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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:

$$V = \frac{m \cdot y \cdot x}{100 \cdot \rho} \tag{1}$$

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 cryo-grinding 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)):

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

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 not affect mechanical properties of the sample bars (Perdomo et al., 2009). A three point bending fixture was used. In order to stay within the linear viscoelastic regime, a frequency of 1 Hz and a strain amplitude of 0.1% were used. The heating temperature range, spanned at 3 °C/min, depended on the moisture contents of the samples. The temperature of the main mechanical relaxation (T_α) was estimated from the slope change in the elastic modulus (E'), the peak in the viscous modulus (E'') or the tanδ maximum, employing the extrapolated onset analysis tool of the Orchestrator (V6.3.2) software. A minimum of three samples for each blend was measured and the values of T_α were averaged.

Neat cassava starch, both native (for the sorption behavior) and transformed (sorption and glass transition behaviors), have been characterized in previous works, using the same procedures (see Madrigal et al., 2011; Perdomo et al., 2009). Therefore, that previous data will be used, wherever needed for comparison purposes below.

3. Results and discussion

3.1. Adsorption characteristics

Moisture adsorption isotherms of native (CS–CFA) and transformed (TCS–CFA) cassava starch blends, determined at 25 °C, are shown in Fig. 1a and 1b, respectively. The moisture content in these figures is normalized to a nonfat weight solid basis. Data from neat CS and TCS in these figures were taken from the work of Madrigal et al. (2011). Differences in the moisture adsorption behavior of native (Fig. 1a) and transformed (Fig. 1b) samples were found to be small. Nevertheless, Fig. 1a shows that, for a constant water activity, the moisture content of samples with highest added CFA level is lower than those with lower CFA levels. This result indicates a decreasing hydrophilic behavior of samples with increasing CFA values. At water activity higher than around 0.85, the blends exhibited a slightly higher moisture adsorption ability than that of cassava starch. Fig. 1b, on the other hand, shows that differences in the sorption behavior of samples are less marked, than those exhibited by native samples. It is also interesting to note that at a_w values higher than around 0.6, the samples with the highest added CFA content exhibited larger equilibrium moisture content, even larger than that of neat transformed cassava starch. This behavior could be attributed to a larger plasticizing effect of this fatty acid level in the transformed cassava starch matrix. This plasticizing effect may be the result of the exposure of a higher amount of more hydrophilic active sites, as for example those coming from the outer surface of the amylose helix or from carboxyl groups of the fatty acid molecules

Results obtained from both, native and transformed samples, indicated that added CFA did not greatly affect the sorption behavior of CS. In all cases, isotherms with sigmoidal forms (type II) were obtained, in accordance to those reported for many starchy products (Al-Muhtaseb, McMinn, & Magee, 2004; Brett, Figueroa, Sandoval, Barreiro, & Müller, 2009; McMinn & Magee, 1999) and particularly for cassava starch (Madrigal et al., 2011; Perdomo et al., 2009). The isotherms presented in Fig. 1a and b are well described by Eq. (2), as indicated by the high and low R^2 and RMSE values; respectively. Table 1 shows these values, as well as the regression constants for each sample analyzed.

3.2. Main mechanical relaxation temperatures (T_α) at different moisture content

Fig. 2 shows a DMTA graph obtained for TCS–CFA blend after being equilibrated in a controlled atmosphere of 75% relative humidity. The figure shows the drop in the elastic modulus and the distinct peaks in the viscous modulus and in the tanδ, at the main

