

Effect of Sucrose on RVA Viscosity Parameters, Water Activity and Freezable Water Fraction of Cassava Starch Suspensions

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ABSTRACT The effects of sucrose on the physical properties of cassava starch aqueous systems were investigated at varied concentrations of cassava starch (5-15% w/w) and sucrose (0-40% w/w). The peak viscosity and the final viscosity during a gelatinization-retrogradation cycle were determined based on a Rapid Visco Analyzer (RVA) test. Sucrose generally increased the viscosity values, while such increments were more pronounced at higher starch concentrations. The water activity and the fraction of freezable water of gelatinized systems decreased with increasing sucrose concentration. These results suggest that the major role of added sucrose is the reduction of water available for starch, thereby increasing effective concentration of starch during gelatinization and enhancing successive retrogradation.

KEYWORDS: cassava starch, sucrose, RVA viscosity, water activity, freezable water fraction.

INTRODUCTION

Starch plays an important role in developing food products, either as a raw material or as a food additive such as a thickener, stabilizer, or texture enhancer.¹ In addition, starch is used to improve the moisture retention, to control the water mobility, and also to maintain the quality of food products during storage.^{2,3}

Since most foods are aqueous systems, the quality of final food products depends strongly on interactions between water and other ingredients as well as the contribution from individual ingredients.⁴ Many polysaccharides have strong capabilities of associating with water and thus can perform as effective agents to control the behavior of water in complex food systems. This should be also the case for starch based foods since the main components of starch are two types of polysaccharides, designated as amylopectin and amylose. When dry native starch granules are suspended in water and then heated, starch granules absorb water and swell to some extent, accompanied by a loss of crystallinity of granules.⁵ A part of amylose separates from amylopectin and leaches out of granules. These phenomena are generally called gelatinization. Then, on cooling and during a subsequent storage at a low temperature, retrogradation takes place, which is the partial recovery of the initially ordered structures of

polysaccharides.⁵ Amylose is mainly responsible for a short term retrogradation (typically, less than a day), while slow developments of the crystallinity of amylopectin may continue for weeks.⁵ Retrogradation must be strictly controlled with respect to starch-based food products since it can be utilized to structuring the product but on the other hand excessive retrogradation can lead to deterioration in qualities (firming or syneresis).

Interactions between starch polysaccharides and water may exhibit dominant influence on properties of the entire system, while other components may affect how starch interacts with water.^{6,7} From practical as well as scientific point of views, many researchers have investigated effects of sugars on gelatinization/retrogradation behavior of starch.⁸⁻¹⁰ Most sugars exhibit anti-plasticizing effects and thus the amount of amylose leaching is reduced in the presence of sugar.^{11,12} The rate of retrogradation may increase during a short storage period in the presence of sugar but may substantially decrease during longer storage.¹³ The presence of sugars also reduces water activity⁸ and decreases considerably the translational mobility of water.¹⁴ A great number of reports in the literature appear to show complicated effects of sugars but those seem to be attributed to a combination of specific sugar-starch interactions, competition between starch and sugar for available

water, and influences on water structure. Understanding the effect of sucrose on viscosity of starch system is important for product and process development such as a breaded or battered coating or a fill viscosity aid for soups and sauces during the initial stages of cooking before sterilization.¹⁵ As a consequence, however, the overall outcome of sugar addition to a specific food product is by far unpredictable.

Cassava starch is predominant over other starches in the industrial production in Thailand and, due to its low price, cassava starch is used as an ingredient to modify the texture of many Thai food products. The goal of our study is to acquire knowledge on interaction between cassava starch and sucrose in food products. Effects of sucrose on gelatinization and short-term retrogradation were analyzed using a Rapid Visco Analyzer (RVA) test. Additionally, effects of sucrose on the water activity and the amount of freezable water were investigated since the knowledge on the state of water is essential in predicting changes in product properties during production and storage.

