

Evolution of Interactions between Water and Native Corn Starch as a Function of Moisture Content

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Received 26 December 2001; accepted 12 March 2002

ABSTRACT: Thermostimulated current spectroscopy, thermogravimetric analysis, and differential scanning calorimetry (DSC) were used to study starch–water systems with moisture contents of 0–50% (on a total weight basis). DSC enabled the calculation of the amounts of bound and free water. The maximum quantity of bound water was detected for a 30% humidity sample. The existence of inter-

actions between water and starch was proved and found to be weakened for samples containing more than 30% water. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2860–2865, 2002

Key words: thermogravimetric analysis (TGA); differential scanning calorimetry (DSC); polysaccharides

INTRODUCTION

Many sectors of the plastics industry are increasing the use of biopolymers because of increasing environmental problems. Therefore, starch is frequently chosen for blending with synthetic polymers to reduce the nonbiodegradable parts of the products. However, there is an increasing tendency to develop fully biodegradable materials, especially in food packaging, as long as processing is maintained at a reasonable cost level. For that, a deeper knowledge of the material itself is needed; for example, in the case of starch, performing processing techniques such as extrusion requires precise knowledge of the raw material and its interactions with water, which is frequently used as a plasticizer and an additive.

Starch is essentially composed of two types of macromolecules: amylopectin and amylose. These components both contain glucose units linked by α -(1,4)-bonds to form linear chains. Unlike amylose, which is mostly linear, amylopectin is highly branched, and the linear chains of glucose units are generally linked to other ones by α -(1,6)-bonds. Their relative proportions depend on the botanic origin.^{1,2}

Glucose units can generate intramolecular and intermolecular hydrogen bonds or bonds with water;³ water molecules inserted between rigid starch chains

act as plasticizers. This property has often been observed with various techniques. Leveque et al.⁴ and Samouillan et al.⁵ applied thermostimulated current spectroscopy (TSC) to study the mobility enhancement of polar groups in keratin and to detect the presence of polar mobile sequences (β modes) in the spectra of collagen, elastin, and valvular leaflets. Moreover, it was proved that the addition of water was also the reason for the decrease in the glass-transition temperature of starch detected by differential scanning calorimetry (DSC) or dynamic mechanical analysis.^{6–8} NMR spectroscopy and sorption microcalorimetry also showed a decrease in the residence time of water in polar groups of starch for different species (potato, wheat, and corn).^{9–11}

Li et al.¹² proposed simplifying the hydration problem by distinguishing water molecules, which create strong interactions with starch, from others. The first category corresponds to the bound water, and the second corresponds to the free water.

Although these works give very interesting information, the diversity of the studied materials is impressive; even corn starch may be different from another starch, any difference depending partly on the extraction of the starch from the raw material. This study was concerned with the behavior of water within raw corn flour containing mostly starch.

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Contract grant sponsor: Région Rhône-Alpes.
Contract grant sponsor: Clextral.

EXPERIMENTAL

Materials

Corn flour (type 36.05, MCT, Ennezat, France) was used for this study. It essentially contained starch

(85% on a dry basis) and proteins and lipids (10 and 1%, respectively, on a dry basis). Flour grains ranged from 200 to 700 μm . Each grain was mainly composed of starch granules. The moisture content (MC) of the flour was estimated to be 13% (on a wet basis).

The actual MC was determined with an MA40 Sartorius infrared dryer (Goetingen, Germany) at 130°C. Afterward, we added deionized water to maize to obtain samples with various total water contents (MC) of 18, 25, 30, 35, 40, and 50% (on a wet basis). They were stored at 4°C for 8 h for equilibration. The MC was checked before each experiment with the infrared dryer at 130°C.

The 0% moisture sample was obtained by the drying of the maize flour at 40°C in a vacuum oven. By the measurement of the weight loss, the humidity ratio (MC) was calculated and evaluated to be less than 2%.

Experiments

Samples containing 0, 13, 18, 25, 30, 35, 40, and 50% water were cooled from 25 to -80°C at a cooling rate of $10^\circ\text{C}/\text{min}$ with a Setaram differential calorimeter (Caluire, France). This procedure converted very mobile liquid free water into crystallized water. The crystallization enthalpy enabled us to determine the percentage of very mobile freezable water (W_f) and unfreezable water (W_u):

$$W_f = \frac{\Delta H}{\Delta H_o} \quad (1)$$

and

$$W_u = \frac{\Delta H_o - \Delta H}{\Delta H_o} \quad (2)$$

where ΔH_o is the crystallization enthalpy of permuted water and ΔH is the crystallization enthalpy of the sample

Other authors such as Li et al.¹² used another available mode that consisted of cooling a sample at a definite rate from room temperature to about -40°C . Then, with heating, a fusion endotherm of water at about 0°C is observed and enables the calculation of W_f and W_u . However, this heating mode was not used here because during heating, metastable crystals may evolve.

