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Effect of Sucrose on the Thermomechanical Behavior of Concentrated Wheat and Waxy Corn Starch−Water Preparations

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The rheological behavior of concentrated starch preparations from two different origins (wheat and waxy corn) was studied in the presence of sucrose by dynamic mechanical thermal analysis (DMTA). Moisture contents ranged from 30 to 60% (w/w wsb), and samples contained 0, 10, or 20 g of sucrose for 100 g of the starch−water mixture. The storage modulus (G') changes during heating depended strongly on water content (in the moisture range studied), and the importance of these variations was dependent upon the starch type. Sucrose addition resulted in a shift to higher temperatures of the increase in G' during heating. Differential scanning calorimetry (DSC) and electron-spin resonance (ESR) analyses were performed in parallel in order to relate the viscoelastic changes to water migrations and to structural disorganization of starch. Sucrose was found to increase the gelatinization temperature and enthalpy of both starches, implying a stabilization of the granular structure during heating. The sugar−water interactions do not appear to be the only way by which sucrose delays starch gelatinization. The obtained results suggest that sugar−starch interactions in the amorphous and/or the crystalline regions of the starch granules should be envisaged.

Keywords: *Starch; gelatinization; sucrose; DSC; DMTA; ESR*

INTRODUCTION

The control of starch gelatinization in food systems is important in obtaining good quality and desirable properties of many food products. Processes such as baking of bread and cakes, extrusion of cereal-based products, thickening, and gelling of sauces and pie fillings are all dependent on proper starch gelatinization (Biliaderis et al., 1980). An important aspect of the endothermic changes associated with starch gelatinization is the role played by ingredients other than starch (and water). Because of the wide range of products that contain it, sometimes at high concentration, sucrose is of particular interest in this context. Although it is essentially considered as responsible for sweet flavor in foods, sucrose also contributes significantly to the structural and textural properties of many different cereal-based products (such as cakes or breads, cookies, and breakfast cereals) by affecting the thermomechanical behavior of the product's other ingredients. Efforts to replace sucrose with other sweetening agents in baked products thus far have been unsuccessful because the alternative, intense sweeteners, do not replace sucrose's abilities to alter the thermal setting properties of starch and/or gluten (Kim et al., 1986).

The effect of sugars on starch gelatinization has been studied by many researchers using a wide range of techniques, for example, light microscopy (Bean and Yamazaki, 1978), rheological measurements (D'Appolonia, 1972), differential scanning calorimetry (Wootton and Bamunuarachchi, 1980; Evans and Haisman, 1982; Kohyama and Nishinari, 1991; Chungcharoen and Lund, 1987; Eliasson, 1992), electron spin resonance (Johnson et al., 1990), and nuclear magnetic resonance (Chinachoti et al., 1991; Lim et al., 1992). While there is no disputing the fact that the presence of sugars increases the temperature of gelatinization of starch in water, the exact mechanism still remains unclear. Moreover, conflicting results concerning changes in gelatinization enthalpy have been reported. Spies and Hoseney (1982) suggested that sugar delays gelatinization through a combination of two independent mechanisms: lowering of the water activity of the sugar solution compared to water and interaction with starch chains to stabilize the amorphous regions of the granule. Evans and Haisman (1982) and Beleia et al. (1996) reported that both displacement of water in the starch granule by dissolved sugar and lowering A_w of the system are responsible for the increased onset temperature of starch gelatinization. Slade and Levine (1989) used a polymeric approach to discuss the effects of sugars on starch gelatinization. They suggested that sugar solutions act as an antiplasticizing cosolvent relative to water, i.e., the replacement of water by sugar diminishes the depressing effect of the aqueous phase on the glass transition temperature (T_g) of starch. Thus, greater energy is required to melt the crystals. On the other hand, Kohyama and Nishinari (1991) suggested that sugars stabilize the crystalline regions of starch and "immobilize" water molecules, whereas starch−sugar interactions where also envisaged by Lim et al. (1992) and Hoover and Senanayaka (1996).

Accordingly, the objective of this study was to try to elucidate the mechanism(s) operative in the gelatinization of starch in the presence of sucrose. Therefore, the experiments were designed to study the rheological behavior of starch dispersions at various water contents during a thermal treatment corresponding to the temperature range used in a thermal processing of a cereal product. To evaluate the relative contributions of amylose and amylopectin, two different starch types were

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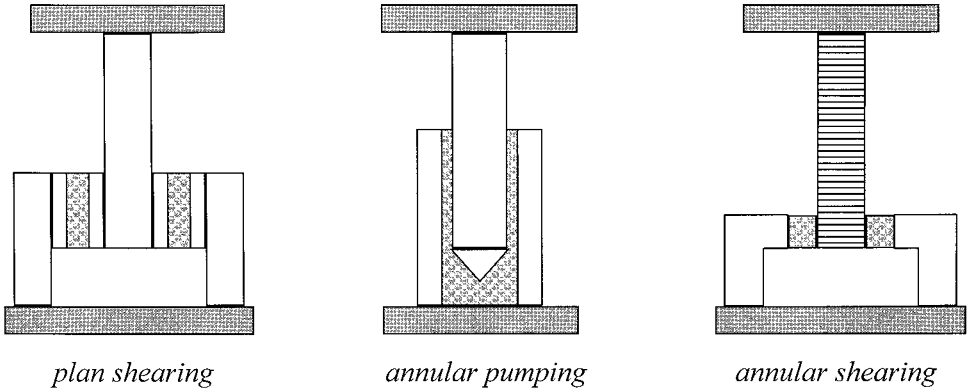

Figure 1. Schematic presentation of the different devices used in DMTA.

used: wheat starch, containing 25% amylose and 75% amylopectin, and waxy corn starch, essentially composed of amylopectin (1% amylose). Sugar concentrations were chosen in a way to be sure that sucrose is always dissolved and no phase separation apparently occurs; indeed, sucrose functionality strongly depends on its physical state. The use of a mixture design allowed optimization of the experiments. Dynamic mechanical thermal analysis (DMTA) was used to observe the viscoelastic behavior of the dispersions during heating. Differential scanning calorimetry (DSC) and electron spin resonance (ESR) analyses were performed in parallel with DMTA measurements, to relate the viscoelastic changes to structural disorganization of starch and water migrations, and to yield information about component interactions in the starch-sugar-water system.

MATERIALS AND METHODS

Sample Preparation. Both wheat and waxy corn starch were provided by Roquette Frères (Lestrem, France). Sucrose (analytical grade) was purchased from Merck (Darmstadt, Germany). Preparations were made with 18 g of starch, and distilled water/or sugar solution was added to give the selected moisture (30, 37.5, 45, and 60% w/w wet basis) and sugar (0, 10, or 20 g of sucrose for 100 g of the starch−water mixture) contents. In the case of sucrose addition, the water-to-starch ratio was kept constant. The samples were manually blended until a homogeneous mixture was obtained and then allowed to stand for at least 1 h at room temperature in a closed environment (the more liquid-like samples being magnetically stirred) before measurements. All tests in this study were performed at least in triplicate; the mean and standard deviations were calculated.

Moisture Content. A few grams of preparations were weighed and placed in an oven at 105 °C for 5 h and then in a desiccator for 1 h before being weighed again. Moisture contents are expressed in grams of water per 100 g of water−starch mixture (even in the presence of sucrose).

Water Activity. Water activity (A_w) was measured with a FA$_{-ST}$/1, GBX hygrometer, using the dew point technique. The average standard deviation was calculated to be 0.5%.

Differential Scanning Calorimetry (DSC). The DSC measurements were carried out with a Perkin-Elmer DSC-7 instrument, calibrated with azobenzene and indium in the positive temperature range. Starch-based preparations (40−85 mg) were weighed in stainless steel DSC pans, which were then hermetically sealed. Samples were heated from 25 to 160 °C at a rate of 10 °C/min. An empty pan was used as the reference. Pans were reweighed at the end of the run to ensure that water was not lost during heating in the DSC. For each endotherm, the overall gelatinization enthalpy ΔH (expressed as J/g of dry starch) and the onset, peak, and end temperatures were reported. Moreover, the partial melting enthalpy was calculated from the onset of the endotherm to 85 °C (per 1 °C step) to plot the curve representing the cumulated enthalpy values versus temperature. The average standard deviation for the enthalpy determination was calculated to be 8% for wheat starch and 8.9% for waxy corn starch.

Dynamic Mechanical Thermal Analysis (DMTA). The small amplitude oscillatory rheological measurements were performed with a Viscoanalyzer (Metravib R.D.S., Limonest, France), equipped with a thermocontrol unit. Three different solicitation modes were used for this study: plan shearing for the more solid-like samples and annular pumping + annular shearing for the more liquid-like samples (for wheat starch above 37.5% water and for waxy corn starch above 45% water). These different modes are showed in Figure 1.

Plan Shearing. Two cylindrical samples (4 mm height × 20 mm diameter) were glued with cyanoacrylate glue (Amatron, England) on outside and inside plates. The inside plates were connected to a sensor, which regulated the amplitude and the frequency of the strain, whereas the outside plates were connected to a sensor, which registered the stress.

