Effect of Moisture Content on the Thermomechanical Behavior of Concentrated Waxy Cornstarch–Water Preparations—A Comparison with Wheat Starch

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ABSTRACT: The rheological behavior of waxy cornstarch preparations at intermediate moisture contents (30 to 60% w/w) was studied by dynamic mechanical thermal analysis (DMTA). Differential scanning calorimetry (DSC) and electron spin resonance (ESR) experiments were also performed in parallel. The results were compared to those obtained previously for wheat starch. DMTA results evidenced a critical moisture content (between 50 and 55%) for waxy cornstarch that delimited a radical change in the rheological behavior both at room temperature and during heating. This critical water content was around 45% for wheat starch.

Keywords: starch, amylose, moisture content, rheological behavior

Introduction

THE AMOUNT AND DISTRIBUTION OF WATER WITHIN STARCH granules is of utmost importance to their physical and chemical properties. An understanding of the role of water and its interplay with heat treatments is crucial in the industrial processing of starch and starch-containing materials as well as in its utilization in many technical and food applications.

When dispersed in excess cold water, starch undergoes a limited swelling (around 5% for wheat starch) (Hoseney and Rogers 1994), but there is no discernible rheological effect on relatively dilute suspensions of starch granules. With sufficient heat, a starch-water system or a starch-containing food material (dough for example) undergoes a series of dramatic changes referred to as gelatinization and pasting. These changes occur within a relatively wide temperature range. The gelatinization temperature range is not a constant, but greatly depends upon the characteristics (water content, dissolved solutes) of the medium (Doublier and others 1987). In excess water, heating results in a suspension of swollen particles composed mainly of amylopectin molecules trapped inside the granules. The continuous phase is a solution of amylose that may also contain amylopectin. Hence, the rheological behavior of such a composite system depends upon diverse parameters. Most of these parameters themselves depend upon the botanical origin of starch and the preparation procedure. Mainly based on microscopical observations, Miller and others (1973) suggested that the rheological behavior of starch is mainly controlled by the organization of dissolved and entangled macromolecules leached out of the granules during gelatinization. This was interpreted as evidence of the major importance of the soluble material. In contrast, several authors (Evans and Haisman 1979; Wong and Lelievre 1981) ascribed a major role to the dispersed phase in determining overall properties and postulated that the continuous phase was of minor importance. Bagley and Christianson (1982) assumed that, due to the absence of soluble material in pastes cooked below 85 °C, viscosity would be governed primarily by the volume fraction of swollen particles. However, several authors reported results showing that amylose could leach out from a temperature as low as 50 °C for wheat starch in excess water (Eliasson 1986; Tester and Morrison 1990). At intermediate water contents, the granules can only partially swell during heating because of a limited available volume. Amylose and amylopectin would be only partially separated, the swollen granules including consequently both amylose and amylopectin. In that case, the 2 key variables of the rheological behavior of concentrated starch preparations during heating would thus be the volume occupied by the granules (closely related to swelling) and their deformability (Rolée and Le Meste 1997, 1999); the amylose is expected to play only a minor role (Keetels 1995).

Recently, Rolée and Le Meste (1999) studied the rheological behavior of wheat starch preparations at intermediate moisture contents (25 to 60% w/w) by dynamic mechanical thermal analysis (DMTA). Differential scanning calorimetry (DSC) and electron spin resonance (ESR) experiments were also performed in parallel. The DMTA results suggested that swelling would occur mainly in the range of temperature corresponding to the first endothermic peak observed with DSC. In the same temperature range, the ESR results suggested an increase in the viscosity of the aqueous phase attributed to improved starch-water interactions and/or to leaching of soluble starch molecules. The increase in volume fraction (ϕ) of the starch granules was assumed to be responsible for the increase in storage modulus during heating, when ϕ reached a volume fraction close to the close-packing volume fraction ϕ_m. The 45% moisture content level appeared to be critical for wheat starch preparations, because of the radical change in thermomechanical behavior around this concentration. Indeed, lower moisture contents would allow the wheat starch granules to reach the close-packing volume fraction at room temperature. Whatever the moisture content in the range 25 to 60%, the storage modulus G'

would be closely related to the deformability of the granules once the volume fraction had reached ϕ_m.

