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The effect of hydrophobic modifications on the adsorption isotherms of cassava starch

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ABSTRACT

Moisture sorption isotherms of native and ten hydrophobically modified cassava starches were determined at 25 °C using a moisture sorption analyzer in an a_w range of 0–0.94. Modified cassava derivates were obtained by modifying native cassava starch (CS) with octenyl succinic anhydride (OSA) and by modifying a carboxymethylated cassava starch (CMCS) with quaternary ammonium salts having different alkyl chain lengths (C_nTAB with $n = 12$, 14, 16, and 18). In comparison to native cassava starch, the results obtained showed that OSA modification yielded a more hydrophobic material for the whole a_w range, while the ionic complexes obtained from CMCS and quaternary ammonium salts produced more hydrophobic starches at low a_w values and more hydrophilic ones at high a_w values. It was found that the experimental data were well represented by the GAB model and that the monolayer water contents decreased with chemical modification. The moisture sorption kinetic parameters showed that water adsorption process became slower in chemically modified starches.

1. Introduction

The hydrophilic nature of native starch limits the development of starch-based products since highly water-sensitive products are obtained, with properties changing when varying ambient relative humidity. Hence, a great amount of research work has been carried out to chemically modify starches in order to obtain less hydrophilic materials. One of the paths that have been tried with both native and carboxymethylated starch is the chemical incorporation of hydrophobic groups such as alkyl ethers or alkyl esters (Biswas et al., 2008; Rivero, Balsamo, & Müller, 2009), polymer chains grafting onto starch (Kaewtatip & Tanrattanakul, 2008), or complex formation with surfactants (quaternary ammonium salts) (Naves & Petri, 2005; Tiitu, Laine, Serimaa, & Ikkala, 2006). Modified starches can be used in different food applications, where native starches are unable to confer desired functional characteristics in the final product; they can also act, when added to polymer blends, as compatibilizers (Chen et al., 2005; Wang, Sun, & Seib, 2001; Zhang & Sun, 2004).

Carboxymethyl starch (CMS) is a starch derivative with high commercial value (Bhattacharyya, Singhal, & Kulkarni, 1995). Its unique properties are given by the presence of negatively charged groups (CH_2COO^-), which impart greater water solubility in the final product and make it suitable for practical applications, such as drilling muds, detergents, food stuffs, tooth pastes, as well as pharmaceuticals (Heinze & Koschella, 2005). As CMS is an anionic polyelectrolyte, it can form complexes with cationic surfactants such as quaternary ammonium salts to obtain interesting CMS/C_nTAB complexes with alkyl chains of different lengths, which impart a hydrophobic character reducing water solubility, an important aspect in the paper processing industry.

Starch modification with OSA was patented by Caldwell and Wurzburg (1953). Incorporation of the hydrophobic group from the alkyl chain within the hydrophilic starch molecule allows the establishment of a strong interaction at the water/oil interface (Trubiano, 1986). As a result, an aqueous solution of modified starch with alkenyl succinates may be employed to stabilize food flavor concentrates, oils in salad dressings, and to encapsulate fragrances and vitamins (Shogren, Viswanathan, Felker, & Gross, 2000; Trubiano, 1986). On the other hand, interest in studying the incorporation of OSA-modified starch in food applications, due to its emulsifying properties, has extensively increased since the US FDA (Federal Drugs Administration) allowed the use of up to 3 wt.% of octenyl succinic anhydride (with respect to starch weight) in chemical reactions (Bhosale & Singhal, 2006).

One way of evaluating the increasing starch hydrophobicity obtained by means of chemical modification is the determination of sorption moisture isotherms. The sorption behavior of chemi-

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cally modified cassava starch with octenyl succinic anhydride or with quaternary ammonium salts having alkyl chains of different lengths has not been addressed before in the literature, as far as the authors are aware. The gravimetric method, one of the most frequently employed methods for sorption characteristic determination, can be carried out statically by means of equilibration under constant relative humidity atmospheres, or dynamically by using controlled atmosphere microbalances. This second technique, a relatively novel one to the food industry, allows adsorption and/or desorption behavior of a sample to be followed by monitoring mass changes while the sample is subjected to various relative humidity atmospheres. This is achieved by the continuous circulation of relative humidity controlled gas over the sample (Bell & Labuza, 2000). One of the advantages of this technique is that it is relatively fast as compared to the static one reducing the experimentation time from weeks to days, as well as the amount of sample needed for completing the isotherm. It also enables the sorption kinetic parameters to be obtained through the software package.

A vast amount of water sorption isotherm models have been proposed in the literature for different products. They include those theoretically derived based on thermodynamic considerations such as the BET (Brunauer, Emmett, & Teller, 1938) and GAB (Van den Berg & Bruin, 1981) models, and semi-empirical and empirical models (e.g. Peleg, 1993; Viollaz & Rovedo, 1999). The GAB equation has been recognized as the most versatile sorption model. When using this model, the monolayer water content represents valuable additional information that can be obtained from sorption isotherm data; it gives information about the minimal water content conferring product stability, including sample caking (Mulet, García-Reverter, Sanjuán, & Bon, 1999).

Starch and starch-based product stability depend on composition, chemical structure, and storage conditions; i.e., temperature and ambient relative humidity (Bertuzzi, Armada, & Gottifredi, 2003; Haque & Roos, 2004). Relationship among these variables will have major effects on physical, chemical, and microbiological characteristics of the product, as well as on the potential practical applications. Therefore, the knowledge of sorption isotherms of these materials is of great importance. Hence, the aim of this work is to determine the moisture sorption isotherms of hydrophobically modified cassava starches using the dynamic technique, as well as to obtain parameters for the evaluation of the moisture sorption kinetic process. The mathematical description of the sorption isotherms of these starches and monolayer water content determination was also addressed in this work.

