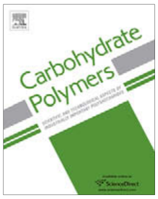
Carbohydrate Polymers 76 (2009) 305–313

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol



Glass transition temperatures and water sorption isotherms of cassava starch

J. Perdomo [a,b], A. Cova [a,b,*], A.J. Sandoval [a], L. García [a,b], E. Laredo [c], A.J. Müller [b,*]

[a] *Depto. de Tecnología de Procesos Biológicos y Bioquímicos, Universidad Simón Bolívar, Aptdo. 89000, Caracas 1080-A, Venezuela*
[b] *Grupo de Polímeros USB, Dpto. de Ciencia de los Materiales, Universidad Simón Bolívar, Aptdo. 89000, Caracas 1080-A, Venezuela*
[c] *Grupo de Física de Sólidos, Universidad Simón Bolívar, Dpto. de Física, Aptdo. 89000, Baruta 1080, Edo. Miranda, Venezuela*

ARTICLE INFO

Article history:
Received 4 August 2008
Received in revised form 23 October 2008
Accepted 28 October 2008
Available online 5 November 2008

Keywords:
Cassava starch
Plasticizing and anti-plasticizing effects
WAXS
DSC and DMTA
Glass transition
Sorption isotherm
Retrogradation

ABSTRACT

The effect of water content on the glass transition temperatures of cassava starch was determined by differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA). Samples were transformed to the amorphous state by compression molding at high temperature (as demonstrated by wide angle X-ray diffraction, WAXS), and then the samples were moisture conditioned. Both DSC and DMTA showed that water anti-plasticized cassava starch at lower moisture contents, and plasticized it at higher water contents. Samples with higher moisture contents stored at room temperature, 45 °C and 80 °C underwent retrogradation as indicated by WAXS. Sorption isotherms of cassava starch showed that for a_w values lower than around 0.85, the sorption capacity decreased with increasing temperature; while the opposite behavior was observed at $a_w > 0.85$. This inversion point ($a_w = 0.85$) was attributed to the fact that more active sites were exposed to the adsorption processes, due to the enhanced molecular mobility promoted in the amorphous regions by starch crystallization.

1. Introduction

Cassava (*Manihot esculenta Crantz*) is an important root crop, which is consumed as food in Venezuela and many other tropical countries in different forms. It is considered a foodstuff of high nutritional value and one of the most economical sources of energy; since the carbohydrate yield is 40% greater than in rice and 20% greater than in corn (Tonukari, 2004). For this reason, processing of cassava root in order to obtain cassava starch has increased in the last decades. Cassava starch, as all other starches, mainly contains two polymers that contribute to its molecular structure: amylose in a percentage varying from 13 to 24% (Hoover, 2001; Rickard, Asaoka, & Blanshard, 1991), essentially a linear molecule, and a non-linear and highly branched molecule, amylopectin, both consisting of glucose repeating units. Both molecules form semicrystalline superstructures (with crystalline and amorphous layers arranged in an onion like structure), where most of the crystalline regions are formed by amylopectin although parts of the amylose molecules are also present in them. Within such a system, the crystalline structure includes a fixed number of water molecules, while the amorphous zones accommodates an increasing amount of moisture depending on the water activity of the atmosphere where the samples are being equilibrated. Consequently, water influences the structure by acting as a plasticizer of the amorphous regions, an effect that causes a depression of the glass transition temperature, T_g.

The glass transition temperature is a very im‘portant physical parameter, which serves to explain the physical and chemical behavior of food systems (Bell & Touma, 1996), and it is defined as the temperature at which the material changes from the glassy to the rubbery state for a given heating rate. The plasticizing effect of water on food biopolymers is very small at low water activity (a_w) values, therefore the T_g associated with the amorphous regions in the sample will be typically high and at room temperature the material will be glassy. Water access will be higher in the rubbery state (at $T > T_g$) than in the glassy state, since the free volume increases above T_g. Increasing water activity, and hence food biopolymer plasticization, causes an increase in the availability of the polar sites to the water molecules due to the enhanced molecular mobility (Al-Muhtaseb, McMinn, & Magee, 2004a). The plasticizing effect of water at constant temperature is identical to the effect of increasing temperature at constant moisture content (Slade & Levine, 1988).

Polymers such as starch are normally found in foods with high hydrophilic capacity. As with other foodstuffs, food stability of starch and starchy products greatly depends on their composition, the surrounding relative humidity and temperature (Bertuzzi, Armada, & Gottifredi, 2003; Haque & Roos, 2004). The way these variables are related to the water present within the food matrix and its glass transition temperature will determine its physical properties, as well as its chemical and microbial stability. Products stored at temperatures lower than their T_g are known to have greater

---

[*] Corresponding authors. Tel.: +58 212 9063974; fax: +58 212 9063971 (A. Cova), tel./fax: +58 212 9063388 (A.J. Müller).
E-mail addresses: auracova@usb.ve (A. Cova), amuller@usb.ve (A.J. Müller).

0144-8617/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2008.10.023

stability over large periods of storage, as compared to those kept at temperatures greater than their T_g (Haque & Roos, 2004; Nowakowski & Hartel, 2002; Roos & Karel, 1992). In this way, food water sorption characteristics obtained at different temperatures and their relation to the glass transition temperature should be studied, so that a better knowledge of food storage conditions which warranty a longer food shelf life can be gained.

One way for presenting food sorption characteristics is through sorption isotherms. They represent the relationship between the water adsorbed or desorbed within the food, and its water activity, at a constant temperature and under equilibrium conditions (Al-Muhtaseb, McMinn, & Magee, 2002). Many other applications of sorption isotherms in food science make their determination useful for food technologists. They include: drying process modeling, design and optimization of driers, food shelf life prediction, modeling of moisture changes taking place within the food during storage, and food packaging selection (Sahin & Sumnu, 2006).

Although sorption data on starchy products are widely available (e.g., Al-Muhtaseb et al., 2004a; McMinn & Magee, 1999), water sorption data for cassava starch presented in the literature are limited to one temperature, normally around room temperature, such as the values presented by Chang, Cheah, and Seow (2000), Chatakanonda, Dickinson, and Chinacohoti (2003), Mali, Sakanaka, Yamashita, and Grossmann (2005), and Mishra and Rai (2006). In other cases, temperature ranges experimented are higher than those normally found in food storage in tropical countries, as in the data presented by Aviara and Ajibola (2002), where the temperature range reported was from 30 to 60 °C. Additionally, the extreme sensitivity to water or temperature plasticization on food biopolymers and their effect on T_g, underlines the importance of determining the moisture sorption characteristics of food materials at different temperatures. In this way, moisture sorption isotherms can be used together with glass transition values as a function of moisture content to define storage conditions that enhance the stability or increase the shelf life of food products.

Taking into account the above, the aim of this study was to determine the glass transition temperatures of amorphous cassava starch and their variation with moisture content, using dynamic mechanical thermal analysis (DMTA), and differential scanning calorimetry (DSC) techniques. Wide angle X-ray scattering, WAXS, was used in order to follow the variations of the crystallinity of the samples with different moisture contents and thermal treatments. Another objective was to determine moisture sorption isotherms at different temperatures (5, 30 and 45 °C), as well as sorption parameters such as monolayer water content values and isosteric heats of sorption.

2. Materials and methods

2.1. Raw material

The cassava starch used (AIM TF 113) was purchased from Agroindustrial Mandioca C.A. and it was produced in the state of Monagas in Venezuela. Its initial moisture content was 16.8 (d.b., or expressed as g/100 g of dry solids, see method below).

