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Effects of monoglycerides on pasting properties of wheat starch after repeated heating and cooling

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ABSTRACT

The effects of repeated heating and cooling on the properties of pastes prepared from a commercial wheat starch (*Triticum aestivum L.*) with added monoglycerides were studied using a Rapid Visco Analyser (RVA). The nanostructure of the freeze-dried pastes was determined by X-ray diffraction and small-angle X-ray scattering. Pastes prepared from the wheat starch alone, or from the starch mixed with tripalmitin, which does not form complexes with starch, produced regular viscosity profiles in the RVA when subjected to multiple heat-cool cycles. In comparison, the effects of adding monoglycerides (or monoacylglycerols) depended on the chain length and saturation of the fatty acid of the monoglyceride. Repeated heat-cool cycles in the RVA of the starch with different monoglycerides induced the formation of complexes of varying stability that influenced the viscosity trace of the paste during multiple heating and cooling cycles. Small-angle X-ray scattering in combination with X-ray diffraction proved useful in describing the nanostructural changes in the RVA pastes induced by monoglycerides and temperature cycling. The results indicate that the functional properties of starch pastes may be manipulated through the strategic selection of an added monoglyceride.

1. Introduction

Starch is a major source of dietary carbohydrate and is used in many food applications as a thickener, texture enhancer, stabilizer and for controlling consistency and moisture retention (Ellis et al., 1998). The characteristics of many foods result from the specific pasting, gelatinization and retrogradation properties of starch, which can be influenced significantly by additives. One of the most important interactions of starch is between amylose and lipids, which can alter both the functional and nutritional characteristics of starchy foods (Hibi et al., 1990; Riisom et al., 1984). Complexation with lipids reduces the solubility of starch in water, alters the rheological properties of pastes, decreases swelling capacity, increases gelatinization temperature and reduces gel rigidity (reviewed by Copeland et al., 2009). From a nutritional perspective, complexation with lipids affects the susceptibility of starch to enzymatic breakdown. Lipids slow down amylose retrogradation, thereby retarding the formation of resistant starch, but conversely, *in vitro* studies have shown that starch complexed with lipids is attacked more slowly by amylases (Crowe et al., 2000; Eerlingen et al., 1994; Jeong and Lim, 2003).

With rising consumer demand for functional foods, methods to evaluate gelatinization and retrogradation behavior of starches are of interest. Instruments such as the Rapid Visco Analyser (RVA, Newport Scientific) are used extensively in empirical studies to characterize the viscosity of starch throughout the gelatinization and retrogradation processes. The RVA has been used to form and characterize starch–lipid complexes (Mira et al., 2005; Tang and Copeland, 2007a), and to investigate the varietal influences on complex formation between lipids and wheat starch (Blazek and Copeland, 2009; Salman and Copeland, 2010). These and most other RVA studies reported in the literature have used a standardized single heat-cool profile, with only a few reports of modified RVA protocols (Batey, 2007; Blakeney and Booth, 2001; Corke et al., 1996; Nelles et al., 2000).

RVA and similar techniques provide valuable information on process adequacy, and can be coupled with diffraction, scattering, thermal and microscopic techniques to enable the food microstructure to be related to functionality. Salman and Copeland (2010) used a novel extended RVA profile, which included repeated heating and cooling to investigate the properties of starch and starch–lipid pastes. The rationale behind using repeated heating and cooling is that various processed foods, such as pasteurized

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foods, convenience, restaurant and mass catering meals, and pre-cooked foods, undergo repeated heating and cooling or are held at elevated temperatures for a period before consumption. Information on the behavior of starch in such systems is very limited. The objectives of the present study were to increase our understanding of the interactions between starch and lipids by exploring the behavior of wheat starch pastes with added monoglycerides (also referred to as monoacylgycerols) during repeated heating and cooling in the RVA. Although food processing is unlikely to include such complex thermal treatments, we chose to extend the number of heat/cool cycles to observe the thermal stability of the starch–lipid complexes. In order to explore the relationship between viscosity and structure of the pastes, RVA measurements were supported by XRD and SAXS analyses of the resulting freeze-dried pastes.

2. Experimental

2.1. Materials

A commercial starch from Penford Australia Pty Ltd (Lane Cove, NSW, Australia) was used in this study. The starch had 25% amylose and other properties as described by Tang and Copeland (2007a). The following monoglycerides (from Sigma–Aldrich, St. Louis, MO, USA, and of at least 99% purity) were investigated: monocaprylin (C8:0), monocaprin (C10:0), monolaurin (C12:0), monomyristin (C14:0), monopalmitin (C16:0), monostearin (C18:0), monopalmitolein (C16:1), monoolein (C18:1), monoerucin (C22:1) and tripalmitin (3xC16:0), where the fatty acid component (Cn:D) is shown in brackets using the standard nomenclature where Cn is the number of carbon atoms and D is the number of double bonds in the fatty acid. All unsaturated monoglycerides had fatty acids in the *cis* configuration. The properties of the lipids used in this study are summarized in Table 1.