2. Materials and methods

2.1. Materials

Cassava starch (AIM TF 113) purchased from Agroindustriales Mandioca C.A., Venezuela, was used in this work. Moisture content determined for native starch as received was 16.8 (expressed in g/100 g of dry solids), according to Perdomo et al. (2009). Native cassava starch (CS), and two types of hydrophobically modified cassava starches; i.e., octenyl succinic anhydride modified cassava starch (CS-OSA) and carboxymethyl modified cassava starch (CMCS) were used in this work.

The modification of cassava starch with octenyl succinic anhydride (OSA) was carried out using microwave radiation following the procedure reported elsewhere (Pérez, 2008; Rivero et al., 2009). The degree of substitution of CS-OSA, DS_{OSA}, was determined using a titration method after acidifying the samples by adding 5 ml of a 0.1 M ethanol HCl solution to a suspension of CS-OSA (1 g in 5 ml ethanol). Then, the product was filtered, washed with deionized water until the chlorides test was negative, and dried under vacuum. In a second step, a suspension of dried CS-OSA powder was prepared in 50 ml DMSO and heated at 70 °C for 10 min; a 0.5 M aqueous NaOH solution was added to the suspension and the excess of alkali was back-titrated with a 0.5 M aqueous HCl solution, using phenolphthalein as indicator. A blank suspension of native unmodified starch was also titrated. DS_{OSA} was determined from $\%OSA$ substitution as follows (Bhosale & Singhal, 2006):

$$\%OSA = \frac{(V_{\mathrm{blank}} - V_{\mathrm{sample}}) \times 0.1 \times c \times 100}{W} \tag{1}$$

where V_{blank} is the HCl volume required for blank titration (ml), V_{sample} the HCl volume for sample titration (ml), W the weight of sample employed (g), and c is the concentration (mol/L) of the HCl solution. Thus,

$$DS_{\mathrm{OSA}} = \frac{162 \times \%OSA}{21,000 - (209 \times \%OSA)} \tag{2}$$

where 162 is the molecular weight of the starch anhydroglucose unit (AGU) (g/mol), 209 the molecular weight of the octenyl succinic group (g/mol), and 21,000 is 100× molecular weight of the octenyl succinic group. All measurements were done in duplicate. Two products with different degrees of substitution were used in this work (CS-OSA1 with $DS = 0.024$ and CS-OSA2 with $DS = 0.031$).

The modification of previously carboxymethylated cassava starches (CMCS1 with $DS = 0.24$ and CMCS2 with $DS = 0.30$) with trimethylalkylammonium bromides having different alkyl chain lengths (C_nTAB with $n = 12$, 14, 16, and 18) was performed following the procedure reported elsewhere (Balsamo et al., 2010, submitted for publication; Contó, 2008) using a molar ratio anhydroglucose unit:C_nTAB of 1:0.75. A total of ten hydrophobic cassava starch types were analyzed. The degree of substitution of the CMCS precursors, DS_{CMCS}, was determined using a titration method (Stojanovic, Jeremic, Jovanovic, & Lechner, 2005) after all carboxylate groups were transformed into carboxyl groups by adding an excess of a 6 M HCl solution to an acetone dispersion of the reaction product. The product was filtered, washed with an aqueous methanol solution, and dried under vacuum. For the titration, 25 ml of a 0.04 M NaOH solution and 75 ml distilled water were added to approximately 0.13 g of CMCS. Then, excess of alkali was back-titrated with a 0.05 M HCl solution, using phenolphthalein as indicator. All measurements were done in duplicate. The DS was determined using Eq. (3):

$$DS_{\mathrm{CMCS}} = \frac{162 \times (V_{\mathrm{blank}} - V_{\mathrm{sample}})c}{W - \left[58 \times (V_{\mathrm{blank}} - V_{\mathrm{sample}})c\right]} \tag{3}$$

where 58 corresponds to the molecular weight of the grafted carboxylate moiety. The average degree of substitution of the complexes, DS_{complex}, was calculated from the nitrogen content obtained by means of the Kjeldhal method using Eq. (4) (Heinze, Haack, & Rensing, 2004):

$$DS_{\mathrm{complex}} = \frac{M_{\mathrm{AGU(X)}} \times \%N}{1401 - [(M_{\mathrm{S}} - 1) \times \%N]} \tag{4}$$

where DS_{complex} indicates the experimental amount of quaternary cations introduced per anhydroglucose unit (AGU), whose average molecular weight, $M_{\mathrm{AGU(X)}}$ was calculated as follows:

$$M_{\mathrm{AGU(X)}} = (58 \times DS_{\mathrm{CMS}}) + 162 \tag{5}$$

$\%N$ is the w/w nitrogen percentage obtained by means of the Kjeldhal method; M_{S} is the molecular weight of the substituent introduced in the AGU unit: $C_{12}TA^{+}$ (228 g/mol), $C_{14}TA^{+}$ (256 g/mol), $C_{16}TA^{+}$ (284 g/mol), and $C_{18}TA^{+}$ (312 g/mol); and 1401 is the nitrogen atomic mass multiplied by 100. The calculated degrees of substitution are listed in Table 1.