2.2. Sample preparation

Solid, amorphous cassava starch bars or films, depending on the analysis, were prepared as follows: powder native starch was moistened up to 25% (wet base, w.b.), by slowly adding water while continuously stirring and left overnight for equilibration. Subsequently, the powder was placed in a plate mould ($52 \times 11 \times 1.5$ mm^3), for DMTA bar samples, or between kapton polymide sheets making a 1 mm powder layer for WAXS and DSC sample films. Compression molded employing a hydraulic press (ADQ 11, model PP25 T) (3500psig) at 135 °C for 20 min, was carried out. The whole assembly was cooled (up to 40 °C) before releasing the pressure, in order to avoid water bubble forming inside the plate. Following decompressing, thin rectangular films for WAXS analysis ($12 \times 10 \times 1$ mm^3), and sample discs for DSC measurements (5 mm in diameter and 1 mm thick), were cut.

Complete transformation of the samples by using this procedure was further confirmed by the absence of residual gelatinization enthalpy, determined by DSC experiments in excess of water in a Perkin Elmer DSC 7 and by WAXS (as indicated below).

2.3. Sample conditioning

Different moisture contents in the molded samples, for DMTA and DSC experiments, were achieved by conditioning samples at room temperature (25 °C) for four weeks at different environments with a varying relative humidity values; i.e., different levels of water activity in the samples ($0.11 \leqslant a_w \leqslant 0.98$) (Greenspan, 1977). Bone dry material was obtained from conditioning film sample discs in P_2O_5 under the same time-temperature conditions. A resulting moisture content of 2.0 ± 0.2% was obtained for these latter samples (see method below).

Amorphous samples to be used in the evaluation of development of crystallinity during storage by means of WAXS analysis, were placed in environment of LiCl, K_2CO_3, KCl, KNO_3 and K_2SO_4 and stored at room temperature, 45 °C and 80 °C for three weeks. Relative humidity values at the three temperatures considered were taken from Greenspan (1977). Crystallinity was also investigated in the native cassava starch.

2.4. WAXS analysis

The WAXS experiments were carried out in a Panalytical X'Pert-Pro system automatic diffractometer equipped with an X'celerator photon counter. The experimental conditions were 45 kV and 40 mA for the X-ray source (Cu Kα, Ni-filtered) and the runs were recorded from 5 to 70° in 2θ with 0.02° steps and 20 s counting time. The crystallinity was measured either by a deconvolution of the experimental trace or a determination of the amorphous fraction and further subtraction from the total diffracted intensity.

2.5. Glass transition temperatures

Glass transition temperatures in samples with different moisture content were measured using two different methods: thermo-mechanical and calorimetric analysis.

2.5.1. DMTA analysis

Thermo-mechanical determination of the glass transition temperatures was carried out in a rheometric solid analyser (Rheometric Scientific, RSA II). Starch bars were placed in a three point bending geometry, and oscillated at a frequency of 1 Hz at a heating rate of 3 °C/min. The temperature range of the measurements depended on the moisture content of the samples. The strain amplitude was maintained at 0.1% in order to remain within the linear viscoelastic range. Starch samples with dimensions of $52 \times 11 \times 1.5$ mm^3 were used and the specimens were coated with vacuum grease and completely wrapped in aluminum foil, to limit weight loss during testing (Pereira & Oliveira, 2000). It was previously confirmed that this procedure did not have any effect on the mechanical properties of the starch bars. Temperature at which a maximum was obtained in the viscous modulus (E''), were determined by using the software Orchestrator (V6.3.2). A minimum of three samples for each moisture content was measured and the values of T_α were averaged.

2.5.2. Moisture loss evaluation during DMTA testing

Weight changes during DMTA analysis were followed in samples previously conditioned at three different moisture contents (low, intermediate and high moisture content levels), at room temperature. Bars preparation and DMTA analysis were carried out as before, with a heating range from 30 to 110 °C. In all experiments, heating started at 30 °C and the experiment stopped at temperature increments of 5 °C, i.e., first experiment stopped at 35 °C, second experiment at 40 °C and, so on. For each moisture content sixteen samples were used (one sample for each run), and weight loss was quantified by weighing the sample before and after experimentation.

2.5.3. DSC analysis

Calorimetric determination of the glass transition temperatures at different moisture contents was carried out in sample discs thermo-moulded and moisture conditioned as stated before. Measurements were done using a DSC 7 (Perkin Elmer), previously calibrated with indium and naphthalene. An amount of 10 ± 0.5 mg of each sample with the adjusted moisture content considered in this work was weighed in hermetically sealed aluminum pans. Each sample was heated from −10 to 110 °C at 5 °C/min, using an empty pan as a reference. The glass transition temperature of the specimens was determined from the midpoint of the heat capacity change observed on the second run, to eliminate the effect of sample history. Three samples of each material were measured and the T_g values obtained from the scans were averaged.

2.6. Moisture sorption isotherms

A static gravimetric method was used to determine the sorption characteristics of the molded cassava starch. Bars of starch were placed in triplicate inside eleven desiccators, each one containing oversaturated salt solutions of known equilibrium relative humidity at the temperatures studied. These environments provided an a_w range of 0.08–0.98, with the following salts used for this purpose: KOH, LiCl, CH_3COOK, $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$, KI, NaCl, $(NH_4)_2SO_4$, KCl, KNO_3 and K_2SO_4. At water activity higher than 0.8, crystalline thymol was placed inside the desiccators to prevent the microbial spoilage of the samples. The desiccators were kept in temperature controlled incubators (±0.5 °C) at 5, 30 and 45 °C for at least four weeks. It was previously demonstrated that during this time, equilibrium was attained (by periodically weighing of the samples). Relative humidity values at the three temperatures considered were taken from Greenspan (1977).

After equilibrium was reached, the moisture content of the equilibrated samples was determined in triplicate. Standard procedure of the AOAC (1990) was used for this determination, which consisted on heating the sample in an atmospheric oven at 130 ± 3 °C for 3 h.

The data obtained were adjusted to different sorption models commonly applied to starchy products (Table 1): BET, Smith, Henderson, Halsey, Oswin, GAB (see Rahman, 1995) and modified GAB (Viollaz & Rovedo, 1999). Linear and non-linear regression statistical analysis were performed, using Statistica™ version 6.0. The quality of the fitting was evaluated through the R^2 and through the mean relative percent error (% E) defined as:

$$E(\%) = \sum_{n=1}^{n}\left[\left|\frac{m_{e,i} - m_{p,i}}{m_{e,i}}\right|\right]\cdot\left[\frac{100}{n}\right] \tag{8}$$

where n is the number of data points, (m_e) and (m_p) are experimentally observed and predicted by the model values of the equilibrium moisture content, respectively. The mean relative percentage error (%E) has been widely adopted throughout the literature to evaluate the goodness of fit of sorption models, with an E value below 10% indicative of a good fit for practical applications (Al-Muhtaseb et al., 2004a; Lomauro, Bakshi, & Labuza, 1985).