Annular Pumping. When samples tend toward liquid-like behavior, plan shearing cannot be used any more, particularly because of creep. In that case, some milliliters of sample were poured into a cylindrical tube with a piston in the center, oscillating with a small amplitude. The tube was glued with cyanoacrylate glue (Amatron, England) onto the sensor registering the stress. The piston was screwed into the sensor, which regulated the amplitude and the frequency of the strain.

Annular Shearing. During the thermal treatment, liquid-like samples became more rigid and annular pumping was not efficient anymore (not reliable modulus as a result of slippage). So annular shearing was used from 52 to 53 °C up to 85 °C as well as for the cooling. This device consisted of coaxial cylinders connected to the sensors. The gap between the two cylinders was 2 mm. The starch dispersion, poured in the cell in the liquid state, before heating, was held in the annular space by capillary force.

To prevent drying during analysis, samples were coated with silicone grease (Rhône Poulenc, France) for plan shearing or with a mineral oil (Nachet, France) for annular pumping and annular shearing. The strain and frequencies were set at 3 μm and 5, 10, 20, and 40 Hz, respectively. Measurements were made in the linear region of viscoelasticity, in which the amplitudes of stress and strain are proportional to each other. Starch samples were heated from 25 to 85 °C (1.5 °C/min) and then immediately cooled to room temperature (−1.5 °C/min) during the analysis. The VA2000 software package provided by Metravib R. D. S. allowed calculation of rheological parameters including storage modulus (G'). The average standard deviation for all the tests was calculated to be 10.4% for wheat starch and 10.2% for waxy corn starch.

Electron Spin Resonance (ESR). The starch-based preparations, being diamagnetic, stable paramagnetic species, must be introduced into the system for ESR studies. We used the 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy (TEMPOL) nitroxide radicals (Aldrich Chemicals, France) (Figure 2),

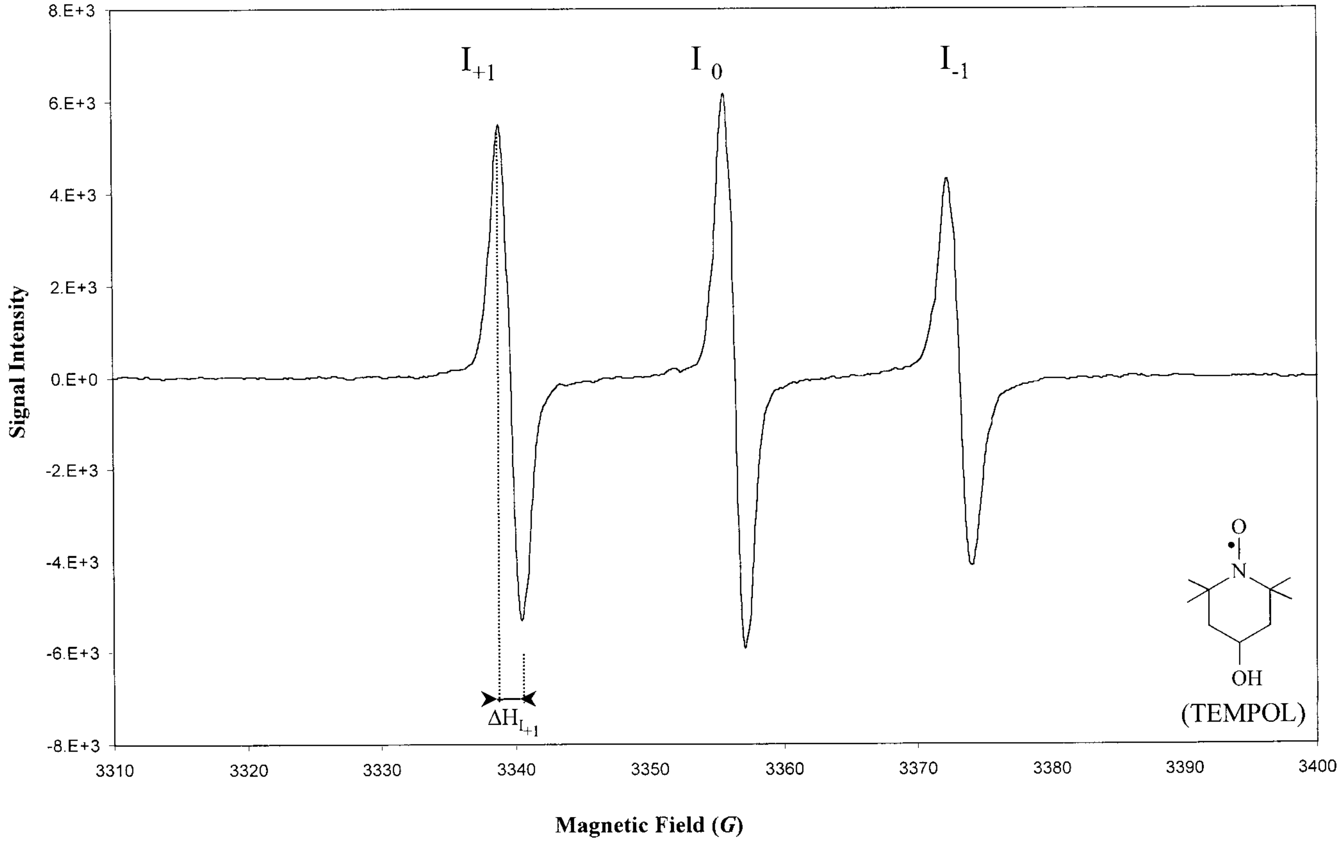

Figure 2. Typical ESR spectrum of a nitroxide free radical (TEMPOL).

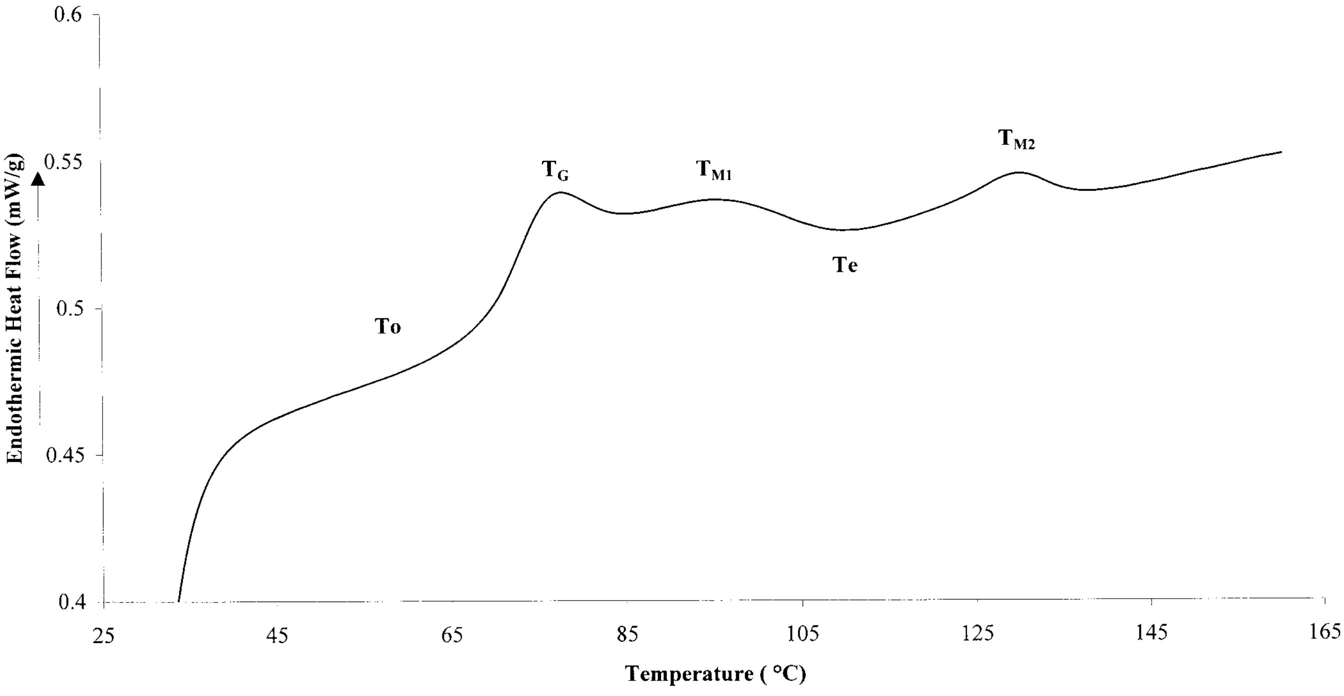

Figure 3. DSC thermogram of wheat starch at 45% water content and 20 g added sucrose. T_o, T_G, T_{M1}, and T_e are, respectively, onset, first peak, second peak, and end temperature of gelatinization. M_2 indicates the amylose–lipid complexes melting peak.

which were dispersed in the aqueous phase (spin probing). Samples were prepared by adding 300 μL of a TEMPOL aqueous solution (2 mg/mL) to distilled water or sugar solution, before being manually mixed to starch (approximate final TEMPOL concentration: 2.4×10^{-7} mol/g of dry starch). The samples were then equilibrated at room temperature by gentle stirring for 24 h before measurements. This technique was applied only to samples with 60% w/w water. Sealed capillary tubes containing the starch-aqueous solution-probe dispersions were placed in a 3 mm diameter ESR sample quartz tube. ESR spectra were recorded with a Bruker EMX spectrometer (Bruker, France), equipped with a nitrogen gas flow variable-temperature controller. The operating microwave frequency and center magnetic field were, respectively, at about 9.42 GHz and 3357 G. The microwave power was 10 mW. Any saturation phenomenon was avoided. The scan rate, time constant, and modulation amplitude were adjusted so that distortion of the spectra was avoided. For all experiments, the temperature was