Table 1
Degree of substitution, DS_{complex}, calculated from nitrogen content (Contó, 2008).

Complex	N (wt.%)	DS
CMS1/C_{12}TAB	1.4	0.23
CMS2/C_{12}TAB	1.6	0.28
CMS1/C_{14}TAB	1.1	0.17
CMS2/C_{14}TAB	1.8	0.34
CMS1/C_{16}TAB	1.3	0.22
CMS2/C_{16}TAB	1.8	0.36
CMS1/C_{18}TAB	2.0	0.45
CMS2/C_{18}TAB	2.2	0.55

2.2. Sorption isotherms

Moisture sorption isotherms of native and hydrophobically modified cassava starches were carried out in an IGASorp moisture sorption analyzer (Hiden Isochema Ltd., UK). It consists on a controlled atmosphere microbalance, in which the relative humidity and the change in sample weight are continuously monitored. Ambients with different levels of relative humidities (RH) are obtained by relative mixing of water vapor and dry ultra high purity nitrogen gas stream to the desired set point. Weight data are acquired and analyzed in real-time to determine kinetic parameters so that the exact point of equilibrium uptake can be predicted. The water uptake process was studied by fitting the changes in weight with a single exponential function. Subsequently, the next desired humidity level is set. The entire process is automatically repeated until the full isotherm has been measured. An amount of 10 ± 1 mg of starch sample was placed inside the balance and the RH was increasingly set as: 0, 8.2, 11.3, 22.5, 32.8, 43.2, 52.9, 68.9, 75.3, 84.3, and 93.6. The maximum time for the total data correction in a RH level or timeout for the RH level to change was 240 min or when the isotherm was stable. The equilibrium criterion for the isotherm stability was taken as the time after which the weight had relaxed to within 1% of the equilibrium uptake. All moisture isotherms were carried out at 25 °C. Data points were collected and plotted as an isotherm by means of the software IGASorp System Software V6.50.42 (Hiden Analytical Ltd.).

2.3. Data analysis

2.3.1. Water sorption kinetics

The kinetics of water sorption at the different RH levels and at a temperature of 25 °C were studied by means of the single exponential function used to fit the water uptake, expressed as in Eq. (6):

$$m(t) = M_\infty + (M_0 - M_\infty)\exp\left(\frac{-t}{K1}\right) \qquad (6)$$

where $m(t)$ is the weight of the sample at time t, M_0 is the initial sample weight, M_∞ is the sample weight at equilibrium and $K1$ is an intrinsic constant related to the settling time (s).

2.3.2. Sorption isotherm modeling

The experimental data obtained corresponding to water activities (a_w) and moisture contents (m) were adjusted to the GAB model described by Eq. (7):

$$m = \frac{m_o \cdot C \cdot k \cdot a_w}{[(1 - k \cdot a_w)(1 - k \cdot a_w + C \cdot k \cdot a_w)]} \qquad (7)$$

where m_o is the monolayer moisture content, C and k are energy constants related to the temperature effect. Nonlinear regression statistical analyses were performed using Statistica$^{\text{TM}}$ version 6.0 (StatSoft, Inc., Tulsa, OK). The quality of the fitting was evaluated through the R^2 and the mean relative percent error (%E) defined as:

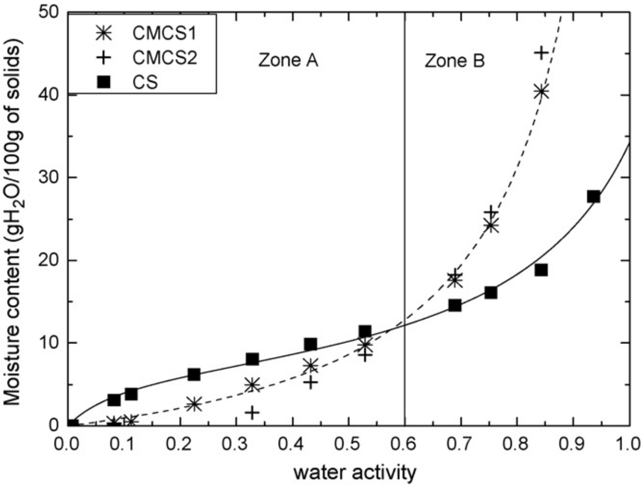

Fig. 1. Sorption isotherms of native cassava starch (CS, solid line) and carboxymethyl cassava starch (CMCS1 and CMCS2, dashed lines).

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

where n is the number of data points, ($m_{e,i}$) and ($m_{p,i}$) are experimentally observed and predicted values by the model 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, McMinn, & Magee, 2004; Lomauro, Bakshi, & Labuza, 1985).

3. Results and discussion

Sorption isotherms of native cassava starch (CS) and carboxymethyl cassava starches (CMCS1 and CMCS2) are shown in Fig. 1. This figure shows that starch carboxymethylation modified the sorption behavior of cassava starch. This modification may be related to differences in chemical structure between native cassava starch and that of the carboxymethyl starch due to the presence of carboxylate groups (COO^-Na^+) in the latter, when it is treated with a NaOH solution after its preparation. These groups lead to a more hydrophilic material, as it is water soluble (Heinze & Koschella, 2005). According to Ping, Nguyen, Chen, Zhou, and Ding (2001) the average number of non-freezable water molecules per each hydrophilic site depends on the chemical nature of the polar site, being 1 for a hydroxyl (–OH), while for a carboxylate group ($-COO^{-+}M$) like the one present in CMCS, this number can increase depending on the size of the counter-ion (M^+), and hence on its ability to undergo dissociation in water. In the case of the $COO^{-+}Na$ group the average number of non-freezable water molecules per hydrophilic site, can reach 4. Apart from the chemical structure difference of the CMCS, it is also different from CS in terms of its physical state, as it exhibits an amorphous structure as compared to the well known semicrystalline structure of CS (Contó, 2008).

