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Effect of acetylation, oxidation and annealing on physicochemical properties of bean starch

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ABSTRACT

Black and Pinto bean starches were physically and chemically modified to investigate the effect of modification on digestibility and physicochemical properties of bean starch. The impact of acetylation, oxidation (ozonation) and annealing on the chemical composition, syneresis, swelling volume, pasting, thermal properties and digestibility of starches was evaluated. The physicochemical and estimated glycemic index (eGI) of the Black and Pinto bean starches treated with ozone were not significantly ($P > 0.05$) different than that of their respective control starches. Annealed starches had improved thermal and pasting properties compared to native starches. Acetylated starches presented reduced syneresis, good pasting properties and lower eGI. Also, all modified starches had increased levels of resistant starch (RS). Therefore, the digestibility and physicochemical properties of bean starch were affected by the type of modification but there were no significant ($P > 0.05$) differences between the Black and Pinto bean starches.
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1. Introduction

Starch is a raw material with several industrial applications, so there has been a growing demand for new starch sources. Legumes can be a good alternative starch source (Adebowale, Henle, Schwarzenbolz, & Doert, 2009). However, native legume starches, such as, from beans have very limited industrial applications due to their low solubility in water, restricted swelling power, poor granule dispersibility, high gelatinization temperatures, higher syneresis and resistance to enzymatic hydrolysis (Hoover, Hughes, Chung, & Liu, 2010). Chemical and physical modification may be necessary to improve functionality of bean starches for industrial applications. Chemical modification can involve the introduction of functional groups into the starch molecule, such as through acetylation and oxidation. Starches can also be physically modified by moist heat treatment and annealing (Adebowale et al., 2009; Hoover et al., 2010; Lopez, Zaritzky, & Garcia, 2010; Singh, Kaur, & McCarthy, 2007).

There have been many studies on the effects of acetylation on starch characteristics from different sources. Li, Gao, Jiang, Huang, and Liu (2011) reported that acetylation of starch resulted in rupturing of starch granules, decrease in relative crystallinity, transition temperature and enthalpy of gelatinization and, increased the thermal stability in starch from *Fritillaria ussuriensis* Maxim (Li et al., 2011). In another study, acetylation of cocoyam starch improved granule swelling and reduced starch solubility. The pasting temperature, setback, peak temperature, enthalpy of gelatinization, and retrogradation of cocoyam starch was reduced after acetylation and oxidation. Also, oxidation of the cocoyam starch resulted in reduced granule swelling and increased starch solubility (Lawal, 2004). Oxidised starch is produced by reaction of starch with an oxidising reagent, hypochlorite being the most common, under controlled temperature and pH. However, hypochlorite causes environmental problems, such as, wastewater disposal. Ozone is one alternative for oxidation of starch because, it does not leave a residue when applied to a food product. Ozone oxidised sago and tapioca starches had reduced swelling power compared to their native starches, while the opposite was found for oxidised corn starch (Chan, Bhat, & Karim, 2009). Pasting properties of ozone treated starches displayed different profiles depending on the ozone generation times. These results showed that under similar conditions of ozone treatment, the extent of oxidation varies among different types of starch (Chan et al., 2009).

Annealing, a heat and water treatment at low temperatures and high water to starch ratio, results in a physical reorganisation of starch granules. Annealing of yam bean starch increased moisture content, decreased the swelling power and starch solubility, and

Abbreviations: T_o, onset temperature; T_p, peak temperature; T_c, end temperature; ΔH_G, gelatinization enthalpy; $T_c - T_o$, gelatinization temperature range; ΔH_R, retro gradation enthalpy; RVU, rapid visco units; HPV, hot paste viscosity; CPV, cold paste viscosity; RDS, rapidly digestible starch; SDS, slowly digestible starch; HI, hydrolysis index; eGI, estimated glycemic index.

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slightly reduced the pasting temperature (Adebowale et al., 2009). Jacobs, Eerlingen, Clauwaert, and Delcour (1995) investigated the effect of annealing on starches from different botanical sources. Annealing was found to increase the endothermic temperatures and enthalpies and change the pasting properties of starch samples (Jacobs et al., 1995).

Physical and chemical starch modifications can alter the digestibility of starch. Starch is classified in three categories depending on the rate and extent of digestion as rapidly digestible starch (RDS), slowly digestible starch (SDS) and resistant starch (RS) (Englyst, Kingman, & Cummings, 1992). Chung, Shin, and Lim (2008) found that acetylation and oxidation of corn starch increased the amount of RS and decreased the SDS but, pregelatinized corn starches had an increase in RDS. Annealing increased the SDS and decreased the RS content in legume starch (Chung, Liu, & Hoover, 2010).

Previously the physicochemical properties of Black and Pinto bean starches from beans grown under different conditions were investigated (Ovando-Martinez, Bello-Perez, Whitney, Osorio-Diaz, & Simsek, 2011). This study was undertaken to determine some functional characteristics of physically (annealed) and chemically (acetylated and oxidation with ozone) modified starches from Black and Pinto beans in order to understand how functional properties of bean starch would be altered.