MATERIALS AND METHODS

Materials

Commercial cassava starch produced in September 1999 for industrial and local home uses was purchased from a starch company (Thai Quality Starch) located in the area of the Ratchaburi province, Thailand, and used throughout the experiment without any further purification. The cassava starch was kept under a controlled temperature (10 ± 2 °C). A proximate analysis of the starch was made according to the AOAC method¹⁶ and the results are shown in Table 1. The amylose content and the approximate molecular size of amylose after sonication determined by high performance size exclusion chromatography¹⁷ are shown in Table 2. Sucrose (Merck, Germany) was a reagent grade quality. Water used in the preparation and ex-

periment was deionized after distillation (Aquatec Water System, Anaheim, USA).

RVA Pasting Properties

Pasting properties of cassava starch were determined using a Rapid Visco Analyzer (Model RVA-4D, Newport Scientific, Narrabeen, Australia) interfaced with a personal computer equipped with Thermocline software (Newport Scientific). The method utilized was modeled after that of Deffenbaugh et al¹⁸ with minor modification. Precalculated amounts of starch (1.59 to 4.79 g) and sucrose (2.8 to 11.2 g) were added to preweighed deionized distilled water in a RVA cannister to achieve a total weight of 28 g for preparing 5 to 15% w/w starch slurries containing 0 to 40% w/w sucrose. Before the measurement, each 28 g starch-sucrose suspension was stirred manually by rotating the plastic paddle of the RVA for 15 to 30 sec to disperse the sample uniformly and to remove starch lumps. The viscosity of the sample was monitored during a thermal treatment, of which results are called pasting profiles (for details, see Newport Scientific, 1995).¹⁹ The temperature profile consisted of equilibrating the starch slurry at 50°C for 1 min, raising the temperature to 95 °C at a heating rate of 6 °C/min, holding the temperature at 95 °C for 5 min, lowering the temperature to 50 °C at 6 °C/min, and holding at 50 °C for the remainder of the run. The total run time was 23 min. Pasting profiles were determined in duplicate in order to confirm the reproducibility of data and evaluated parameters were averaged.

Water activity and freezable water measurements

Precisely weighed amounts of cassava starch and sucrose were suspended in deionized water and dispersed at room temperature by stirring with a magnetic stirrer. Five to 15% w/w of starch dispersions containing 0, 10, 20, 30 and 40% w/w sucrose were prepared. The experiments for water activity and freezable water measurements were arranged in a factorial design. The dispersions were heated at 90 °C for 15 min in a temperature controlled water bath. The gelatinized samples were cooled at room temperature up to 12 hours before the water activity and freezable water measurements.

Table 1. Compositions of cassava starch.

Composition	% (w/w) ^a
Moisture	12.27 ± 0.13
Protein	0.11 ± 0.01*
Fat	0.07 ± 0.02*
Fiber	0.12 ± 0.03*
Ash	0.25 ± 0.03*

^a Mean ± standard deviation.

* dry basis.

Table 2. Molecular size and content of amylose in cassava starch.

Degree of polymerization	2760 ± 30 ^a
Amylose content (% w/w, dry basis)	17.0 ± 0.21 ^a

^a Mean ± standard deviation.

The water activity was determined using a thermoconstanter (Novasina, Zurich, Switzerland) at 25 °C. The apparatus was calibrated before sample measurements using standard saturated salt solutions (SAL-98, SAL-90, SAL-75, SAL-53, SAL-33, Novasina). Water activity values were recorded after 1 h equilibration at 25 °C. Measurements were done in two replications.

Differential scanning calorimetry (DSC) was used to evaluate the fraction of freezable water in sample dispersions with varied sucrose contents. Ten to 20 mg of each sample was weighed directly into DSC pans and then the pans were hermetically sealed. A sealed empty DSC pan was used as a reference. The sample and reference pans were cooled down to -70 °C or below to ensure complete freezing within 15 to 45 min using liquid nitrogen and then heated up at a constant rate (1.0 °C/min) using a DSC apparatus (Pyris-1, Perkin-Elmer, USA). The enthalpy change due to the melting of ice in a sample was determined as the area under the endothermic curves, and then converted into the fraction of freezable water according to the procedure by Pongsawatmanit and Miyawaki.⁴ The instrument constant of the apparatus was determined using a standard material (deionised water) with a known latent heat of the phase transition at a certain temperature. The sample was weighed before and after the measurement to confirm that no weight was lost. Measurements were done at least twice.