The present work has been conducted with similar methods and techniques on preparations containing a starch from another botanical origin, the waxy cornstarch. The main interest of this starch was its very low ratio of amylose (about 1%). A comparison with the results obtained for wheat starch should permit us to discuss the interpretations previously suggested and to estimate the possible influence of amylose on the rheological behavior and structural changes of starch and on the properties of the aqueous phase at intermediate moisture contents during heating.

Materials and Methods

Sample preparation

Waxy cornstarch (waxilys 200; Roquette Frères, Lestrem, France) was used for all investigations. Preparations were made with 18 g of starch (dry matter: 16.06 g) and distilled water was added until moisture contents of 30, 35, 40, 45, 50, 55, and 60% (w/w wb) were obtained. The manual blending was continued until a homogeneous mixture was obtained then the mixture was allowed to rest for at least 1 h at room temperature in a closed environment; the more liquid-like samples (moisture contents above 50%) were magnetically stirred.

Differential scanning calorimetry

Thermograms were obtained with a Perkin-Elmer DSC-7 differential scanning calorimeter, equipped with a TAC/7 DX thermal analysis data station (Perkin-Elmer, St Quentin en Yvelines, France), calibrated with azobenzene and indium in the positive temperature range. Fractions of starch preparations (40 to 85 mg) were weighed and hermetically sealed in stainless steel DSC pans. All traces were normalized to 1 mg of starch. The scanning temperature range and the heating rate were 25 to 140 °C and 10 °C/min, respectively. An empty pan was used as an inert reference. All tests were performed at least in triplicate. The partial melting enthalpy was calculated from the onset of the endotherm to 85 °C (every 1 °C) to plot the curve representing the cumulated enthalpy values as compared with temperature. The average standard deviation was calculated to be 8.9%.

Dynamic mechanical thermal analysis.

The small amplitude oscillatory rheological measurement was performed with a viscoanalyzer (Metravib R.D.S., Limonest, France), equipped with a thermocontrol unit. The temperature was monitored by a thermoprobe at ± 0.5 °C. Plan shearing was used for the more solid-like samples (moisture contents lower than 50%). For the more liquid-like samples, 2 different devices were used depending on the range of temperature: annular pumping up to approximately 63 °C, then annular shearing up to 85 °C. This change in device was necessary because during the thermal treatment, liquid-like samples became more rigid and annular pumping was no longer efficient. These different modes are showed in Figure 1.

Plan shearing. The main characteristic of this device was that 2 cylindrical samples of the same size were needed. Starch samples were 3 mm high × 15 mm dia or 4 mm high × 20 mm dia. They were vertically glued with cyanoacrylate glue (Amatron, Provins, France) 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 that registered the stress.

Annular pumping. About 1.5 ml of sample was poured into a cylindrical cell. A piston was oscillating with small amplitude in the center of the cell, which was glued with cyanoacrylate glue (Amatron, Provins, France) 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. This device consisted of coaxial cylinders connected to the sensors. The gap between the 2 cylinders was 2 mm. The sample dispersion, poured in the cell in the liquid state before heating, was held in the annular space by capillary force.

To prevent drying during the thermal treatment, starch samples were coated with silicone grease (Rhône Poulenc, Lyon, France) with the aid of a small brush for plan shearing. For annular pumping and annular shearing, a mineral oil (Nachet, Dijon, France) was used. The strain and frequencies were set at 3 μm and 5 Hz, respectively. First, strain sweep tests were performed at different temperatures in order to confirm that measurements were run in the linear range of viscoelasticity. Then, starch samples were heated from 30 to 85 °C (1.5 °C/min) during the mechanical analysis. The highest temperature was 85 °C, beyond which starch granules might be damaged (Tester and Morrison 1990). All tests were performed at least in triplicate. At 30% moisture content, numerous tests were needed because of the difficulty to obtain samples with the required shape.

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 10.2%.

Electron spin resonance

Hydrated starch has no paramagnetic activity, so the spin-probing technique was employed, in which a compound with a nitroxyde radical, possessing a stable free electron, is added to the system. The ESR spectra reflect the motion of the small paramagnetic probe that depends on the probe size and on the solvent viscosity. The size and polarity of the probes influence their accessibility to microenvironments and their behavior in a network: a smaller probe may stay relatively mobile where, for steric reasons, a larger molecule may have a reduced mobility. The 4-hydroxy,2,2,6,6-tetramethyl-piperidine N-oxyl (TEMPOL) radical (MW 172.2g mol^{-1}) was purchased from Aldrich Chemicals (Strasbourg, France).