Table 1. Water Activity (A_w) Measurements of Starch Dispersions at Room Temperature

water content (w/w)	sucrose content (g)					
	wheat starch			waxy corn starch		
	0	10	20	0	10	20
30	0.966	0.957	0.913	0.961	0.919	0.909
37.5	0.977	0.958	0.940	0.977	0.942	0.922
45	0.983	0.958	0.942	0.980	0.957	0.943
60	0.991	0.989	0.958	0.981	0.965	0.959

varied stepwise every 2 °C between 25 and 85 °C and the samples were allowed to reach temperature equilibrium (3 min) before recording the spectra. The rotational correlation time (τ_c) of the paramagnetic radical (representing the time during which the molecule remains in a given orientation) was determined as

$$\tau_c = (6.65 \times 10^{-10})(\Delta H_{I+1})[(I_{+1}/I_{-1})^{1/2} - 1] \qquad (1)$$

deduced from the Freed and Fraenkel (1963) theory, where I_{+1} and I_{-1} are the peak to peak height of the lines I_{+1} and I_{-1}, respectively, and ΔH_{I+1} is the width of the I_{+1} line (Figure 2). The rotational diffusion coefficient (D_{rot}), representing the probe mobility, is inversely proportional to τ_c:

$$D_{rot} = 1/(6\tau_c) \qquad (2)$$

Conventional ESR is sensitive to mobility in the range $10^{-11} < \tau_c < 10^{-7}$ s. The average standard deviation was calculated to be 8.8% for wheat starch and 8.1% for waxy corn starch.

RESULTS

Water Activity (A_w) Measurements. One method of measuring the water's reactive ability in a solution is to determine the A_w, i.e., the ratio of the vapor pressure of the solution to the vapor pressure of pure water, which indicates the chemical potential of the water. As shown in Table 1, addition of sucrose decreased the A_w value of starch preparations, and this effect was more pronounced at lower water contents. Moreover, the higher the sucrose content, the more pronounced the effect of water content on water activity. A_w of all samples was measured at room temperature.

Melting of Ordered Regions Studied by DSC. Figure 3 shows an example of a DSC curve obtained for wheat starch with 45% water and 20 g of sucrose. The first endotherm ($G + M_1$) was assigned to amylopectin double helix dissociation and crystals melting, whereas the second one (M_2) was attributed to amylose−lipid complexes melting. Only preparations with 60% water and 20% sucrose showed a single (G) endotherm. At lower moisture and sugar contents, M_1 was developed as a shoulder of G at a higher temperature. The biphasic endotherm has been characterized by the onset (T_o), first peak (T_G), second peak (T_{M1}), and end temperature (T_e) of gelatinization.

T_o, T_G, and T_e are plotted as response surfaces in Figure 4. The x and y axes represent the sucrose and water-to-starch ratio variables, respectively. When increasing levels of sucrose were added to wheat starch, T_o, T_G, and T_e all increased, and this effect was greater at lower water-to-starch ratios. It can be seen (Figure 4) that T_e is not as much affected as T_o and T_G by the addition of sucrose but depends strongly on the water content. Moreover, when the sucrose concentration increased, the shoulder on the high-temperature side of the endotherm progressively disappeared. Thus, sucrose addition results also in a narrower gelatinization temperature range. The third transition (M_2) also shifted to higher temperatures in the presence of sucrose (results not shown).

Num.	T_e (°C)
1	98.0
2	102.0
3	107.0
4	111.0
5	116.0
6	120.0
7	125.0
8	130.0
9	134.0
10	139.0
11	143.0

R=1.000

Num.	T_G (°C)
1	62.0
2	65.0
3	68.0
4	71.0
5	74.0
6	77.0
7	80.0
8	83.0
9	86.0

R=1.000

Num.	T_o (°C)
1	44.0
2	48.0
3	52.0
4	56.0
5	60.0
6	64.0

R=1.000

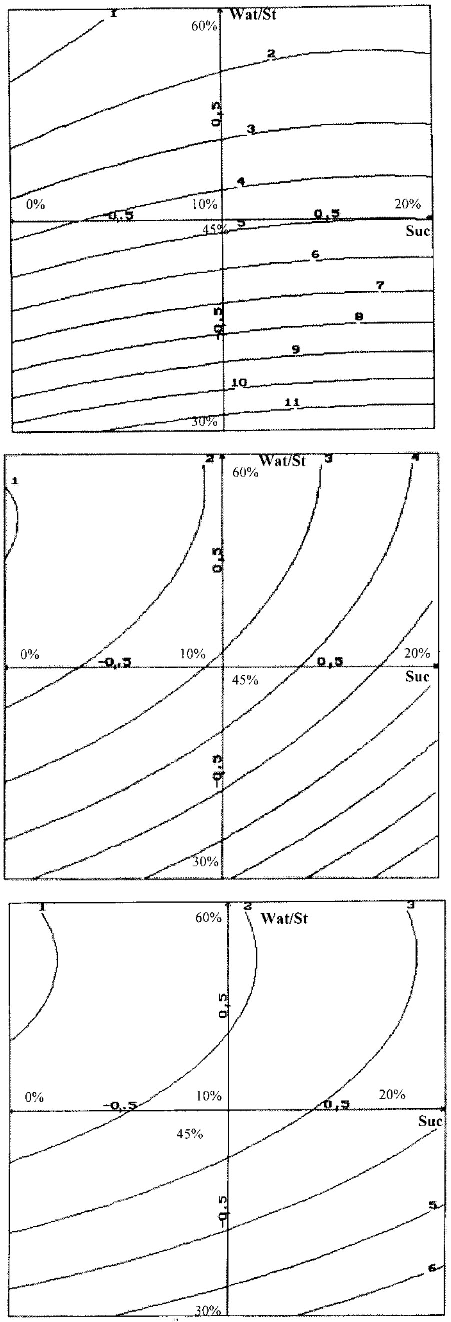

Figure 4. Influence of water and sucrose content on T_o, T_G, and T_e temperatures of gelatinization of wheat starch (graphics obtained with the NEMROD software).

Partial melting enthalpy of wheat starch up to 85 °C is displayed in Figure 5. The higher the moisture content, the faster and more pronounced the melting of starch ordered zones in the temperature range considered. When sucrose was added to the starch−water system (Figure 6), the melting of the amylopectin crystals shifted to higher temperatures and the total enthalpy of gelatinization (ΔH) increased. At 60% w/w moisture content, ΔH was of 14.3 ± 0.3 J/g of dry starch without added sucrose, whereas it was of 15.8 ± 0.4 J/g of dry starch at 20% sucrose.

Waxy corn starch showed only the first endothermic transition (no amylose−lipid complexes). The influence

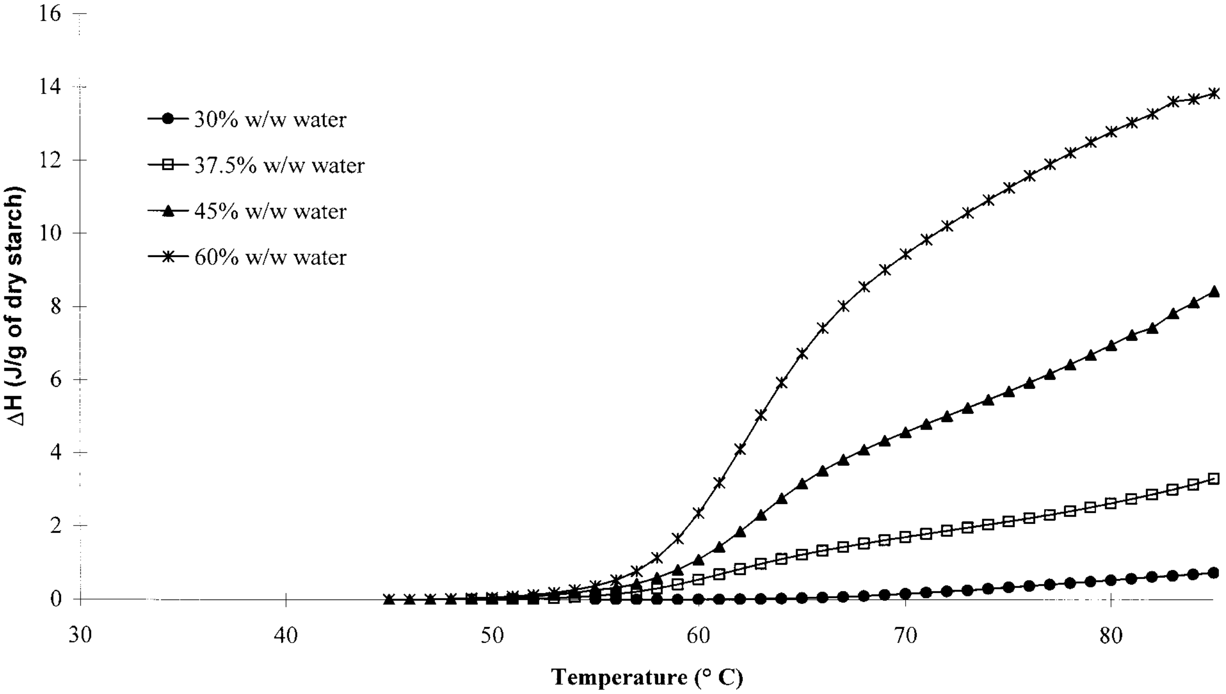

Figure 5. Partial melting enthalpy for wheat starch dispersions as a function of temperature (moisture contents expressed on a wet starch basis).