The sorption behavior exhibited by both native cassava starch and carboxymethyl starches (Fig. 1) indicated that for $a_w < 0.6$ incorporation of the carboxylate groups decreases the material hydrophilicity (zone A), while for $a_w > 0.6$ their hydrophilicity was significantly greater than that of CS (zone B). For CMCS1 in zone A, the material adsorbed between 14 and 90% less water than native cassava starch, while CMCS2 adsorbed between 25 and 96% less water. These results seem to be contradictory, as more hydrophilic groups are being incorporated to the starch molecule and hence more adsorbed water would be expected. On the other hand, the amount of adsorbed water by amorphous materials should be greater than that of semicrystalline materials, due to the broken structure of the granule, which leads to an increase in the number of active sites exposed after starch transformation (Wootton & Bamunuarachchi, 1978). However, these results are in agreement with those obtained by Contó (2008) by means of FTIR, where a decrease and almost disappearance of the 1649 cm^{-1} band, associated to bond-water adsorption, was observed for CMCS1 and CMCS2, respectively. Contó (2008) established that this decreasing effect is associated to the changes taking place on the starch structure due to chemical modification and to starch gelatinization occurring during the CMCS synthesis. Perdomo (2006) found that amorphous cassava starch, kept in an ambient with $a_w < 0.6$, adsorbed less water than native cassava starch which is in agreement with the results shown in Fig. 1. The adsorption ability of native potato starch–protein systems were also found to be greater than those of the same systems previously transformed by extrusion process in the whole range of water activity considered, which was attributed to the structural changes taking place during extrusion reflected in new arrangements of adsorption sites, to which water molecules bond (Wlodarczyk-Stasiak & Jamroz, 2008).

Zone B in Fig. 1, illustrates a change in the water adsorption behavior of the carboxymethyl cassava starches (CMCS1 and CMCS2) with respect to the native cassava starch (CS). For CMCS1 in zone B, the material adsorbed between 20 and 181% more water than native cassava starch, while CMCS2 adsorbed up to 207% more water than the latter at the highest water activity value considered (0.94). In this case, the higher moisture contents (mainly free water) in the carboxymethyl starches (corresponding to a_w values greater than 0.6), enhanced molecular mobility exposing the hydrophilic groups incorporated in the starch upon modification. This is the reason why carboxymethyl starches are water soluble, while native cassava starch is not.

By comparing CMCS1 and CMCS2 in Fig. 1, it can be noted that in zone B CMCS2 adsorbed slightly more water than CMCS1 due to the greater degree of substitution (greater amount of hydrophilic carboxylate groups) of CMCS2. On the other hand, it can also be observed that CMCS2 adsorbed less water than CMCS1 in zone A, which agreed with FTIR results presented by Contó (2008) as mentioned above.

The formation of ionic complexes between carboxymethylated starch and quaternary ammonium salts having different chain lengths altered the sorption behavior in comparison with native starch, as indicated in Figs. 2 and 3. Two zones can be depicted in these figures, zone C and zone D. In zone C, the CMCS/C_nTAB starches exhibit higher hydrophobicity than native cassava starch, represented in the figures by the solid line. In zone D, on the contrary, they tend to be more hydrophilic than native starch.

The behavior exhibited by modified starches in zone C is attributed to the hydrophobic effect of the introduced alkyl groups coming from the quaternary ammonium salts and also because its precursor material (CMCS) exhibit higher hydrophobicity than native cassava starch, as mentioned above. Starches belonging to CMCS2/C_nTAB system (Fig. 3) have a stronger hydrophobic character than those belonging to the CMCS1/C_nTAB group (Fig. 2), since they absorb between 12 and 51% less water when the lowest chain length is considered (CMCS2/C_{12}TAB), and between 11 and 73% when the longest length chain is present (CMCS2/C_{18}TAB). This behavior can be attributed to the different degree of substitution of the two CMCS (CMCS2 > CMCS1); i.e., CMCS2 has a larger number of hydrophobic alkyl chains, which decreases water adsorption.

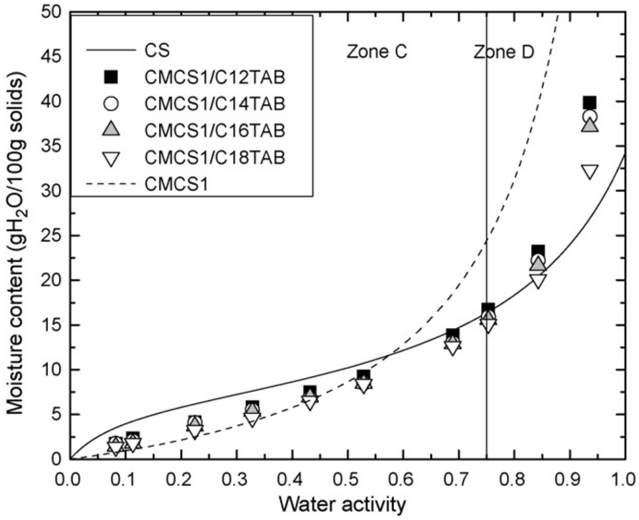

Fig. 2. Sorption isotherms of native cassava starch (CS, solid line), carboxymethyl cassava starch (CMCS1, dashed line), and carboxymethyl modified cassava starches (CMCS1/C_nTAB) at 25 °C.