The water content of the monolayer was determined from the BET (a_w up to 0.35) and GAB (a_w up to 0.90) equations, and the effect of temperature on the sorption isotherms was evaluated through the Clausius–Clapeyron equation:

$$q_{st} = -R\left[\frac{\mathrm{d}(\ln a_w)}{\mathrm{d}(1/T)}\right]_m \tag{9}$$

where q_{st} is the net isosteric heat of sorption (J/mol), T is the absolute temperature (K), and R is the universal gas constant (8.314 J/mol K). By plotting $\ln(a_w)$ vs $1/T$ for a given constant starch average moisture content, the net isosteric heat of sorption q_{st} could be obtained from the slope of the curve. The total heat of sorption (Q_{st}), was determined from Eq. (10).

$$Q_{st} = q_{st} + \lambda_{\mathrm{vap}} \tag{10}$$

were λ_{vap} is the heat of vaporization of pure water (assumed constant with temperature for the temperature range considered here and equal to 44.09 kJ/mol, Cassini, Marczak, & Noreña, 2006).

3. Results and discussion

3.1. WAXS analysis

The native cassava starch crystallizes in the A structure which is more frequent in starch obtained from cereals. The 3D structure found in the crystalline part of A structured starches is monoclinic, space-group B2 and with cell parameters a = 21.24 Å, b = 11.72 Å, c = 10.69 Å and γ = 123.5° (Imberty, Chanzy, Pérez, Buléon, & Tran, 1988). These authors demonstrated that 4 water molecules can be accommodated per unit cell, and that they are localized between the chains. These ordered chains form a parallel aggregate of short amylopectin segments which are radially placed in the granule structure as proposed by Lineback (1986).

In Fig. 1 the WAXS spectra for native cassava starch and transformed starch samples stored at 25 °C are shown. The A structure for the native starch is observed together with the amorphous state of the transformed starch. The crystallinity determination resulted from subtracting the amorphous halo profile adequately weighted from the diffraction spectrum given by the semi-crystalline sample. X_c is calculated by:

$$X_c = \frac{\int_{\theta=8^\circ}^{\theta=60^\circ}(I_{\mathrm{hkl}}(\theta) - I_{BG}(\theta))\mathrm{d}\theta}{\int_{\theta=8^\circ}^{\theta=60^\circ}(I_{\mathrm{total}}(\theta) - I_{BG}(\theta))\mathrm{d}\theta} \tag{11}$$

where $I_{\mathrm{hkl}}(\theta)$ is the contribution of Bragg peaks originated from the crystalline component, the total scattered intensity is $I_{\mathrm{total}}(\theta)$ and a linear background is subtracted from both.

The crystallinity degree for the native starch was found to be X_c = (38 ± 1)%.

When the transformed samples were equilibrated at 25 °C at different water activities, the starch remained amorphous until a_w = 0.973 when the retrogradation of part of the amorphous starch to the crystalline A structure was observed as seen in Fig. 2 curve (a). Upon equilibrating the amorphous samples at 45 °C at different water activities, the spectra obtained showed a 100% amorphous state when stored at a_w values $\leqslant$ 0.817. WAXS spectra for samples stored at higher a_w atmospheres (i.e., 0.870 and 0.961) showed the typical Bragg reflections of the A structure described above. Another series of experiments was performed by equilibrating the amorphous starch at 80 °C at different water activities In Fig. 2, curve (b), the WAXS spectrum of the retrogradated starch at 80 °C is shown to reach a very close crystallinity degree as compared to the starch equilibrated at 25 °C. The difference

Table 1
Isotherm equations for experimental data fitting and their range of applicability.

Model	Mathematical expression	a_w range of applicability	Equation
BET	$\frac{m}{m_o} = \frac{C \cdot a_w}{(1-a_w)(1-a_w+C \cdot a_w)}$	<0.50	(1)
Smith	$m = A + B \cdot \ln(1 - a_w)$	0.50–0.95	(2)
Henderson	$m = \left(-\frac{\ln(1-a_w)}{A}\right)^{1/B}$	0.50–0.95	(3)
Halsey	$m = \left(-\frac{A}{\ln a_w}\right)^{1/B}$	0.10–0.80	(4)
Oswin	$m = A \cdot \left(\frac{a_W}{1-a_W}\right)^B$	NA[a]	(5)
GAB	$m = \frac{m_o \cdot C \cdot k \cdot a_w}{[(1-k \cdot a_w)(1-k \cdot a_w+C \cdot k \cdot a_w)]}$	<0.95	(6)
Modified GAB	$m = \frac{A \cdot B \cdot C \cdot a_w}{[(1-C \cdot a_w)(1-C \cdot a_w+B \cdot C \cdot a_w)]} + \frac{A \cdot B \cdot C \cdot D \cdot a_w^2}{(1-C \cdot a_w)(1-a_w)}$	<1	(7)

[a] Not available. In this work it was used in the whole range of a_w experimented. In Eqs. (3) and (6), m_o represents the monolayer moisture content.

among the three annealing temperatures was the water activity threshold necessary to observe the rise of crystallinity in the samples. At 25 °C, 45 °C and 80 °C the minimum water activities to observe 3 dimensional order were 0.973, 0.870 and 0.789, respectively, whereas the final crystallinity at the highest water activity was similar. This indicates a saturation of the starch sites available for the sorption process. Also the width of the Bragg peaks was larger for the recrystallized starch than for the native starch which results from the formation of more imperfect crystals as the retrogradation proceeds.

3.2. Glass transition temperatures

In order to evaluate moisture loss during DMTA experiments, a weight loss study was carried out. Fig. 3 shows the weight loss for cassava starch bars at low, intermediate and high moisture levels. As shown in this figure, in all cases weight loss began to increase from around 55 °C, and it was kept below 1% at temperatures lower than 100 °C, irrespective of the moisture content considered. Samples with moisture contents of 17.9 and 27.3% (d.b.) exhibited weight loss between 1% and 1.8% at temperatures greater than 100 °C. These results indicate that as expected the higher the moisture content the higher the resulting weight loss. However, this fact should not represent a big constrain in this type of experiment, as samples with high moisture content are expected to have transition temperatures below those at which weight loss becomes meaningful.

The temperature of the main relaxation, T_α, was determined by means of DMTA analysis at different moisture contents. Fig. 4 shows typical DMTA curves as a function of temperature for amorphous cassava starch with a moisture content of 18.4% (d.b.). In most cases, the temperature of the maxima of the relaxation modes (T_α) obtained by DMTA for all samples were quite reproducible with a variation coefficient of less than 10%, in particular for those temperatures obtained from E'' data. Fig. 4 shows the typical behavior of a viscoelastic material going through the glass transition, characterized by a significant drop in the elastic modulus ($E'(T)$), and a maximum in the storage modulus, while a maximum is also observed in tan δ(T). As in some cases, it was not possible to easily detect the drop in the elastic modulus, the transition temperatures reported in this work were taken from the maxima in the loss modulus ($E''(T)$). It is also worth noting in Fig. 4, the broad peak obtained from tan δ(T), suggesting a wide relaxation-time spectrum as it should be expected for a food system. Chung and Lim (2004) reported wide and bimodal tan δ peaks, for normal rice starch which indicate an heterogeneous amorphous phase that might be induced by the presence of crystals. They also observed two very broad transitions by DSC that were attributed to these two T_g processes.

