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Glass transitions and physical aging of cassava starch – Corn oil blends

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ABSTRACT

Glass transition temperatures and physical aging of amorphous cassava starch and their blends with corn oil were assessed by differential scanning calorimetry (DSC). Two enthalpic relaxation endotherms, well separated in temperature values, were exhibited by neat amorphous cassava starch with 10.6% moisture content, evidencing two amorphous regions within the starch with different degrees of mobility. The phase segregation of these two amorphous regions was favored by added corn oil at low moisture contents during storage. The presence of amylose–lipid complexes in this matrix, may also affect the molecular dynamics of these two amorphous regions at low moisture contents. Increasing moisture content, leads to a homogeneous amorphous phase, with an aging process characterized by a single enthalpic relaxation peak. In all cases, after deleting the thermal history of the samples only one glass transition temperature was detected (during DSC second heating runs) indicating that a single homogeneous amorphous phase was attained after erasing the effects of physical aging. Trends of the enthalpic relaxation parameters were also different at the two moisture contents considered in this work.

1. Introduction

Glassy polymers can experience physical aging as a consequence of their desire to approach thermodynamic equilibrium after undergoing their glass transition temperature (Struik, 1978). This enthalpy reduction process simultaneously decreases both, free volume and segmental mobility, as the system approaches a pseudo-equilibrium state. Similar to synthetic polymers, physical aging is an important phenomenon in amorphous starch and starchy materials in general. Many starchy products are processed under high temperature and relative low moisture conditions; and later consumed in the glassy state, as for example snacks and breakfast cereals. Changes occurring during physical aging are often responsible for storage-induced changes and for quality deterioration. These effects should be controlled for the sake of long term stability of starchy products (Champion et al., 2000; Chung & Lim, 2006). Physical aging leads to significant changes in the material properties such as densification, increased brittleness and decreased permeability; which make it a phenomenon of particular interest from both, scientific and technological points of view (Badii et al., 2005; Kim et al., 2003; Lourdin et al., 2002).

The physical aging of different glassy polymers has been investigated by means of dilatometry and differential scanning calorimetry (DSC). DSC is probably one of the most popular techniques to study physical aging. During aging, which is usually induced by annealing at temperatures close but lower than the glass transition temperature (T_g), the sample loses enthalpy as it approaches equilibrium. When the sample is heated during a DSC scan, the enthalpy is regained by the superheated glass. As the enthalpy must rapidly increase in the superheated glass in order to attain the value of the rubbery state, an endothermic process develops and a peak appears just above or around the glass transition temperature range. The area under this endothermic peak is equal to the enthalpy value that was regained by the sample and should be approximately similar to that lost during aging. Apart from allowing reliable temperature control of heating and cooling rates, the DSC experiments can also be performed at constant moisture content, as the sample can be encapsulated in hermetic pans.

Although enthalpic relaxation has been widely studied in starch (Borde et al., 2002a; Borde et al., 2002b; Chung & Lim, 2003; Chung & Lim, 2004; Chung et al., 2004; Kalichevsky et al., 1992; Kim et al., 2003; Lourdin et al., 2002), only limited work has been carried out in more complex systems (e.g., Gonzalez et al., 2010), where interactions with other added food components such as other

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biopolymers, water and oil, might have an effect on the associated endothermic event. The heterogeneity of a system (i.e., the presence of two coexisting phases for instance) might play an important role in determining the relaxation behavior of starchy samples. Madrigal, Sandoval, & Müller (2011) reported two endothermic events from first DSC heating scans of cassava starch blended with different levels of corn oil, and containing low moisture content, after being kept at room temperature for 4 weeks for moisture equilibration purposes. These double peaks corresponded to two different enthalpic relaxation events correlated with two different T_g in the material. They were also evidenced by two peaks exhibited by the same samples in tan δ curves obtained by dynamic mechanical thermal analysis. It was shown, by these authors, that the greater the corn oil content added to cassava starch, the lower the moisture content at which the enthalpic relaxations appeared, which indicated that this oily component favored phase separation and molecular mobility during storage. Consequently, the aim of this study was to carry out a more systematic study on the appearance of such enthalpy relaxation endotherms, and to determine the aging parameters of cassava starch when corn oil was added.

2. Materials and methods

2.1. Raw material

Native cassava starch (CS) donated by Inveyuca (PDVSA Agrícola), located in San Tomé (Anzoategui state, Venezuela) was used. Its initial moisture content was 14.4% (dry basis, d.b.). Commercial corn oil (CO) Mazeite® was bought from a local supplier.

2.2. Sample preparation

Transformation of native samples into amorphous materials by thermo-moulding required their moisture content to be around 25%. Humidified CS was prepared by slowly adding the required amount of distilled water to the CS. The humidified CS–CO blends, on the other hand, were prepared by simultaneously adding CO by slow dripping, in a proportion of 1, 5 and 10 g/100 g of CS, and distilled water to the CS. The required levels of water and corn oil were added separately, but at the same time using two different plastic containers from which the liquids were squeezed drop by drop onto the starch compound. Accordingly, samples with 25% moisture content (wet basis), and the required amount of CO, were obtained in each case. The amount of water added to reach 25% moisture content was calculated considering the initial moisture content of CS. Continuous mixing of samples was applied during addition of water and CO, by using a laboratory mixer at medium speed. Lumps were eliminated by sieving the samples, before being stored in plastic bags at 10 °C overnight to equilibrate moisture content within the sample.

Transformed cassava starch (TCS) and TCS–CO blends were obtained by compression moulding in a ADQ11 (model PP25T) hydraulic press. The samples were placed between kapton sheets and moulded at 3900 psi and 160 °C for 30 min. Pressure was maintained during cooling of the amorphous samples to a temperature of 30 °C, so as to avoid expansion. It has been demonstrated in a previous work by means of DSC in excess of water and wide angle scattering X-rays that these thermo-moulded conditions fully transformed cassava starch to the amorphous state (García et al., 2012; Luk et al., 2013; Madrigal et al., 2011; Perdomo et al., 2009). Samples were cut into small discs (diameter 4 mm and thickness of 1 mm) of approximately 10 mg in weight.