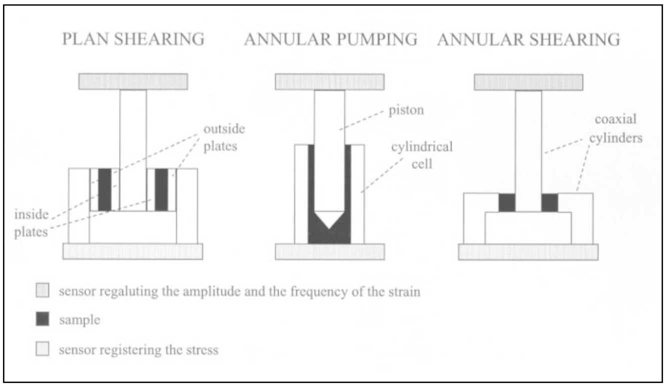

Figure 1—Schematic cross sections of the different devices used for DMTA.

Because of its small size, this probe has the possibility to diffuse into the starch granules, so it can be dispersed in the aqueous phase inside and outside the granules. When preparing the samples, 300 µl of a TEMPOL aqueous solution (2 mg/ml) were added to distilled water, then manually mixed with starch (approximate final TEMPOL concentration: 2.44×10^{-7} mol/g of dry starch). Sealed capillary tubes containing aliquots of the samples were placed in 3 mm-dia ESR sample quartz tubes, and ESR spectra were collected using a Bruker EMX spectrometer (Bruker, Nissembourg, France) with a nitrogen-flow temperature control. The operating frequency and center field were respectively at about 9.42 GHz and 3357 G. The spectra were recorded at a microwave power of 10 mW. Any saturation phenomenon was avoided. The scan rate (20.97 s for 100 G), time constant (81.92 ms), and modulation amplitude (0.40 G) were adjusted so that distortion of the spectra was avoided. For all experiments, the temperature was varied stepwise, every 2 °C, between 25 and 85 °C and the sample was stabilized for 3 min before recording the spectra. All ESR experiments were carried out in triplicate. The average standard deviation for all the tests was calculated to be 8.1%.

The rotational correlation time (τ_c) was determined from the relation:

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

deduced from the Freed and Fraenkel (1963) theory where ΔH_{I+1} is the width of the I_{+1} line, $I_{+1,}$ and I_{-1} are respectively the height of the lines I_{+1} and I_{-1} (Figure 2).

The conventional ESR method was used, allowing mobility measurements in the range $10^{-11} < \tau_c < 10^{-7}$ s. The rotational diffusion coefficient (D_{rot}) was evaluated from the rotational correlation time (τ_c) (Nordio 1976):

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

Results and Discussion

Thermal disordering

The DSC curves for waxy cornstarch were strongly affected by the mass fraction of water (Figure 3), over the 30 to 60% water content range.

The water dependence of the thermal behavior of waxy cornstarch was similar to that of wheat starch (Rolée and Le Meste 1999). However, the curves appeared somewhat less complicated because of the absence of contributions from amylose, including the amylose-lipid complexes. As the water content was lowered, several transitions became apparent. The endotherm (G) observed at high moisture content developed a trailing shoulder (M_1), which shifted to higher temperatures and became predominant when the water content was decreased. On the opposite, the first peak (G) remained located in the same temperature range and its area progressively decreased when the water content was decreased. At 30% moisture content, the first endothermic peak almost disappeared. Total enthalpies of 16 J/g (db) were estimated for the highest moisture contents studied. All of these results are in agreement with previous studies (Donovan 1979; Ghiasi and others 1982; Maurice and others 1985; Gidley and Cooke 1991).