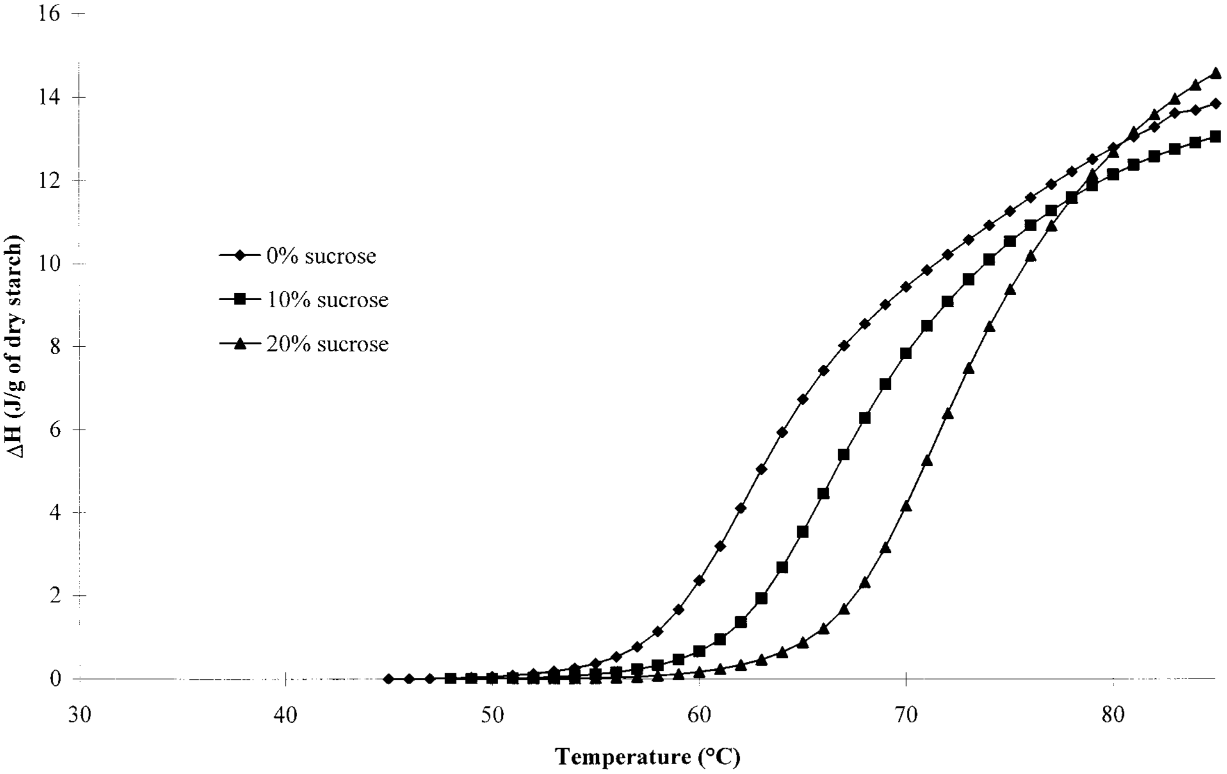

Figure 6. Effect of sucrose on partial melting enthalpy of wheat starch dispersions at 60% w/w (wsb) moisture content.

of sucrose on this transition was similar as for the wheat starch system (results not shown): increase in transition temperature and in ΔH. However, the melting of waxy corn starch ordered zones began at a higher temperature, in comparison with wheat starch (Figure 7), and the melting enthalpy was higher also, in the presence as well as in absence of sucrose.

Viscoelastic Behavior of Starch–Water–Sucrose Preparations. Changes in the storage modulus (G') of 0% sucrose wheat starch systems as a function of water content, determined during heating and cooling, are shown in Figure 8. The observed changes in modulus were not frequency dependent in the frequency range considered; thus, only the 5 Hz results are shown and discussed.

The initial storage modulus ($G'_i = G'$ at 25 °C) increased as moisture content decreased. For dispersions with 30–45% moisture content, G'_i was relatively high (2×10^5–2×10^6 Pa), whereas it was very low (0.5 Pa) for the 60% moisture content dispersions. Upon

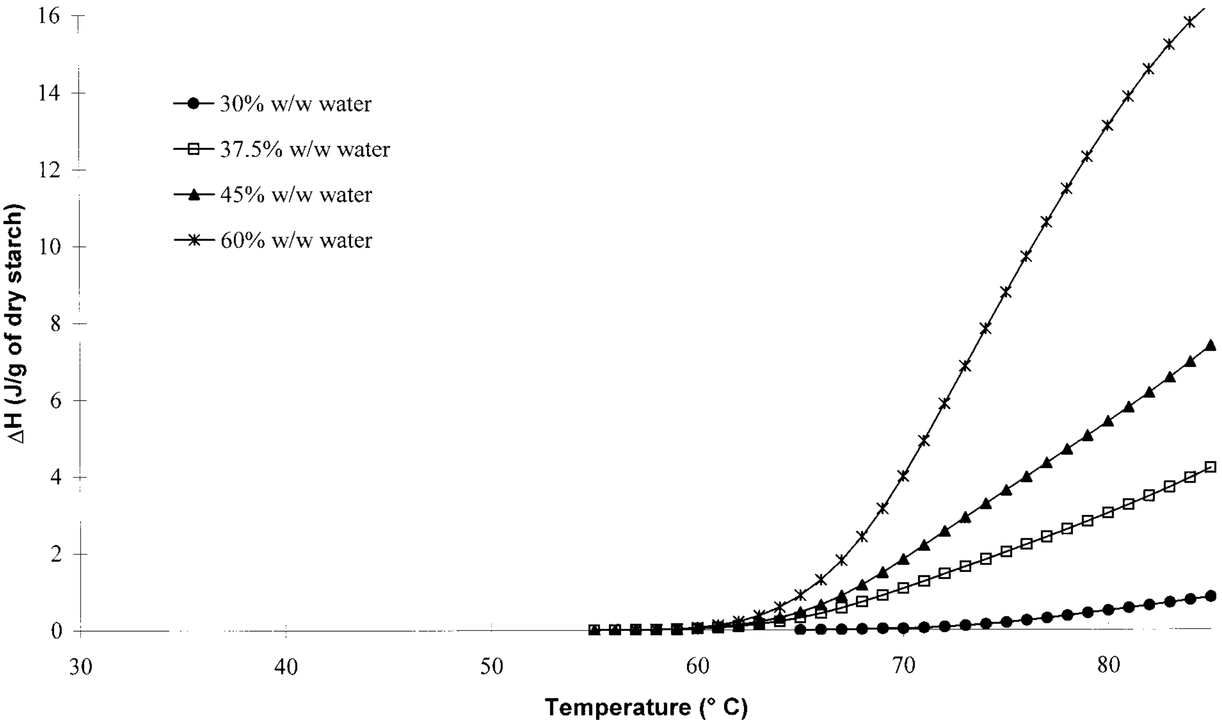

Figure 7. Partial melting enthalpy for waxy corn starch dispersions as a function of temperature (moisture contents expressed on a wet starch basis).

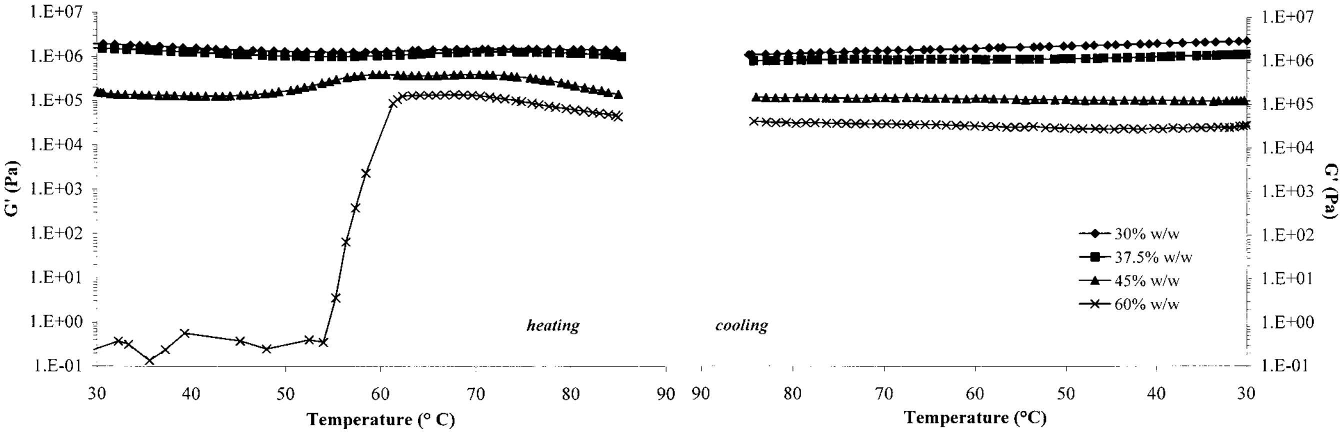

Figure 8. Storage modulus changes for wheat starch dispersions as a function of water content (w/w wsb) during heating and cooling.

heating, the more concentrated dispersions (moisture content ranging from 30 to 45%) did not show important viscoelastic changes. The storage modulus G' decreased slightly up to 45−60 °C, then an increase was observed up to a maximum at about 60−75 °C, followed by a decrease until the end of heating. For samples with 60% moisture, G' increased very strongly from 55 °C and reached a maximum value at around 68 °C, then decreased slightly up to 85 °C. These results are in good agreement with those of Rolée and Le Meste (1998). During cooling, G' increased slightly.

