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Effects of acid-hydrolysis and hydroxypropylation on functional properties of sago starch

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ABSTRACT

In this study, sago starch was hydrolyzed by 0.14 M HCl for 6, 12, 18, and 24 h, and then modified by propylene oxide at a concentration of 0–30% (v/w). The effects of hydrolysis and etherification on molecular weight distribution, physicochemical, rheological, and thermal properties of dually modified starch were estimated. Acid hydrolysis of starch decreased the molecular weight of starch especially amylopectin, but hydroxypropylation had no effect on the molecular weight distribution. The degree of Molar substitution (DS) of hydroxypropylated starch after acid hydrolysis ranged from 0.007 to 0.15. Dually modified starch with a DS higher than 0.1 was completely soluble in cold water at up to 25% concentration of the starch. This study shows that hydroxypropylation and hydrolysis have synergistic effects unlike individual modifications. Dually modified sago starch can be applied to dip-molding for food and pharmaceutical processing because of its high solubility and low tendency for retrogradation.

1. Introduction

Starch is an abundant polysaccharide, and its properties differ according to plant source. Applications of native starch in food products are based on these inherent properties. However, some inherent functional properties, such as insolubility in water, tendency for retrogradation, opacity of cooked paste, and low flow, have restricted the applicability of starch in their native forms [1,2]. Many attempts have been made to overcome the disadvantages of starches and to develop industrial scale applications [3]. Modification of starch can be carried out physically, chemically, enzymatically, and genetically. Chemical modification of starch is the most common because it can be readily controlled, and the principal actions of chemical modifications are well understood compared with those of other methods of starch modification [4]. Depolymerization (i.e., acid-thinned hydrolysis or oxidation) and derivatizations (i.e., etherification or esterification) using chemical reagents are typical modifications that have a wide range of application in the starch industry [5]. Chemical modification causes changes in the molecular structure or introduces functional groups, thus improving the applicability of plant-derived materials in food and non-food industries [6–8].

Starches can be stabilized through reaction with monofunctional reagents. In these reactions, hydroxyl groups of the starch are converted into larger ether or ester groups to block interchain associations. This process tends to stabilize pastes and gels by giving them a reduced tendency to undergo retrogradation [9]. Hydroxypropyl starch (HPS) is a popular modified starch that is widely used in food industry. Hydroxypropylation of starches can cause high paste clarity, low tendency for retrogradation, freeze–thaw stability, and high solubility in cold water after cooking [10,11].

Molar substitution (DS), molecular weight distribution, and distribution of functional groups are the factors that characterize the properties of HPS. HPS also has good film formation properties. The properties of HPS film, such as mechanical, water vapor, and aroma permeability, have been investigated previously [12–14].

Generally, native starches have a low degree of substitution because of their limited degree of reaction on the granule surface. Karim et al. [15] observed that enzymatic hydrolysis prior to the hydroxypropylation of corn starch could improve the yield in the etherification process. Whistler et al. [16] also reported similar improvements in the esterification of corn starch after enzymatic hydrolysis. Researchers assume that hydrolysis gives the substituent groups more access to the subsurface of granules where it can react efficiently, resulting in the increased degree of substitution.

Acid-thinned hydrolysis changes the physicochemical properties of starch but does not alter its granular structure. Previous

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studies show that the gelatinization parameters (i.e., gelatinization temperature and enthalpy) increase upon hydrolysis [17,18]. The tendency for retrogradation of acid-thinned starch also increases because of an increase in the concentration of linear chains. The viscosity and average molecular weight of hydrolyzed starch decreases, whereas the solubility and gel strength of acid-thinned starch increase relative to the untreated starch [19]. Hydroxypropylation introduces a hydrophilic bulky group to the starch chains and improves solubility. Hydroxypropylation also decreases the tendency for retrogradation and improves thermal properties [20]. Therefore, the combination acid-thinned hydrolysis and hydroxypropylation should increase solubility and overcome the disadvantages of native starch.

The effect of two common methods of chemical modification on the solubility of sago starch was evaluated. Acid hydrolysis is an inexpensive and effective method for increasing sago starch solubility [18]. The etherification of sago starch in different substitution levels of propylene oxide was also examined [21]. In this study, sago starch was first hydrolyzed and then hydroxypropylated to evaluate the synergistic effect of dual modification on sago starch. Thermal properties, molecular weight distribution, solubility, and other functional properties were evaluated.

2. Materials and methods

2.1. Materials

Sago starch (13% moisture, 0.21% fiber, 0.18% fat, 0.12% ash, and 0.11% protein; 28% amylose, and 72% amylopectin) was purchased from SIM Company Sdn. Bhd. (Pulau Penang, Malaysia). All chemicals were of analytical grade.