Fig. 5 shows the determination of the glass transition temperatures by DSC studies, obtained from transformed cassava starch at different moisture contents. This figure shows an evident antiplasticizing effect of water (i.e., the T_g values increase as the moisture content increases in the samples) at moisture contents lower than 11.4% (d.b.). At higher moisture content, water plasticizes the cassava starch resulting in the expected decrease of T_g with increasing moisture content. A similar trend for T_α in amorphous cassava starch with moisture content was obtained from DMTA measurements, as shown in Fig. 6. This figure depicts the variation of transition temperatures with moisture contents as obtained by both DMTA and DSC studies for the whole range of moisture contents considered in this work. Although information obtained from DSC and DMTA techniques are not strictly equivalent as they probe molecular mobilities under different experimental conditions, a good agreement between mechanical and calorimetric measurements can be observed in Fig. 6. The transition temperature measured at the maximum of $E''(T)$ (at 1 Hz and 3 °C/min heating) is in most cases very close to the T_g's measured by DSC at 5 °C/min heating. Similar correspondence between the maximum of the loss modulus with calorimetric measurements have been reported in the literature. Cocero and Kokini (1991) found that the glass transition temperatures measured on glutenin with moisture content between 4 and 14%, by DSC (at 5 °C/min) were in agreement with those corresponding to the peak in the loss shear modulus (G'') determined at a frequency of 1 Hz and a heating rate of 5 °C/min. Likewise, work carried out on different single food biopolymers evidenced approximately the same temperature for that obtained from the peak in E'' (at 1 Hz and 2 °C/min heating), and the T_g determined at 10 °C/min on a DSC (Kalichevsky, Blanshard, & Tokarczuk, 1993; Kalichevsky, Jaroszkiewicz, & Blanshard, 1992b; Kalichevsky & Blanshard, 1993).

Fig. 6 was divided into three zones according to the transition temperature variation with moisture content: zone I for moisture content below a value around 11% where an anti-plasticizing effect of water is evident; zone II corresponding to intermediate moisture

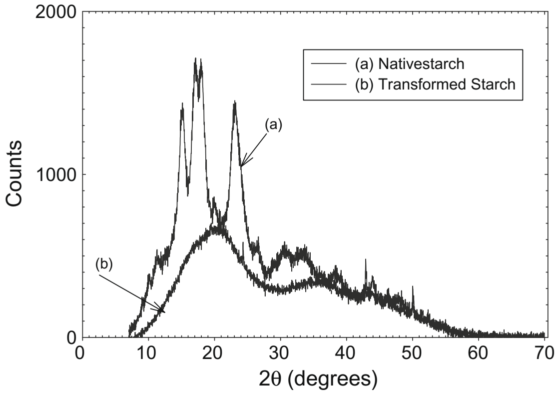


Fig. 1. X-ray diffraction patterns for native cassava starch ($m = 16.8\%$ db) and for amorphous cassava starch equilibrated at ambient conditions. Cu Kα Radiation (Ni-filtered).

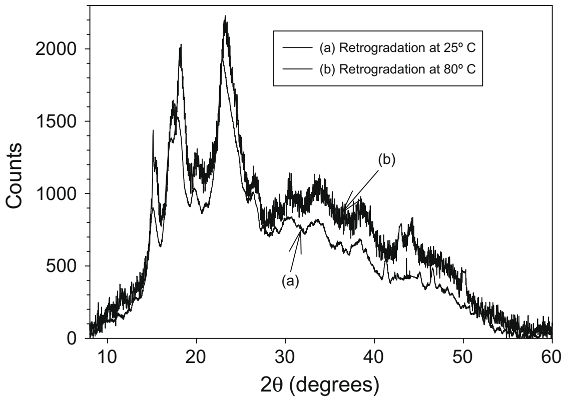


Fig. 2. WAXS patterns showing the retrogradation of transformed cassava starch after equilibration at 25 °C and 80 °C, over saturated K_2SO_4 solution for 3 weeks. Cu Kα Radiation (Ni-filtered).

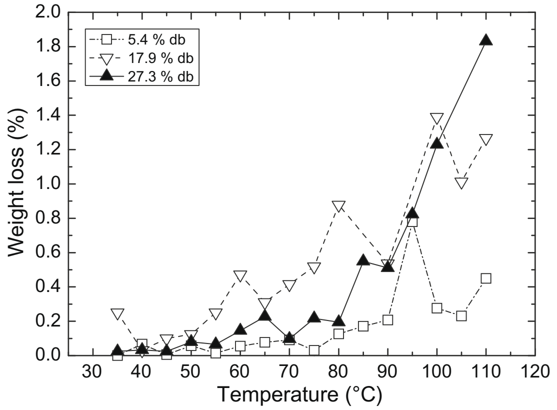


Fig. 3. Weight loss during DMTA experimentation for cassava starch with different initial moisture contents.

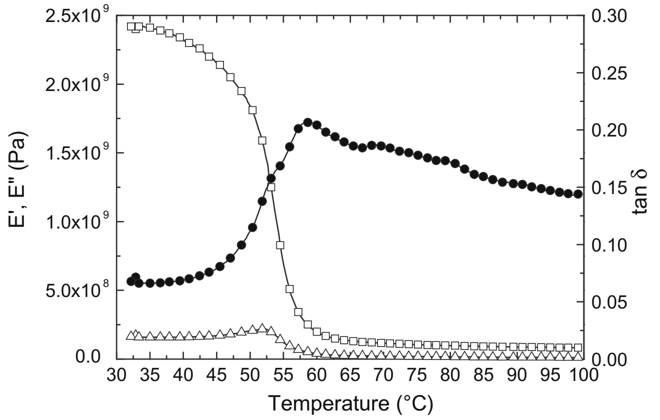


Fig. 4. Typical DMTA curves (□ E', Δ E'' and ● tan δ) as a function of temperature for amorphous cassava starch with moisture content of 18.4 g/100 g of dry solids.

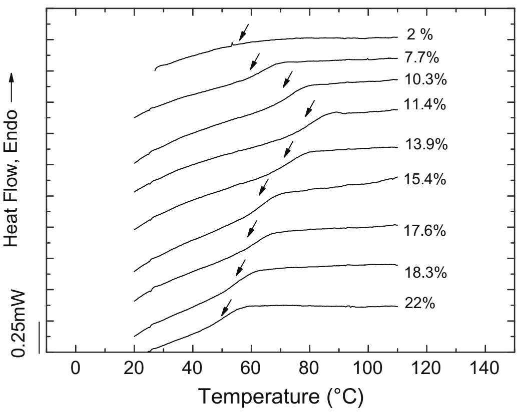


Fig. 5. Typical DSC curves, as a function of temperature for amorphous cassava starch with different moisture contents.

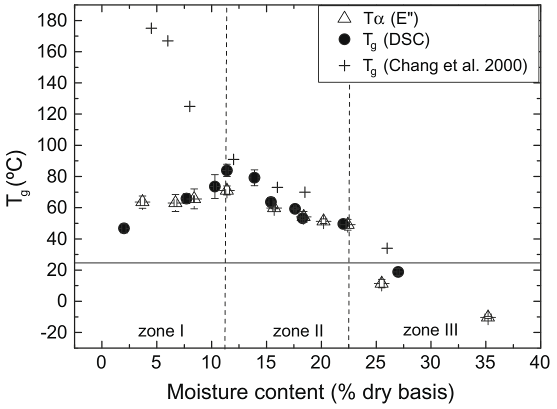


Fig. 6. Glass transition temperature of cassava starch, as function of moisture content, measured by DSC and DMTA experiments, and data presented by Chang et al. (2000) for tapioca starch. The horizontal solid line represents the conditioning temperature of the amorphous cassava starch bars.

content (11–23%) where water acts as plasticizer and the experimental data exhibits an exponential decay curve, whose tendency seems to stabilize towards a T_g of around 50 °C; and zone III or the zone of high moisture content (>23%) where a larger plasticizing effect of water on cassava starch was observed. The horizontal line in Fig. 6 indicates the sample conditioning temperature, illustrates the physical state of the samples; i.e., points above this line are for samples in the glassy state, while points below it correspond to samples in the rubbery state.

