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Effects of stearic acid and gamma irradiation, alone and in combination, on pasting properties of high amylose maize starch

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ABSTRACT

The effects of stearic acid and gamma irradiation on pasting properties of high amylose maize starch (HAMS) were studied. Stearic acid (0%, 1.5%, and 5%) was added to HAMS, and then irradiated at 0, 30, and 60 kGy before pasting. Stearic acid increased the paste viscosity of un-irradiated HAMS from 420 mPa s to 557 and 652 mPa s for 1.5% and 5% stearic acid, respectively. This observation related well with the formation of type II amylose–lipid complexes, with melting temperatures of about 100–120 °C. Gamma irradiation (30 and 60 kGy) reduced pasting viscosity of HAMS. Pasting of gamma irradiated HAMS resulted in the formation of type I amylose–lipid complexes, with melting temperatures and enthalpies ranging from 82 to 102 °C and 0.22 to 1.85 J/g, respectively. Stearic acid addition followed by irradiation creates means of producing different types of amylose–lipid complexes from HAMS for industrial utilization.

1. Introduction

Starch is considered the second largest biomass, next to cellulose (Zhang, Huang, Luo, & Fu, 2012). It is stored as discrete semi-crystalline granules in higher plants, and consists of two main components, namely essentially linear amylose and highly branched amylopectin (Gallant, Bouchet, & Baldwin, 1997). High amylose maize starches are produced from maize with amylose extender *ae* mutant (Shi, Capitani, Trzasko, & Jeffcoat, 1998). They are reported to have the ability to form strong gels (Raphaelides & Georgiadis, 2008). High amylose maize starches can be used in the preparation of biodegradable films (Bader & Göritz, 1994), resistant starch (Lay Ma, Floros, & Ziegler, 2011), and nano-sized starch particles (Kim & Lim, 2009). They can also be used as fat replacers (eg. in cake icings) (Singh & Byars, 2011).

High amylose maize starch has limited commercial utilization compared to normal maize starch due to challenges in processing them at normal conditions (i.e. 60–90 °C), and therefore require temperatures above 130 °C to completely gelatinize and disperse (Case et al., 1998), which may contribute to high energy utilization and cost of production. In a previous study by Ocloo, Minnaar, and Emmambux (2014), the effects of stearic acid and gamma irradiation on some functional, structural and molecular characteristics of native high amylose maize starch were investigated. The major findings from that study showed that gamma irradiation depolymerised both amylose and amylopectin components of native high amylose maize starch. Gamma irradiation also decreased the gelatinization temperature of native high amylose maize starch (Ocloo et al., 2014).

Gamma irradiation produces free radicals that are able to induce molecular changes and fragmentation of starch molecule (Chinnaswamy, 1993; Ciesla, Zoltowski, & Mogilevsky, 1991; Liu, Ma, Xue, & Shi, 2012; Ocloo et al., 2014; Sabularse, Liuzzo, Rao, & Grodner, 1992). These changes have been reported to reduce the pasting properties of starches, for example normal maize starch (Chung & Liu, 2009). Gamma irradiation (30 kGy) has also been reported to decrease transition temperatures and melting enthalpies of endogenous amylose–lipid complexes in wheat and potato starches (Cieśla & Eliasson, 2003, 2007b) and wheat flour (Cieśla & Eliasson, 2005), due to gamma irradiation-induced depolymerization. Cieśla and Eliasson (2007a) reported similar effects when 1-mono-lauroyl glycerol was mixed with wheat and potato starches.

Starches have been modified to improve their functional properties and utilization using stearic acid (D'Silva, Taylor, & Emmambux, 2011; Raphaelides & Georgiadis, 2008; Wokadala, Ray, & Emmambux, 2012). High amylose maize starch has been modified with sodium-palmitate (Fanta, Kenar, Byars, Felker, & Shogren, 2010), palmitic and oleic acid (Fanta, Felker, Shogren, &

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Salch, 2008) and lauric, myristic, palmitic and stearic acid and their salts (Fanta, Shogren, & Salch, 1999) to produce spherulites and inclusion complexes through jet cooking. Addition of stearic acid to starches has been reported to reduce first pasting peak viscosity and increase second pasting peak viscosity of other starches, such as normal maize starch (Nelles, Dewar, Bason, & Taylor, 2000; Wokadala et al., 2012) and teff starch (D'Silva, Taylor, & Emmambux, 2011; Wokadala et al., 2012). The above phenomena have been attributed to formation of amylose lipid inclusion complexes in these starches (D'Silva, Taylor, & Emmambux, 2011; Nelles, Dewar, van der Merwe, & Taylor, 2003; Nelles et al., 2000; Wokadala et al., 2012). Amylose with different degree of polymerization (molecular weight) can produce different types of amylose–lipid complexes (Gelders, Vanderstukken, Goesaert, & Delcour, 2004; Godet, Buleon, Tran, & Colonna, 1993). Starches with higher amylose contents have been reported to produce more amylose–lipid complexes compared to those with lower amylose contents (Eliasson, Finstad, & Ljunger, 1988).

Very low pasting viscosity values (<10 BU) have been reported for high amylose maize starch (Hylon V) using Brabender Visco-amylograph (Chang, He, & Huang, 2013). Jane et al. (1999) also reported similar low pasting viscosities (<10 RVU) when high amylose maize starches (Hylon V and VII) were pasted using Rapid Visco Analyser (RVA). These researchers attributed the observed pasting viscosity values to incomplete gelatinization.

