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Anti-plasticization of cassava starch by complexing fatty acids

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ABSTRACT

The effect of adding 1–8% amylose complexing fatty acids (CFA), such as linoleic and oleic acids, on the glass transition temperature (T_g) of cassava starch (CS) with moisture content varying from 5 to 35% (dry basis) was studied. The main relaxation temperature (T_α), associated with the glass transition temperature of the samples (T_g), was determined by dynamic-mechanical-thermal analysis. The plasticizing behavior of water in the blends was evidenced by a decrease of T_α values with moisture content. The effect of CFA on CS was found to be a function of moisture content. At low moisture (<11%) it caused an anti-plasticization effect, while at higher moisture contents it produced plasticization. The anti-plasticizing effect of CFA on CS was attributed to amylose–lipid complex formation.

1. Introduction

Cassava, a widely available root in tropical countries has a short shelf life of between 24 and 48 h after being harvest (González & Pérez, 2003; Soares, Grossmann, Silva, Caliari, & Spinosa, 1999). Incorporation of this commodity in different processed foods, mainly in starch form, could increase its potential consumption. This implies mixing with other food ingredients, such as protein, other carbohydrates, and lipids sources; among others. In such a matrix, interactions take place, which greatly affect the processing parameters, as well as the final quality of the products.

One of the main processing options for starchy materials is the use of extrusion to obtain expanded snacks or ready to eat breakfast food. During this process, the starchy matrix is subjected to an intense thermo-mechanical treatment within the heated extruder barrel and it also expands at the die exit. The foamed structure, characteristic of this type of products, is finally formed when expansion ceases at the glass transition temperature (Della Valle, Vergnes, Colonna, & Patria, 1997; Fan, Mitchell, & Blanshard, 1994, 1996; Moraru & Kokini, 2003).

During extrusion, food-oils act as lubricants with the disadvantage of decreasing the processing efficiency when high oil levels, such as 17–25%, are added (Camire, 2000; Huber, 2000). Nevertheless, oils can cause a plasticization effect because they contain mainly hydrophobic but also hydrophilic groups, which can interact with similar moieties in starch biopolymers. It is well known (Banks & Greenwood, 1971; Godet, Tran, Delage, & Buleon, 1993) that the amylose helical cavity is hydrophobic; i.e., it can be filled with compounds such as iodine, alcohols or fatty acid. On the other hand, the outer surface of the amylose helix is hydrophilic, due to the presence of active hydroxyl groups. When oil is added to starch, the carboxyl groups of the fatty acid molecules will be preferentially excluded to the outer amylose helical cavity due to steric hindrance (Buleón, Colonna, Planchot, & Ball, 1998; Snape, Morrison, Maroto-Valer, Karkalas, & Pethrick, 1998). Hence, amylose/lipid complexes can develop. This type of complexes formed during extrusion cooking conditions, when fatty acids or monoglycerides are present in at least 0.3% within the starch matrix (Bhatnagar & Hanna, 1994; Cova, Müller, Laredo, & Sandoval, 2012; Lazou & Krokida, 2011; Mercier, Charbonniere, Grebaut, & de la Gueriviere, 1980). Macromolecular degradation of manioc (cassava) starch during twin-screw extrusion is usually less extensive due to amylose–lipid complexation, in particular when oleic acid is used (Colonna & Mercier, 1983).

In a previous work, the plasticizing effect of vegetable oil on cassava starch was reported, as evidenced by a decrease in the glass transition temperature with corn oil addition, at moisture content levels found in extrusion cooking (Madrigal, Sandoval, & Müller, 2011). Horvat, Emin, Hochstein, Willenbacher and Schuchmann (2013) reported an increase in expansion of extruded corn starch due to the addition of medium-chain triglycerides, a phenomenon more related to the extensional properties of starch melts. Addition of this oil source increased significantly the extrapolated pressure drop at the entrance of the die (Bagley pressure), a result that might be caused by the formation of amylose–lipid complexes.

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Linoleic and oleic acids (with lipid numbers of 18:2 and 18:1, respectively) are the major fatty acids found in vegetable oils (Zambiazi, Przybylski, Weber, & Barbosa, 2007). In the case of corn oil, widely used in the Venezuelan food industry, they represent 80–85% of the fatty acid composition, with 50–60% and 25–30% of linoleic and oleic acids, respectively (Archile et al., 1997; Zambiazi et al., 2007). These fatty acids increase the amount of complexed starch to high levels (Colonna & Mercier, 1983; Cova et al., 2012; Schweizer, Reimann, Solms, Eliasson, & Asp, 1986; Snape et al., 1998; Zhong & Sun, 2005). The presence of amylose/lipid inclusion complexes in food formulations is important since they determine starch texture in the solid state (Parker & Ring, 2001). These components act either as plasticizers or anti-plasticizers, shifting the glass transition temperature (Gaudin, Lourdin, Forssel, & Colonna, 2000; Madrigal et al., 2011; Orford, Parker, Ring, & Smith, 1989; Perdomo et al., 2009; Ross & Karel, 1991). Thus, processing, phase behavior and mechanical properties of water–starch systems depend not only on the moisture content, but also on the level of other food ingredients (such as lipids). Hence, the aim of this work is to study the effect of complexing fatty acid addition on the glass transition temperatures and sorption behavior of cassava starch.