Although the plasticizing effect of water on starchy products, as found in this work for moisture contents greater than around 13%

(d.b.) and represented by zone II and zone III in Fig. 6, is fairly well established in the literature (e.g., Bizot et al., 1997; Brent, Mulvaney, Cohen, & Bartsch, 1997; Cuq & Icard-Verniėre, 2001; Sandoval, Nuñez, Müller, Della Valle, & Lourdin, 2008), the water anti-plasticizing effect (zone I in Fig. 6), has been only reported to occur on their mechanical properties. It has been established that at low moisture contents, small amounts of sorbed water by a water compatible glassy polymers can increase the structural order, compactness, rigidity and brittleness of polymeric systems, acting therefore as anti-plasticizer (Pittia & Sacchetti, 2008). This mechanical anti-plasticization has been reported on starchy products subjected to extrusion conditions such as extruded corn meal (Halek, Paik, & Chang, 1989), extruded flat bread (Fontanet, Davidou, Dacremont, & Le Meste, 1997; Marzec & Lewicki, 2006), breakfast cereals (Gondek & Lewicki, 2006) and on cassava starch (Chang et al., 2000). No anti-plasticizing effect of water on food systems, reflected on glass transition temperatures determined either by DSC or DMTA, has been reported in the literature, as far as the authors are aware. On the contrary, it has been suggested that the first and earlier sorbed water molecules might cause mechanical anti-plasticization in glassy food polymers independently of their kinetic effects in lowering the T_g of the neat polymer (Slade & Levine, 1995). However, in our case, as presented in Fig. 6, the shift in T_g values to higher temperatures at low moisture contents (or anti-plasticization effect) has been clearly and reproducibly observed by both DSC and DMTA experiments.

In Fig. 6 it is also worth noting the behavior of the region III, where a more pronounced plasticizing effect of water at higher moisture content (above 23%) can be seen. As shown in this figure, the data reported by Chang et al. (2000) also exhibited a slope change in the curve of the plasticizing effect of water on tapioca starch for moisture contents greater than about 18%. This change in the plasticizing effect of water at higher moisture content deserves an explanation since it should be expected that a maximum plasticization at high moisture content is reached at slow varying T_g. This opposedly observed behavior could be related to the fact that the samples conditioned at 25 °C corresponding to zone III are in rubbery state as compared to those in zone II which were in glassy condition. Additionally, the sample with the highest moisture content (equilibrated at 25 °C in a 97.3% humidity ambient) showed the existence of crystalline regions (it had retrograded) as previously mentioned. Under such conditions chain ordering in amorphous starch is plausible as the system was in the rubbery state, as indicated by the horizontal line on Fig. 6.

During this retrogradation phenomenon a large amount of water would be squeezed out of the crystals (since the crystals contain only 4 water molecules per unit cell), increasing the amount of water into the amorphous rubbery domain. Hence, an increase in the plasticizing effect of the amorphous region of cassava starch will lead to a faster decrease in T_g with moisture content, as observed in zone III of Fig. 6. As indicated before from the X-ray diffraction patterns, samples confined to zone II (which were in the glassy state) did not exhibit retrogradation. Contrary to the expected behavior, i.e., the glass transition temperatures are generally expected to be higher as crystallinity increases due to the reduced motion of the amorphous phase when co-existing with a crystalline phase (Farhat, Mousia, & Mitchell, 2001; Kalichevsky, Jaroszkiewicz, Ablett, Blanshard, & Lillford, 1992a; Zeleznak & Hoseney, 1987), in this work a higher water-plasticizing effect was obtained as the tendency to retrogradate occurred in the samples with high moisture contents. An increase in crystallinity, above 20 and 30%, has been found to decrease glass transition temperatures of polymeric systems such as poly ethylene terephthalate (PET) and poly ether ether ketone (PEEK), respectively (Jonas & Legras, 1993; Murayama, 1987). Meanwhile, Laredo, Grimau, Müller, Bello, and Suarez (1996) reported the same degree of crystallinity/T_g relationship for bisphenol-A polycarbonate within a crystallinity range of 0–20%.

Fig. 6 shows that the experimental glass transition temperatures obtained from DSC experiments in cassava starch within the plasticizing regions agree well with those presented by Chang et al. (2000) for tapioca starch. Although no anti-plasticizing effect evidenced by calorimetric measurements was reported by these authors, which may be attributed to the botanical origin of these two cassava starches.

3.3. Sorption isotherms

Sorption isotherms experimentally obtained for cassava starch at temperatures of 5, 30 and 45 °C are presented in Fig. 7. The equilibrium moisture content at each water activity shows the mean value of 3 identical experiments. Each isotherm shown in Fig. 7 indicates that the equilibrium moisture content increases with increasing water activity. The sigmoidal shape found is typically reported as a Type II isotherm (Al-Muhtaseb et al., 2002), according to Brunauer's classification (Brunauer, Deming, Deming, & Troller, 1940). This is in agreement with some other researchers, who found this behavior in cassava starch (Chang et al., 2000; Chatakanonda et al., 2003; Mishra & Rai, 2006; Sanni, Atere, & Ayoade, 1997), and for other starchy materials, such as: potato starch (Al-Muhtaseb et al., 2004a; Boki & Ohno, 1991; Chatakanonda et al., 2003; Mishra & Rai, 2006), corn starch (Boki & Ohno, 1991; Palou, López-Malo, & Argaiz, 1997; Mishra & Rai, 2006), wheat and rice starches (Boki & Ohno, 1991).

Fig. 7 also shows the effect of temperature on the moisture sorption characteristics of cassava starch. It can be seen from this figure that for water activity values lower than around 0.85, as expected in an exothermic moisture sorption process, the equilibrium moisture content decreases with increasing temperature (at constant water activity), indicating that the starch become less hygroscopic. However, for a_w values higher than 0.85 an isotherm cross-over with temperature is observed, i.e., the equilibrium moisture content increased with temperature for a given a_w value.

Isotherm cross-over behavior with temperature has been widely observed in high-carbohydrate foods such as banana, sugar beet root, sultana raisins, barley malt, and soy protein–sugar system, among others (Wolf, Spiess, & Jung, 1973; Iglesias, Chirife, & Lombardi, 1975; Saravacos, Tsiourvas, & Tsami, 1986; Barreiro, Fernández, & Sandoval, 2003; Cassini et al., 2006). All of these

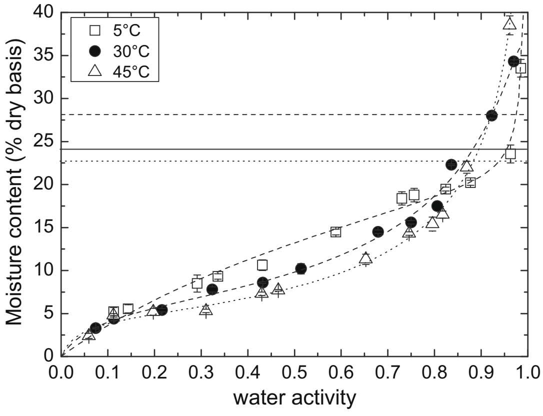


Fig. 7. Sorption isotherms of cassava starch for a temperature range between 5 and 45 °C (□ 5 °C, ● 30 °C, Δ 45 °C). Modified GAB fits are represented on the graph (dash sigmoid line 5 °C, solid sigmoid line 30 °C, dotted sigmoid line 45 °C). The horizontal lines represent the moisture content at which the T_g value of, 5 °C (dashed line), 30 °C (solid line), and 45 °C (dotted line) are attained.

authors reported this behavior and attributed it to the endothermic dissolution of sugars at elevated water activity. Nevertheless, the material considered here is neat starch, for which the isotherm inversion with temperature at high water activity (or moisture content), could be more related to a greater exposure of active sites or hydrophilic groups at high a_w or water contents as the temperature increases, as indicated by Brett and Figueroa (2005). These authors presented evidence that relates the isotherm cross-over of oat flour and rice flour with temperature, to the onset of glassy to rubbery state transition taking place for the highest temperature sorption curve at high moisture contents or a_w's.