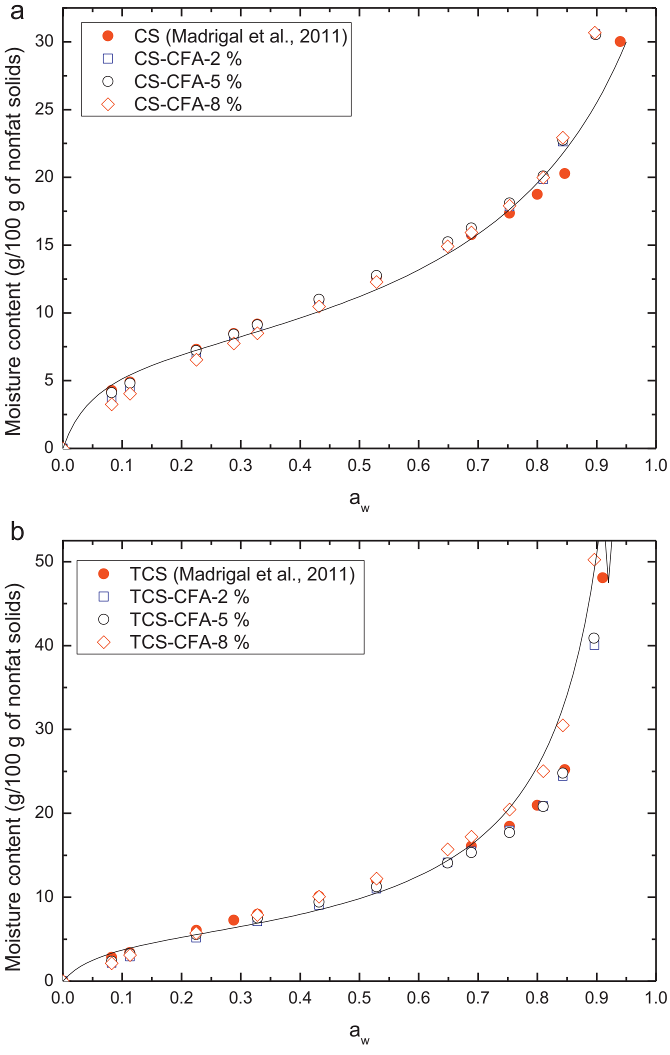

Fig. 1. Adsorption isotherms of cassava starch and cassava starch–complexing fatty acid blends at 25 °C; (a) in their native (CS–CFA) and (b) transformed (TCS–CFA) forms. As an example the GAB model fitting of one data set per figure is drawn as a solid line (i.e., cassava starch for (a) and TCS–CFA-8% for (b)).

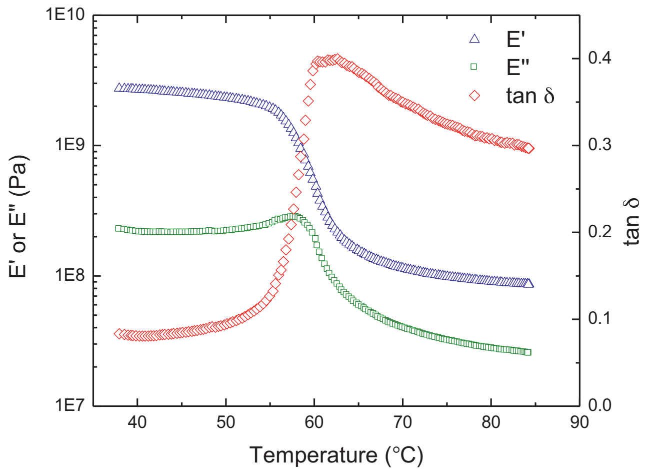

Fig. 2. DMTA graph obtained for TCS–CFA-2% blend after being kept in a controlled atmosphere of 75% of relative humidity at room temperature.

Table 1
Fitting parameters for the GAB model applied to adsorption data of native and transformed CS–CFA blends at 25 °C.

