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Effect of two different lipid sources on glass transition temperatures and tensile properties of corn semolina

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ABSTRACT

The effect of adding corn oil (CO) and corn germ (CG) on the thermal and mechanical properties of corn semolina (CS) was investigated. The lipids concentration employed were 2% and 3% of CO or CG. The thermal transitions were studied in a moisture content range of 3–27% (d.b.), by means of dynamic mechanical thermal analysis (DMTA) and differential scanning calorimetry (DSC) techniques. Wide angle X-ray scattering (WAXS) experiments showed that type-V amylose–lipid complexes were formed with the native lipids within the corn semolina during thermo-moulding and that re-crystallization to a type-A structure, favored by the added lipids, occurred upon storage in high relative humidity (RH) environments. Two thermal events were observed during the first DSC scan and tanδ DMTA curves. The first one appearing at around 55–60 °C was attributed to a possible phase separation or ageing phenomenon taking place during storage of the samples, while the second was ascribed to the glass transition temperature of CS. It was found that addition of both, CO and CG, reduced the moisture content required for these transitions to appear. The expected decrease in the glass transition temperatures with moisture content was well described by the Gordon–Taylor equation. The addition of CO and CG also causes plasticization of CS. Hence, corn germ meal can be used as a lipid source that is more convenient to handle than liquid fats. However, the CS T_g values were independent of the lipids content. Tensile properties of CS and CS-lipid systems were found to be influenced by the moisture content, the physical state of the samples, and their composition.

1. Introduction

Corn semolina is mainly composed of starch. It is a sort of coarse ground meal with many applications in the food industry. Main differences in requirements for these applications rely on particle sizes and lipid composition. Corn semolina is widely used as a raw material for the processing of ready to eat breakfast formulations, as well as for snacks obtained by extrusion processes; for which a lipid composition of around 1% is normally used (Llo et al., 2000). During this process the material is subjected to a severe thermo-mechanical treatment (with specific mechanical energy ranging from 100 to 1000 kJ kg^{-1} and operating temperature as high as 180–190 °C) for a short period of time (20–40 s depending on type of extruders) (Harper, 1989; Riaz, 2000), leading to a powdery-molten material transition within the extruder. At the end, the material is dramatically expanded at the extruder die by the water evaporation from the starchy matrix. For these products maximum expansion of 500% increase in product diameter has been observed (Moraru and Kokini, 2003). During this expansion, which ends when the cooling material temperature reaches that of the glass-rubber transition range, the texture of the product is established (Fan et al., 1994, 1996; Della Valle et al., 1997; Moraru and Kokini, 2003). The knowledge of the glass transition temperatures is then very important, as the characteristics of the expanded product will depend on the difference between the processing material temperature and its glass transition temperature, during extrusion cooking. Texture of this type of products, as measured in terms on their mechanical properties, is a key factor for their acceptance by the consumers.

Although data are available for glass transition temperatures of cereal-based matrixes, and particularly for corn, studies on the role of other food ingredients normally used in extrusion are not that extensive. Kaletunç and Breaslauer (1993) studied the glass transition of high-amylopectin extrudate corn flour by means of DSC, finding that it decreased rapidly from 103 to 40 °C in a moisture content range of 0–11% (d.b.). Nicholls et al. (1995) reported ranges of glass transition temperatures for waxy maize starch from 30–130 °C for

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decreasing moisture content values from 15% to 5% measured by DMTA, finding that these values were 20–30 °C higher than those of obtained for wheat gluten. Brent et al. (1997), also using DMTA measurements reported T_g values in a range of −3–48 °C for de-germed corn meal with moisture content varying from 36% to 22% (w.b.), respectively. These authors also found that the glass transition values for pregelatinized corn starch and pregelatinized waxy maize starch were similar to corn meal at a similar moisture content of 27%. In all these previous works, the expected decrease of glass transition temperature values with increasing moisture contents was obtained. Apart from the plasticizing effect of water, other ingredients such as sugar have also been found to decrease the glass transition temperature of non-expanded maize and wheat extrudates (Carvalho and Mitchell, 2001). At all sugar levels (0%, 10% and 20%), it was reported that coarse semolina of durum wheat was less plasticized by water, compared with maize flour and maize grits. For this sugar contents, glass transition temperatures of maize extrudates, determined by DMTA, varied from −10 to 120 °C in a moisture content range of 35–10%. Values of T_g for a specific moisture contents of 10% for corn flour and corn starch were given by Chanvrier et al. (2005). These authors reported glass transition temperatures of 100 °C for the former and 107 °C for the latter.

High levels of lipid addition (e.g., 17–25%) during extrusion cooking have been found to decrease the process efficiency, since at such levels, this ingredient acts as lubricant (Camire, 2000; Huber, 2000). However, a plasticizing action should also be expected, as already pointed out by Madrigal et al. (2011). This plasticization effect is believed to occur because of the hydrophobic–hydrophilic groups present in natural oils, which can interact with similar moieties in starch biopolymers. It has been pointed out before (Banks and Greenwood, 1971; Godet et al., 1993) that the amylose helical cavity is hydrophobic; i.e., it can be filled with compounds such as iodine, alcohols or fatty acids. On the other hand, on the outside surface of the helix, active hydroxyl groups are exposed together with the carboxyl groups of the fatty acid molecules, which are located outside the helical cavity due to steric hindrance (Buleón et al., 1998; Snape et al., 1998).