Moisture equilibration at different levels was carried out by storing amorphous samples during four weeks in controlled environments generated by the following eleven different oversaturated salt solutions at 25 °C: KOH (8.2%), LiCL (11.3%), $MgCl_2$ (32.8%), K_2CO_3 (43.2%), $Mg(NO_3)_2$ (52.9%), KI (68.9%), NaCl (75.3%), $(NH_4)_2SO_4$ (80.9%), KCl (84.3%), KNO_3 (95.4%), and K_2SO_4 (97.3%). The numbers in parenthesis indicate the relative humidity in each environment (Greenspan, 1977). In order to prevent microbial spoilage of samples, crystalline thymol was placed inside the environments with relative humidity greater than 80%. It has been proven that at ambient temperature, thymol does not affect the sample water sorption (Sandoval et al., 2011).

2.3. Moisture and lipid content determination

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 were dehydrated in an atmospheric oven at 130 ± 3 °C for 3 h, until constant weight.

The amount of lipid in the TCS–CO blends was assessed by means of the method No. 922.06 of the AOAC (1990). To do this, transformed blends were cryo-ground and sieved in an Ultra-centrifugal Mill ZM 200 (Retsh®) into a fine powder (0.20 mm particle size), by a Soxhlet extraction with hexane preceded by an acid hydrolysis (Weibull method). The procedure was detailed in a previous work (Madrigal et al., 2011).

2.4. Differential scanning calorimetry (DSC) analysis

Thermal transitions of TCS and TCS–CO blends with different moisture contents were determined by DSC analysis, using a DSC 7 (PerkinElmer™), previously calibrated with indium. This equipment employs an ultra-high purity nitrogen gas purge. An amount of 10 ± 1 mg of each sample, after being moisture equilibrated in atmospheres with different relative humidity levels, was weighed in hermetically sealed aluminum pans. Experimental moisture content of each sample was determined before performing DSC measurements. Each sample was heated from 0 to 115 °C, at a heating rate of 5 °C/min, using an empty pan as a reference. Two heating scans were performed in each case, the first one carried out to erase any aging event occurring during sample storage, and the second one to determine the glass transition temperatures. By using the Pyris Thermal Analysis Software (V 8.0.0.0172), the glass transition temperatures were estimated from the midpoint of the heat capacity change observed during the second heating scan. Two to three samples of each material were measured and the T_g values obtained from the scans were averaged.

2.5. Physical aging in TCS–CO samples with different levels of moisture content

Physical aging experiments of TCS–CO blends with two selected moisture contents (i.e., 8.6 and 14.9%) were carried out. This was implemented to study the physical aging in samples with low and intermediate moisture contents, since they displayed different physical aging behavior (see below). To do this, after moisture equilibration, selected disc samples were hermetically sealed in aluminum pans and placed in vials sealed with bakelite screw caps. They were then introduced in a water bath kept at a temperature at least 30 °C above that at which the enthalpic relaxation peak was observed during the first heating scan of each particular sample. After a heating for 10 min, the samples were transferred to a thermal bath containing silicone to perform aging experiments by annealing the samples at a temperature of $T_a = 35$ °C. Aging times varied from 1 to 192 h and two samples were analyzed for each aging time. Subsequent DSC experiments, as detailed previously, were carried out (i.e., two heating scans in each aged sample).

3. Results and discussion

3.1. Sample characterization

The average lipid content values for the transformed blends as determined by the Weibull method were 1.1 ± 0.1, 4.6 ± 0.2 and 6.9 ± 0.3 (%, d.b.), which were very close to the nominal values fixed in the experiments (1, 5 and 10%); except for the sample with 10% added corn oil. This difference was due to the compression molding procedure which squeezed out oil from the sample andt his fact was more pronounced for the blend with the highest nominal lipid content. Discussion of results from transformed CS–CO blends will be done in terms of the experimentally determined lipid content values; i.e., 1.1, 4.6 and 6.9% of CO.

3.2. First DSC heating scans of TCS and TCS–CO blends

Thermal transitions of moisture conditioned TCS and TCS–CO blends were determined from DSC heating scans. Fig. 1 shows the first heating runs for these samples. In all cases, enthalpic relaxation peaks, indicating sample aging during storage were observed.

Fig. 1a shows first heating runs for neat TCS at different moisture contents. In the moisture content range in between 12.8% and 18.2% a clear single endothermic relaxation peak is observed in each aged sample. These peaks move toward lower temperatures as the moisture content of the sample is increased, from 89.2 to 53.4 °C, as expected, since the T_g values of TCS should depend on water content.

It is interesting to note that in TCS containing 10.6% moisture content two enthalpic relaxation peaks were observed. The upper and lower inset plots in Fig. 1a show first and second DSC heating scans for five replicates of this sample after being moisture equilibrated. The inset plot shows that the appearance of these two endothermic peaks in the first heating runs were reproducible in spite of base line fluctuations and in some cases the presence of noise in the data. It must be noted that these measurements were performed at the limit of resolution of the equipment, as indicated by the *y* scale bar (which represents only 0.01 mW). The first relaxation appears at around 50 °C and the second one at approximately 100 °C. Conversely, in all the replicates, only one endothermic event was evidenced in the DSC second heating scans (lower inset plots in Fig. 1a), which corresponded to that of a single glass transition temperature of non-aged samples (i.e., samples whose thermal history was erased during the first heating scan).

Sub-T_g endotherms of glassy amorphous amylopectin with intermediate moisture content (12–15%), occurring at around 50 °C, have been reported by Kalichevsky et al. (1992). This endothermic event was not detected immediately after rescanning but it appeared after storage. The origin of such sub-T_g endotherm was studied by Thiewes and Steeneken (1997) using native and amorphous potato starches aged by means of a two-stage aging procedure, at 30 and 70 °C. These authors demonstrated that the origin of such an endotherm is due to enthalpy relaxation rather than carbohydrate-water interactions, as previously reported by other authors (Appelqist et al., 1993; Gidley et al., 1993; Yuan & Thompson, 1994). Chung and Lim (2004) reported dual glass transitions for amorphous rice starch after moisture equilibration at 14.5%, but before aging. One T_g occurring at 56.7 and the other at 71.4 °C; the upper one being similar to that of amorphous waxy rice starch appearing at 70.7 °C. The presence of two different amorphous regions; a less restricted and a more restricted one, was given by these authors as a plausible explanation for such a bimodal endothermic transition.