The G' curves of wheat starch−sucrose blends exhibited features similar to that of wheat starch with different water contents and are not shown here. However, the addition of sucrose was found to delay the G' increase during heating (Figure 9); it did not significantly affect the G' increase on cooling.

Waxy corn starch showed no increase in G' during heating (in the presence as well as in absence of sucrose), except for the 60% water preparations (Figure 10). For the samples with 37.5 and 45% moisture, the storage modulus decreased slightly up to 70 °C and then more steeply until the end of heating. Samples with 60% moisture content showed an increase in G', starting slightly from 25 to 60 °C then strongly from 60 to 70 °C. At 70 °C, G' started to decrease. On subsequent cooling, G' increased slightly. Moreover, waxy corn starch gave stiffer and more crumbly preparations than wheat starch (higher initial modulus). Because of this difficulty to form the samples, it was not possible to perform measurements at 30% water. The effect of added sucrose on G' evolution was similar to that observed for wheat starch (results not shown).

Motional Behavior of TEMPOL in Starch−Sucrose−Water Dispersions Studied by ESR. For all the sucrose contents, the ESR spectra of TEMPOL in 60% moisture content wheat or waxy corn starches displayed a symmetrical triplet signal (in the temperature range studied from 25 to 85 °C), similar to that of the probes in an aqueous solution. These spectra

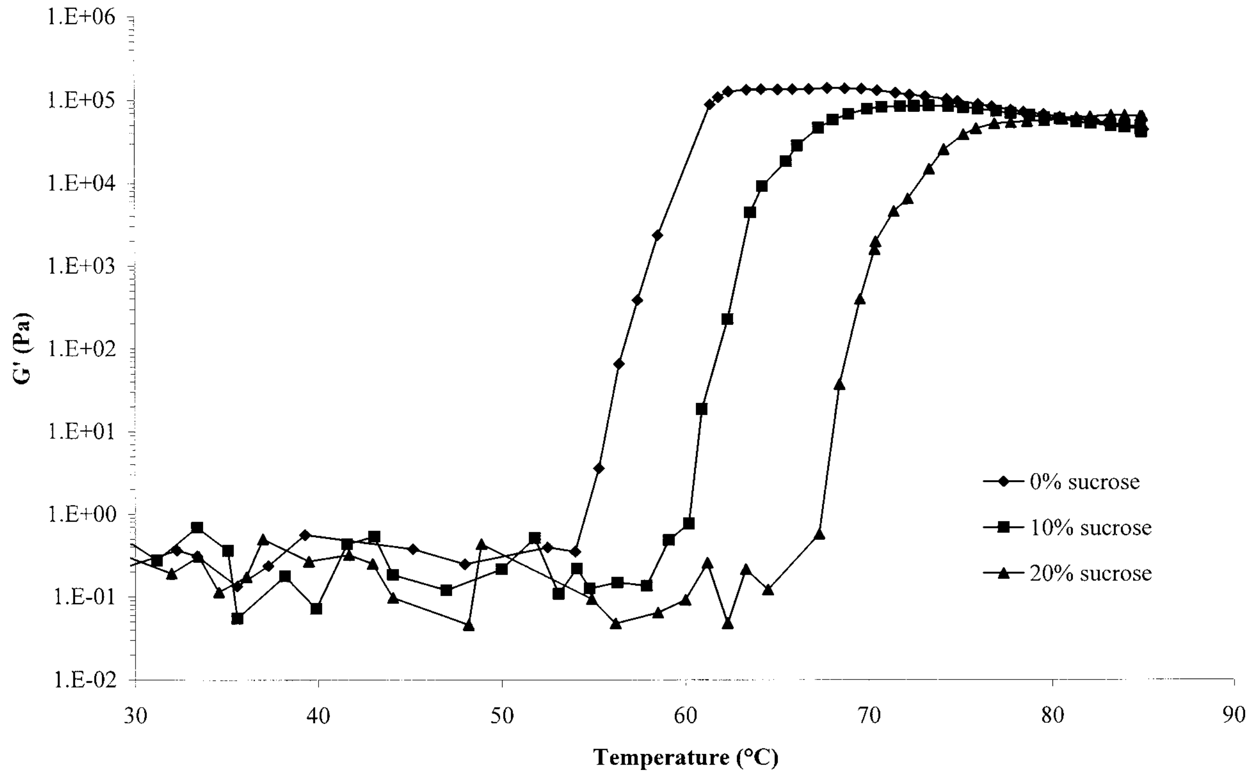

Figure 9. Effect of added sucrose on the storage modulus of 60% water content (w/w wsb) wheat starch dispersions during heating.

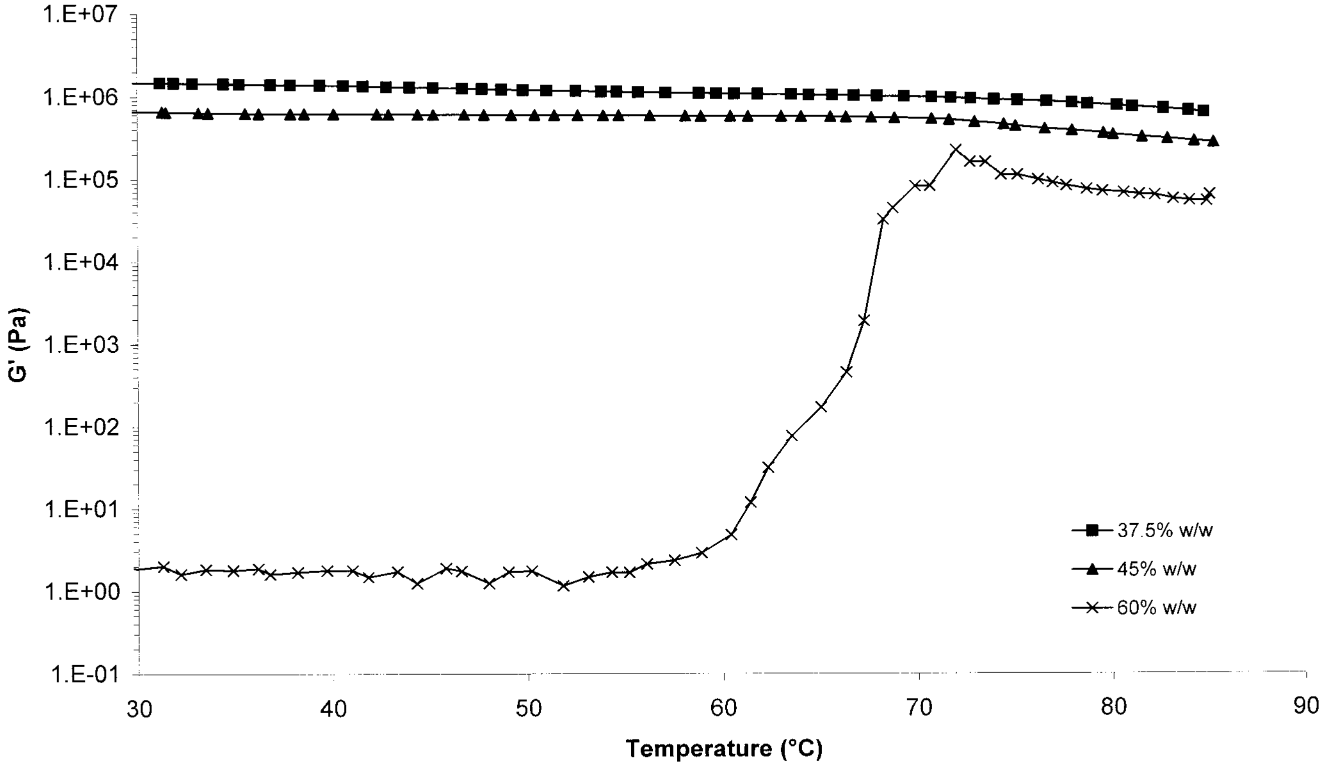

Figure 10. Storage modulus changes for waxy corn starch dispersions as a function of water content (w/w wsb) during heating.

represent rapid isotropic motions. However, the calculated rotational diffusion coefficients (D_{rot}) for starch–sucrose–water systems (Figure 11) were found to be lower than the values for the probes in sucrose–water solutions (at 25 °C $D_{rot} \cong 10^{10}$ s^{-1} for the 20% sucrose solution).