Compared to native starch, the greater adsorption of water of the modified starches in zone D, a region of higher water activity, can be attributed to the following reasons: (a) in the CMCS/C_nTAB system the starch has lost its crystalline structure (Balsamo et al., 2010) and (b) more free volume exists among chains due to the higher size of the functional group introduced, which allows greater water incorporation. In other words, a competence of hydrophobization due to the introduced alkyl group vs hydrophilization due to physical structure effect exists.

By comparing the sorption behavior of the CMCS/C_nTAB systems with their corresponding precursor material; i.e., CMCS (Figs. 2 and 3), it can be noted that for $a_w < 0.45$ the complexes are slightly less hydrophobic than CMCS, and for $a_w > 0.45$ the precursor is more hydrophilic. This fact can be attributed again to a competence effect between the complex size and hydrophobic character. At low moisture contents (low a_w values), there is a greater free volume due to the presence of the long alkyl chains (C_{12}–C_{18}), whose size is bigger than the CMCS carboxylate group. As a consequence water molecules can be adsorbed in major proportion because they become more mobile and can reach the active sites and bound themselves more easily. Conversely, at

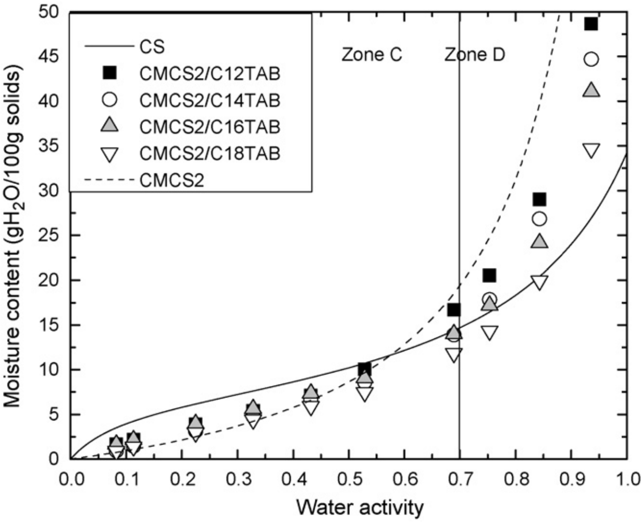

Fig. 3. Sorption isotherms of native cassava starch (CS, solid line), carboxymethyl cassava starch (CMCS2, dashed lined) and carboxymethyl modified cassava starches (CMCS2/C_nTAB) at 25 °C.

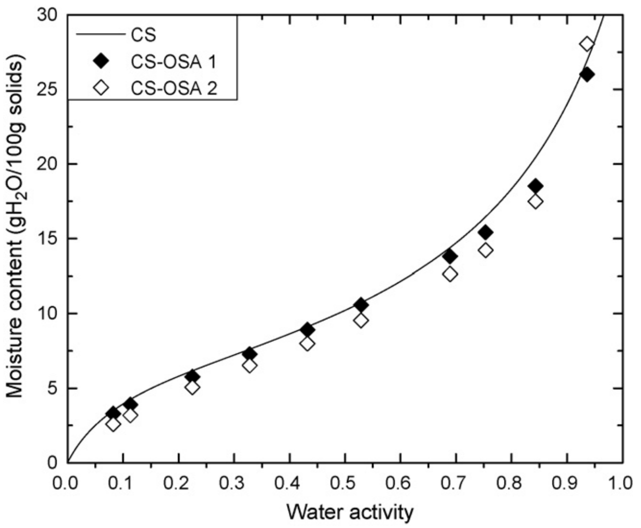

Fig. 4. Sorption isotherms of native cassava starch (CS, solid line) and modified octenyl succinic anhydride modified starches (CS-OSA1 and CS-OSA2) at 25 °C.

high moisture contents (high a_w values), the hydrophobic character introduced by the complex governs the adsorption behavior, decreasing the amount of adsorbed water with increasing chain length.

Esterification of cassava starch with octenyl succinic anhydride (OSA) involves incorporation of at least one alkyl chain with eight carbon atoms to the starch anhydroglucose unit. This OSA incorporation leads to a slight increase of the material hydrophobicity (as compared with unmodified native CS) over the whole range of water activity, as is clearly indicated in Fig. 4. The figure shows that for a given a_w value, the equilibrium moisture contents reached by CS-OSA1 and CS-OSA2 were lower than for native cassava starch, represented by the solid line in Fig. 4. The figure also shows that the greater the degree of substitution (CS-OSA2 > CS-OSA1), the higher the material hydrophobicity, since a larger number of OSA groups are incorporated and the 8-carbon alkyl chain has no affinity for water. CS-OSA1 adsorbs between 2 and 10% less water than native cassava starch, while the water adsorption for CS-OSA2 resulted in between 7 and 24% less water adsorption than that of native cassava starch.

From a water adsorption point of view, the advantage of the OSA-modified cassava starch, compared to the CMCS/C$_n$TAB system, is that an enhanced hydrophobic capacity is obtained over the whole range of water activity, even when the sample contains a much lower degree of substitution (i.e., one order of magnitude lower than that of the CMCS modified sample). This behavior can be attributed to the fact that OSA-modified starch has a smaller size alkyl chain than the C$_n$TAB systems, which generates less free volume for water to be arranged.