2. Materials and methods

2.1. Materials

Two common bean cultivars (Black 8025 and Pinto Durango) were used for this experiment. Both cultivars were grown under temporal (rain fed) conditions in Ocampo, were planted in July 2008 and harvested in October 2008. Samples were donated by National Institute of Research Forest, Agricultural and Livestock (INIFAP) of Celaya, Guanajuato, Mexico.

2.2. Preparation of native and modified bean starch samples

Bean starch was isolated from milled bean flour according to the method of Otto, Baik, and Czuchajowska (1997). For acetylation, starches (75 g) were dispersed in 375 ml of distilled water and stirred for 20 min. The pH of the starch slurry was adjusted to pH 8 using 1 M NaOH followed by the slow addition of 7.65 g of acetic anhydride, while simultaneously stirring and maintaining the pH between 8 and 8.5. Then, the pH was adjusted to 4.5 with 0.5 M HCl and the reaction was allowed to proceed for 5 min. The starch was recovered by centrifugation and washed with 500 ml of distilled water (3x), then dried at 30 °C during 48 h (Sathe & Salunkhe, 1981). Bean starches were exposed to ozone gas using an ozone generator (OS-8C; Ozone Solutions, Inc.; Sioux Center, IA) equipped with an ozone monitor (model 450 M, Advanced Pollution Instrumentation, Inc., San Diego, CA) to prepare the ozonated bean starches. Samples (75 g) were placed in a cylindrical acrylic container for ozone gas treatment for 30 min with a gas flow of rate 2.5 L/min and ozone concentration of 1500 ppm. The sample was considered fully treated when the amount of ozone gas entering the cylinder was similar to the amount of ozone leaving the cylinder (Sandhu, Manthey, & Simsek, 2012). For annealing, starch dispersions were prepared by adding 150 ml of distilled water to 75 g starch in a sealable container. The suspension was heated at 50 °C in a water bath for 24 h. Then, the starch suspensions were centrifuged and dried at 30 °C for 48 h (Atichokudomchai, Varavinit, & Chinachoti, 2002).

2.3. Chemical composition

Crude protein was determined using a Leco combustion nitrogen analyzer according to approved method 46–30, AACC (American Association of Cereal Chemists and Approved Methods Committee, 2000). The amylose (AM), amylopectin (AP) content were determined by High Performance Size Exclusion Chromatography (HPSEC) analysis (Grant, Ostenson, & Rayas-Duarte, 2002; Ovando-Martinez et al., 2011).

2.4. Determination of starch molecular weight

The apparent average molecular weight distribution of the samples was determined by HPSEC analysis. Weight-averaged molecular weights of the starch samples were calculated using a series of gel permeation chromatography grade dextrans as standards. The dextran standard molecular weights were as follows: 48,600, 147,600, 273,000, 409,800, 667,800, 1.4 million, and 5–40 million Da (Grant et al., 2002; Ovando-Martinez et al., 2011).

2.5. Gel permeation chromatography (GPC)

Starch was fractionated to obtain AM and AP using Gel permeation chromatography (GPC) as previously described (Ovando-Martinez et al., 2011). Fractions were collected (2 ml, measured for 9 min) and every third fraction was selected to determine the amount of oxidation by the uronic acid assay and the identification of AM and AP by the blue value assay.

The blue value was determined by adding 100 μl of I_2/KI solution (0.2 g I_2, 2 g KI in 100 ml of 0.1 M acetate buffer pH 5, diluted 10x) to 100 μl of sample. The absorbance was read to 630 nm. The uronic acid was determined dissolved (200 μl of each fraction) in 1.2 ml of sulphuric acid and cooled for 5 min. The samples were mixed and heated in a boiling water bath for 5 min, then samples were cooled in an ice water bath for 5 min, and 20 μl of m-hydroxydiphenyl reagent was added. The absorbance was read at 494 nm.

2.6. Swelling volume and pasting properties

The swelling volume of the native and modified bean starches was determined according to the method described by the Huang, Schols, Jin, Sulmann, and Voragen (2007) and Huang, Schols, van Soest et al. (2007). Bean starch was weighed into aluminium cans and deionized water was added. Samples were equilibrated at 25 °C for 30 min and then heated at 50, 60, 70, 80 or 90 °C for 30 min using a Rapid Visco Analyzer. The samples were cooled to room temperature and centrifuged at 1000 rpm for 15 min. The supernatant was measured. Finally, the swelling volume was calculated from the gel volume of each sample and was reported in ml/g of sample. Pasting properties of bean starch samples were determined using a Newport Scientific Rapid Visco-Analyzer (RVA) according to AACC approved method 76-21 (American Association of Cereal Chemists and Approved Methods Committee, 2000).

2.7. Differential scanning calorimetry (DSC)

Thermal characteristics of native and modified bean starches were studied with a Perkin–Elmer Differential Scanning Calorimeter, DSC-7. Samples (3.5 mg) were weighed into aluminium pans and deionized water (8 μl) was added. The pans were sealed hermetically and kept at room temperature overnight before analysis. The samples were heated at 10 °C/min from 20 to 120 °C. An empty aluminium pan was used as a reference. From the curve, enthalpy of gelatinization (ΔH), the onset (T_o), peak (T_p) and end (T_c) temperatures were obtained using the data processing software