



Impact of annealing and heat-moisture treatment on rapidly digestible, slowly digestible and resistant starch levels in native and gelatinized corn, pea and lentil starches [☆]

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ABSTRACT

Impact of annealing (ANN) and heat-moisture treatment (HMT) on rapidly digestible starch (RDS), slowly digestible starch (SDS), resistant starch (RS), and expected glycemic index (eGI) of corn, pea, and lentil starches in their native and gelatinized states were determined. ANN was done for 24 h at 70% moisture at temperatures 10 and 15 °C below the onset (T_o) temperature of gelatinization, while HMT was done at 30% moisture at 100 and 120 °C for 2 h. The swelling factor (SF), amylose leaching (AML) and gelatinization parameters of the above starches before and after ANN and HMT were determined. SF and AML decreased on ANN and HMT (HMT > ANN). The gelatinization temperatures increased on ANN and HMT (HMT > ANN). However, the gelatinization temperature range decreased on ANN but increased on HMT. Birefringence remained unchanged on ANN but decreased on HMT. The Fourier transform infrared (FT-IR) absorbance ratio of 1047 cm^{-1} /1022 cm^{-1} increased on ANN but decreased on HMT. ANN and HMT increased RDS, RS and eGI levels and decreased SDS levels in granular starches. HMT had a greater impact than ANN on RDS, RS, and SDS levels. In gelatinized starches, ANN and HMT decreased RDS and eGI, but increased SDS and RS levels. These changes were more pronounced on HMT. This study showed that amylopectin structure and interactions formed during ANN and HMT had a significant impact on RDS, SDS, RS and eGI levels of starches.

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1. Introduction

Starch is classified into rapidly digestible starch (RDS), slowly digestible starch (SDS), and resistant starch (RS) according to the rate of glucose release and its absorption in the gastrointestinal tract (Englyst, Kingman, & Cummings, 1992). RDS is the starch fraction that causes a sudden increase in blood glucose level after ingestion, and SDS is a starch fraction that is digested completely in the small intestine at a lower rate as compared to RDS. RS is the starch portion that cannot be digested in the small intestine, but is fermented in the large intestine. A number of physiological effects have been ascribed to RS (Haralampu, 2000; Sajilata, Singhal, & Kulkarni, 2006), whereas studies on the health benefits of SDS are limited (Lehmann & Robin, 2007). The health benefits of RS have been reported as prevention of colon cancer, hypoglycemic effects, substrate for growth of the probiotic microorganisms, reduction of gall stone formation, hypocholesterolemic effects,

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inhibition of fat accumulation, and increased absorption of minerals (Sajilata et al., 2006). The potential health benefits of SDS are linked to a stable glucose metabolism, diabetes management, mental performance, and satiety (Lehmann & Robin, 2007). Among granular starches, maize, waxy maize, sorghum and legume starches have been shown to contain high amounts of SDS, due to the interplay of optimal granule size, channelisation and the interaction of protein or other surrounding material (Lehmann & Robin, 2007; Zhang, Ao, & Hamaker, 2006; Zhang, Venkatachalam, & Hamaker, 2006). The glycemic index (GI), which characterizes the carbohydrate in different foods, is ranked on the basis of the postprandial increase in blood glucose (Jenkins, 2007; Jenkins et al., 1982). Low GI foods, by virtue of the slow digestion and absorption of their carbohydrate, produce a more gradual rise in blood glucose and insulin levels, and are increasingly associated with health benefits. Low GI foods have thus been associated with reduced incidence and prevalence of heart disease, diabetes, and also some forms of cancer (Brand-Miller, 2007; Brand-Miller, Hayne, Petocz, & Colagiuri, 2003; Jenkins, 2007; Roberts, 2000; Wolever & Mehling, 2002). FAO/WHO (1998) recommended an increased intake of low GI foods, with emphasis on diabetics and subjects with

impaired glucose tolerance. In the recent WHO reports (FAO/WHO, 2003), the preventive potential of low GI diets in relation to obesity and diabetes was graded as 'possible'. The evidence for such a possibility was recently strengthened by many clinical studies demonstrating a positive relation between dietary GI and insulin resistance, and prevalence of metabolic syndrome (Brand-Miller, 2007; Jenkins, 2007; Mckeown et al., 2004). In accordance with the definition, the GI must be confirmed *in vivo* by clinical trials. However, GI evaluation in human can be difficult and costly, therefore studies measuring *in vitro* digestion have been done in order to expect *in vivo* effects (Goni, Garcia-Alonso, & Saura-Calixto, 1997; Granfeldt, Björck, Drews, & Tovar, 1992). They suggested that the *in vitro* procedure had a high correlation with *in vivo* glycemic response and thus could be useful in the estimation of the GI. Legume starches have been known to exhibit a lower glycemic index than cereal or tuber starches due to high levels of amylose, large amount of viscous soluble dietary fiber and strong interactions between amylose chains (Hoover & Zhou, 2003).