Sorption data obtained for native cassava starch and for all hydrophobically modified cassava starches studied were fitted to the GAB model, and the results are presented in Table 2. The table also shows R^2 and the mean relative percent error (%E). The GAB model was chosen as it is widely used in modeling sorption behavior of starchy products (Perdomo et al., 2009), and particularly modified starches (Bravo-Osuna, Ferrero, & Jiménez-Castellanos, 2005; Maia, Cornejo, Ascheri, Maia, & Rocha-Leao, 2004), and emulsified edible films (Phan The, Debeaufort, Voilley, & Luu, 2009), where hydrophilic and hydrophobic components coexist.

Table 2
Fitting parameters for the GAB model applied to sorption data of native and hydrophobically modified cassava starches.

Sample	m_o	C	k	R^2	%E
Native CS	6.80	13.07	0.81	0.990	5.64
CS-OSA 1	6.37	13.63	0.81	0.996	2.48
CS-OSA 2	5.12	14.92	0.87	0.993	6.12
CMS1	10.77	0.83	0.94	0.999	26.37
CMS1/C$_{12}$TAB	5.87	5.07	0.90	1.000	1.57
CMS1/C$_{14}$TAB	5.29	5.51	0.92	1.000	2.53
CMS1/C$_{16}$TAB	5.68	4.18	0.90	0.999	3.60
CMS1/C$_{18}$TAB	6.53	2.91	0.85	0.999	2.06
CMS2	5.97	−279.65	0.99	0.966	588.19
CMS2/C$_{12}$TAB	7.61	2.43	0.91	0.999	5.87
CMS2/C$_{14}$TAB	5.75	2.76	0.95	1.000	5.24
CMS2/C$_{16}$TAB	5.87	4.46	0.92	1.000	1.38
CMS2/C$_{18}$TAB	5.64	2.86	0.89	1.000	4.35

Table 2 shows that in all cases, very good fits were obtained, as evidenced by the high R^2 values (>0.990) and mean relative percent errors lower than 7%, except for the CMCS. It may also be noted in this table that the monolayer water content of the native cassava starch was 6.80 g water/100 g of dry solids, while it slightly decreased with the OSA modification, as indicated by the corresponding values obtained for CS-OSA1 and CS-OSA2 (6.37 and 5.12 g water/100 g of dry solids, respectively). This result is in agreement with the increasing hydrophobic character induced by the degree of substitution already discussed above and has also been observed by Phan The et al. (2009) in starch-emulsifier films and by Bravo-Osuna in methyl methacrylate-starch copolymers. In the same way, Chen, Kou, and Lai (2009) reported decreasing sorption capacity and monolayer water content of tapioca starch/decolorized hsian-tsao leaf gum films with increasing amount of surfactants, which imparted hydrophobicity to the films.

Monolayer water content values obtained for native cassava starch are within the range presented for starchy products, which have been reported to be between 5.1 and 8.6 g water/100 g of dry solids (Rahman, 1995). Higher values have been reported for cassava starch; for instance, Chatakanonda, Dickinson, and Chinacohoti (2003) reported a monolayer water content value at 25 °C of 7.93 g water/100 g of dry solids, while Sangeetha (2006) found a value of 9.54 g water/100 g of dry solids at a temperature of 20 °C. Monolayer water content values of amorphous cassava starch ranging from 4.5 to 12.7 g H$_2$O/100 g of dry solids were reported by Perdomo et al. (2009) in a temperature range of 45–5 °C.

Table 2 also shows that an increase in material hydrophobicity, due to OSA modification, causes an increase in the C constant, which is related to the water–substrate interaction energy. A C constant increase was also observed by Chen et al. (2009) in tapioca starch/decolorized hsian-tsao leaf gum films with increasing amount of surfactants. According to these authors, a greater amount of energy is required for the molecule adsorption on the active sites, which was in concordance with the increase in the degree of hydrophobicity of the sample. However, studies carried out by Bravo-Osuna et al. (2005) in methyl methacrylate-starch copolymers and Phan The et al. (2009) in emulsified edible films, showed a decrease of the C constant with increasing hydrophobicity degree. These authors stated that this behavior might be related to a weaker water–copolymer interaction caused by the presence of methyl methacrylate.

By considering the k constant in Table 2, which takes into account the difference between the chemical potential of the sorbate's pure liquid state and in the upper layers (Timmermann, Chirife, & Iglesias, 2001), very little variation with OSA modification can be observed; this is due to the fact that sorption behavior of the modified starches at high water activity was similar. This behavior was not appreciated in the case of the CMCS/C$_n$TAB systems. For these systems the value of k is slightly higher than the presented by the native cassava starch; this increase indicates that at high values of water activity the material is capable of absorbing more water (Timmermann et al., 2001). This behavior is consis-

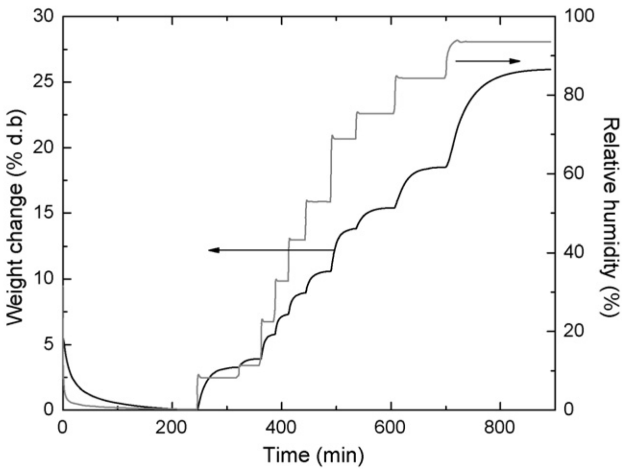

Fig. 5. Sorption kinetics for the octenyl succinic anhydride modified starch (CS-OSA1) at 25 °C.

tent with that observed in Zone D, where the complexes are more hydrophilic than native cassava starch and therefore more water is adsorbed.