The results presented in this work previously shown that cassava starch samples stored at room temperature tended to crystallize when conditioned at high relative humidity. On the other hand, at 45 °C (the highest temperature tested in this work), it was clearly shown that samples stored at the two higher relative humidities (87% and 96.1%), i.e., the two last points in the 45 °C isotherm of Fig. 7, did show crystallinity development upon conditioning at that temperature. Hence, it can be suggested that as water is being squeezed out of the crystals due to the crystallization process, the amount of water adsorbed into the rubbery amorphous starch matrix will be greater, which in turn, due to its plasticizing effect will increase molecular mobility. Consequently, an increase of the available hydroxyl groups for sorption enhancement will be promoted. The deviation in the sorption capacity of starches as possibly linked to the onset of the glass transition range has also been previously suggested in the literature (Van den Berg, 1981; Al-Muhtaseb et al., 2004a; Brett & Figueroa, 2005). The horizontal lines in Fig. 7 indicate the moisture contents at which the glass transition temperatures were those corresponding to the isotherm determinations (read from Fig. 6): i.e., 23% (45 °C, dot line), 24% (30 °C, solid line) and 28% (5 °C, dash line). The experimental sorption data at the temperatures experimented, above each corresponding line are in the rubbery state which would explain the unexpected increase of moisture contents in samples kept at 30, and 45 °C and the last point of the 5 °C isotherm.

Sorption data for cassava starch available in the literature have been in most cases presented at one temperature, normally around ambient temperature (Chang et al., 2000; Chatakanonda et al., 2003; Mali et al., 2005; Mishra & Rai, 2006). In other cases temperature ranges different from those experimented here have also been presented. Aviara and Ajibola (2002) presented desorption equilibrium moisture content data, obtained from a temperature range of 30 to 60 °C over water activity range of 0.07 to 0.88, and their results did not evidence isotherm cross-over with temperature, probably due to the unexperimented high relative humidity atmosphere. Nevertheless, the sorption characteristics of cassava starch determined in a temperature range of 25–45 °C in a wide range of water activity (0.1–0.96) did not evidence isotherm cross-over (Sanni et al., 1997). Nonetheless, results presented in this work for amorphous cassava starch are in line with the cross-over/T_g relationship reported by Brett and Figueroa (2005).

Moisture sorption isotherm for the cassava starch obtained at the three temperatures considered in this work (5 °C, 30 °C, 45 °C), were fitted to seven models most frequently used to fit starchy sorption behavior (Table 1), and the results are shown in Table 2. Evaluation of the quality of model fittings was carried out through the determination of the mean relative percentage error (% E), and the (R^2) measurements and the corresponding values are also shown in Table 2. This table shows that, except from the BET and Henderson models fitted at 45 °C, all the models described well the experimental sorption behavior of cassava starch in the range of temperatures considered, as indicated by R^2 values greater than 0.90 and mean relative errors lower than 10%. On the other hand, Table 2 also shows that GAB and modified GAB models better described the sorption behavior of cassava starch in the whole range considered in this work. This result is in agreement with the literature, as the GAB model has been widely recognized for predicting the sorption behavior of foodstuffs, particularly on different starches such as: cassava (Chatakanonda et al., 2003; Mishra & Rai, 2006), potato (Al-Muhtaseb et al., 2004a; Chatakanonda et al., 2003; Mishra & Rai, 2006) and corn (Mishra & Rai, 2006).

The monolayer water content, as determined by the BET and GAB models at temperatures of 5, 30 and 45 °C are also presented in Table 2. Irrespective of the equation used in their calculation, the monolayer water content decreased as the temperature increased, as expected (Table 2). This fact has been attributed in the literature to a reduction of the active sites in the food matrix due to chemical and physical changes (e.g., reduction in hydrogen bonding degree), taking place as the temperature increases, the extension of which will depend on food nature (Al-Muhtaseb et al., 2004a; Aviara & Ajibola, 2002). The water content associated to the monolayer of cassava starch analyzed in the 5–45 °C range, varied from 0.071 to 0.043 g water/g dry solids, when the BET model was considered and from 0.127 to 0.045 g water/g dry solids from the GAB model. Similar values have been reported by Chatakanonda et al. (2003) for native cassava starch at 25 °C (0.074 using BET model and 0.079 by the GAB model), and by Mishra and Rai (2006), who reported a GAB calculated monolayer water content of 0.0954 g of water/g dry solids at 20 °C. Likewise, Table 2 shows that moisture contents associated to the monolayer calculated using BET equation were lower than those calculated using GAB equation for the whole temperature range considered, which is in agreement with results observed by several authors and summarized by Rahman (1995) and Timmermann, Chirife, and Iglesias (2001). These differences have been attributed to the fact that BET model focuses on surface adsorption in the first layer, while the GAB model takes into account sorbed water properties in the multilayer region (Bell & Labuza, 2000).The net isosteric heat of sorption and the isosteric heat of sorption were determined from Eqs. (9) and (10). Variations of the isosteric heat of sorption with moisture contents (MC), for a range between 0.075 and 0.175 g/g dry solids, was determined in this work and it can be expressed as:

$$Q_{st} = 67.87e^{-2.26MC}(R^2 = 0.990) \qquad (12)$$

The isotherm crossing-over already mentioned precluded from taking higher values of moisture content in the net isosteric heat calculation. The isosteric heat of sorption was found to decrease with increasing moisture content, as expected. It has been established that during the initial stages of the sorption process at low moisture content, there are more active sites on the food surface covered by a monolayer of water, with a higher energy of binding than those existing at higher moisture content (multilayer water) (Al-Muhtaseb, McMinn, & Magee, 2004b; Iglesias & Chirife, 1976). The decreasing behavior of the isosteric heat of sorption with increasing moisture content has been also observed in other starchy products such as: cookies and corn snacks (Palou et al., 1997), starch powder (Al-Muhtaseb et al., 2004a), corn (Samapundo et al., 2007), and starchy flours (Brett & Figueroa, 2005).

4. Conclusions

Measurements of glass transition temperatures determined by DSC and DMTA in a wide range of moisture content (2–35%, dry basis), and determination of sorption characteristics of cassava starch in a temperature range of 5–45 °C were carried out in this work. Very good correspondence was obtained between calorimetric (DSC) and mechanical (DMTA) measurement of the glass transition. Three different effects of water as plasticizing agent were observed on cassava starch. For moisture contents lower than around

Table 2
Fitting parameters for the mathematical expressions applied to sorption data of amorphous cassava starch at different temperatures.