Laredo et al. (2009) performed combined WAXS and thermally stimulated depolarization current (TSDC) experiments on amorphous transformed cassava starch. They found a cooperative relaxation mode at higher temperatures that was attributed to the dielectric manifestation of the dynamic glass transition. This cooperative relaxation process exhibited a bimodal distribution that shifted to higher temperatures as moisture was reduced in the measuring cell spanning a large temperature interval (from −73 to 50 °C). The authors postulated the coexistence of two amorphous zones with different rigidities to explain the bimodal relaxation time distribution observed by TSDC when these phases become mobile at increasing temperatures. The less rigid amorphous zones within the TCS examined by Laredo et al. was attributed to the original disordered phase present in native starch while the second and more rigid amorphous regions, were thought to be originated by the melting of the crystalline lamellae during the transformation process.

Taking into consideration the results reported by Laredo et al. and the fact that the two transitions observed for the TCS with 10.6% moisture content (upper inset plot in Fig. 1a) disappeared during the second heating DSC scan (lower inset plot in Fig. 1a), we postulate that the appearance of these two enthalpic relaxation are probably due to the development of structural heterogeneity or in other words to the formation of two amorphous phases during the storage period in the TCS employed here. There seems to be a critical moisture content below which physical aging allows the separation of the two types of amorphous phases whose T_g values differ by almost 50 °C and are very difficult to detect. After the thermal history is erased, the sample transforms into a homogenous melt sample, that later vitrifies during cooling from the melt. In a second heating scan, only one amorphous phase can be initially detected unless the sample is left to age for a considerable amount of time.

Although the low temperature endothermic peak (occurring at around 50 °C) was only detected in the first DSC scan of TCS samples with 10.6% moisture content (Fig. 1a and upper inset plot in it), its occurrence was evidenced in samples with different moisture contents, when they were blended with corn oil (TCS–CO samples). These enthalpic relaxation peaks can be observed in Fig. 1b–d for TCS–CO-1.1%, TCS–CO-4.6% and TCS–CO-6.9%, respectively. The figures show that irrespectively of the amount of CO added, two endothermic peaks, named hereafter PI and PII, were exhibited by the blends at low moisture contents. The higher transition temperature (PII) is more dependent on moisture content than the lower temperature one (PI). PII shifts toward PI with increasing moisture content, and both peaks finally merge at higher water contents. A similar behavior to that shown in Fig. 1b–d, has already been reported by Madrigal et al. (2011) in cassava starch blended with corn oil. In line with the results presented by these authors, Fig. 1b–d show that the greater the corn oil added levels, the lower the moisture content needed for PI to appear; i.e., 10.2% (Fig. 1b), 8.5% (Fig. 1c) and 6.4% (Fig. 1d) for samples with added corn oil of 1.1, 4.6 and 6.9%, respectively. Hence, these results also evidenced the synergistic action between water and corn oil for favoring molecular mobility within the starchy matrix during the physical aging process occurring during sample storage.

3.3. Glass transition temperatures of TCS and TCS–CO blends

Glass transition temperatures were determined form the midpoint of the heat capacity change during the second DSC heating scans for TCS and TCS–CO blends (graphs not shown), and the results are presented in Fig. 2. These second heating runs were performed after: (a) fully melting the aged samples and erasing their thermal history (during a first heating scan) and (b) performing a cooling run from the melt in the DSC. In all cases, only one endothermic event was observed in the DSC second heating scans. Fig. 2a shows the glass transition temperatures of TCS with different moisture contents. The figure also shows data reported by