2.2. Dual modification of sago starch

Acid-thinned hydrolysis: About 40% sago starch slurries were prepared by adding 400 g starch (db) with 0.14 N hydrochloric acid (HCl) solution at 50 °C to a final weight of 1000 g according to the modified Wang and Wang [22] method [18]. The suspension was incubated at different times (6, 12, 18, and 24 h) at 50 °C to prepare sago starch with different molecular weights. Preliminary experiments showed that incubation times lower than 6 h did not have significant effects on sago starch, and incubation for 24 h decreases the molecular weight, and the starch solution has not film formability. Suspensions were stirred at 200 rpm in an orbital incubator shaker (Jeio Tech SI-. 600R, Seoul, South Korea) to prevent sedimentation. After a specific length of time (6, 12, 18, and 24 h), the slurries were neutralized with NaOH (1%) to a pH 5.5, washed three times with two-fold volume of distilled water, and filtered by a Whatman filter paper 4. The starches were dried in an oven at 40 °C overnight.

Hydroxypropylation: Hydrolyzed hydroxypropylated sago starch (HHSS) was prepared using the method of Hjermstad [23] with some modifications [15,21]. Sodium sulfate (20%, w/v, based on the total solution) was added to the hydrolyzed starch slurry (20%, w/v) and stirred. The pH was adjusted above 10.5 with NaOH (5%). As an etherifying agent, propylene oxide was added to constitute 10%, 20%, and 30% of the dry weight of the hydrolyzed starch. For each concentration, the reaction flask was capped and the mixture was stirred at room temperature for 30 min. The suspension was then incubated for 24 h at 40 °C. To prevent sedimentation, the mixture was stirred at 200 rpm in an orbital incubator shaker SI-600R (JEIOTech, Seoul, Korea). Next, using HCl (10%), the pH of the suspensions was neutralized and adjusted to 5.5. The samples were washed immediately with distilled water. The starch cakes obtained were washed with distilled water until the sulfate content was negative according to the $BaCl_2$ test. The samples were dried in an oven at 40 °C until the moisture content was approximately 10%. The samples were ground using a hammer mill and sieved to the size of 250 μm. HHSS was prepared in triplicate using different hydrolysis sago starches, and the mean of the values was determined.

2.3. Molecular weight distribution after dual modification by gel permeation chromatography (GPC)

GPC measurements were taken by a chromatograph equipped with a PerkinElmer Series 200 pump, Knauer Smartline 2300 refractive index detector, Knauer Smartline column thermostat, Shodex Ohpak SB-G guard column, and Shodex OHpak SB-806MHQ column. Elution was carried out using a 5 mM LiBr in DMSO/DMF (75/25) solution as the mobile phase at a flow rate of 0.3 mL/min. The temperature of the columns was maintained at 60 °C. A calibration curve was constructed using 12 pullulan standards (2560, 1660, 788, 404, 212, 112, 47.3, 22.8, 11.8, 5.9, 1.32, and 0.342 kDa).

A starch concentration of 0.25% and a sampling volume 100 μL were used. To obtain more reliable results, the starch samples were dissolved in the same solvent used as eluent in the GPC system. For better solubilization, the sols were heated in an oil bath at 120 °C for 10 min. The warm (approximately 40 °C) solution was filtered through a 0.45 μm membrane (Whatman 25 mm GD/X, GMF), allowed to cool down, and then injected into the HPLC system [18]. For each samples three replicated using for GPC and the mean of the values was determined.

2.4. DS estimation of propylene oxide

The hydroxypropyl content of the hydrolyzed starches was determined according to the method of Johnson [24] and expressed as DS [21]. The method involves the hydrolysis of the hydroxypropyl group to propylene glycol, which in turn is dehydrated to propionaldehyde and the enolic form of allyl alcohol. These products were measured spectrophotometrically at 590 nm after reacting with ninhydrin reagent (3% ninhydrin in 5% $Na_2S_2O_5$) to form a purple color. MS was calculated as follows:

$$\mathrm{DS} = \frac{162W}{100 - (M-1)W}$$

where W is the equivalent hydroxypropyl group in 100 g of starch, and M is the molecular weight of C_3H_6O [11,25].

2.5. Solubility and swelling power

The method described by Liu et al. was used to determine the solubility and swelling power of the different dually modified sago starches [26]. Briefly, 0.5 g of dually modified starches (db) was weighed and placed in a centrifuge tube with 40 mL of distilled water. The tubes were heated at different temperatures (i.e., 30 °C, 50 °C, 70 °C, and 90 °C) in a shaking water bath for 30 min. The tubes were cooled down to room temperature and centrifuged at 1670 × g for 20 min. The supernatant was carefully poured out and dried overnight at 120 °C. Solubility was determined as the ratio of dried supernatant to dry starch (%), and swelling power was calculated as the ratio of sediment weight to dry starch (g/g). Triplicate measurements were obtained for each starch at each temperature. To measurement the maximum solubility in cold water, different concentrations of dually modified sago starch (from 1% to 20%) were prepared with deionized water. Dispersions were heated up to 90 °C for 30 min and cooled down to room temperature. The maximum concentration that shows liquidity after cooling was considered as the maximum solubility in cold water [18].