For wheat starch, a slight decrease in D_{rot} was observed from 25 to 45 °C, followed by a more pronounced decrease up to about 60 °C. Then, D_{rot} gradually increased with further heating to 85 °C. In the presence of sucrose, and at room temperature, the overall D_{rot} gradually increased with the concentration of the sucrose–water solution. Moreover, the temperature induced decrease in D_{rot} was shifted to higher temperatures, but the same minimum value as for the starch-water system alone was attained ($\cong 2.50 \times 10^9$ s^{-1}).

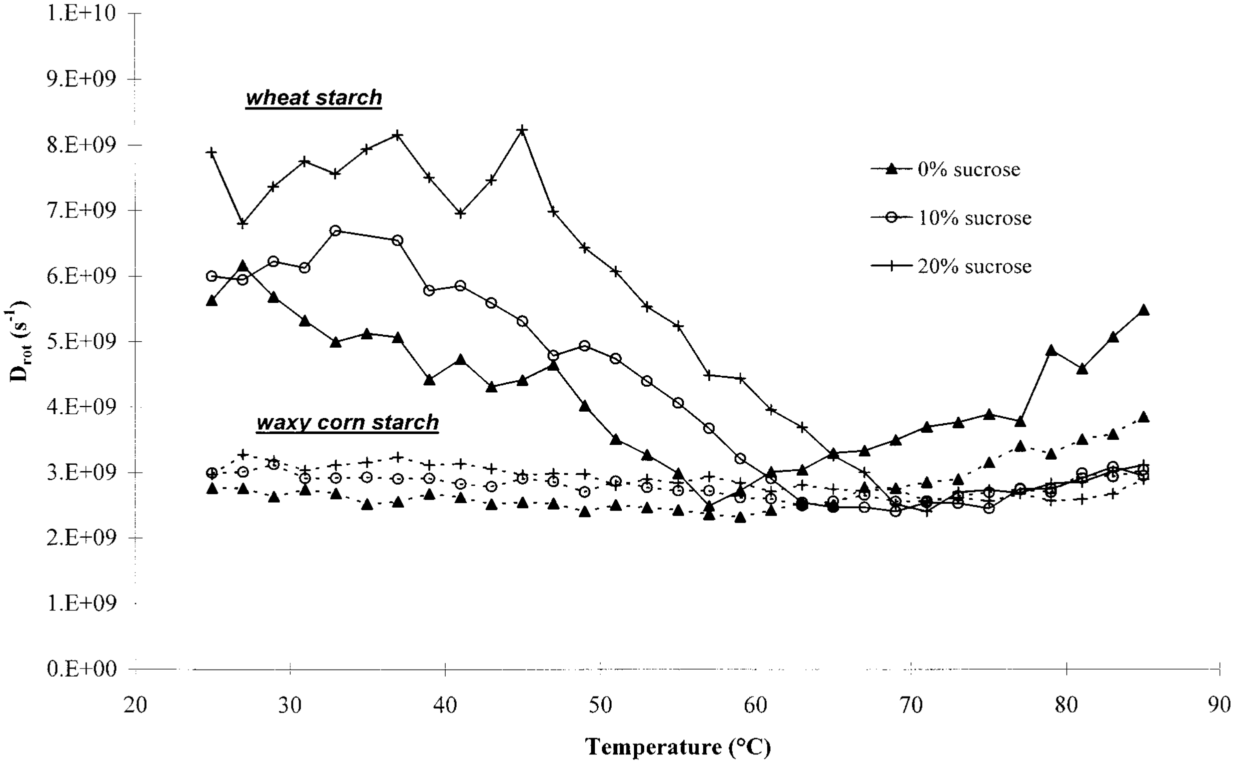

Figure 11. Effect of sucrose on the rotational diffusion coefficient of spin probes (TEMPOL) dispersed in the aqueous phase of 60% water content (w/w wsb) wheat and waxy corn starch dispersions during heating.

Above this temperature, the gradual increase of D_{rot} till 85 °C indicated a smaller and less rapid increase in probe mobility than for dispersions without added sucrose.

In presence of sucrose, the D_{rot} evolution as a function of temperature, demonstrated a similar evolution for the waxy corn starch preparations with the same moisture content (Figure 11). However, a much lower probe mobility than for wheat starch was evidenced, and the sucrose effect was not significant.

DISCUSSION

Effect of Water. DSC curves were strongly affected by the water content. Previous studies (Donovan, 1979; Biliaderis et al., 1980) have already shown the major role played by the water−starch ratio. When the water level is reduced, crystal melting starts at approximately the same temperature, but the gelatinization temperature range widens, so less crystallites disappear within the temperature range considered (25−85 °C) (Figures 5 and 7).

The storage modulus measured at 25 °C, as well as its evolution during heating, also strongly depend on water content. DMTA measurements (Figures 8 and 10) showed that the more concentrated dispersions (30−45% moisture) exhibited first a high initial modulus, which could be explained by the tight packing of compressed granules, then only slight viscoelastic changes upon the heating−cooling cycle, which might be related to the limited structural disorganization in the temperature range considered and to the limited swelling of the individual granules, restricted by the space available.

The strong rigidity increase observed from about 55 °C for dispersions with 60% moisture could be attributed to the progressive swelling of starch granules that begin to fill the sample volume still available, thus inducing a transition from a liquid system, with particles dispersed in a continuous aqueous liquid phase, to a system nearly packed with more or less deformable particles. According to Rolée and Le Meste (1997), below close-packing, the shear modulus appears to be independent of the particle size and increases with the volume fraction ϕ of the filler, in accordance with an empirical equation of Eilers and van Dijk (Ferry, 1980). According to this model proposed for hard spheres, when granules start to touch each other, G' increases dramatically and tends toward an asymptote corresponding to ϕ_m (ϕ_m is the maximum volume fraction corresponding to close-packing of starch granules).

In fact, we observed that G' reached a maximum and then it decreased up to 85 °C. In this range of temperature, DSC results (Figures 5 and 7) showed evidence of melting/dissociation of ordered zones. The decrease in rigidity (G') was more pronounced for the more hydrated samples, as expected from the observed effect of water on the melting behavior. In agreement with the suggestion of Lii et al. (1996), continuous heating provides the energy to break down the residual crystalline structure of the granule, causing G' to drop down. Moreover, when the granules are in contact the friction forces may lead to a deformation of the granules and a decrease in the strength of the transient network formed (Champenois et al., 1998).

The increase in the rigidity of the dispersions during cooling is mainly ascribed to formation of a gel in the aqueous continuous phase. It is known that, during heating, some amylose molecules can leach out of the granules, due to the incompatibility of amylose and amylopectin and the higher mobility of amylose compared to amylopectin (Keetels, 1995). The gelation of solubilized amylose in the continuous phase may form a hardening gel between the granules. However, the contribution of amylopectin in the short-term hardening is not excluded. No significant effect of the water content on the increase in stiffness of starch dispersions on cooling was observed.

Effect of Sucrose. As anticipated, when sucrose was added into the starch dispersions, the T_o, T_G, and T_e values increased with the increment of sucrose concentration (Figure 4). Even when DSC results are plotted as a function of total water content (w/w wb), sucrose still raises significantly the gelatinization temperature of starch. This effect was even more pronounced at lower water-to-starch ratios. This was also observed by Chungcharoen and Lund (1987) and Eliasson (1992) when sucrose was added to rice or potato starches, respectively. However, T_e was only slightly raised by sucrose (whereas it was strongly affected by the water−starch ratio), resulting in a narrower gelatinization temperature range. The enthalpy of gelatinization (ΔH) was also found to increase in the presence of sucrose.

Most workers report a similar increase of the gelatinization temperature in the presence of sugars (Evans and Haisman, 1982; Kim et al., 1986; Buck and Walker, 1988; Kohyama and Nishinari, 1991; Eliasson, 1992; Lii et al., 1997). Different approaches have been used to explain the delay of starch gelatinization in the presence of sugar. Some have purely thermodynamic grounds (Lelievre, 1976; Evans and Haisman, 1982); they thus assume that the system is at equilibrium. These approaches rely on the Flory−Huggins theory of polymer melting and consider the volume fraction of diluents, the water activity, or the ratio of water activity over the water volume fraction as controlling parameters. The theoretical models also take into consideration the specific interaction parameters between the different components of ternary systems.

Indeed, the increase in the gelatinization temperature has been attributed to the sugar's ability to limit the availability of water for starch, i.e., to reduce the chemical potential of water (D'Appolonia, 1972; Hoseney et al., 1977). Thus, reactions involving water may require more thermal energy than they would in pure water (Spies and Hoseney, 1982; Beleia et al., 1996). However, A_w does not appear to be the only factor delaying starch gelatinization in sucrose solutions. At equal A_{ws}, salts (i.e., NaCl) delay gelatinization much less than does sucrose (Spies and Hoseney, 1982; Evans and Haisman, 1982). Moreover, it can be seen from Figure 4 that samples with the same A_w, but with different sucrose contents (i.e., 45 g of water/10 g of sugar−60 g of water/20 g of sugar wheat starch samples in Table 1), did not exhibit similar gelatinization temperatures. This suggests that some factors, other than A_w, also affect starch gelatinization in sucrose solutions and probably indicates some specific interactions between starch and solutes.