Sample	Constants	CS	CS–CFA blend		
			2%	5%	8%
Native	M_m	9.28	6.66	6.89	6.65
	C	12.0	19.6	21.5	15.2
	K	0.673	0.862	0.852	0.866
	R^2 (RMSE)	0.999 (0.110)	0.989 (0.964)	0.989 (0.955)	0.990 (0.926)
Transformed[a]	M_m	7.51	4.86	4.74	5.25
	C	8.07	16.4	22.9	15.7
	K	0.838	0.976	0.983	0.998
	R^2 (RMSE)	0.998 (0.417)	0.985 (1.48)	0.983 (1.60)	0.991 (1.43)

M_m in g water/g of nonfat solids. C and K dimensionless.

[a] Data for transformed CS were taken from Madrigal et al. (2011).

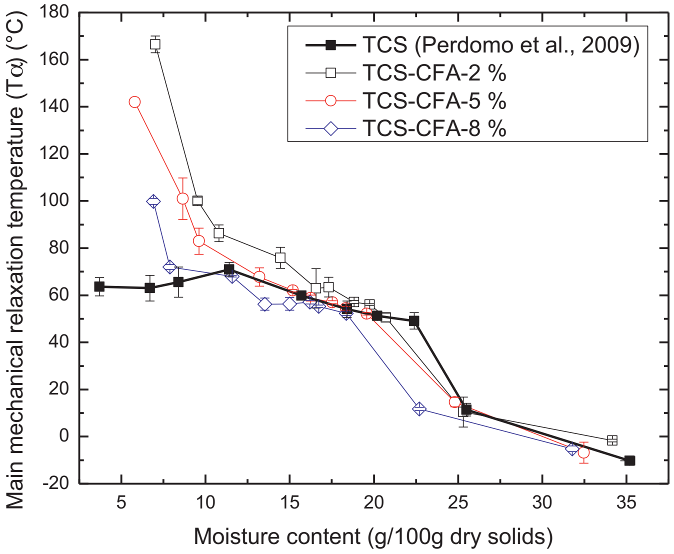

Fig. 3. Main mechanical relaxation temperatures of TCS–CFA blends as a function of moisture content, measured by the maximum in E'' from DMTA experiments, and data presented by Perdomo et al. (2009) for TCS.

relaxation temperature, normally associated with the glass transition temperature (T_g) in this type of transformed matrix. Graphs such as those shown in Fig. 2 were obtained in most cases and good reproducibility was achieved. In order to compare with data obtained from neat TCS in a previous work (Perdomo et al., 2009), the peak in E'' was chosen for the main mechanical temperature determination.

Fig. 3 shows the main relaxation temperatures as a function of moisture content for the three blends analyzed here and for those reported by Perdomo et al. (2009). Both sets of data exhibit different behaviors depending on the moisture content range of the sample. At low moisture content (i.e., less than 11%), a large plasticizing effect of water was observed for the three blends; i.e., small variations of moisture content greatly affect T_α values. This effect was more pronounced for TCS–CFA-2% and then, in decreasing order, for TCS–CFA-5% and TCS–CFA-8%. At intermediate moisture content range, the plasticizing effect of water was less pronounced for the three blends, which agree well with the behavior observed for TCS. For the higher moisture content range (i.e., greater than 20%), a more pronounced plasticizing effect of water was observed. This effect has been pointed out before for cassava starch by several authors (Chang, Cheah, & Seow, 2000; García, Cova, Sandoval, Müller, & Carrasquel, 2012; Madrigal et al., 2011; Perdomo et al., 2009). This phenomenon has been attributed to the re-crystallization of transformed cassava starch at high moisture contents, where water availability increases (i.e., since water is segregated from the crystals) (Perdomo et al., 2009). In general terms, Fig. 3 does not show large differences among the main mechanical relaxation temperatures of TCS and TCS–CFA blends at intermediate and higher moisture contents values.

3.3. *Effect of added complexing fatty acids*

The effect of added CFA can also be seen in Fig. 3. This figure shows that for low and intermediate moisture content ranges, the main relaxation temperatures decreased with the amount of added CFA. This decrease is more marked for low moisture content (lower than around 15%), than for intermediate moistures. At higher moisture content, the decrease of the main relaxation temperatures with added CFA is less pronounced. This plasticization effect of CFA on TCS could be attributed to hydrophilic-hydrophobic interactions taking place when oil sources are mixed with starch; as previously shown by Madrigal et al. (2011) in a similar system composed of corn oil and cassava starch blends.