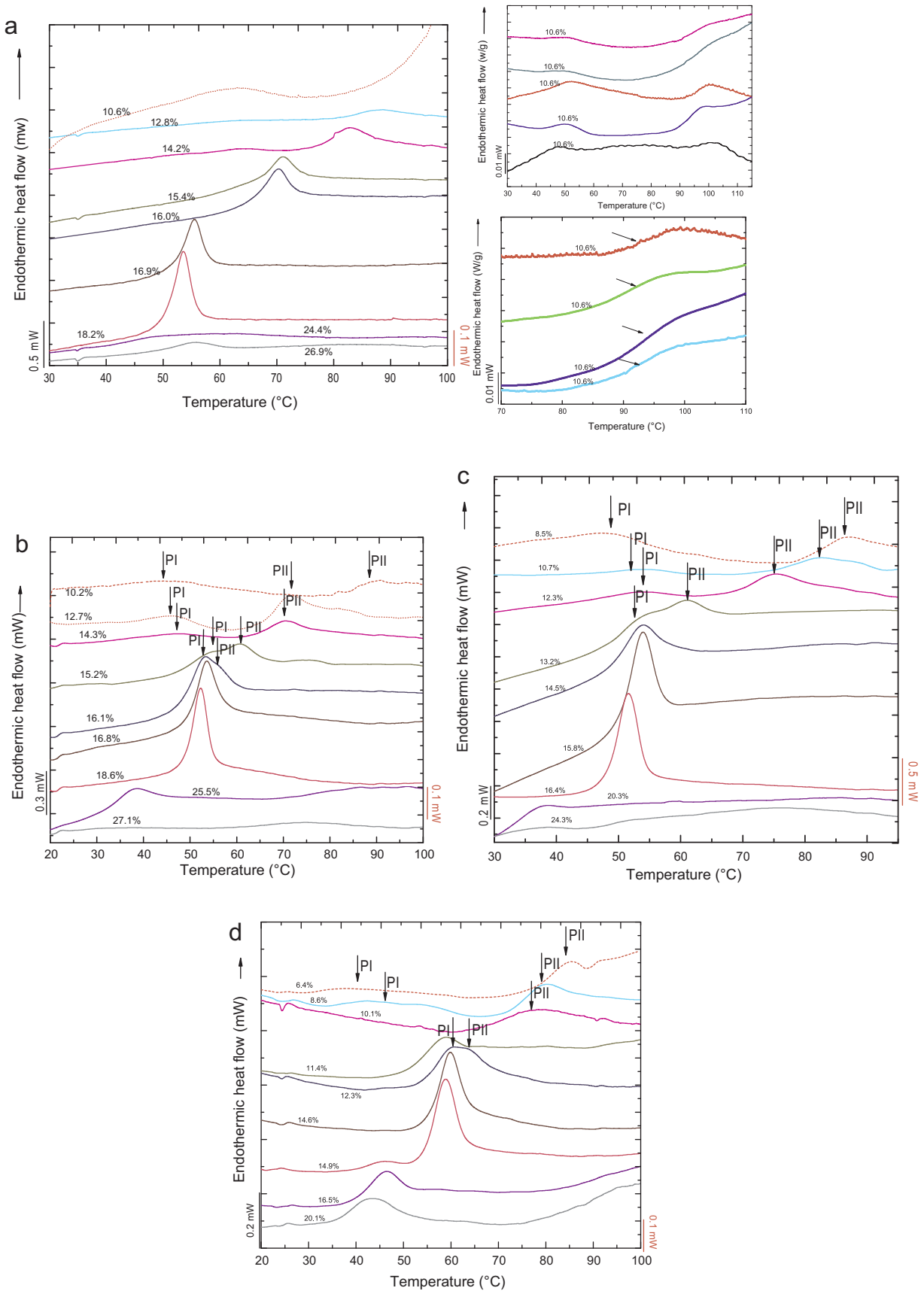

Fig. 1. First DSC scans for (a) TCS, (b) TCS–CO-1.1%, (c) TCS–CO-4.6%, and (d) TCS–CO-6.9%. In Fig. 1a, DSC heating scan of sample with 10.6% of moisture content is read on the right-side scale and the other DSC scans on the left-side scale. The upper and lower inset plots in Fig. 1a correspond to replicates of first and second DSC heating scans for TCS with moisture content of 10.6%.

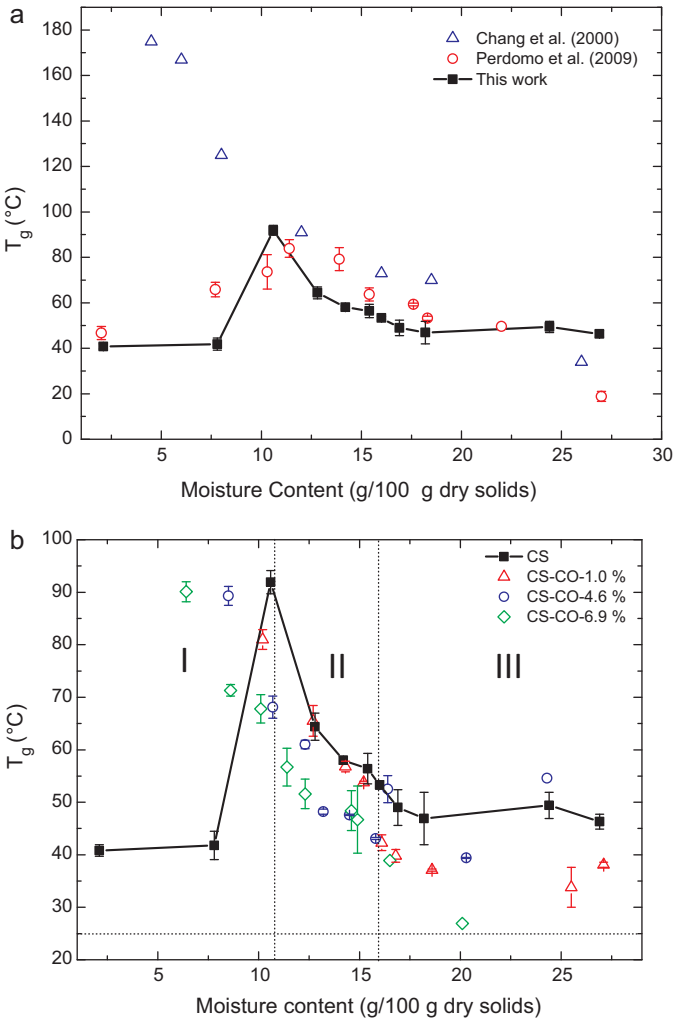

Fig. 2. Glass transition temperatures as a function of moisture content for (a) TCS and (b) TCS–CO blends.

Chang et al. (2000) and Perdomo et al. (2009). It is interesting to note in this figure, differences among the reported glass transition temperatures of cassava starch, which may be due to their different origins. In all cases, the plasticizing effect of water can be seen for moisture contents greater than around 11%. The anti-plasticizing effect of water reported by Perdomo et al. (2009), for moisture content values lower than 11%, was consistent with data obtained in this work.

Fig. 2b shows the effect of moisture content on T_g values of the three different TCS–CO blends. In all the blends, water acted as plasticizing agent for the whole range of moisture content tested. It is also worth noting that, as previously reported by Madrigal et al. (2011), the addition of corn oil to cassava starch did prevent the anti-plasticization effect of water at moisture contents lower than 11%. For moisture contents greater than this value Fig. 2b shows that added corn oil plasticized corn starch (i.e., at any constant moisture content greater than 11%, glass transition temperatures decreased with increasing contents of added corn oil). For moisture contents lower than 11%, Fig. 2b shows that corn oil anti-plasticized cassava starch as recently reported by Luk et al. (2013) i.e., glass transition temperatures of the blends are greater than those of the neat TCS.