RESULTS AND DISCUSSION

Effect of sucrose on RVA viscosity parameters

The pasting curves of cassava starch dispersions without sucrose are shown in Fig 1. Below an onset temperature of gelatinization (usually below 50 °C), starch granules are insoluble in water and the viscosity of an aqueous dispersion remains low. When starch granules are heated above the gelatinization temperature in the presence of water, the granules absorb a large amount of water and swell to many times their original size and the viscosity increases. The temperature at the onset of this rise in the viscosity can be considered as the starting point of gelatinization and is defined as the pasting temperature in the RVA test.¹⁹ The pasting temperature gives an indication of the minimum temperature required for cooking starch suspensions. The peak viscosity (Fig 1) is considered to represent the equilibrium point between swelling and rupture of starch granules. Swelling of granules, accompanied by leaching of amylose, increases the viscosity, while

granules may rupture during further heating, which results in a decrease in the viscosity. During the holding period at 95 °C, the sample remains subjected mechanical shear stress, which can lead to further disruption of starch granules and amylose-leaching. Leached-out amylose molecules are more or less aligned in the direction of flow, which contributes to shear-thinning or a breakdown in viscosity. As the sample is subsequently cooled down to 50 °C, the viscosity increases to a final viscosity, which is attributed to the retrogradation or reassociation of amylose molecules. Both the peak viscosity and the final viscosity for cassava starch-water systems increased with increasing cassava starch content (Fig 1). The pasting temperature was not much influenced by the starch concentration. In general, the gelatinization temperature of starch increases only slightly with increasing starch concentration and the retrogradation is much enhanced.¹¹⁻¹³ The results in Fig 1 appear to be in line with these general observations.

RVA viscosity profiles were strongly affected by adding sucrose to cassava starch-water systems (Fig 2). Both the peak viscosity and the final viscosity increased with increasing sucrose content (Fig 2), which is similar to the effect of increasing starch concentration (Fig 1). At a certain starch concentration, the pasting temperature increased with increasing sucrose content (Fig 3). Such anti-plasticizing effects of sucrose indicate that a cassava starch-water system containing a higher amount of sucrose will require a higher energy to gelatinization. Since it is known that a reduction of the water content can affect gelatinization of starch in a similar manner,²⁰ increasing pasting temperature may be due

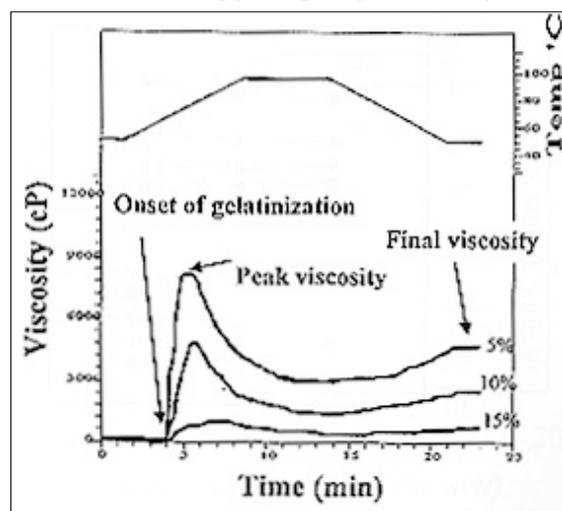


Fig 1. RVA viscosity profiles of 5, 10 and 15% w/w cassava starch suspensions.

to the inhibition of the hydration of starch granules.²¹ In concentrated systems, the competition between sucrose and starch for water, which is necessary for swelling and gelatinization of starch granules, may be critical. In the present case, however, anti-plasticizing effects were observed only when sucrose was added (Fig 2) and were not recognized when the starch concentration was increased (Fig 1). Quantitative analyses of changes in gelatinization behavior have revealed that effects of sugars are much larger than those predicted by considering the reduction of the amount of water due to the hydration by sugar.¹¹ Additionally, it has been believed that sugars interact with starch chains in the amorphous regions of starch granules to stabilize those regions.⁸ If the gelatinization needs to occur at higher temperatures for some reason, the gelatinization mechanism may be altered.^{6, 22} Therefore, understanding delay in starch gelatinization is crucial for improving the texture and other quality of starch-based products,

such as cakes containing relatively high contents of sucrose.