Thermogravimetric analysis (TGA) experiments were conducted on 13, 18, 25, 30, 35, 40, and 50% MC samples with a Setaram TGC 85. The procedure was performed at a heating rate of $10^\circ\text{C}/\text{min}$ from 25 to 250°C under a dry helium flow of 5 L/h. A mass of 50 mg was chosen to study the evolution of weight as a function of temperature so that we could observe wa-

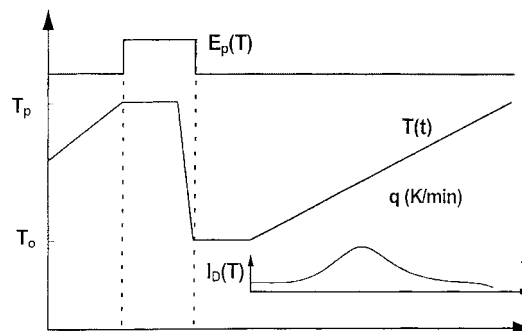


Figure 1 Principle of the thermostimulated current spectroscopy (TCS) technique.

ter evaporation because only water vaporizes and no degradation occurs in this temperature range.¹³

For TCS measurements, each sample (0, 13, 23, 30, 35, and 50% MC) was placed between two plane condenser electrodes and surrounded by a guard ring in Teflon to hold the corn flour in position. This cell was put in an environment in which ambient water was eliminated by pumping. Afterward, dry helium was introduced to ensure good thermal exchanges and to obtain nonnoisy electric signals. Figure 1 describes the TSC procedure. A static electric field (E_p) was applied to the sample at the polarization temperature (T_p) during a time (t_p) sufficient to orient molecular segments, which were mobile enough at a temperature lower than or equal to T_p . Then, this unbalanced dipolar configuration was frozen via quenching at a certain temperature (T_o) with liquid nitrogen. The electric field was cut off, and the condenser was connected to a very sensitive electrometer (Keithley 642, Cleveland, OH) with a sensitivity of 10^{-17} -A. A linear increase in temperature (rate = q) triggered a progressive relaxation of previously oriented dipoles, resulting in a depolarization current [$I_D(T)$]. Relaxation spectra, showing the depolarization current versus the temperature, were obtained for MCs of 0, 13, 18, 25, 30, 35, 40, and 50% with the following polarization conditions: $T_p = 0$ or 20°C for 0% moisture, $t_p = 2$ min, $E_p = 150$ V/mm, $q = 7^\circ\text{C}/\text{min}$, and $T_o = -180^\circ\text{C}$.

All the experimental data were verified at least twice.

RESULTS

Figure 2 shows a thermogram that was obtained for the various samples. No exotherm is noticeable for an MC lower than 30%. With eqs. (1) and (2), the experimental data enabled us to evaluate the percentage of unfreezable water. In Table I, the results are given on a total water basis (A), on a total weight basis (B), and on a dry basis (C). Freezable water on a total weight basis (D) is given for samples containing more than 25% water. As expected, the freezable water quantity

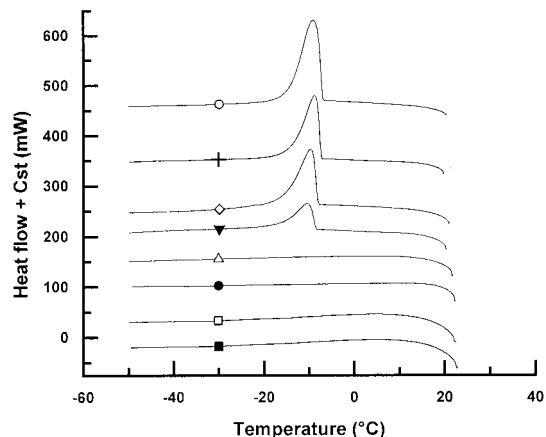


Figure 2 DSC thermograms for MCs of (■) 0, (□) 13, (●) 18, (△) 25, (▼) 30, (◇) 35, (+) 40, and (○) 50% by cooling from 25 to -80°C .