3.4. The effect of added corn oil on the aging of cassava starch with two different moisture contents

Physical aging of TCS–CO-6.9% blends was studied in samples with two different moisture contents. From the first DSC heating scans of Fig. 1d, two samples were selected: one exhibiting two enthalpic relaxation peaks; i.e., CS–CO-6.9% with a moisture content of 8.6% and another with a single enthalpic relaxation peak; i.e., CS–CO-6.9% with 14.6% of moisture content. These samples exhibited glass transition temperatures in the second DSC heating runs of 71 and 48 °C, respectively (Fig. 2b). Physical aging was carried out at a T_a = 35 °C from 1 to 192 h. Hence, the (T_g–T_a) for samples with 8.6 and 14.6% moisture contents resulted in 36 and 13 °C, respectively. The first and second DSC heating scans of the aged samples after different aging periods of time are shown in Fig. 3(a through d).

The first DSC heating scans at different aging times, ranging from 1 to 192 h, for CS–CO-6.9% with 8.6% and 14.9% moisture contents are shown in Fig. 3a and b, respectively. Fig. 3a shows a bimodal or double enthalpic relaxation behavior appearing in a range of 45–90 °C, which became more distinctive as aging time proceeded. Bimodal enthalpic relaxations, with different enthalpy values, have been observed in native potato starch samples with 16% moisture content treated with a two-stage aging procedure at different temperatures, 70 °C for 0, 20 and 96 h, followed by aging at 30 °C for 100 h (Thiewes & Steeneken, 1997). According to these authors, the first peak, appearing at a temperature around 60 °C decreased in intensity with aging time; while the second peak, at 90–100 °C, increased in magnitude and shifted towards higher temperatures, as the aging time proceeded. Both endotherms were attributed to enthalpy relaxation due to aging occurring at 30 °C and 70 °C, respectively. A plausible explanation for dual enthalpic relaxation has been the existence of two different amorphous regions or phases, as argued by Chung and Lim (2004) for rice starch. Some other works have suggested the coexistence of less restricted and more restricted amorphous regions within partially crystallized synthetic polymers, such as partially crystallized or semicrystalline PET (poly(ethylene terephthalate)) (Diego et al., 1999; Montserrat & Cortes, 1995; Zhao et al., 2001; Zhao et al., 2002). These authors stated that double T_g could appear when there is some degree of crystallinity within the polymeric matrix.

In line with these works in synthetic polymers, the two peaks that became more distinctive as aging times proceeded, as shown in Fig. 3a, could also be attributed to the enthalpic relaxation of two amorphous zones (i.e., two amorphous phases) with different degrees of mobility. Apart from the plausible presence of two different amorphous regions in net amorphous cassava starch as seems to be indicated by the upper inset plot of Fig. 1a and the work carried out by Laredo et al. (2009), in case of the TCS–CO blends phase segregation may be increased by the presence of amylose–lipid complexes. Dual relaxation was firstly reported in this type of blend (CS–CO) by Madrigal et al. (2011), and in other biopolymer blends at low moisture contents, such as cassava starch–protein concentrate by Garcia et al. (2012). Subsequent work carried out by Luk et al. (2013) on cassava starch-complexing fatty acid blends reported the role of the amylose–lipid complex in this type of starch matrix, which was more prominent at low moisture content (<11%). Under these conditions, these complexes might act as physical cross-linking, varying the degree of mobility of the amorphous phases co-existing within such a system studied in this work.

Fig. 3b shows the first DSC heating scans exhibited by TCS–CO-6.9% sample with 14.9% of moisture content as aging time proceeded. The figure shows the gradual appearance of a single endothermic peak at around 45 °C, that increases in size and shifts toward higher temperatures, with increasing aging time. This behavior widely found in synthetic polymers, biopolymers and