2. Materials and methods

2.1. Raw material

Native cassava starch (CS) codified as AIM TF was bought from *Agroindustria Mandioca* (*Monaga state, Venezuela*). Its initial moisture content, determined as specified below, was 16.6% (w.b., g/100 g). Linoleic acid ($C_{18}H_{32}O_2$, CAS-No. 60-33-3) approx. 60%, Sigma–Aldrich was used. Carbon-13 nuclear magnetic resonance (NMR) analysis of this product yielded the following composition: linoleic acid: 58%, oleic acid: 32%, and linolenic acid: 0.5%. Commercial data for this reagent (here after named CFA) were given as: molar mass: 280.46 g/mol, density: 0.903 g/ml and flash point greater than 113 °C.

2.2. Sample preparation

Blends of cassava starch and three levels of CFA were prepared: 2, 5 and 8%; and hereafter denoted as: CS–CFA-2%, CS–CFA-5% and CS–CFA-8%, respectively. The required volume (V in mL) of CFA to be added to the starch was calculated as:

$$V = \frac{m \cdot y \cdot x}{100 \cdot \rho} \quad (1)$$

where m is the amount of cassava starch in the blend (g), y the solid fraction of the cassava starch, ρ the density reported by the reagent commercial data (g/mL), and x the desired CFA level in the blend (%, v/w).

In preparing the blends, CFA was added drop by drop, spaced 30 s apart, to CS under continuous mixing, in an Oster® mixer, for 30 min. Sieving of the sample and subsequent additional mixing was carried out during 10 min. These blends were humidified by water adsorption, in a water saturated atmosphere (100% relative humidity), at room temperature (25 °C), so that samples reached a moisture content (wet basis, w.b.) of 25%. Crystalline thymol was placed inside this atmosphere in order to prevent microbial spoilage. It has been previously shown that, at ambient temperature, this antimicrobial agent does not affect the sorption behavior of the sample (Sandoval, Guilarte, Barreiro, Lucci, & Müller, 2011). Moistened samples were placed in plastic bags and stored under refrigeration for 24 h for further thermo-molding.

Test bars for Dynamic Mechanical Thermal Analysis (DMTA) were obtained by compression molding. The moistened samples were loaded in stainless steel molds fitted with Kapton sheets (for easy sample removal after molding) in a hydraulic press (ADQ 11, model PP25T) at 140 °C for 30 min under a pressure of 3700 psig. Cooling of the samples was carried out under pressure in order to avoid water bubbles from forming inside the materials. Rectangular bar samples (58.0 mm × 14.0 mm × 2.0 mm) of transformed material were obtained.

Moisture equilibration of the transformed blend specimens at different levels was achieved by storage under thirteen different controlled relative humidity atmospheres, during four weeks at room temperature (25 °C). A previous weight loss/gain study indicated that this time was enough to reach equilibrium. Saturated salt solutions of: KOH (0.082), LiCl (0.113), CH_3COOK (0.225), $MgCl_2$ (0.328), K_2CO_3 (0.432), $Mg(NO_3)_2$ (0.529), $CoCl_2$, (0.649), KI (0.689), NaCl (0.753), $(NH_4)_2SO_4$, (0.810), KCl (0.843), KNO_3 (0.936), and K_2SO_4 (0.973); were used to obtain the controlled atmosphere environments. The numbers in parenthesis indicate the water activity of the saturated salt solutions (Greenspan, 1977). At water activity greater than 0.8, crystalline thymol was placed inside the control atmosphere desiccators in order to prevent microbial spoilage of samples.

In all cases, moisture content of samples was determined in triplicate by means of the AOAC (1990) standard method (No. 925.10). For this, 2 g of sample was dehydrated in an atmospheric oven at 130 ± 3 °C for 3 h, until constant weight.

2.3. Sorption properties measurements

A dynamic vapor sorption technique was used to determine moisture sorption isotherms of native and transformed CS–CFA blends at 25 °C. An IGASorp moisture sorption analyzer (Hiden Isochema Ltd., UK), detailed elsewhere (Cova, Sandoval, Balsamo, & Müller, 2010; Madrigal et al., 2011) was employed.

An amount of 10 ± 1 mg of powder sample (native or transformed) was placed inside the sorption analyzer and dried in a zero relative humidity ambient for 3 h at 30 °C, before the adsorption process began. Relative humidity was then automatically increased from 0 to 94% by means of the software IGASorp System Software V6.50.42 (Hiden Analytical Ltd.). Ambients with different relative humidities levels were obtained by mixing water vapor and dry ultra high purity nitrogen gas. The equilibrium criterion for the isotherm stability was taken as the time after which the weight had relaxed to within 1% of the equilibrium uptake.

Transformed blends were converted into powder by cryogrinding and sieving (0.20 mm) in an Ultra-centrifugal Mill ZM 200 (Retsh®), before adsorption isotherm determination. Data points were collected and plotted as an isotherm by means of the software IGASorp. Isotherm data were exported to Microsoft Excel software.

The experimental adsorption data obtained, corresponding to water activities (a_w) and moisture contents (M) were adjusted to the GAB model (Eq. (2)):

$$M = \frac{M_m \cdot C \cdot K \cdot a_w}{(1 - K \cdot a_w) \cdot (1 - K \cdot a_w + C \cdot K \cdot a_w)} \quad (2)$$

where M_m is the monolayer moisture content of GAB model, and C and K are energy constants. Matlab v. 2007R-B (The MathWorks, Inc.) was used to perform nonlinear regression statistical analyses. The adequacy of the regression was evaluated using the coefficient of determination (R^2) and the root mean square error (*RMSE*).

2.4. Dynamic Mechanical Thermal Analysis (DMTA)

A rheometric solid analyser (Rheometric Scientific, RSA II) was used to perform DMTA measurements. Weight loss during testing was prevented by coating the test bars with vacuum grease and completely wrapping them in aluminum foil (Pereira & Oliveira, 2000). It has been previously confirmed that this procedure does