Although several contradictory interpretations have been suggested for the biphasic profile at intermediate moisture contents, it is now widely admitted that the redistribution of water within the sample during heating plays a key role (Donovan 1979; Evans and Haisman 1982; Liu and others 1991; Liu and Lelievre 1992; Beleia and others 1996; Garcia and others 1996; Rolée and Le Meste 1999). The similarities in thermal curves for waxy corn and wheat starches indicate that the melting endotherms may be largely accounted for by the amylopectin portions of the starch granules. Even if amylose seems to play a minor role, its contribution remains unclear. The endothermic peak present at high temperature for wheat starch corresponding to the melting of amylose-lipid complexes was, of course, not observable for waxy cornstarch. As the gelatinization endotherm would represent essentially the difference between the endothermic energy, associated with melting of crystallites, granule swelling and denaturation, and the exothermic energy associated with hydration of starch and formation of the amylose-lipid complexes (Kugimiya and others 1980), the absence of amylose in waxy starches may generate a higher endothermic energy. The results obtained with the waxy cornstarch seem to confirm this hypothesis since our values of enthalpies of gelatinization, as those currently found in literature, are high compared to most of the non-waxy starches. In the same way, potato and cassava starches contain no lipids and, hence, no amylose-lipid complexes can form; as for waxy cornstarch,

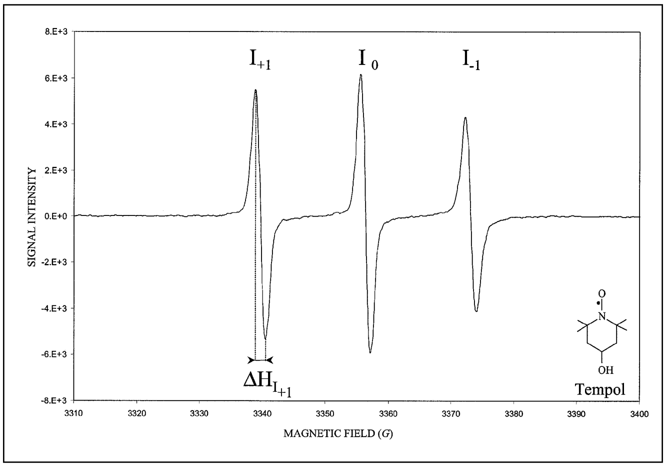

Figure 2—Typical ESR spectrum of a nitroxyde free radical (TEMPOL).

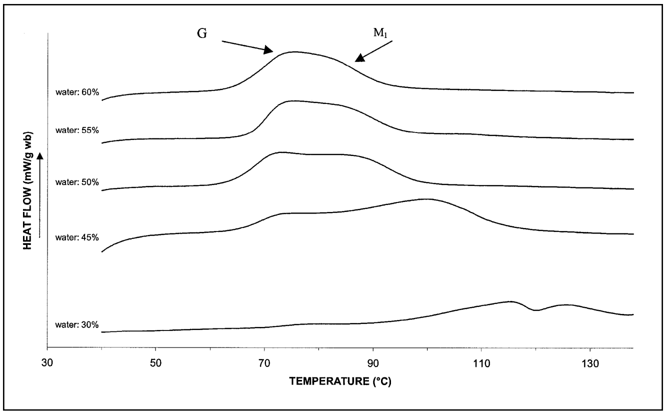

Figure 3—Differential scanning calorimetry thermograms of waxy starch preparations at intermediate moisture contents (30 to 60% w/w, wb). G and M_1 indicate the 2 successive endothermic peaks.

enthalpies of gelatinization currently found in literature for both starches are relatively high, tending to reinforce the previous hypothesis.

Though similarities existed in the DSC traces for waxy corn and wheat starches, a clear difference could also be observed at the highest moisture contents studied. Indeed, for wheat starch, a main peak and a shoulder were observed, but for waxy cornstarch, 2 partly superimposed peaks were visible. This difference is highlighted in the partial melting enthalpy plot (Figure 4a and 4b).

For wheat starch, at the highest moisture contents studied, the melting enthalpy grew up steeply with temperature at the beginning of melting (in an approximate range of 10 °C), then an inflection point was observed around 65 °C and the rate of enthalpy increase slowed down. For waxy cornstarch, no inflection point was observed, the enthalpy increased almost linearly up to 85 °C. This difference could be due, at least partly, to the exothermic formation of amylose-lipid complexes, thus inducing above 65 °C an underestimation of the enthalpy of melting for wheat starch. Normal cornstarch, with approximately the same amylopectin/amylose ratio as wheat starch, was observed to exhibit a similar 2 step melting process with an apparent lower rate of melting above 75 °C (Rolée and Le Meste 1997).