There is no doubt that when sucrose is added to the system it "binds" some of the water and, thus, lowers the amount of water available for starch hydration and gelatinization. However, as reported above (see Effect of Water), the level of water does not alter T_o and T_G (above a water content of 35% w/w wb) (Donovan, 1979), although the upper end (T_e) of the gelatinization range is moved to higher temperatures with decreasing water content. In contrast, when sucrose was added, T_o and T_G both increased, which should not be the case if the only function of sucrose would be to decrease the amount of water available for starch hydration. This was also pointed out by Spies and Hoseney (1982) and Kim et al. (1986). In fact, when the shape of the gelatinization endotherm is regarded, the addition of sucrose seems to be consistent with additional solvent in the system: instead of broadening, the base of the peak narrows somewhat when sucrose is present, and the double endotherm changes into a single one under certain conditions. Ghiasi et al. (1983) reported that sucrose loses its ability to bind water as the temperature increases. Apparently, water becomes available for starch gelatinization and may explain the narrowing of the gelatinization temperature range in the presence of sucrose.

Evans and Haisman (1982) proposed the following equation based on the Flory−Huggins theory to predict the direction and relative magnitude of the effect of many different solutes on the gelatinization temperature:

$$1/T_m - 1/T^\circ_m \cong (T^\circ_m - T_m)/(T^\circ_m)^2 \cong K[1 - \ln(a_w/v_1)] \quad (3)$$

T_m is the melting point of the system under consideration, T°_m the melting point of the pure crystalline polymer, a_w the water activity, v_1 the volume fraction of the water, and K a constant. The onset and end temperatures of gelatinization of both wheat and waxy corn starches are plotted as a function of the logarithm of water activity divided by the volume fraction of water in the dispersions in Figure 12. It can be observed that the theory fits reasonably well the experimental data when the end temperature is considered, which means that the main variable affecting T_e is the ratio a_w/v_1. Nevertheless, some discrepancy is observed with the onset temperature. This could be due to the fact that thermodynamic equilibrium may be reached at the end of the gelatinization process, whereas other factors may affect the beginning of the endothermic event.

A kinetic approach has also been proposed to explain the influence of sugars on starch gelatinization. Native starch being a partially crystalline polymer, water acts as a plasticizer, which depresses the glass transition temperature (T_g) of the amorphous regions and enhances the mobility of chains, thus facilitating the crystallites melting. Depending on the relative proportions of water, sugar, and starch, sugars can be considered as having either a "plasticizing" or an "antiplasticizing" effect on starch. The antiplasticizing effect of sugars, when sugar replaces water in recipes, has been used to explain the delay in the onset of starch gelatinization transitions (Slade and Levine, 1989). In our experiments, sucrose addition was accompanied by an increase in the volume fraction of aqueous phase. However, using the Couchman−Karasz equation (Couchman and Karasz, 1978) to predict the influence of this aqueous phase on the glass transition temperature (T_g) of the preparation, it appears that the sugar solution acts as an antiplasticizer (increase in T_g) comparatively to the preparation with the same starch−water ratio but without sugar. This antiplasticizing effect, i.e., reduction in the flexibility of the amorphous regions, may contribute to the delay of the gelatinization process.

The results concerning the gelatinization enthalpy are conflicting: ΔH has been reported to be unaffected by the addition of sugars (Evans and Haisman, 1982; Eliasson, 1992), but increased (Kim et al., 1986; Kohyama and Nishinari, 1991; Lii et al., 1997) as well as

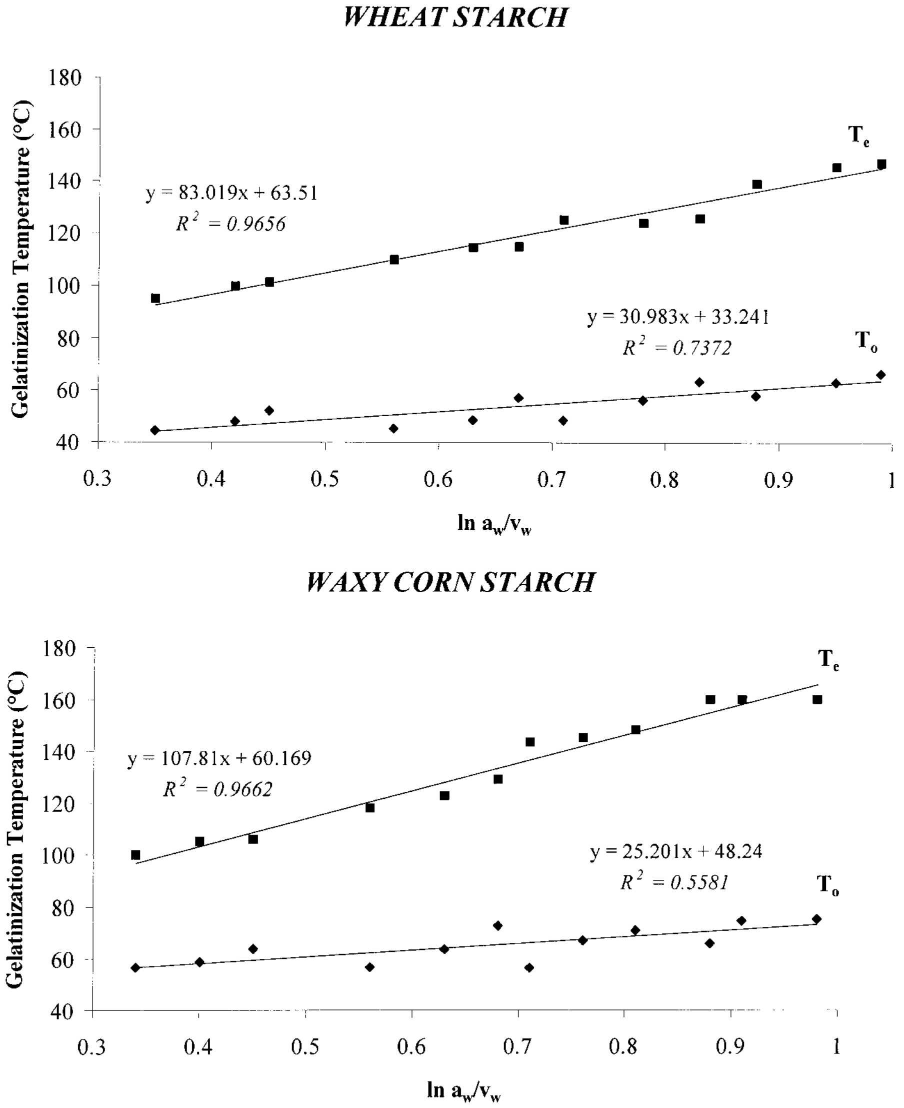

Figure 12. Onset and end temperatures of gelatinization of wheat and waxy corn starches vs the logarithm of water activity divided by the volume fraction of water.

decreased values (Wootton and Bamunuarachchi, 1980; Chungcharoen and Lund, 1987; Buck and Walker, 1988) have also been reported in the presence of sugar. In the present study, the water-to-starch ratio was kept constant when sucrose was added, whereas in other investigations the aqueous phase-to-starch ratio was kept constant. If the sugar addition also means a decrease in water addition, ΔH might very well decrease. Thus, the differences in sample preparation, starch-water ratio and starch variety or granular structure might explain the different results obtained concerning the enthalpy of gelatinization.

Nevertheless, the influence of sugars on starch hydrothermal behavior cannot be completely explained by the effect of sucrose on the properties of water and sucrose-starch interactions should also be considered. The increase in melting enthalpy and temperature of starch crystallites in the presence of sucrose implies a stabilization of the semicrystalline structure during heating. Hoover and Senanayake (1996) observed a similar increase of gelatinization enthalpy of oat starches in the presence of sugars and postulated an effect of starch−sugar interactions. Moreover, they also observed a decreased amylose leaching (at 95 °C) in the presence of sugars, suggesting that sugar molecules penetrate the starch granule and interact with amylose chains in the amorphous regions (cross-link formation between hydroxyl groups of sugar molecules with those on adjacent amylose chains). The formation of “sugar bridges” would decrease starch chain flexibility and granular swelling. Consequently, the ability of the amorphous regions to destabilize starch crystallites during gelatinization (Donovan, 1979) would be inhibited (Hoover and Senanayake, 1996). Moreover, Sobczynska et al. (1990) concluded from ^{17}O and ^{13}C NMR data that sucrose should interact with the glucose residues of the starch to increase the chain rigidity before the onset of gelatinization, creating a need for more energy to break the starch−sucrose−water bonds. Furthermore, Hansen et al. (1989) have shown by ^{13}C NMR studies the interaction sites to occur with G1, G5, G6, F1, and F6 carbon atoms (G-glucose moiety; F-fructose moiety) of the sucrose molecule and that the native granular structure likely was necessary for these interactions to occur. Finally, Tomasic et al. (1995) interpreted the sugar−starch interactions in terms of formation of starch−low-molecular sugar complexes. These authors clearly stated that the increase in enthalpy and temperature of gelatinization should be due to the capacity of starch to form inclusion complexes with many mono-, di-, and trisaccharides. The formation of these inclusion complexes is governed by the swelling of starch, which opens the interior of granules for weakly penetrating sugar molecules and by the conformational fitness of sugar molecules and glucose units of starch.