2.2. Complexing index of starch with different lipids

The amount of lipid required to saturate the starch was assessed by allowing excess lipid to react with starch in dilute solution, as described by Blazek and Copeland (2009). Starch (20 mg) was freed of endogenous lipids and dissolved in 5 ml of deionized water and lipid (5 mg) dissolved in ethanol (0.1 ml) was added to the starch solution. The mixtures were incubated for 60 min at 80 °C in a shaking water bath. The complexing index (CI) of starch was measured by the method of Gilbert and Spragg (1964) with modifications as follows. An aliquot of starch solution (0.1 ml) was added to 5 ml of deionized water and 0.05 ml of iodine solution (0.13% w/v I_2 and 0.3% w/v KI in water) was added with mixing. The absorbance at 620 nm was read after 30 min at 25 °C. The complexing index, CI, was calculated from:

$$CI = 100(A_S - A_{S.L})/A_S$$

where A_S and $A_{S.L}$ are the absorbances of the starch solution without and with added lipid, respectively.

2.3. Pasting properties

Pasting properties of the starch samples were analyzed in a Rapid Visco Analyser RVA-4 (Newport Scientific, Warriewood, Australia) using a mixture of starch (3 g, 10% moisture) and 25 g of deionized water. Lipids (30 mg) were added directly to the RVA canister at a final concentration of 1.1% (w/w) per weight of starch. This ratio of lipid to starch was below the ratio of approximately 15% (w/w) at which maximum complexation was measured (Blazek and Copeland, 2009). An RVA profile consisting of 15 repeated heat-cool cycles of 12 min each was employed. This profile featured a constant mixing speed of 160 rpm with temperature profile of a single heat-cool cycle as follows: hold at 50 °C for 1 min, increase to 95 °C over 3 min 42 s (rate 12.1 °C per minute), hold at 95 °C for 2 min 30 s, decrease to 50 °C over 3 min 48 s (rate 11.8 °C per minute) and hold at 50 °C for 1 min. This profile was based on the one heat-cool cycle STD1 profile described in the Thermocline software supplied with the instrument and is subsequently referred to as 15STD1. Analyses were performed on duplicate starch samples. Starch pastes from the RVA were frozen at −80 °C, freeze-dried and ground into a powder using a mortar and pestle for the XRD and SAXS analyses.

2.4. X-ray diffraction

XRD measurements of freeze-dried pastes, deposited as approximately 1 mm-thick film in the sample holder, were made with a Difftech Mini Materials Analyzer X-ray diffractometer (GBC Scientific Equipment Pty. Ltd.). The X-ray generator was equipped with a cobalt anode (λ = 0.178897 nm) operating at 1 kV and 3.36 mA. X-ray diffraction patterns were acquired at room temperature (20 ± 1 °C) over the 2θ range of 5°–35° at a rate of 0.50° 2θ per minute and a step size of 0.05° 2θ. The Igor software package (Wavemetrics, Lake Oswego, Oregon) was used for curve fitting as described by Lopez-Rubio et al. (2008). The curve fitting operation was carried out iteratively with each iteration refining the fitting coefficients to minimize chi-squared, which is defined as:

$$\sum \left(\frac{y - y_i}{\sigma_i} \right)^2$$

Table 1
Properties of the RVA pastes. Melting temperatures of the lipids (T_m) are from Sigma Aldrich product data sheets and Lindman (1984). Complexing index (CI) was calculated from the affinity for the formation of starch–lipid complexes in commercial wheat starch in dilute solution as described in the text. Relative change in viscosity during the first five cycles and in final viscosity after 15 cycles were calculated from comparison to starch-only paste, i.e. 336.7 and 278.7 RVU, respectively.

Mixture	Tm (°C)	CI (%)	Max viscosity of first 5 cycles (RVU)	Relative change (%)	Final viscosity after 15 cycles (RVU)	Relative change (%)
starch-only	–	0.0	336.7	0.0	278.7	0.0
monocaprylin (C8:0)	–	6.1	338.3	0.5	277.3	−0.5
monocaprin (C10:0)	51	21.0	343.6	2.0	130.4	−53.2
monolaurin (C12:0)	60	92.1	422.7	25.5	128.0	−54.1
monomyristin (C14:0)	68	94.1	397.4	18.0	136.6	−51.0
monopalmitin (C16:0)	74	94.7	473.2	40.5	218.2	−21.7
monostearin (C18:0)	78	94.4	353.3	4.9	376.0	34.9
monopalmitolein (C16:1)	–	94.3	370.1	9.9	206.6	−25.9
monoolein (C18:1)	35	95.0	398.9	18.5	381.4	36.9
monoerucin (C22:1)	52	94.8	316.6	−6.0	388.3	39.3
tripalmitin (3xC16:0)	66	6.7	336.1	−0.2	278.1	−0.2