The effect of lipids on gelatinization and retrogradation has been extensively studied in the literature (Paton, 1987; Wang and White, 1994; Lin et al., 1997; Siswoyo and Morita, 2001; Miyoshi, 2002; Chiotellia and Le Meste, 2003). However, the effect of the type of added lipids; i.e., from oil or germ, on the glass transition temperature of corn semolina has not been addressed. Consequently, the aim of this work was to study the effect of these two lipid sources on the glass transition temperatures of corn semolina at low to intermediate moisture contents. The effect of oil addition on the mechanical properties of corn semolina will also be addressed.

2. Materials and methods

2.1. Raw material

Both corn semolina (CS) M80 and corn germ (CG) used in this work were kindly donated by *Refinadora de Maíz Venezolana C.A.* (*Remavenca, Venezuela*). The commercial corn oil (CO) Mazeite® was bought locally. Initial lipid content of CS was 0.92% (see method below).

Sample approximate composition (i.e., moisture, fat, protein, ash, total dietary fiber and carbohydrate contents) was determined on CS and CG. Standard procedures from AOAC (1990) were used in the following analyses: Moisture content by the atmospheric oven N° 925.10, fat content (Soxhlet method N° 922.06), protein content (micro-Kjeldahl method N° 960.52) with a conversion factor of 6.25, and ashes (method N° 923.03). Total dietary fiber was determined as recommended by Lee et al. (1992) using an α-amylase, protease and amyloglucosidase enzymatic system for the hydrolysis. The carbohydrate content was determined by difference.

2.2. Sample preparation

Native corn semolina had 0.92% lipid content. Preliminary experiments showed that upon adding 5% lipids, only 3% remained after thermo-moulding because exudation occurred. Therefore, the effect of adding 2% and 3% of lipids on CS was investigated. These lipid contents were achieved by adding the appropriate amount of CO or CG to CS. Accordingly, five samples were studied: CS, CS-CO-2%, CS-CO-3%, CS-CG-2%, and CS-CG-3%.

The CS-CG blends were obtained by mixing both powders in a food powder mixer (BOLAFIX®) for 30 min. Initial moisture content of all samples was adjusted to 30% (wet basis, w.b.) in order to have enough water content so that transformation into amorphous material by thermo-moulding could be achieved. Distilled water was added, together with the CO (in case of CS-CO blends), to CS and to CS-CG, under continuous stirring in a laboratory blender (Oster®) at medium speed. The samples were packed in plastic containers, sealed and left overnight to reach equilibrium.

Transformed or amorphous CS, CS-CO and CS-CG blends were carried out as in previous works (Farhat et al., 2003; Chanvrier et al., 2006; Perdomo et al., 2009; Sandoval et al., 2009; Madrigal et al., 2011; García et al., 2012). They were obtained by placing the moistened blends in $12 \times 10 \times 2$ mm^3 frames between Kapton® polyimide sheets and subjected them to a pressure of 3500 psig in a hydraulic press (ADQ 11, model PP25T). Simultaneous heating to 140 °C was applied for 20 min. Further cooling of the whole assembly up to 40 °C was done under pressure in order to avoid water bubble forming inside the samples. Following decompressing, thin rectangular films of $12 \times 10 \times 2$ mm^3 and discs of approximately 4 mm in diameter were obtained for DMTA and DSC experiments, respectively. The absence of residual gelatinization enthalpy in the amorphous samples, by means of DSC experiments in excess of water (1:3) carried out in a Perkin Elmer DSC 7, was used to confirm the complete transformation to the amorphous state.

Equilibration of the amorphous blends to different constant moisture contents was achieved by storing them in different controlled relative humidity (RH) environments for 3 weeks at room temperature (25 °C). It was previously determined that this time was enough to reach equilibrium. The controlled atmosphere environments were obtained with saturated salt solutions. Crystalline thymol was placed on a watch glass inside the higher RH controlled atmosphere environments (>80%) to prevent microbial growth in the samples being moisture conditioning. It has been recently showed that, at room temperature, it does not affect the sorption characteristics of the samples (Sandoval et al., 2011). As the moisture content of samples after thermopressing was about 30%, the moisture equilibration was attained by desorption.

2.3. Wide angle X-ray scattering (WAXS) experiments

Native and amorphous CS, as well as amorphous CS-CO-3% and CS-CG-3% were analyzed by WAXS. These experiments were done in a Panalytical X'Pert-Pro system with an automatic diffractometer equipped with an X'celerator photon counter for fast data acquisition. The excitation voltage and current were 45 kV and 40 mA for the copper X-ray source (Kα, Ni-filtered). The angular sweeps were recorded from 5° to 60° in 2θ with 0.02° steps and 20 s counting time. The analysis of the material was carried out on samples $(10 \times 12 \times 1)$ mm^3 right after transformation or further equilibration during 3 weeks in controlled RH environments. Oversaturated solution of K_2CO_3 (9.2% d.b.), NaCl (14.5% d.b.), KCl (18% d.b.), KNO_3 (27.3% d.b.) and K_2SO_4 (33.4% d.b.) were used at room temperature to generate the required environments; the