As previously stated, the amylose helical cavity is hydrophobic, so that the fatty acid can be accommodate within it; whereas at the outer surface of the helix active hydroxyls are exposed together with the carboxyl groups of the fatty acid molecules (Banks & Greenwood, 1971; Buleón et al., 1998; Godet et al., 1993; Snape et al., 1998). The formation of the amylose–lipid complex has been reported to increase dramatically with 1% of added linoleic acid in extruded drum-dried wheat flour (Schweizer et al., 1986), and with 2% of oleic acid in extruded manioc starch (Colonna & Mercier, 1983). On the other hand this complex has also been reported to occur for thermo-molded oil–starchy matrix (Cova et al., 2012). Wide angle X-ray scattering experiments showed that type-Vh amylose–lipid complexes are formed during thermo-molding of corn semolina with intrinsic (0.92%) or added (3%) lipids in the form of corn oil or germ (Cova et al., 2012).

It is also worth noting in Fig. 3, that the addition of CFA to CS seems to prevent the anti-plasticizing effect of water on neat TCS reported by Perdomo et al. (2009), for low moisture contents (6–11%). Data points for this region were redrawn in Fig. 4 to plot the main relaxation temperatures as a function of added CFA. The main relaxation temperatures of 0% CFA, with the different moisture contents (shown in the graph), were taken from Perdomo et al. (2009). The figure shows that, in all cases, the smallest amount of added CFA (i.e., 2%) caused an increase in the main relaxation temperatures of TCS. Further addition of CFA (at levels of 8%-CFA) decreased the main relaxation temperatures to values close to that of neat TCS (around 70 °C) for blends with moisture contents of 8–11%. For the lowest moisture contents (6–7%), TCS–CFA-8% blends exhibited a larger T_α value (around 100 °C).

The increase of the main relaxation temperatures of TCS–CFA blends in comparison with that of the neat TCS represents an anti-plasticizing effect, which, as shown in Fig. 4, decreases with

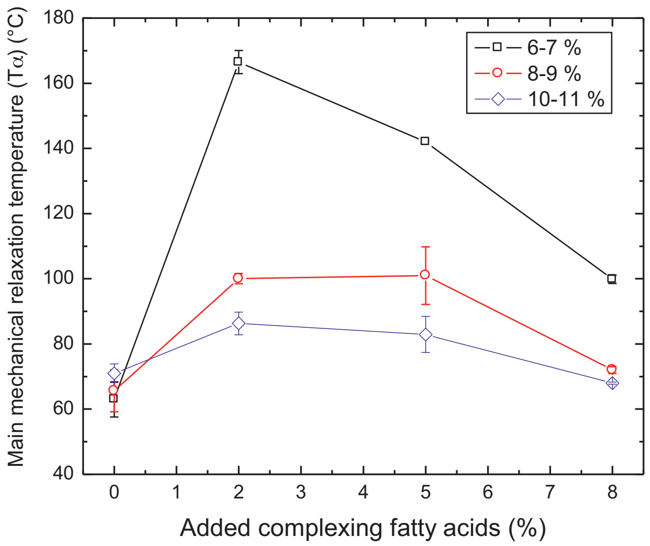

Fig. 4. Main mechanical relaxation temperatures of TCS–CFA blends as a function of CFA content, at low moisture content (6–11%, d.b.). Data at 0% CFA were taken from Perdomo et al. (2009).