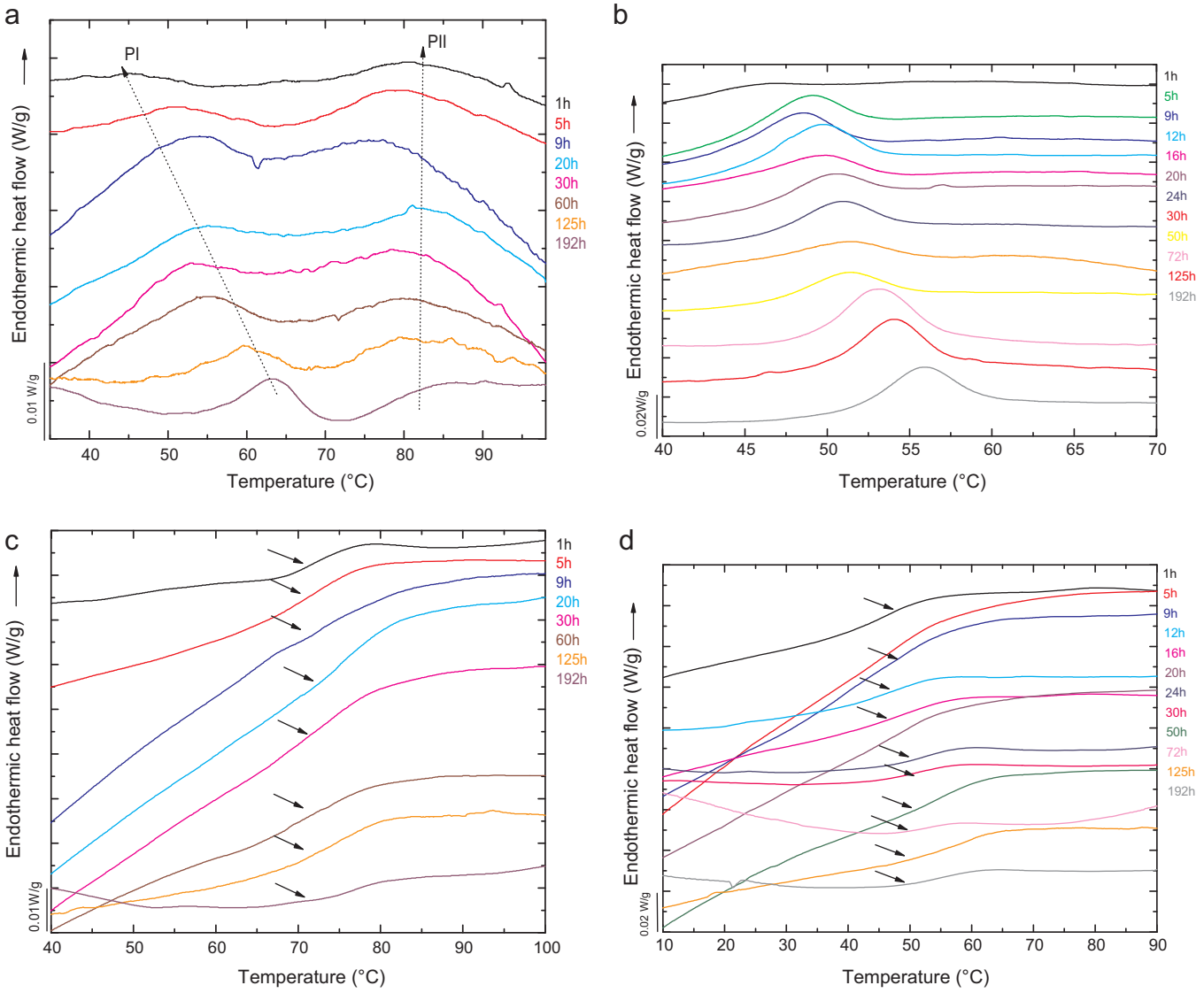

Fig. 3. First (a and b) and second (c and d) DSC scans for TCS–CO-6.9% with moisture contents of 8.6% (a and c) and 14.9 (b and d) at different ageing times (shown in the graphs).

lower molecular weight biological materials such as sugars (Chung & Lim, 2003b; Hutchinson et al., 1999; Noel et al., 2005) has been attributed to the difference in molecular mobility and free volume of samples with different degrees of aging or densification. It has been demonstrated, through mechanical testing and calorimetry, that physical aging leads to an increase in stiffness of the materials and a shift in the mechanical relaxation that corresponds to the glass transition to longer times (Chung & Lim, 2004; Lourdin et al., 2002; Noel et al., 2005).

Second DSC heating scans at different aging times, ranging from 1 to 192 h, for CS–CO-6.9% with 8.6% and 14.6% of moisture content are shown in Fig. 3c and d, respectively. The figures show that as expected the glass transition temperature of de-aged samples (after the rejuvenation process provided by the high temperature melting performed by the first heating run in the DSC) remains around the same value; i.e., 73–74 °C (Fig. 3c) and 46–49 °C (Fig. 3d) for samples with 8.6% and 14.6% of moisture contents, respectively. It has to be pointed out that; as shown by Fig. 3d, once thermal history of the samples is erased; the two enthalpic relaxation associated to amorphous zones with different degrees of mobilities (or to two T_g) disappeared. Hence, sample homogeneity or a unique amorphous zone within it with only one T_g can be assumed after immediate DSC scanning of de-aged samples.

3.4.1. Relaxation parameters

3.4.1.1. Enthalpy relaxation. The enthalpy recovery due to structural relaxation during physical aging depends on aging times. The enthalpy values for the two relaxation peaks (Fig. 3a) and for the single peak (Fig. 3b), were measured by the integration of the area under the peaks and plotted as a function of aging time in Fig. 4a and b.

Fig. 4a shows that, as expected for an enthalpic relaxation process, the enthalpy recovery of CS–CO-6.9% with a moisture content of 8.6% for both peaks increased with aging times as free volume and molecular mobility decreased with increasing aging time (Montserrat, 1992; Montserrat, 1994). In both cases, the plateau is reached rapidly during the early stages of the aging process ($t_e < 30$ h). At the beginning of aging ($t_e \leq 30$ h) there is more chain mobility, which explain the initial rapid increase in enthalpic values. This mobility decreases as the system approaches pseudo-equilibrium ($t_e \geq 30$ h). Fig. 4a also shows enthalpy variations, from the beginning to the end of the enthalpy recovery process, of

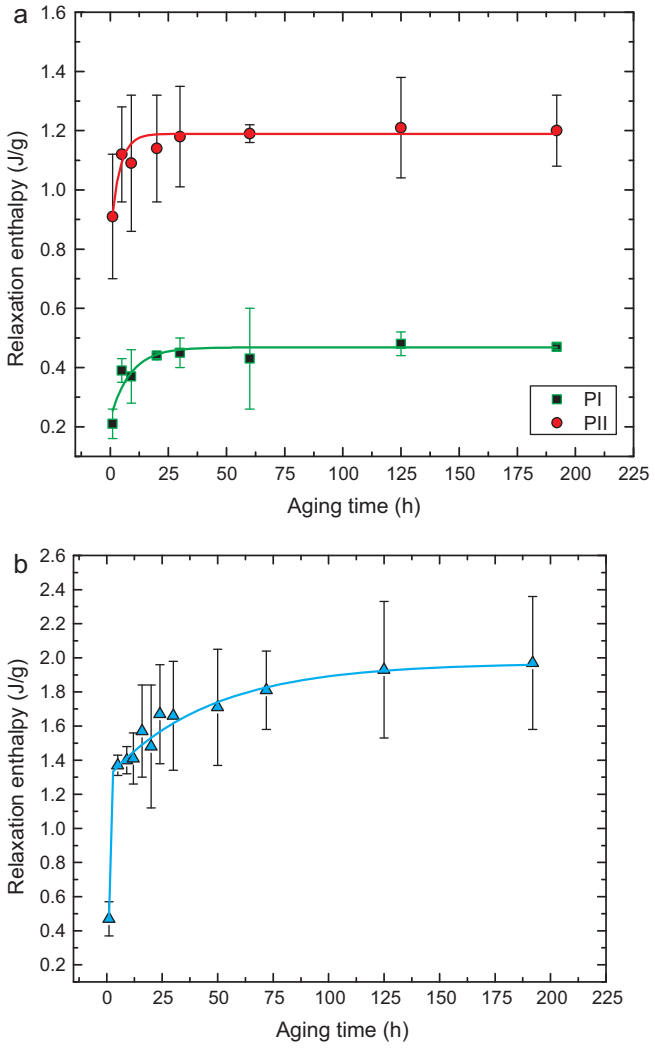

Fig. 4. Relaxation enthalpies as a function of aging times for TCS–CO-6.9% with moisture content of 8.6% ((a) T_a = 35 °C, T_g = 71 °C) and 14.9%, ((b) T_a = 35 °C, T_g = 48 °C).