This present study determines the effects of stearic acid and gamma irradiation, alone and in combination, on pasting properties of high amylose maize starch with the aim of producing amylose–lipid complexes under pressure in a rheometer. There is no published report on pasting of high amylose maize starch under pressure in the literature.

2. Materials and methods

2.1. Materials

High amylose maize starch (Hylon VII®) was purchased from Ingredion Incorporated® (Westchester-USA). The amylose content as measured according to the method described by Yun and Matheson (1990) using amylose/amylopectin assay kit from Megazymes (Megazyme International, Bray, Ireland) was 61.62 ± 2.97%. Stearic acid (AR) was purchased from Sigma–Aldrich Company (St. Louis, MO, USA). All other reagents used in this study were analytical grade.

2.2. Methods

2.2.1. Addition of stearic acid into high amylose maize starch

Stearic acid (0%, 1.5% and 5%) was added to high amylose maize starch on dry weight basis using the procedure of D'Silva, Taylor, and Emmambux (2011). In brief, stearic acid was solubilized in absolute ethanol and then the starch added and stirred. The mixture was covered with parafilm and aluminum foil and then incubated in the shaking water bath at 50 °C for 30 min with a speed of 120 rpm. The ethanol used in the solubilization was evaporated in an oven at 40 °C.

2.2.2. Gamma irradiation

About 40 g of high amylose maize starch samples were packaged and then irradiated at a commercial gamma irradiator facility run by Synergy Sterilisation SA (Pty) (Isando, South Africa) using ^{60}Co source. Samples were irradiated at target doses of 0, 30 and 60 kGy (Actual irradiation doses were 0, 30.8 and 61 kGy) with a mean dose rate of 0.02 kGy/min. Irradiation was repeated three (3) times. Samples were stored at 8 °C for further analyses.

2.2.3. Pasting of high amylose maize starch samples

Irradiated and un-irradiated high amylose maize starch (with and without stearic acid) suspensions (10% w/w) were pasted by initially stirring at 960 rpm at 50 °C for 10 s, heating to 120 °C at 10 °C/min and holding at this temperature for 10 min at 160 rpm and then cooled to 90 °C with a rheometer (Physica MCR 101, Anton Paar Germany GmbH) under a pressure of 500 kPa). The pastes were further held at 90 °C for 90 min and then cooled to 50 °C at 160 rpm. The pastes were then frozen in liquid nitrogen for about 20 min and stored at −20 °C. The frozen samples were finally freeze-dried for 5 days in a freeze dryer (Intruvac Lyophilizer model BKL, South Africa) at −45 °C and pressure of −85 kPa. The freeze-dried samples were then milled using mortar and pestle. Samples were packaged and stored at 8 °C prior to analysis. The initial pasting condition (heat at 120 °C for 10 min) was introduced to effect gelatinization of high amylose maize starch, since high amylose maize starch can only paste above 100 °C (Case et al., 1998). The second stage of pasting (heat at 90 °C for 90 min) was to create the conditions for the formation of amylose–lipid complexes, since crystalline type II amylose–lipid complexes are reported to be formed at 90 °C (Biliaderis & Galloway, 1989; Biliaderis & Seneviratne, 1990; Karkalas, Ma, Morrison, & Pethrick, 1995). The accessory in the rheometer was made up of a cup with a stirrer; and a magnetic coupling head that capture the resistance to flow in the cup to the load cell.

2.2.4. Differential Scanning Calorimetry (DSC)

The thermal properties of the pasted freeze-dried un-irradiated and irradiated high amylose maize starch (with and without added stearic acid) samples were analyzed using a high pressure Differential Scanning Calorimetry (DSC) system with STARe® software (HPDSC-827, Mettler Toledo, Greifensee, Switzerland). The procedure reported by Wokadala et al. (2012) was used. The instrument was previously calibrated using indium (T_o = 156.62 °C, Heat flow = −28.55 J/g). Starch sample (10 mg, db) was weighed into a crucible and about 30 mg distilled water added. The pan was sealed and equilibrated for at least 4 h under ambient temperature. Heating was conducted from 30 °C to 160 °C at a rate of 10 °C/min under pressure (4.00 ± 0.01 MPa). The reference material was an empty pan. The melting-transition characteristics of the amylose–lipid complexes (onset temperature (T_o), peak temperature (T_p) and enthalpy (ΔH)) were then determined.

2.2.5. Wide angle X-ray scattering (WAXS)

The X-ray diffractograms of the freeze-dried pasted un-irradiated and irradiated high amylose maize starch (with and without added stearic acid) samples were taken using the X-ray diffraction (XRD) (X'Pert-Pro PANanalytical diffractometer) (Eindhoven, the Netherlands). Dried pasted high amylose maize starch samples were equilibrated at 95% relative humidity (using a 22% glycerol solution) (Darfour, Ocloo, & Wilson, 2012) for 5 days at about 25 °C. The XRD operating conditions were: 45 kV, 40 mA and Cu $K_\alpha 1$ (0.154 nm). Samples were scanned from 5° to 30° (2θ) with an exposure time of 16 min 14 s, a step size of 0.026° and a time/step ratio of 224 s (Wokadala et al., 2012). A plot of relative intensity peaks against 2 theta peaks was then obtained. Relative crystallinity of the freeze-dried starch samples was calculated as percent integrated area of crystalline peaks to the total integrated area above a straight baseline (Cheetham & Tao, 1998). Diffraction spacing (d-spacing) for the identified peaks was calculated using the Bragg's equation ($n\lambda = 2d \sin\theta$) (Singh, Ali, Somashekar, & Mukherjee, 2006).