The disorganization of crystallites seems to be facilitated in wheat starch compared to cornstarch (waxy and normal). Indeed, melting started at a lower temperature for wheat starch. This difference between wheat and corn could not be attributed to amylose, as the onset temperature for the melting of normal cornstarch crystallites was similar to that of the waxy cornstarch (Rolée and Le Meste 1997). This apparent higher thermal stability of the crystallites in corn and waxy cornstarches might reflect a different organization of the molecules, either within the crystalline domains or between the crystalline and the amorphous domains.

Rheological behavior

Storage modulus (G') as compared with temperature was plotted for all moisture contents studied (Figure 5).

As for wheat starch (Figure 6), the initial storage modulus ($G'_i = G'$ at 30 °C) increased as moisture content decreased. For dispersions with 55 and 60% water content, G'_i was low (10 to 100 Pa) whereas G'_i was very high for dispersions with 30 to 50% moisture content ($5 \times 10^5 – 1.2 \times 10^6$ Pa).

For samples with 55 and 60% water, *G′* increased very strongly from 55 to 60 °C and reached a maximum value at around 70 °C, before decreasing slightly up to 85 °C (Figure 5). In such dispersions with quite high moisture contents, an increase in volume fraction of starch granules has been shown to be responsible for this *G′* increase during heating (Bagley and Christianson 1982; Doublier and others 1987; Rolée and Le Meste 1997). The dominant effect of the progressive swelling of starch granules, subsequent to the crystallite melting in this range of temperature, led to a maximum occupancy of the available space by the swollen granules. Due to the resulting increase in the granule-granule interactions, the system formed a «gel» with a crystal-like package of the granules. This state has also been assimilated to a transient network formed by the granules, which could eventually disrupt during further heating (Champenois and others 1998). Wheat starch dispersions in the 50 to 60% moisture content range were shown to behave in a similar way (Rolée and Le Meste 1999). However, the *G′* increase was shifted towards higher temperatures for the waxy cornstarch. This result is in agreement with DSC results showing the higher thermal stability of the crystals of waxy cornstarch. Moreover, we noticed that waxy cornstarch dispersions reached their maximum *G′* value at about 70 °C after a continuous increase, whereas for wheat starch dispersions a very steep increase in modulus was first observed up to about 55 °C, followed by a more reduced increase to approximately 65 °C (Figure 5 and 6).

At least 2 events could be responsible for this difference. First, this could be due to the polydispersed granules (2 populations) of native wheat starch, whereas waxy cornstarch has only one population of granules, as described in the literature (Galliard and Bowler; 1987 Rolée and Le Meste 1997). For wheat starch, the straight increase in *G′* would reflect the rapid packing of the large population of granules during heating. Some available spaces between these large packed granules could allow the smallest granules to swell further and reinforce gently the rigidity of the system. Secondly, when the granules get closed-packed, contact between the granules might occur either directly, which might be the case for waxy cornstarch, or, as suggested by Eliasson (1986) for wheat starch, the contact might also involve amylose that

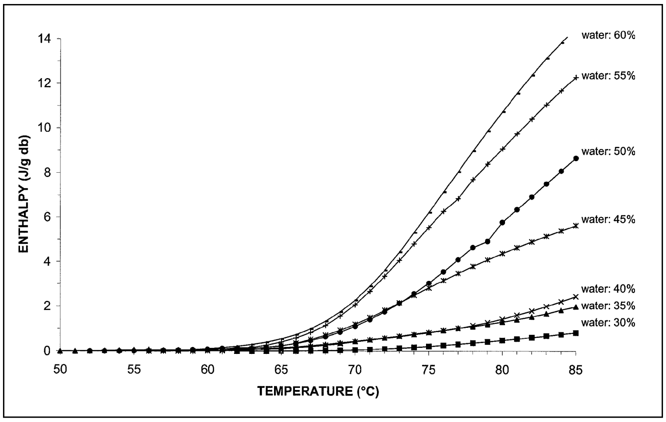

Figure 4a—Partial melting enthalpy as a function of temperature for waxy cornstarch preparations (moisture contents given on graph expressed on a wb).