0.2–0.5 J/g and 0.9–1.2 J/g for PI and PII, respectively. Results shown in Fig. 4a demonstrate that the CS–CO-6.9% sample with a moisture content of 8.6% exhibited the existence of two distinct amorphous regions within the system, as only the amorphous regions in starch experience aging phenomena.

Fig. 4b shows the increasing enthalpy values with aging times for CS–CO-6.9% sample with 14.6% moisture content. The figure shows that in case of a higher moisture content sample, the increase in enthalpy is more progressive towards a pseudo-equilibrium enthalpic state, reaching the plateau at longer times ($t_e \geq 125$ h). However, the increase in recovered enthalpy values is more marked than that observed in samples with lower moisture contents (Fig. 4a). For $t_a \leq 30$ h the enthalpy relaxation increased from 0.47 to 1.7 J/g. As aging time proceeded changes in enthalpy values are smaller, reaching a plateau at a value of about 2 J/g in an aging time of 125 h. Kim et al. (2003) reported an increase of relaxation enthalpy values with aging time from 1 to 2 J/g in potato starch with 16% of moisture content, aged at 33 °C for 180 h. Other aging temperatures, such as 25, 42 and 50 °C were also studied by these authors.

The behavior shown in Fig. 4a and b illustrates the role of water in the aging process, which contributes to higher molecular mobility and free volume in the early stages of aging. The figures show that, as expected, samples with greater moisture content relaxed more; i.e., exhibited higher enthalpy values, than that with lower moisture content. Additionally, greater chain mobility within this sample due to the lower (T_g–T_a), is also expected to contribute to its greater relaxation. This behavior has been reported by different starchy and proteinaceous materials such as: gelatinized starch (Appelqvist et al., 1993; Gidley et al., 1993; Shogren, 1992; Yuan & Thompson, 1994), native starch (Chung et al., 2002), and gelatin in the glassy state (Badii et al., 2005).

Apart from the moisture content implicit differences between the two samples, the mentioned heterogeneity and the role that amylose-lipid may be playing at low moisture content in the one exhibiting the two relaxation peaks (CS–CP-6.9% with moisture content of 8.6%), might also have played an important role in the observed behavior. As in the case of synthetic polymers, such as PEEK and PET; i.e., the relaxation rate decreases with increasing crystallinity, since the crystallites seems to act as a physical crosslinks, retarding the relaxation process (Mukherjee & Jabarin, 1995; Tant & Wilkes, 1981; Yoshida, 1995). Chung et al. (2004) reported that for a fixed aging time enthalpy relaxation of rice starch increased with decreasing crystallinity. The relaxation enthalpy was positively correlated with the amount of amorphous material.

3.4.1.2. Onset and peak temperatures of the relaxation endotherm. In a DSC scan, the temperature at which the endothermic peak of the enthalpy recovery appears, increases with aging time. Onset and peak temperatures of the relaxation endotherms exhibited by CS–CO-6.9% with 8.6% (Fig. 3a) and 14.6% (Fig. 3b) of moisture contents, were plotted as a function of temperature and shown in Fig. 5a through d.

Fig. 5a and b show the onset and peak temperatures as a function of aging time for CS–CO-6.9% with 8.6% of moisture content. The figures show that a linear relationship was obtained for onset temperatures of the two peaks (PI and PII); and for the peak temperature of PI. A poor linear relationship and a negative slope (around zero) were obtained for the variation of peak temperature of PII with aging time, indicating that it was independent on aging time (Fig. 5b).

A linear positive relationship between the peak temperature and the logarithmic values of aging time is a typical behavior of synthetic polymers, as well as of amorphous starchy materials as reported by several authors (Chung & Lim, 2004; Shogren, 1992; Thiews & Steeneke, 1997). However, Montserrat (1994) reported that peak temperatures were practically constant with changes in aging time, when the difference between the aging and glass transition temperatures (T_g–T_a) was less than 10 °C, since the system had achieved a structural equilibrium. In the sample studied here, CS–CO-6.9% with 8.6% of moisture content, this difference was much higher than this value (T_g–T_a = 36 °C). Consequently, the behavior exhibited by the sample in Fig. 5b; i.e., the independence of peak temperature on aging time (PI), and the non-logarithmic linear relationship (PII) of the relaxation process could be attributed to the structural heterogeneity of this sample already mentioned.

The variation of onset and peak temperatures for CS–CO-6.9% with 14.9% of moisture content is shown in Fig. 5c and d, respectively. The figures show that, these temperatures behaved differently when the moisture content of the sample increased. In fact, as expected the shape of the curve resulted similar to that of enthalpy relaxation as a function of aging times (Chung & Lim, 2004; Shogren, 1992; Thiews & Steeneke, 1997) i.e., a very rapid variation at short aging times, which tends to slow down with further increases of aging time, as can be noted from the inset plots in Fig. 5c and d.

