicka (2005) reported that the specific surface area, micro- and mesopore volume and mean pore diameter of potato starch granules increased after F/T treatment. F/T treatment was reported to cause leaching of amylopectin (Tao et al., 2015), while HA treatment caused leaching of amylose (Wang & Copeland, 2012a). The aim of the present study was to determine the effects of F/T and HA pre-treatments on corn starch granules, and how these effects influence reactivity of the starch with OSA, and the physico-chemical properties of the derivatized starch. The results obtained in the present study should be of interest for food and other applications of OSA-modified starches.

2. Materials and methods

2.1. Materials

Corn starch (amylose content 24.1%) and high-purity (97%) OSA were purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO, USA). HCl-isopropyl alcohol solution (0.2 mol/l) was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). All other chemicals used in this study were of analytical grade.

2.2. Freeze/thawing treatment

Corn starch (30 g, dry weight) was weighed accurately into polypropylene bags, and 60 ml distilled water were added. The bags were sealed and the starch and water were mixed uniformly by shaking. The samples were frozen at −20 °C for 22 h, and thawed at room temperature for 2 h. The freezing-thawing process was repeated for 10 or 20 cycles, after which the samples were centrifuged at 3500g for 15 min. The sedimented starch was resuspended in absolute ethanol and filtered with suction. The resulting starch cake was dried under a gentle air stream and stored in a sealed plastic bag at 4 °C. The resulting products are subsequently referred to as 10F/T-starch and 20F/T-starch, respectively.

2.3. Hydrothermal-alkali treatment

Three sets of corn starches (30 g, dry weight) were suspended in 85.7 ml of distilled water by magnetic stirring in a water bath at 50 °C to obtain 35% (w/w) starch suspensions. The pH of the suspensions was adjusted to 8.5 with a 3% NaOH solution. After incubation for 1 h, one starch suspension was cooled to 35 °C and reacted with OSA as described in Section 2.3, the modified starch was referred to as OSA-HA-starch. The other sets of starch suspensions were dried either by freeze-drying or ethanol-dehydration, producing starch samples referred to as HAF-starch and HAED-starch, respectively.

2.4. Preparation of OSA modified starch

Native and pre-treated corn starches (30 g, dry weight) were suspended in distilled water with agitation (200 rpm) to obtain a 35% (w/w) starch suspension. The pH of the suspension was adjusted to 8.5 with a 3% NaOH solution. The OSA reagent, diluted five times with absolute alcohol (v/v), was added slowly over 2 h to the above starch suspension to a final concentration of 3% based on dry starch weight. A separate sample of native starch was mixed with a high concentration of OSA (15% w/w starch) for use as a control in some analyses. The reaction was performed at pH 8.5 and 35 °C for a further 4 h, after which 3% HCl solution was added to adjust the pH to 6.5. The reaction mixture was centrifuged at 4500g for 10 min. The sedimented starch was washed three times with distilled water and alcohol, respectively, to remove the residual OSA. The washed starch samples were filtered with suction and dried under a gentle air stream. The dried starch was ground gently using a pestle and mortar, and passed through a 100 mesh sieve.

2.5. Determination of the degree of substitution

The degree of substitution (DS), defined as the average number of hydroxyl groups substituted per glucose unit (Song, He, Ruan, & Chen, 2006), was measured by titration according the method of Ruan, Chen, Fu, Xu, and He (2009) with slight modifications as follows. The OSA-starch samples (2 g, dry weight) were weighed accurately and dispersed in 125 ml of HCl-isopropyl alcohol solution (0.2 M) with stirring for 30 min. Aqueous isopropyl alcohol solution (90% v/v, 100 ml) was added and the slurry stirred for an additional 10 min. The suspension was centrifuged and the precipitate was washed with 90% isopropyl alcohol solution until no Cl^- ions were detected using 0.1 M $AgNO_3$ solution. The washed starch was resuspended in 120 ml of distilled water and heated in a boiling water bath for 20 min with stirring. The starch solution was titrated with 0.1 M standard NaOH solution using phenolphthalein as an indicator. Native starch, titrated as for the OSA-modified starch, was used as a blank. The DS was calculated by the following equation:

$$DS = \frac{0.162 * (A * M)/W}{1 - \left[0.209 * (A * M)/W\right]}$$

where A is the titration volume of NaOH solution (ml), M is the molarity of NaOH solution, and W is the dry weight (g) of the OSA starch.

The reaction efficiency (RE) was calculated as follows:

$$RE = \frac{\text{Actual DS}}{\text{TheoreticalDS}} * 100\%$$

The theoretical DS was calculated based on the assumption that OSA reacted quantitatively with starch to form the ester derivative.

2.6. Differential scanning calorimetry (DSC)

The thermal characteristics of native, pretreated and OSA-modified starches were measured using a differential scanning calorimeter (200 F3, Netzsch, Germany) equipped with a thermal analysis data station and data recording software. The sample preparation and heating procedures were as described in Wang and Copeland (2012b). A starch: water ratio of 1:3 (w/v) was used in the present study to determine the thermal properties of the starches. The samples were heated from 20 to 100 °C at a heating rate of 10 °C/min. An empty aluminum pan was used as the reference.

2.7. Pasting properties

The pasting properties were analysed using a Rapid Visco Analyser (RVA) (Perten Instruments, Warriewood, Australia). Starch (2.5 g dry weight) and distilled water were added successively into aluminum canisters to make a total weight of 28.0 g. The starch slurries were mixed uniformly by the paddle before analyzing according to STD 1 protocol provided with the RVA instrument. Peak viscosity (PV), trough viscosity (TV), final viscosity (FV), and pasting temperature (PT) were obtained from the RVA profiles. The breakdown (BD) and setback (SB) were calculated using the Thermocline software provided with the instrument.