Annealing (ANN) and heat-moisture treatment (HMT) are two hydrothermal methods that have been used to modify starch digestibility. ANN of starch is a physical treatment of starch granules in the presence of heat and water. During ANN starch granules in excess (>60% w/w) or at intermediate water content (40% w/w) are held at a temperature above the glass transition temperature (T_g) but below the onset (T_0) temperature of gelatinization for a set period of time (Hoover & Vasanathan, 1994a; Tester & Debon, 2000). The following changes have been shown to occur in all starches on ANN: (1) increase in granule stability, (2) crystalline perfection, (3) starch chain interactions within the amorphous and crystalline domains of the granule, (4) formation of double helices, (5) increase in gelatinization temperatures, (6) narrowing of the gelatinization temperature range, (7) decrease in granular swelling, and (8) decrease in amylose leaching. However, depending on the starch source, crystallinity, amylose–lipid interactions, and susceptibility towards acid and enzyme hydrolysis have been shown to increase, decrease or remain unchanged on ANN (Hoover & Manuel, 1996a; Hoover & Vasanathan, 1994a; Jacobs & Delcour, 1998; Tester & Debon, 2000; Waduge, Hoover, Vasanathan, Gao, & Li, 2006). HMT is also a physical modification technique that involves treatment of starch granules at low moisture levels (<35% moisture w/w) for a certain time period (15 min–16 h) and at temperatures (84–120 °C) above T_g but below the gelatinization temperature. In all starches, increase in gelatinization temperatures, widening of the gelatinization temperature range, decrease in granular swelling and amylose leaching, and an increase in thermal stability have been shown to occur on HMT. However, depending on the starch source, changes to the X-ray pattern (B to A + B), formation of amylose–lipid complexes, disruption of crystallinity, and increase or decrease in enzyme susceptibility have also been shown to occur on HMT (Gunaratne & Hoover, 2002; Hoover & Manuel, 1996b; Hoover & Vasanathan, 1994b).

Several attempts have been made to generate RS by ANN and HMT (Brumovsky & Thompson, 2001; Haralampu, 2000; Haralampu & Gross, 1998; Jacobasch, Dongowski, Schmiedl, & Muller-Schmehl, 2006; Lehmann & Robin, 2007; Sajilata et al., 2006; Shi & Trzasko, 1997; Vasanathan & Bhatt, 1998). However, there is a dearth of information on the effect of ANN and HMT on the formation of SDS. Shin, Kim, Ha, Lee, and Moon (2005) showed that the hydrothermal treatment (50% moisture at 55 °C for 12 h) of sweet potato starch increased the SDS level from 15.6% to 31.0%. Niba (2003) investigated the effect of heat treatment, storage temperature and time on the digestibility of various flours (maize, yam, rice, potato, plantain, and cocoyam). For all flours, the SDS content was increased by autoclaving and parboiling, but significantly reduced by microwaving, compared with the raw flour. However, the increased RS and SDS in granular starch

by ANN and HMT were not heat stable. The lack of thermal stability of SDS and RS represents a limitation on their use as food ingredients.

The objective of this study was to compare the impact of ANN and HMT (under different time–temperature regimes) on SDS, RS and eGI levels in different starch sources (corn, pea and lentil starches) subjected to *in vitro* α -amylolysis.

2. Materials and methods

2.1. Materials

Pea (*Pisum sativum* L.) cultivar (1674-13) and lentil (*Lens culinaris*) cultivar (CDC Meteor) were obtained from the Crop Development Centre, University of Saskatchewan, Canada. Pea and lentil starches were extracted from seeds using the procedure of Chung et al. (2008). Normal corn starch (cat. no. S-4126), pancreatin from porcine pancreas (cat. no. P-7545, activity 8× USP/g) and invertase (ED 3.2.1.26) grade VII from Bakers yeast (355 U/mg) were purchased from Sigma Chemical Company (St. Louis, MO, USA). Amyloglucosidase (EC 3.2.1.3., 3300 U/mL) and glucose oxidase-peroxidase assay kit (cat. no. K-GLUC) were purchased from Megazyme (Megazyme International Ireland Ltd., Bray, Ireland).

2.2. Hydrothermal treatment

2.2.1. Annealing

Starch slurries (70% moisture) were incubated at 10 and 15 °C below the onset temperature (T_0) of gelatinization for 24 h in a water bath. At the end of the incubation period, samples were centrifuged (2000g) for 10 min and supernatant was decanted (no amylose or soluble carbohydrate was detected in the supernatant). The annealed starches were washed once with deionized water and air dried at room temperature, ground and passed through a 120-mesh screen.

2.2.2. Heat-moisture treatment

Starch samples were weighed into glass containers. Starch moisture content was brought to 30% by adding the appropriate amount of distilled water. The starch samples were mixed thoroughly during the addition of water. The containers were sealed, kept for 24 h at ambient temperature, and then placed in a forced air oven at 100 or 120 °C for 2 h. Afterwards the containers were opened, and the starch samples air dried to uniform moisture content (~10%).

2.3. Apparent amylose content

Apparent amylose content was determined using the method of Williams, Kuzina, and Hlynka (1970).

2.4. Amylopectin chain length distribution

Isoamylase debranching of whole starch accompanied by high performance anion exchange chromatography with pulsed amperometric detection (HPAEC–PAD) was used to determine the average chain length (CL) and the branch chain length distribution of the native starches (Liu, Gu, Donner, Tetlow, & Emes, 2007).

2.5. Swelling factor (SF)

SF of native, ANN, and HMT starches when heated at 80 °C in excess water was measured according to the method of Tester and Morrison (1990). The SF is reported as the ratio of the volume of swollen granules to the volume of dry starch.

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