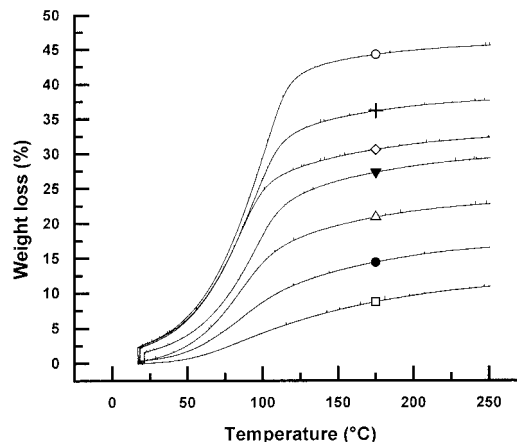


Figure 3 Weight loss versus temperature for MCs of (□) 13, (●) 18, (△) 25, (▼) 30, (◇) 35, (+) 40, and (○) 50%.

increased with the water content. However, the unfreezable water quantity (C) did not vary and reached a maximum of 30%.

Figure 3 shows the evolution of weight loss as a function of temperature for 13–50% humidity samples. Water vaporization occurred faster from 25 to about 110°C and tended to stop beyond 110°C as the weight loss reached a threshold. The derivative of weight as a function of temperature was drawn (Fig. 4) so that we could observe more precisely the influence of the humidity ratio on water evaporation. The temperature of the extreme of the derivative related to the maximum of water loss increased with MC within 13–30% (Fig. 5). Moreover, beyond MC = 30%, the maximum was shifted to a lower temperature, that is, 86°C for MC = 35%. Then, the value of this temperature rose again from 35 to 50%. Moreover, the more important the MC is, the greater the value is of the derivative, that is, the weight loss. It becomes identical for samples containing 35% or more water within the low temperature range of about $25\text{--}60^{\circ}\text{C}$.

Figure 6 shows complex TSC spectra of samples containing 0, 13, 23, 30, 35, and 50% water from -180 to 20°C . Two relaxation modes are noticeable: the first, β_1 , was around -130°C , and the other, β_2 , was around -60°C . They depended on the water content. With increasing water concentration, the I_D maxima increased, and the noise on the signals became more pronounced. Besides, the I_D maxima shifted to lower temperatures for the whole MC range. The plot of the reciprocal of T_{β_i} ($i = 1$ or 2) as a function of MC yielded a linear curve fit for the data between 0 and 23% water (Figs. 7 and 8) with the correlation coefficients $R^2 = 0.9995$ and 0.9999 for T_{β_1} and T_{β_2} , respectively. This evolution can be described with the following equations, the MC, which is expressed as a weight percentage, being replaced by the mass fraction of water [$x(\text{water})$]:

$$\frac{1}{T_{\beta_1}} = 4 \times 10^{-3} \cdot x(\text{water}) + 0.0059$$

TABLE I
Evaluation of the Percentage of Bound and Free Water

Moisture Content (MC) of TH (%)	ΔH (J/g of water)	% Bound water ^a (on a total water basis)		% Bound water (on a dry basis)	% Free water (on a total weight basis)
		$A = 100 \times \frac{(\Delta H_0 - \Delta H)}{\Delta H_0}$	$B = A \times \text{TH}$		
100	-267.5	0.0	0.0	0.0	100.0
50	-177.3	33.7	16.9	33.7	33.1
40	-149.5	44.1	17.6	29.4	22.4
35	-116.3	56.5	19.8	30.4	15.2
30	-66.3	75.2	22.6	32.2	7.4
25	—	—	—	—	—
18	—	—	—	—	—
13	—	—	—	—	—
0	—	—	—	—	—

^a ΔH_0 represents the enthalpy of crystallization for bulk water (TH = 100%) = -267.5 J/g.