Similarly, the rheological behavior of starch-sucrose mixtures did not seem to be controlled by water availability as expressed by A_w (samples with the same A_w did not show similar viscoelastic behaviors), but rather to be sensitive to the amount of aqueous phase. The delay of G' increase during heating of starch dispersions in the presence of sucrose (Figure 9) corresponds to the delay of starch gelatinization observed by DSC. This shift to higher temperatures can be related to the greater volume of aqueous phase present in the dispersion. When sucrose dissolves in water, each gram creates about 0.6 cm^3 of additional volume (Hoseney and Rogers, 1994). In fact, the higher the sucrose concentration in the starch dispersion, the lower the initial value of ϕ, the volume fraction occupied by the granules ($\phi_{0\%} > \phi_{10\%} > \phi_{20\%}$), and hence, the later the preparation will reach the concentration corresponding to ϕ_m (close-packing) during heating. It has been shown (Savage and Osman, 1978; Lelievre, 1984; Hoover and Senanayake, 1996) that the presence of sucrose, at a concentration greater than 20% w/w, inhibits granular swelling (sucrose > glucose > fructose). These results are in good agreement with the findings of Lii et al. (1997), who reported that addition of polyols to the starch-water system, results in a higher temperature of the initial G' increase and the G' maximum due to delaying and restricting the swelling of starch granule.

To detect any change in the interactions occurring at the molecular level, we used the ESR spin probe technique, which gives a measure of probe mobility in the aqueous phase (Figure 11). At 60% moisture content, the water−starch system is discontinuous. The granules contain some water and are also surrounded by an aqueous continuous phase. The spin probe, added to this system, is distributed throughout both continuous and dispersed phases (because of its small size: MW = 172, the probe can diffuse inside the granules) and, therefore, may experience two different molecular environments. Thus, the ESR spectrum is expected to reflect the properties of the aqueous phase both within and outside the granules. The rotational diffusivity of the probe is inversely proportional to microscopic viscosity (η) of the aqueous phase approximated by the modified Debye−Stoke−Einstein equation:

$$D_{\rm rot} = kT/8\pi\eta r^3 C \qquad (4)$$

k is the Boltzmann's constant, T the absolute temperature, r the radius of the diffusing molecule, and C the coupling parameter representing the amount of solvent that is dragged with the molecule when it moves (Kowert and Kivelson, 1976). At room temperature, the motion of TEMPOL was slowed when starch was added to water or sucrose solutions. Pearce et al. (1985) and Biliaderis and Vaughan (1987) obtained similar results with another water-soluble probe (TEMPO). Reduced probe mobility is thought to result from the ability of starch to change the local aqueous environment experienced by the probe (i.e., environment of higher “microviscosity”). When a starch−water dispersion is stored overnight after preparation, the starch granules absorb water from the system and swell reversibly to some extend. Thus, the mobility of the probes is restricted as a consequence of starch-water interactions.

The addition of sucrose (10 or 20%) to a wheat starch−water system resulted in an increased $D_{\rm rot}$, indicating higher probe mobility in the aqueous phase with increasing sucrose concentration (Figure 11). At low temperatures, we can assume that the added sucrose “retains” water in the aqueous phase and, thereby, limits starch hydration. The water vapor sorption isotherms of amorphous sucrose and wheat (or waxy corn) starch at 25 °C (Iglesias and Chirife, 1982) show that, for water activities higher than 0.45, the affinity of sucrose for water is greater than that of starch for water. This supports the previous hypothesis. The higher the sucrose content, the greater the amount of aqueous phase outside the granules, and the less visible the effect of starch on the probe mobility. The findings of Johnson et al. (1990), showing higher spin probe mobility at the same water content in a mixture of starch and sucrose (ratios of starch-to-sugar-to-water ranging from 1:0.5:2 to 1:3:2) than in starch alone, confirm our results. Moreover, in a study on the mobility of water in starch−sucrose systems, using oxygen-17 NMR, Chinachoti and Stengle (1990), showed that for samples equilibrated at A_w of 0.88, 0.93, and 0.97, the amount of NMR-active water (the mobile fraction of water) increased greatly with increasing levels of added sucrose (0, 10 or 20% db), and hence, the mobility of water increased as additional water was accommodated by the added sucrose. The limited hydration of starch in the presence of sucrose is in agreement with the previous hypothesis of a reduced flexibility of the amorphous chains.

The pronounced decrease in $D_{\rm rot}$ observed from 45 °C to a minimum value at 60 °C for the wheat starch dispersions without added sucrose indicates an increasing “microviscosity” in the environment of the nitroxide radical, induced by increased starch−water interactions. The reduction in probe mobility occurred just before the onset of starch melting as revealed by DSC (Figure 6). These results suggest that some organized structures disappear in wheat starch during heating (rupture of starch−starch interactions), before any visible endothermic destruction of long-range order is observed with DSC, and affects the properties of water. The $D_{\rm rot}$ minimum occurred at higher temperatures in the presence of sucrose. Lim et al. (1992) found similar results for wheat starch−sucrose−water dispersions at 10, 20, and 30% starch concentrations, using ^{17}O NMR. They observed that when sucrose was added at a concentration ranging from 0.5 to 1.5 M at the same starch concentration, the temperature at which the transverse relaxation rate (R_2) maximum (minimum mobility) occurred gradually increased with the sucrose concentration. As the $D_{\rm rot}$ diminution was attributed to the rupture of starch−starch bonds in the profit of starch−water ones, it seems that sucrose stabilizes the ordered structure of native starch even at temperatures below those corresponding to the gelatinization endothermic events. Above the temperature of minimum mobility, $D_{\rm rot}$ gradually increased as temperature increased, but at a slower rate in the presence of sucrose. In this temperature range, DSC results (Figure 6) showed improved starch crystal melting. This progressive increase in the mobility of the probe dissolved in the aqueous phase can be attributed to the higher overall molecular mobility at higher temperatures, which makes crystal melting more easy. The inversion of the sucrose effect possibly means that, in this temperature range, the loss of ordered starch structure (more important in the absence of sucrose) becomes the dominant phenomenon controlling aqueous phase mobility. More work is needed in order to elucidate the exact mechanism responsible for this evolution.

Effect of the Starch Origin. The melting of waxy corn starch ordered zones began at a higher temperature in comparison with wheat starch (Figure 7). Gudmundsson and Eliasson (1992) reported that starches with higher gelatinization temperature than other starches, either have more perfect crystallites and/or higher glass transition temperature (T_g) of their amorphous phase. It is also possible that there is a higher crystallinity within the waxy corn starch granules than those of wheat starch. Moreover, the results of DMTA measurements indicate that the swollen waxy corn starch granule is more rigid than the wheat starch one. Keetels (1995) presumed that entanglements are present between the amylopectin molecules in a starch granule. The branched structure of the amylopectin molecules may contribute to the higher stiffness of waxy corn starch. The higher initial storage modulus could also be attributed to a higher ϕ of the waxy corn granules, since swelling is probably a property of amylopectin (waxy starches swell much more than the normal ones) (Tester and Morrison, 1990; Navarro et al., 1996).

The ESR results showed a lower probe mobility of waxy corn starch in comparison with wheat starch at the same water and sucrose contents, and D_{rot} was not significantly affected by sucrose addition, although the same trend (as for wheat starch) was present. These results could be explained by the greater affinity for water of this type of starch (lower A_w), which limits the water availability for the probes, whatever the temperature. To support these results, wheat and waxy corn starch dispersions of equal weight, in excess of water (90% w/w wb), were prepared and allowed to stand overnight in a closed environment under magnetic stirring. Then, both preparations were allowed to sedimentate for 24 h. Waxy corn starch clearly showed a greater volume of sediment, meaning greater affinity for water in comparison with wheat starch. In that case, sucrose is not able to slow the rapid hydration and subsequent swelling of starch granules. A more thorough study on the comparison of wheat and waxy corn starches, which estimates the possible influence of amylose on the thermomechanical behavior and on the properties of the aqueous phase, is proposed by Rolée et al. (1999).

CONCLUSION

Understanding the effect of sucrose on starch gelatinization is important for improving texture and shelf life of starch-based products and for better process control, to meet specific functional requirements of baked products. Parallel investigations combining the dynamic rheological and differential scanning calorimetric measurements were essential to interpret the thermomechanical behavior of the starch–sucrose–water system, while electron spin resonance measurements gave information about the molecular origin of changes and/or interactions.

The results of this study have shown that sucrose increases the thermal transition temperatures and the enthalpy of gelatinization of wheat and waxy corn starches. The delaying effect of sucrose was greater at lower water-to-starch ratios. Waxy corn starch showed some differences in thermomechanical behavior in comparison with wheat starch.

Since the gelatinization process is governed by the volume fraction and deformability of swollen granules and by the structural disorganization of ordered regions, the sucrose effect need to be considered to influence these factors. The great dependence on water content of the concerned parameters must also be taken into account. The obtained results suggest that the delay of starch gelatinization in the presence of sucrose is due to an interplay of factors such as lowered A_w of the system, increased volume of sucrose–water cosolvent, antiplasticization properties of sugars relative to water, and stabilization of the granular structure due to starch–sucrose interactions. Additional research is needed to obtain a better knowledge of the organization of amylose and amylopectin into the granular structure, to understand the exact mechanism of the starch–sucrose interaction. Moreover, an investigation of starch gelatinization at higher sucrose levels should permit to detect the occurrence of a phase separation between starch and sugar, a fairly common phenomenon in high sugar content products such as cakes and cookies.

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