Monolayer content values for the CMCS/C$_n$TAB systems were lower than those of the native cassava starch, indicating the effect of hydrophobicity due to the incorporation of the trimethylalkylammonoim group. In the case of CMCS2/C$_n$TAB, Table 2 clearly shows the effect of increasing chain length, as the monolayer content value decreases with increasing number of carbon atoms in the substituting chain, a fact that evidences the increasing hydrophobicity of the modified starches.

Table 2 also shows that in all cases, the C constants for the CMCS/C$_n$TAB systems were lower than that for native cassava starch, which would again indicate a weakening of the water-modified starch interactions, caused by the presence of modifying groups when complexes between CMS and quaternary ammonium salts are formed, which decrease the amount of bound water molecules. Even though the constant C for all modified starches was lower than that of the native cassava starch, no specific trend was observed for this parameter, as the chain length of the complex increased.

One of the advantages of determining the sorption isotherm with a controlled atmosphere microbalance, such as the one used in this work, is that kinetic data can also be continuously recorded during the whole sorption process, as shown in an example in Fig. 5. Variation of the kinetic constant $K1$ with RH and weight change for the native and hydrophobically modified starches considered in this work are shown in Figs. 6 and 7. In both cases, it can be observed that native cassava starch presents the lowest values of $K1$ for all RH considered, indicating that it has a faster water sorption kinetics.

Fig. 6 shows the variation of the kinetic constant $K1$ with RH for native and OSA-modified cassava starches. It can be observed from this figure that the kinetic constant $K1$ slightly increases for modified starches, indicating that chemical modification of cassava starch with octenyl succinic anhydride makes the sorption process slower. On the contrary, values for the kinetic constant $K1$ for the CMCS/C$_n$TAB system (Fig. 7) exhibited a larger increase with respect to native cassava starch, particularly at low activity water ambients.

It is also worth noting that the kinetic constant $K1$ for native cassava starch goes through a minimum at RH ambient range between 20 and 40%, indicating that the sorption kinetics is faster. Lower water sorption resulted at low RH (<20%), and even lower at higher RH ambients (>40%). A similar behavior was reported by Van Nieuwenhuijzen, Meinders, Tromo, Hamer, and van Vliet (2008) in starch and protein-based wheat flour. In case of low RH ambients, this behavior may be attributed to the fact that the sorption process is initiated with a dry material, having a lower free volume available for water, making difficult its transport to the active sites and hence the water transport velocity in the material is slow. As the sorption process proceeds and the moisture content is higher, the polymer hydration takes place by water molecules, which leads to polymer swelling and increases its free volume, increasing in this way the water transport velocity. If the RH is continuously increased, the material swelling degree may increase and so may the particle size, reducing in this way the effective surface area. Additionally, under these conditions, agglomeration and compaction of the material (i.e., caking phenomenon) can take place, which would considerably reduce water transport velocity, evidenced by the increase in the kinetic constant $K1$ values shown in Fig. 6. This phenomenon of agglomeration occurring at high RH ambients has been reported before (Haque & Roos, 2004; Jouppila & Roos, 1994).

Yu, Schmidt, Bello-Pérez, and Schmidt (2008) determined the water diffusion coefficient of corn starch under adsorption process

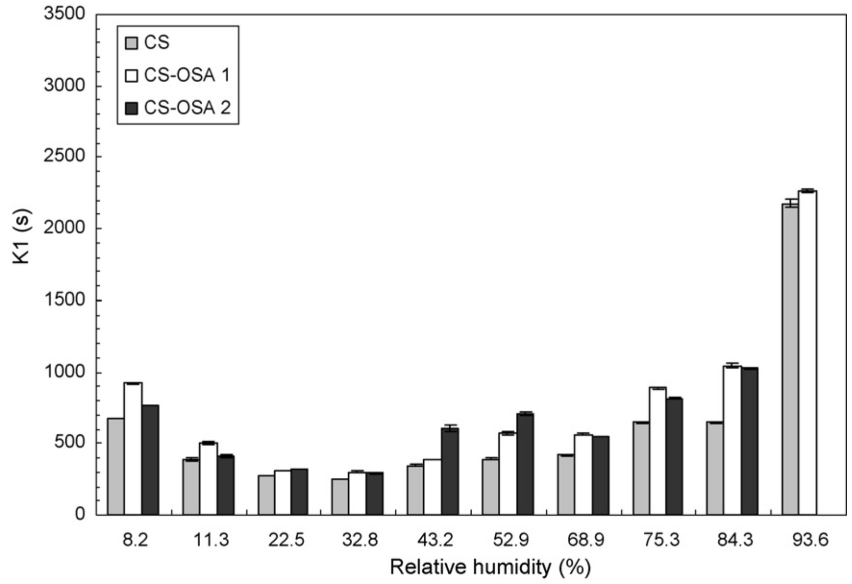

Fig. 6. Variation of the kinetic constant $K1$ with relative humidity for native cassava starch and for octenyl succinic anhydride modified starches, at 25 °C.