Model	Constants	Gelatinized cassava starch		
		5 °C	30 °C	45 °C
BET	m_o	0.071	0.059	0.043
	C	13.78	12.86	32.46
	R^2	0.994	0.962	0.680
	E (%)	1.84	5.03	16.4
Smith	A	0.076	0.034	0.017
	B	−0.158	−0.219	−0.212
	R^2	0.910	0.980	0.981
	E (%)	7.47	4.73	3.87
Henderson	A	27.73	32.90	37.08
	B	1.783	1.711	1.658
	R^2	0.996	0.991	0.962
	E (%)	2.66	6.14	12.2
Halsey	A	0.016	0.011	0.011
	B	1.737	1.745	1.646
	R^2	0.984	0.974	0.981
	E (%)	2.66	8.7	8.79
Oswin	A	0.119	0.100	0.086
	B	0.321	0.446	0.468
	R^2	0.952	0.983	0.984
	E (%)	8.78	5.10	7.82
GAB	m_o	0.127	0.060	0.045
	C	7.570	19.93	33.07
	K	0.538	0.862	0.908
	R^2	0.992	0.983	0.990
	E (%)	4.95	5.04	8.04
Modified GAB	A	0.254	0.061	0.046
	B	8.250	15.823	30.452
	C	0.192	0.854	0.889
	D	0.004	0.000	0.000
	R^2	0.988	0.994	0.996
	E (%)	1.48	0.26	1.09

11% water anti-plasticized cassava starch, while a plasticizing effect was obtained for higher moisture contents in two different fashions; i.e., from 11 to 23%, an exponential decrease of T_g with moisture content was obtained, and an unexpected rapid decrease of T_g with moisture content was obtained at values greater than 23%. This greater plasticizing effect of water at high moisture content was attributed to cassava starch retrogradation, which was confirmed by X-ray diffraction, and resulted in more water coming into the amorphous matrix, as it was expelled from the crystalline regions within the sample. A sigmoidal shape, characteristic of Type II isotherms, was found for cassava starch in a temperature range of 5–45 °C. The inversion (or cross-over) points exhibited at a water activity of around 0.85, was explained by the result of more active sites exposed in virtue of the enhanced molecular mobility due to the water being squeezed out of the crystals upon crystallization. The experimental sorption data were fitted to several models, however, GAB and modified GAB models were the more appropriate according to their E and R^2 values. The monolayer water content, whether determined by BET or GAB models, were found to be inversely related to temperature and their values ranging from 0.071 to 0.045 g/g (dry basis). The net isosteric heat of sorption was found to decrease with increasing moisture content, as expected. An exponential relationship was found to describe this variation, within the moisture content range considered in this work.

Acknowledgements

The authors acknowledge the financial support for this work from the National Fund for Science and Technology *FONACIT* in Venezuela through Grant G-2005000776.

References

Al-Muhtaseb, A., McMinn, W., & Magee, T. (2002). Moisture sorption isotherm characteristics of food products: A review. *Transactions of the Institution of Chemical Engineers Part C, 80*, 118–127.

Al-Muhtaseb, A. H., McMinn, W., & Magee, T. (2004a). Water sorption isotherm of starch powders Part 1: Mathematical description of experimental data. *Journal of Food Engineering, 61*(3), 297–307.

Al-Muhtaseb, A. H., McMinn, W., & Magee, T. (2004b). Water sorption isotherm of starch powders Part 2: Thermodynamic characteristics. *Journal of Food Engineering, 62*(2), 135–142.

AOAC (1990). *Official methods of analysis*. Arlington: Association of Official Analytical Chemists.

Aviara, N. A., & Ajibola, O. O. (2002). Thermodynamics of moisture sorption in melon seed and cassava. *Journal of Food Engineering, 55*(2), 107–113.

Barreiro, J. A., Fernández, S., & Sandoval, A. J. (2003). Water sorption characteristics of six row barley malt (*Hordeum vulgare*). *Lebensmittel-Wissenschaft und-Technologie, 36*, 37–42.

Bell, L., & Labuza, T. (2000). *Moisture sorption. Practical aspects of isotherm measurements and use*. USA: American Association of Cereal Chemists, Inc..

Bell, L., & Touma, D. (1996). Glass transition temperatures determined using a temperature-cycling differential scanning calorimeter. *Journal of Food Science, 61*(4), 807–810.

Bertuzzi, M. A., Armada, M., & Gottifredi, J. C. (2003). Thermodynamics analysis of water vapour sorption of edible starch based films. *Food Science Technology Institute, 9*(2), 115–117.

Bizot, H., Le Bail, P., Leroux, B., Davy, J., Roger, P., & Buléon, A. (1997). Calorimetric evaluation of the glass transition in hydrated, linear and branched polyanhydroglucose compounds. *Carbohydrate Polymers, 32*(1), 33–50.

Brent, J. L., Mulvaney, S. J., Cohen, C., & Bartsch, J. A. (1997). Thermomechanical glass transition of extruded cereal melts. *Journal of Cereal Science, 26*(3), 301–312.

Brett, B., & Figueroa, M. (2005). *Moisture sorption characteristics of starchy products. Oat flour and rice flour*. B.Sc. thesis, Simón Bolívar University, Venezuela (in Spanish).

Boki, K., & Ohno, S. (1991). Equilibrium isotherm equations to represent moisture sorption on starch. *Journal of Food Science, 56*, 1106–1110.

Brunauer, S., Deming, L. S., Deming, W. E., & Troller, E. (1940). On the theory of Van der Waals adsorption of gases. *Journal of the American Chemical Society, 62*, 1723–1732.

Cassini, A. S., Marczak, L. D. F., & Noreña, C. P. Z. (2006). Water adsorption isotherms of texturized soy protein. *Journal of Food Engineering, 77*, 194–199.

Chang, Y. P., Cheah, P. B., & Seow, C. C. (2000). Plasticizing effects of water on physical properties of tapioca starch films in the glassy state. *Journal of Food Science, 65*, 445–451.

Chatakanonda, C., Dickinson, L., & Chinacohoti, P. (2003). Mobility and distribution of water in cassava and potato starches by H and H NMR. *Journal of Agricultural and Food Chemistry, 51*, 7445–7449.

Chung, H. J., & Lim, S. T. (2004). Physical aging of glassy normal and waxy rice starches: Thermal and mechanical characterization. *Carbohydrate Polymers, 57*(1), 15–21.

Cocero, A. M., & Kokini, J. L. (1991). The study of the glass transition of glutenin using small amplitude oscillatory rheological measurements and differential scanning calorimetry. *Journal of Rheology, 35*(2), 257–270.

Cuq, B., & Icard-Vernière, C. (2001). Characterisation of glass transition of durum wheat semolina using modulated differential scanning calorimetry. *Journal of Cereal Science, 33*(2), 213–221.

Farhat, I. A., Mousia, Z., & Mitchell, J. R. (2001). Water redistribution during the recrystallisation of amylopectin in amylopectin/gelatin blends. *Polymers, 42*(10), 4763–4766.

Fontanet, S., Davidou, S., Dacremont, C., & Le Meste, M. (1997). Effect of water on mechanical behaviour of extruded flat bread. *Journal of Cereal Science, 25*(3), 303–311.

Gondek, E., & Lewicki, P. P. (2006). Antiplasticization of cereal-based products by water Part II: Breakfast cereals. *Journal of Food Engineering, 77*, 644–652.

Greenspan, L. (1977). Humidity fixed points of binary saturated aqueous solution. *Journal of Research of the National Bureau of Standards-A. Physics and Chemistry, 81A*(1), 89–96.

Halek, G. W., Paik, S. W., & Chang, K. L. B. (1989). The effect of moisture content on mechanical properties and texture profile parameters of corn meal extrudates. *Journal of Texture Studies, 20*, 43–55.

Haque, M., & Roos, Y. (2004). Water sorption and plasticization behavior of spray-dried lactose/protein mixtures. *Food Engineering and Physical Properties, 69*(8), 384–391.