Positive effects of sucrose on increasing peak viscosity were enhanced at higher starch concentrations (Fig 4). The peak viscosity is considered to reflect the water-binding capacity of starch granules although its interpretation cannot be made in a straightforward manner. It is because adding sugar should cause a retardation of gelatinization, a decrease in the amount of amylose-leaching, and yet increases in effective concentrations or local concentrations of granules or leached-out amylose molecules. On the other hand, the final viscosity can be considered as a parameter reflecting the texture quality of relatively fresh starch products. The final viscosity values also increased with increasing sucrose and cassava starch contents (Fig 5). When the final viscosity is plotted on a logarithmic scale (Fig 5b), the slopes of fitted lines were almost independent of the sucrose content

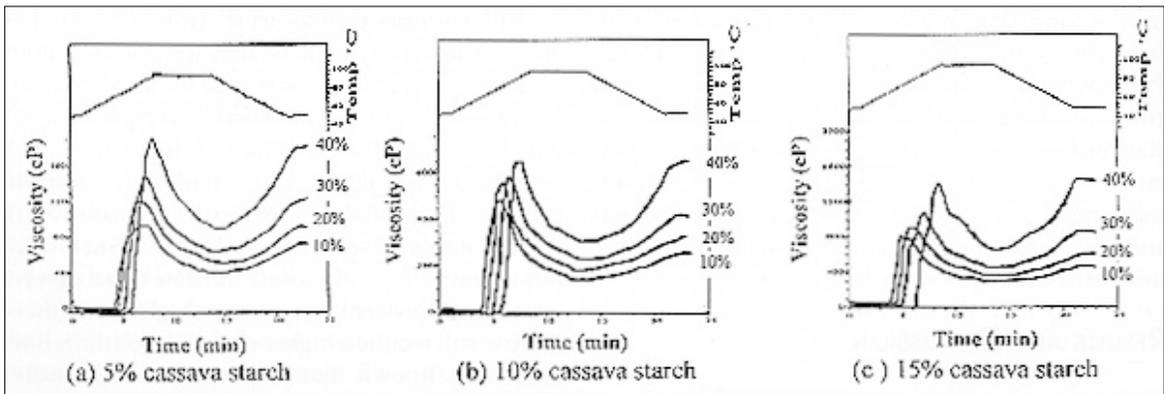


Fig 2. RVA viscosity profiles of cassava starch suspensions containing 10, 20, 30 and 40% w/w sucrose.

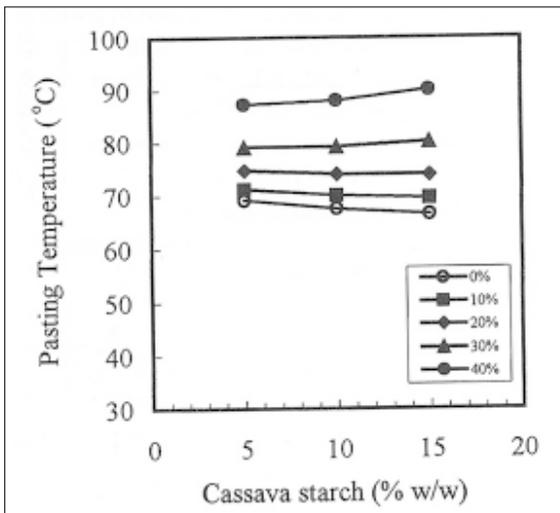


Fig 3. Pasting temperatures of cassava starch suspensions with 0, 10, 20, 30 and 40% w/w sucrose.