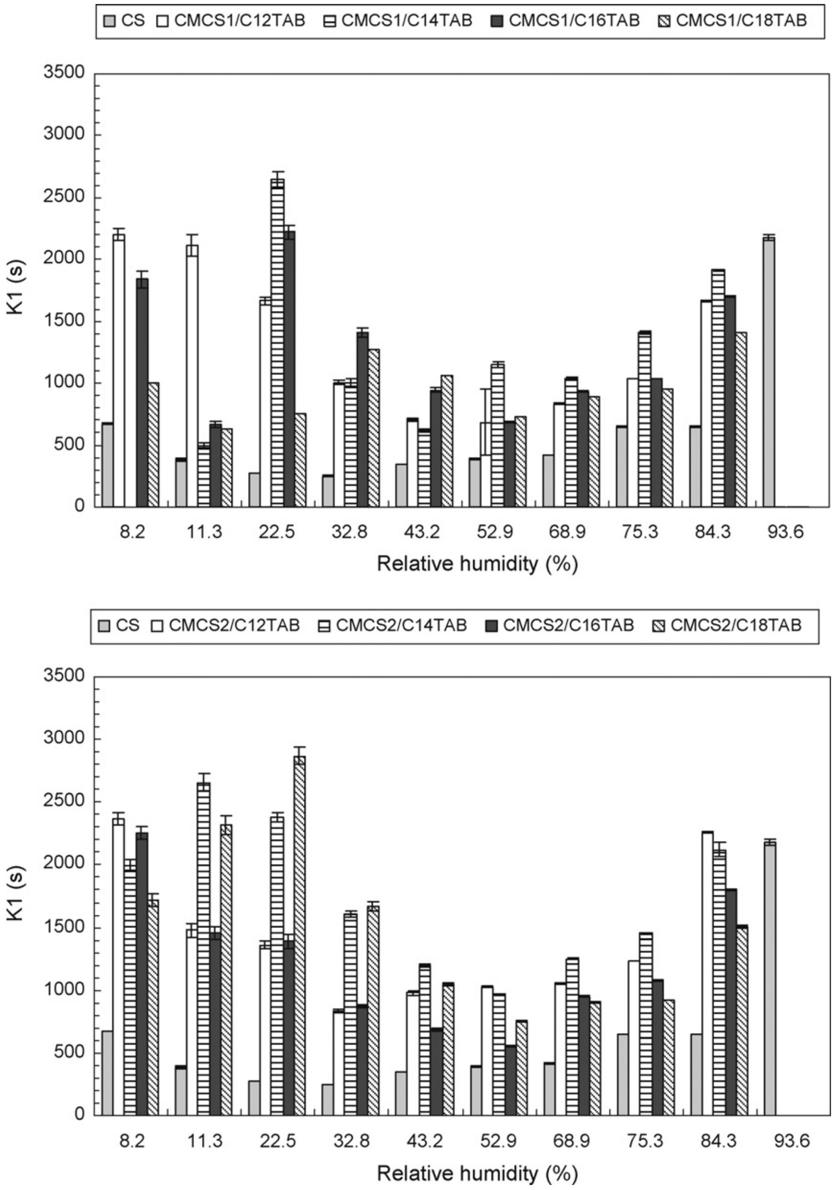

Fig. 7. Variation of the kinetic constant $K1$ with relative humidity for native cassava starch and for starch ionic complexes (CMCS1/C_nTAB and CMCS2/C_nTAB) at 25 °C.

for different RH values (between 10 and 80%) and found a maximum value for this parameter at RH ambients of 50%. It was postulated that the occurrence of such a maximum may be due to a change in the diffusion coefficient; i.e., from a vapor diffusion at low RH to liquid diffusion at high RH ambients. This behavior has also been observed by Karathanos, Villalobos, and Saravacos (1990) in corn starch gels. In Fig. 6, it may also be noted that chemical modification of cassava starch with octenyl succinic anhydride does not change the general trend, as the kinetic constant $K1$ for native cassava starch also exhibited a minimum in the 20–40% RH range. The minimum in the kinetic constant $K1$ for the CMCS/C_nTAB system (Fig. 7) was moved towards RH values between 43% and 68%. The reason why such behavior is exhibited is still not clear. Further studies are necessary to define this mechanism in more detail.

By looking at the kinetic constant values obtained for the different materials in the CMCS/C_nTAB system (Fig. 7), no clear trend was observed as the chain length of the quaternary ammonium salt increases, since each material behaves differently. Consequently, it can be said that water sorption kinetic is a very complex process that is affected by many factors, such as physical state, the ambient (RH) in which is kept, and chemical structure, among others.

4. Conclusions

Moisture sorption isotherms of native and ten hydrophobically modified cassava starches were determined at 25 °C using a dynamic gravimetric method. It was found that cassava starch modification with octenyl succinic anhydride (OSA) leads to a more hydrophobic material than native cassava starch, increasing hydrophobicity with degree of substitution. Incorporation of the quaternary ammonium moiety to the carboxymethyl starch caused a dual sorption behavior along the isotherm; i.e., greater hydrophobicity than native cassava starch at low a_w values and the opposite at high a_w values. This behavior was attributed to the competing effects of the hydrophobic nature of the CMCS/C_nTAB complexes and the large size of the introduced alkyl chains that can induce a large free volume where water molecules can easily accommodate. The adsorption experimental data of all the materials considered were well represented by the GAB model and the monolayer water contents decreased with the hydrophobic nature of the material. It was also shown that chemical modification of cassava starch slows down the water adsorption process.

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