Hoover, R. (2001). Composition, molecular structure, and physicochemical properties of tuber and root starches: A review. *Carbohydrate Polymers, 45*, 253–267.

Iglesias, H., Chirife, J., & Lombardi, J. (1975). Water sorption isotherms in sugar beet root. *Journal of Food Technology, 10*(3), 299–308.

Iglesias, H. A., & Chirife, J. (1976). Isosteric heat of water vapour sorption on dehydrated foods Part I: Analysis of the differential heat curves. *Lebensmittel-Wissenschaft und-Technologie, 9*, 116–122.

Imberty, A., Chanzy, H., Pérez, S., Buléon, A., & Tran, V. (1988). The double-helical nature of the crystalline part of A-starch. *Journal of Molecular Biology, 201*(2), 365–378.

Jonas, A., & Legras, R. (1993). Relation between PEEK semicrystalline morphology and its subglass relaxation and glass transition. *Macromolecules, 26*, 813–824.

Kalichevsky, M. T., Jaroszkiewicz, E. M., Ablett, S., Blanshard, J. M. V., & Lillford, P. J. (1992a). The glass transition of amylopectin measured by DSC, DMTA and NMR. *Carbohydrate Polymers, 18*, 77–88.

Kalichevsky, M. T., Jaroszkiewicz, E. M., & Blanshard, J. M. (1992b). Glass transition of gluten. 1: Gluten and gluten–sugar mixtures. *International Journal of Biological Macromolecules, 14*(5), 257–266.

Kalichevsky, M. T., & Blanshard, J. M. (1993). The effect of fructose and water on the glass transition of amylopectin. *Carbohydrate Polymers, 20*(2), 107–113.

Kalichevsky, M. T., Blanshard, J. M., & Tokarczuk, P. F. (1993). Effect of water content and sugars on the glass transition of casein and sodium caseinate. *International Journal of Science and Technology, 28*(2), 139–151.

Laredo, E., Grimau, M., Müller, A., Bello, A., & Suarez, N. (1996). Influence of aging and cristallinity on the molecular motions in Bisphenol-A polycarbonate. *Journal of Polymer Science, 34*, 2863–2879.

Lineback, D. R. (1986). Current concepts on starch structure and its impact on properties. *Journal of the Japanese Society of Starch Science, 33*, 80–88.

Lomauro, C. J., Bakshi, A. S., & Labuza, T. P. (1985). Evaluation of food moisture sorption isotherms equations Part I. Fruit, vegetable and meat products. *Lebensmittel-Wissenschaft und-Technologie, 18*, 111–117.

Mali, S., Sakanaka, L. S., Yamashita, F., & Grossmann, M. V. E. (2005). Water sorption and mechanical properties of cassava starch films and their relation to plasticizing effect. *Carbohydrate Polymers, 60*, 283–289.

Marzec, A., & Lewicki, P. P. (2006). Antiplasticization of cereal-based products by water Part I: Extruded flat bread. *Journal of Food Engineering, 73*, 1–8.

McMinn, W. A., & Magee, T. R. (1999). Studies on the effect of temperature on the moisture sorption characteristics of potatoes. *Journal of Food Process Engineering, 22*, 113–128.

Mishra, S., & Rai, T. (2006). Morphology and functional properties of corn, potato and tapioca starches. *Food Hydrocolloids, 20*, 557–566.

Murayama, T. (1987). Dynamic mechanical properties. In H. Mark, N. Bikales, C. Overberger, & J. Menges (Eds.). *Encyclopedia of Polymer Science & Engineering* (Vol. 5, pp. 690–723). New York: John Wiley & Sons, Inc.

Nowakowski, C. M., & Hartel, R. W. (2002). Moisture sorption of amorphous sugar products. *Journal of Food Science, 67*, 1419–1429.

Palou, E., López-Malo, A., & Argaiz, A. (1997). Effect of temperature on the moisture sorption isotherms of some cookies and corn snack. *Journal of Food Engineering, 31*, 85–93.

Pereira, P., & Oliveira, J. (2000). Measurement of glass transition in native wheat flour by dynamic mechanical thermal analysis (DMTA). *International Journal of Food Science and Technology, 35*, 183–192.

Pittia, P., & Sacchetti, G. (2008). Antiplasticization effect of water in amorphous foods. A review. *Food Chemistry, 106*, 1417–1427.

Rahman, S. (1995). Water activity and sorption properties of foods. In *Food properties handbook* (pp. 1–86). USA: CRC Press Inc.

Rickard, J., Asaoka, M., & Blanshard, J. (1991). The physicochemical properties of cassava starch. *Tropical Science, 31*, 189–207.

Roos, Y. H., & Karel, M. (1992). Crystallization of amorphous lactose. *Journal of Food Science, 57*, 775–777.

Sahin, S. Y., & Sumnu, S. G. (2006). Water activity and sorption properties of food. In *Physical properties of food* (pp. 193–228). USA: Springer.

Samapundo, S., Devlieghere, F., De Meulenaer, B., Atukwase, A., Lamboni, Y., & Debevere, J. M. (2007). Sorption isotherms and isosteric heats of sorption of whole yellow dent corn. *Journal of Food Engineering, 79*, 168–175.

Sandoval, A. J., Nuñez, M., Müller, A. J, Della Valle, G., Lourdin, D. (2008). Glass transition temperatures of a starchy ready to eat breakfast cereal formulation and its main components determined by DSC and DMTA. Carbohydrate Polymers, in press, doi:10.1016/j.carbpol.2008.11.019.

Sanni, L., Atere, C., & Ayoade, K. (1997). Moisture sorption isotherms of fufu and tapioca at different temperatures. *Journal of Food Engineering, 34*, 203–212.

Saravacos, G. D., Tsiourvas, D. A., & Tsami, E. (1986). Effect of temperature on the water adsorption isotherm of sultana raisins. *Journal of Food Science, 52*(2), 381–383. 387.

Slade, L., & Levine, H. (1988). Structural stability of intermediate moisture foods. A new understanding. In J. M. V. Blanshard & J. R. Mitchell (Eds.), *Food Structure: Its creation and evaluation* (pp. 115–147). London: Butterworths.

Slade, L., & Levine, H. (1995). Glass transitions and water–food structure interactions. *Advances in Food and Nutrition Research, 38*, 103–269.

Timmermann, E. O., Chirife, J., & Iglesias, H. A. (2001). Water sorption isotherms of foods and foodstuffs: BET or GAB parameters? *Journal of Food Engineering, 48*, 19–31.

Tonukari, N. (2004). Cassava and the future of starch. *Electronic Journal of Biotechnology, 7*(1), 5–8.

Van den Berg, C. (1981). *Vapour sorption equilibria and other water–starch interactions: Physico–chemical approach*. Ph.D. Thesis, Agricultural University Wageningen, The Netherlands. In Al-Muhtaseb et al. (2004a).

Viollaz, P. E., & Rovedo, C. O. (1999). Equilibrium sorption isotherms and thermodynamic properties of starch and gluten. *Journal of Food Engineering, 40*(4), 287–292.

Wolf, W., Spiess, W.E. & Jung, G. (1973). Die Wasserdampfsorptionsisothermen einiger in der Literatur bislangwening berücksichtigter lebensmittel. *Lebensmittel-Wissenschaft und Technologie*, 6, 94. In Iglesias, H., & Chirife, J. *Handbook of food isotherms: Water sorption parameters for food and food components*. London. UK: Academic Press, Inc., 1982, p. 27.

Zeleznak, K. J., & Hoseney, R. C. (1987). The glass transition in starch. *Cereal Chemistry, 64*, 121–124.