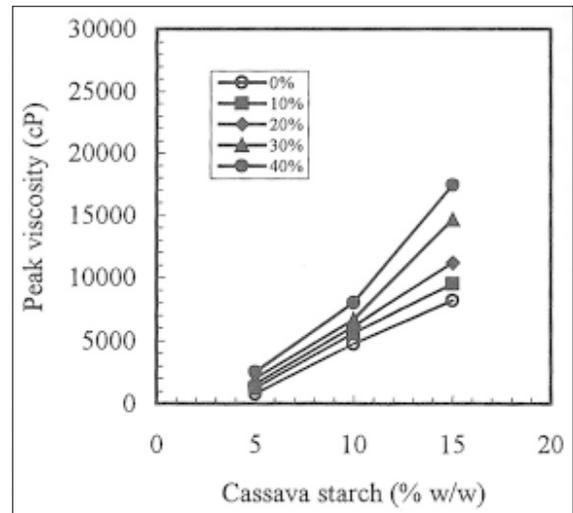


Fig 4. Effects of sucrose content on peak viscosity values of cassava starch suspensions.

(Table 3). These results indicate that changes in the final viscosity by adding sucrose at any starch concentrations can be roughly predictable if we have experimental data sets at a certain starch concentration, despite complicated interactions between sugar and starch at molecular levels.

Effect of sucrose on water activity and freezable water fraction

Since water is the major component in most foods, physicochemical properties of water have strong influences on physicochemical behavior of foods during processing and storage, and even affect sensory properties of foods.²³ The activity of water and the fraction of freezable water appear to be good measures for evaluating the state of water in food systems.²⁴

Water activity correlates well with the stability of foods in terms of chemical reactions and microbial

growths.¹⁰ Figure 6 shows water activities of cassava starch dispersions at various sucrose concentrations. The water activity values of cassava starch dispersions were nearly independent of the starch concentration for the systems containing 0 to 20% w/w sucrose. At sucrose concentrations higher than 20% w/w, the water activity decreased significantly with increasing starch concentration. The water activity value of the thickest dispersion that contained 40% w/w sucrose and 15% w/w cassava starch was about 0.94, suggesting that the overall water activity is dominated by free water in the examined systems. Due to the colligative property of water, the water activity tends to be dominated by the amount of low molecular weight substances, that is sucrose in the present case.²⁴

The fraction of freezable water, which is indicative of the amount of free water in an unfrozen system, decreased with increasing cassava starch content from 5 to 15% w/w at any certain sucrose concentrations (Fig 7). The water activity of the cassava starch dispersions was, in contrast, much less dependent on the starch concentration especially at low sucrose concentrations (0 to 20% w/w, Fig 6).

Table 3. Linear regression parameters for plots of log(final viscosity) and starch concentration.

Sucrose (% w/w)	slope	R ²
0	0.20	0.95
10	0.19	0.97
20	0.19	0.99
30	0.20	0.98
40	0.20	0.98

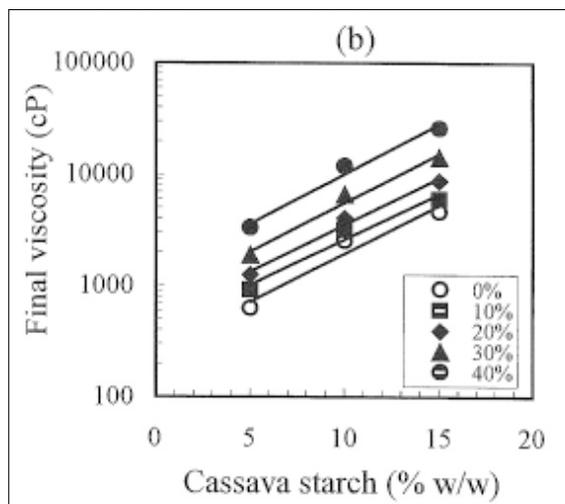
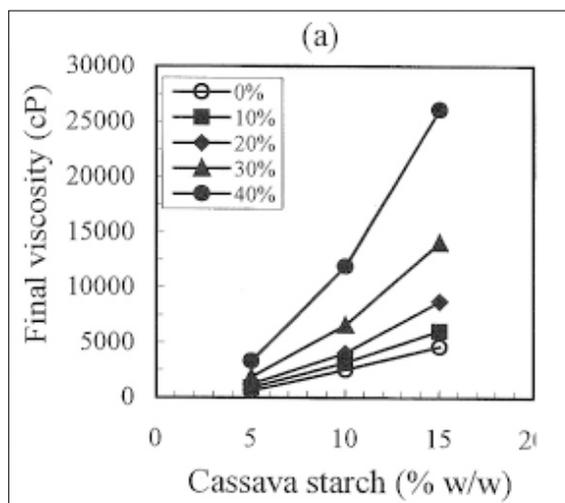