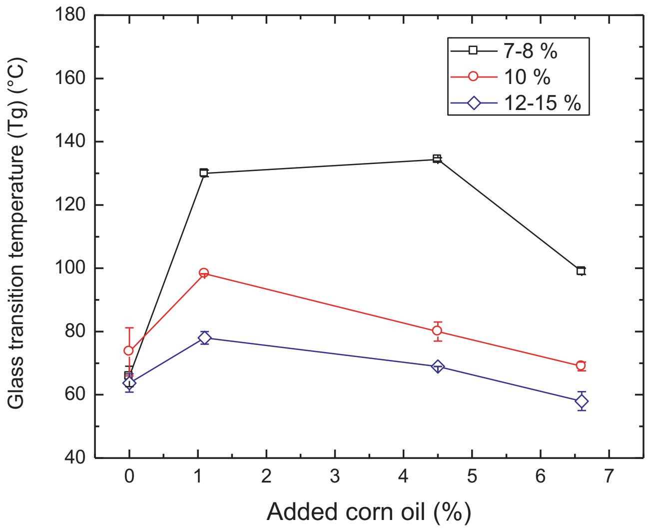

Fig. 5. Main mechanical relaxation temperatures of TCS–corn oil blends as a function of added corn oil, at low moisture content (7–15%, d.b.) as reported by Madrigal et al. (2011).

increasing moisture content. This anti-plasticizing effect could be explained by an increase in density of the sample as amylose–lipid complexes are formed when CFA is added (Bhatnagar & Hanna, 1994; Colonna & Mercier, 1983; Cova et al., 2012; Zhong & Sun, 2005). Hence, it seems that in the presence of such low water contents, the amylose–lipid complexes might act as physical cross-links, increasing the density and rigidity of the sample. In such conditions, the starchy matrix increased its structural order with the consequent increase of the main relaxation temperature.

The anti-plasticizing effect of water on starchy materials has been documented by changes in their mechanical properties under high deformation (Chang et al., 2000; Fontanet, Davidou, Dacremont, & Le Meste, 1997; Gondek & Lewicki, 2006; Halek, Paik, & Chang, 1989; Marzec & Lewicki, 2006), and in their glass transition temperatures (Perdomo et al., 2009). However, as far as the authors are aware, no anti-plasticizing effect of fatty acids, such as CFA, on starchy materials, has been reported in the literature.

However, it is noteworthy that the results presented here are consistent with a previous work on cassava starch blended with corn oil levels of 1.1, 4.5 and 6.6% (Madrigal et al., 2011). Glass transition temperatures (T_g) reported by these authors and obtained from differential scanning calorimetry measurements, are plotted as a function of added corn oil in the range of low moisture content (7–15%, d.b.), and shown in Figure 5. It is remarkable that data plotted in this figure behave in a similar way to those shown in Fig. 4. Therefore, oil-sources, such as corn oil and CFA, can both show plasticizing and anti-plasticizing effects in low hydrated starch matrixes. Another natural starch plasticizer with anti-plasticizing behavior when used in small amounts is sorbitol. It has been shown, that it does not always behave as a plasticizer, but on the contrary, it frequently shows an anti-plasticizing behavior depending on its concentration in the starch matrix (Gaudin et al., 2000).

The anti-plasticizing effect of CFA on starchy materials, demonstrated in this work, needs to be considered during processing (e.g., extrusion cooking), since it affects their glass transition temperature and probably their rheology. These are two aspects of particular importance during expansion of extruded starchy-foods.

4. Conclusions

The main mechanical relaxation temperatures of TCS–CFA blends with a wide range of moisture contents were determined by DMTA analysis. In all blends these temperatures decreased with moisture content. The effect of added CFA to CS depended on the moisture content of the blends. An anti-plasticizing effect of CFA was found for moisture contents lower than 11%, while a plasticizing effect was obtained for larger moisture contents. This result is consistent with results obtained in a previous work for cassava starch–corn oil blends. The formation of amylose–lipid inclusion complexes may be responsible for the anti-plasticizing effect of CFA, by acting as physical cross-linking.

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