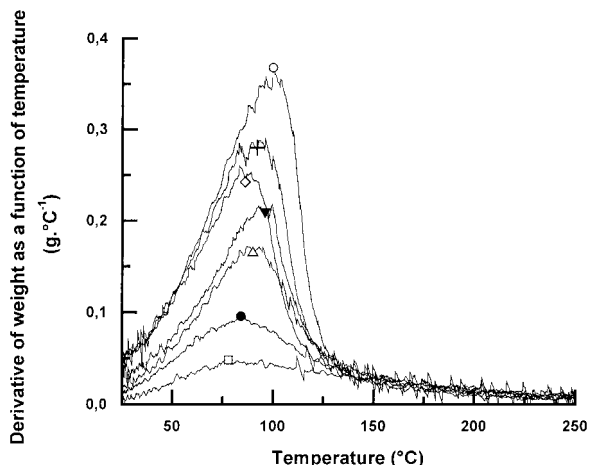


Figure 4 Derivative of weight as a function of temperature for MCs of (□) 13, (●) 18, (△) 25, (▼) 30, (◇) 35, (+) 40, and (○) 50%.

$$\frac{1}{T_{\beta 2}} = 4 \times 10^{-3} \cdot x(\text{water}) + 0.0037$$

which can be turned into other equivalent relations:

$$\frac{1}{T_{\beta 1}} = \frac{x(\text{water})}{T_1(\beta_1)} + \frac{x(\text{corn})}{T_2(\beta_1)} \quad (3)$$

where $T_1(\beta_1) = 101 \text{ K } (-172^\circ\text{C})$ and $T_2(\beta_1) = 169 \text{ K } (-104^\circ\text{C})$ and

$$\frac{1}{T_{\beta 2}} = \frac{x(\text{water})}{T_1(\beta_2)} + \frac{x(\text{corn})}{T_2(\beta_2)} \quad (4)$$

where $T_1(\beta_2) = 130 \text{ K } (-143^\circ\text{C})$ and $T_2(\beta_2) = 270 \text{ K } (-3^\circ\text{C})$.

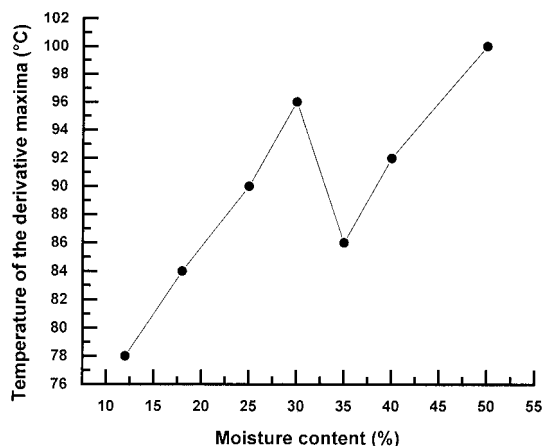


Figure 5 Temperature of the derivative maxima versus MC from 13 to 50%.

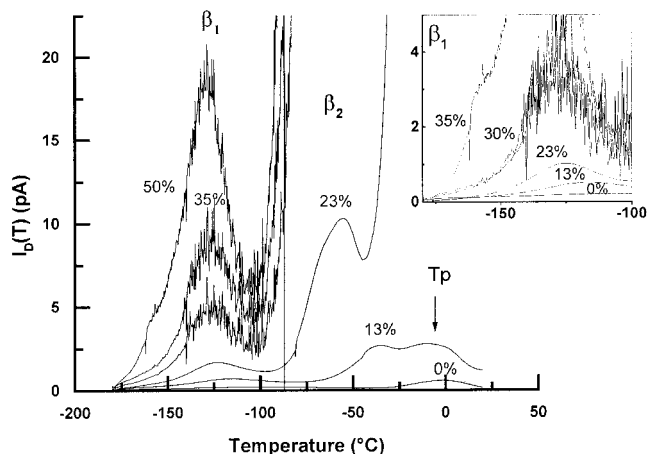


Figure 6 TSC spectra for the 0, 13, 23, 30, and 50% MC samples at low temperatures.

DISCUSSION

Determination of bound and free water

Because some of the water is very mobile and free, it can generate a conduction current that is recorded as a noise in TSC complex spectra (Fig. 6). Indeed, the existence of free water in samples appears on TSC signals for MCs exceeding 30%. Equations (3) and (4), reliable within a humidity range of 0–23% only, also highlight this particular limit of 30% water. These equations are similar to some kind of Fox's law,¹⁴ generally applied for the α -mode variations through dielectric or mechanical analysis to determine the glass transition of a copolymer or polymer blend. Water cannot be considered a solvent as soon as a significant quantity becomes very mobile, that is, not bound to starch, and probably phase-separates. Therefore, eqs. (3) and (4) do not fit the experimental data for 30% moisture. T_1 , which represents the relaxation temperature of bound water without corn flour [$x(\text{water}) = 1$], is only a calculated value for the two β modes