The semi-logarithm behavior of both, onset and peak temperature, with aging time shown in Fig. 5c and d exhibited a discontinuity in the linear trend as the starchy matrix approaches

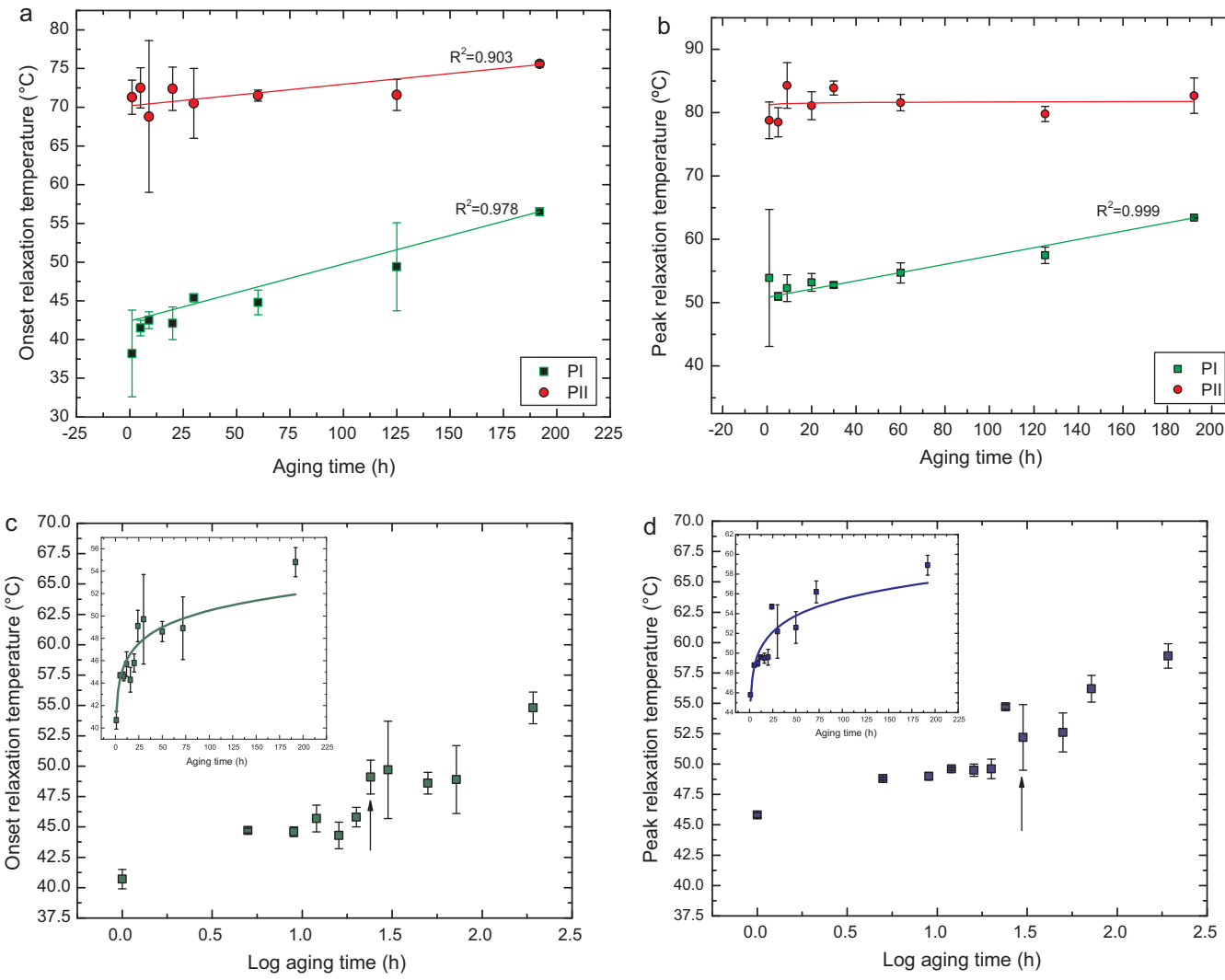

Fig. 5. Onset (a and c) and peak (b and d) temperatures as a function of aging times for TCS–CO-6.9% with moisture contents of 8.6% (a and b), and 14.9% (c and d).

an enthalpic pseudo-equilibrium (pointed out with arrows in both figures). This discontinuity divided the aging process in two stages: (i) an early aging zone; for 0 h < t_a < 24 h, and (ii) a late aging zone for 24 h < t_a < 192 h. Two stages of aging, the first one from 0 to 50 h and the second one from 50 to 250 h, have been reported by Chung et al. (2004) for native and partially melted rice starch. These authors also reported that the plot trends of enthalpy relaxation and peak temperature as a function of aging time had similar shapes.

4. Conclusions

Thermal transitions after physical aging of TCS and TCS–CO blends with different moisture contents were determined from first and second DSC heating scans. Two well reproducible endothermic peaks, occurring at around 50 and 100 °C, were observed during the first DSC heating scan in neat TCS with 10.6% moisture contents, which disappeared after immediate reheating in the calorimeter. This double enthalpic relaxation behavior transition is probably a manifestation of structural heterogeneity within amorphous cassava starch characterized by two amorphous regions or phases with different degrees of mobility. This phase segregation was enhanced by added corn oil, as indicated by the wider moisture content range of samples presenting bimodal thermal transition during first DSC heating scans evidencing the synergistic actions between water and corn oil favoring molecular mobility within starchy matrices during physical aging. Differences among glass transition temperature values of amorphous cassava starches reported by other authors and the ones presented in this work, underlined the relevance of botanical origins. The role of water and corn oil on glass transition behavior of TCS analyzed in this work was consistent with previous works in similar blends. The behavior during physical aging of TCS–CO blends depended on their moisture content. At low moisture content (in this work 8.6%), dual enthalpic transitions appeared at around 45 and 90 °C, and became more distinctive as the aging time proceeded. As with neat TCS, the two endotherms reflecting these relaxations processes disappeared after first DSC heating scans, indicating that once the sample storage history is erased, the amorphous matrix became a homogeneous system with one amorphous phase. Increasing moisture content (in this work to 14.9%), promoted homogeneity of samples and physical aging was then characterized by one endothermic peak, which also disappeared after immediate re-heating of the sample in the calorimeter. Enthalpy recovery of both, samples with two relaxation peaks and the one with a unique relaxation endotherm, increased with aging times towards an equilibrium enthalpic state. The peak temperatures of the two relaxation process occurring at low moisture content, were independent on aging time for PII and varied linearly for PI. At higher moisture content the expected semi-logarithmic

relationship between these two parameters was exhibited by the sample.

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