Fig 5. Effects of sucrose content on final viscosity values of cassava starch suspensions. The viscosity was plotted on linear (a) and logarithmic (b) scales.

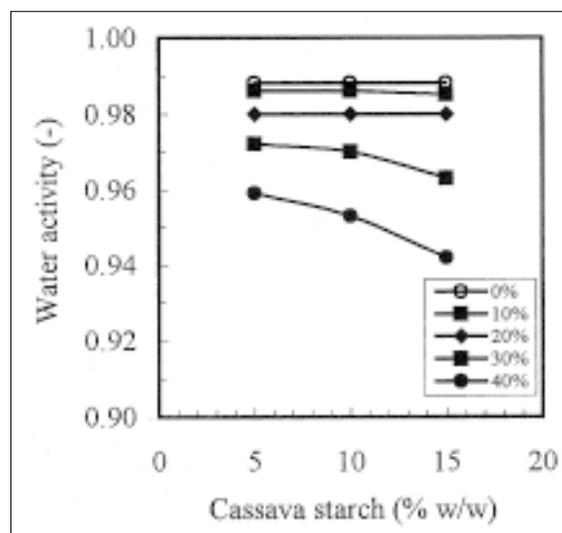


Fig 6. Water activity of cassava starch suspensions with 0, 10, 20, 30 and 40% w/w sucrose.

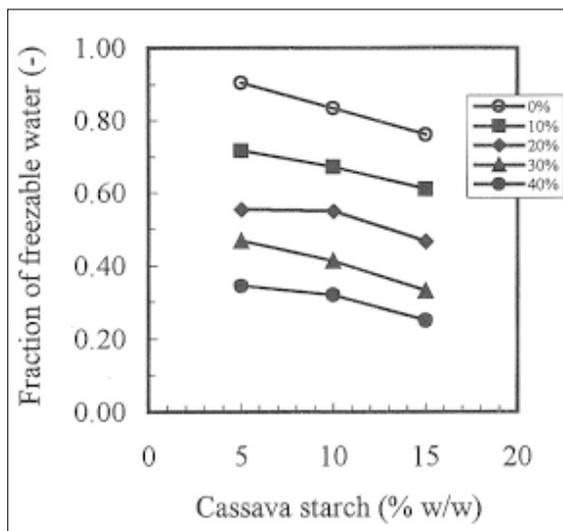


Fig 7. Fraction of freezable water of cassava starch suspensions with 0, 10, 20, 30 and 40% w/w sucrose.

Sucrose decreased the fraction of freezable water more significantly compared with the water activity (eg the fraction of freezable water of the thickest dispersion that contained 40% w/w sucrose and 15% w/w cassava starch was about 0.20). The stability of food products is expected to be improved by decreasing the fraction of freezable water. Further investigation is needed to reveal if the stability of food products is improved by increasing concentration of sucrose and/or starch even though the water activity remains high.

In conclusion, anti-plasticizing effects of sucrose were recognized in aqueous dispersions of cassava starch during gelatinization. Although sucrose is known to reduce the amount of amylose-leaching, sucrose enhanced both the peak viscosity and the final viscosity in RVA tests, suggesting that the effective concentration of amylose was increased by reducing the amount of water available. This hypothesis was supported by the determination of the total amount of free water, which was significantly decreased with increasing sucrose concentration.

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