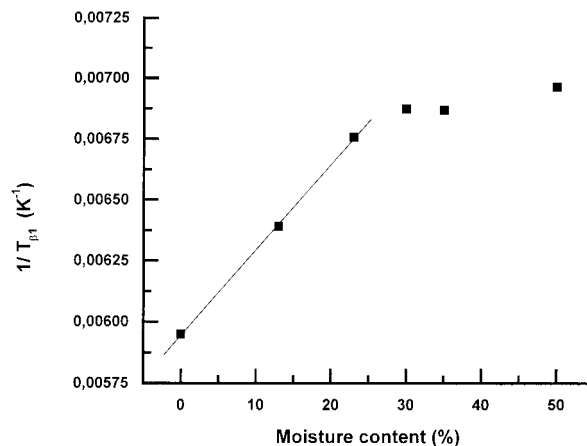


Figure 7 Inverse of the β_1 peak temperature versus MC for the 0, 13, 23, 30, 35, and 50% humidity samples.

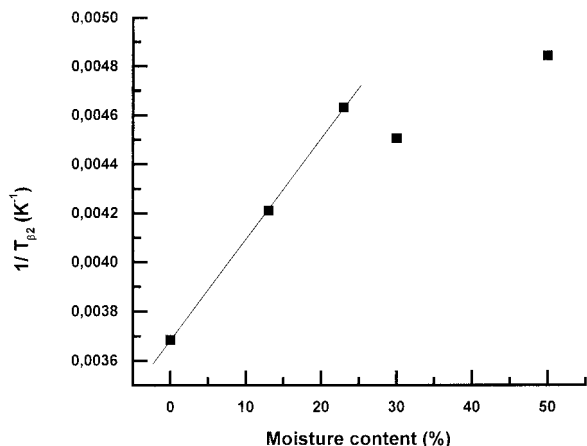


Figure 8 Inverse of the β_2 peak temperature versus MC for the 0, 13, 23, 30, and 50% humidity samples.

because it depends on bonds between water and polar segments of starch. Moreover, the values of T_1 (-172 and -143°C) do not correspond to the two relaxation temperatures of pure and, therefore, free water located at -113 and -93°C , as shown by depolarization current techniques,¹⁵ even though a comparison seems delicate because the experimental conditions are different. The appearance of an exotherm at about 0°C for humidity ratios greater than 30% in DSC thermograms (Fig. 2) corresponds to free water crystallization because the other components are already in the solid state. DSC experiments permit us to evaluate the proportions of free and bound water (Table I). Therefore, the concentration of free water increases from 7.4 to 33.1% when the MC is raised from 30 to 50%. The appearance of free water from 30% moisture shows that the polymer may have created all the possible interactions with water, and the water, which is likely to be bound, cannot exceed 33% on a dry basis. This specific limit at MC = 30% was also evoked by Li et al.¹² in a study on a waxy corn starch, although they found a slight increase in the bound water content beyond 30% moisture. By carrying out TSC experiments on keratin, which is a protein and not a polysaccharide like starch, Leveque et al.⁴ noticed a boundary at a water content of 25%, beyond which the intensity of the thermocurrent did not change, whereas the amplitude dropped below 25%.

Evolution of interactions between water and starch

Water was proved to play the role of a plasticizer in starch by establishing hydrogen bonds with the hydroxyl groups of starch.^{3,11} In general, the greater the water content was, the more accentuated this phenomenon was.³

Although adding excess water beyond a 30% MC increases the concentration of free water, the number of hydrogen bonds between water and hydroxyl

groups of starch does not increase but remains constant: the percentage of bound water on a dry basis is evaluated from the DSC experiments at about 30% (on a dry basis), whatever the humidity ratio is in the range of 30–50% (Table I).

Even though the number of interactions between water and starch is stabilized beyond 30% moisture, the strength of these bonds declines. In fact, the TGA experiments show that all the water, free or bound, is nearly evaporated at 110°C for the initial 35% moisture humidity sample. However, the samples containing only 25 or 30% humidity are still losing weight at this temperature because they still contain an amount of water that is more difficult to extract (Fig. 4). Moreover, the maximum quantity of evaporated water occurs at a lower temperature, 86°C , for 35% moisture, instead of 96°C for 30% moisture. Of course, the maxima are again shifted to higher temperatures when the water content exceeds 35% (86°C for 35%, 92°C for 40%, and 100°C for 50%), but it brings out only that, in this case, there is more water to eliminate. Therefore, the maximum is delayed by a kinetic phenomenon. The curves for 35, 40, and 50% humidity join within the range 25– 70°C , and they separate only when the water is almost extracted, after the maximum rate has been attained.

The similar weight losses of 35, 40, and 50% moisture samples in the range of 25– 70°C mean that water evaporates very easily at an identical rate and that this phenomenon concerns mainly free water. Indeed, the bonds of free water are weaker, and their strength does not evolve with the humidity ratio.

Regarding the four small water contents, those lower than 35% (where water should be totally or almost in the bound state), the temperature corresponding to the maxima of the weight loss tends to rise with the MC (Figs. 4 and 5). The highest temperature, 96°C , is reached for 30% water. In this latter sample, water and starch have formed the maximum number of bonds between each other, and this value should be the threshold for the appearance of free water. Free water represents only 7.4% of the total weight, which is not enough to weaken the metastable balance of the interactions that exist between water molecules and polar hydroxyl groups of starch.

The TSC analysis (Figs. 7 and 8) shows that the two β modes (ca. -130 and -60°C) put in relief two kinds of bonds between water and starch. The relaxations at about -130°C can be attributed to complex movements of very mobile and small polar groups of starch as the peak temperature is low. It may concern small sequences with hydroxyl groups because this mode is greatly influenced by water, which can form hydrogen bonds; indeed, when MC increases, the relaxation peak is shifted toward lower temperatures because the mobility of starch chains is enhanced by water. This plasticizing effect of water is also noticeable for the

other β relaxation, but at a higher temperature of -60°C . Then, this mode could be associated with bigger dipoles, involving stiffer segments of chains such as glucose cycles. Water molecules alone would not trigger these relaxations. The maxima of the depolarization current are visible for dehydrated products. This may indicate that the hydroxyl groups of starch can interact together to form some intramolecular or intermolecular bonds. In addition, obtaining a dipolar relaxation at a low temperature for ice crystals would require acute precautions, such as those used by Jeneveau and Sixou¹⁵ to study water, the use of deionized and very pure water, and a very low heating rate (0.05 K s^{-1}).

Dry starch may form intramolecular or intermolecular interactions. Added molecules of water can competitively establish several hydrogen bonds with polar hydroxyl groups of starch and become the so-called bound water, the unique state of water until 25% moisture (Table I). This mechanism strengthens with an increasing humidity ratio. The maximum of potential bonds between water and starch must be attained at 30% moisture as some of the water starts to appear in the free state. These molecules directly bound to the hydroxyl groups of starch form the first layers of water.⁴ Adding more water brings free water in which water molecules can preferentially create other bonds with the water molecules already present in the medium. These additional water molecules can constitute several additional water layers that can be inserted between two starch chains, and the mobility of the polymer chains is enhanced through this plasticizing effect of water. However, when a molecule of the bound water creates a bond with another water molecule, this mechanism may destroy one of the various bonds between starch and water. Therefore, the total interaction strength between this water molecule and the polymer decreases even if the same quantity of molecules remains bound (30% on a dry basis). In fact, free water molecules, known to be very mobile, can create bonds with other bound water molecules, increasing their mobility. Besides, this interpretation is in agreement with the works of Li et al.¹² and Tanner et al.,¹¹ who observed the enhancement of water molecule mobility and a decrease in the residence time for water molecules, respectively, with NMR spectroscopy, independently of the specific limit at 30%. However, because the percentage of bound water does not change above 30% moisture, there is a balance between water molecules creating bonds with starch and other molecules destroying such links. Even if the

value of the MC above which these mobility mechanisms become nonnegligible depends on the analysis techniques and experimental conditions, all these results corroborate the same kinds of phenomena.

CONCLUSIONS

The effects and mechanisms of starch hydration were studied with DSC, TGA, and TSC. With the addition of water, a characteristic change in behavior was observed with a 30% water content.

Adding more than 30% water (on a weight basis) to a mixture of starch and water increases the free water content, whereas the maximum percentage of bound water is found to be 30% on a dry basis. Higher MCs weaken interactions between water and starch. This can be explained by bonding mechanisms. At low MCs, water molecules create hydrogen bonds with hydroxyl groups of starch; these first layers of water molecules already permit small chain motions. Increasing the humidity ratio brings more water molecules, which can potentially establish bonds with the first water molecules already present in the medium. These additional layers of water contribute to moving away starch chains, which become more mobile. Whatever the humidity ratio is, water has a plasticizing effect on starch chains, the mobility of which is accentuated.

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