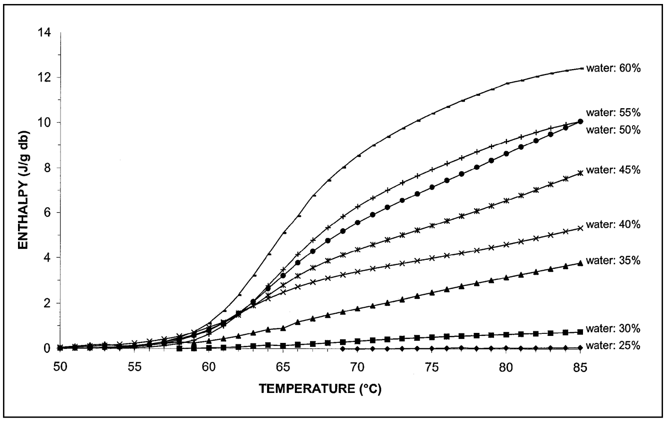

Figure 4b—Partial melting enthalpy as a function of temperature for wheat starch preparations (moisture contents given on graph expressed on a wb) (Rolée and Le Meste 1999).

has leached out, at least partly, from the granules. A thin layer of leached amylose wrapping the granules could generate indirect granule-granule contacts, and thus explain the gentle *G'* increase preceding the maximum *G'* value.

Once granules are in close contact, *G'* would then be sensitive to the intrinsic softness, that is, deformability of the granules, closely related to the swollen state and the remaining ordered zones. The values of the modulus for closed packed suspensions of both waxy corn and wheat starch suggest that the granular material is in the rubbery state. Heating above the temperature where the maximum in *G'* is observed provides energy to break down the residual crystalline structure of starch, causing *G'* to drop down (Figure 5b) (Lii and others 1996). As for wheat starch, DSC results on waxy cornstarch (Figure 4a and Figure 4b) showed evidence of melting/dissociation of ordered zones in this range of temperature.

The dispersions having the highest G'_i (moisture content ranging from 30 to 50%) did not show pronounced viscoelastic changes up to 65 to 70 °C (Figure 5). However, further heating up to 85 °C induced a *G'* decrease. For such moisture contents, the granules were already interacting at room temperature. The high initial modulus of the dispersions could be explained by the tight packing of compressed granules. Not enough space was available for the granules to further swell and consequently no *G'* increase was observed, unlike the higher moisture contents studied. These concentrated dispersions composed of packed granules were then sensitive to the intrinsic softness of the granules during the whole heating. The *G'* decrease observed from 65 to 70 °C to 85 °C was then explained by the same reasons as previously accounted for the dispersions with 55 and 60% water contents, that is, crystal melting and subsequent decrease in the granule rigidity.

Motional behavior of probes (TEMPOL) dispersed in the aqueous phase studied by ESR

ESR proved to be an appropriate technique to detect changes in the properties of the water phase within starch dispersions (Biliaderis and Vaughan 1987; Rolée and Le Meste 1999). In this case, ESR is not a direct method, but is used to measure the rotational mobility of a water-soluble probe (TEMPOL) dispersed in the aqueous medium of the suspension. The rotational diffusivity of a probe dispersed in a homogeneous liquid medium can be described by the modified Stokes-Einstein equation:

$$D_{rot} = kT/8\pi\eta r^3C$$

where k is the Boltzmann constant, T the absolute temperature, η the viscosity of the medium, 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). Rolée and Le Meste (1999) emphasized that, in heterogeneous systems such as concentrated starch-water dispersions, the relevant parameter should be the viscosity of the diffusion medium (that is, aqueous phase). This viscosity is expected to be sensitive to the interactions between water and the starch molecules and thus to starch structural disorganization such as the disruption of low energy starch-starch interactions (melting) and subsequent increase in starch-water hydrogen bonding.

At room temperature, like over the entire temperature range studied, 3 line spectra similar to those of probes in water were obtained (not shown). This behavior is generally interpreted in terms of isotropic fast motion. The calculated rotational diffusion coefficients (Figure 7) were found to be lower than the values for the probe in water. The observed slower motion in the presence of starch suggests that the probe experienced an environment of higher viscosity. A previous work (Rolée and Le Meste 1999) suggested that this higher viscosity would be due to a reduced mobility of water molecules involved in the starch-water interactions. Indeed, starch molecules become partly hydrated as soon as the starch-water dispersion is prepared, and the granules swell reversibly to some extent. This would decrease the mobility of probe molecules. It can be noticed that only one population of probes was observed, that is, probes inside and outside the granules could not be distinguished. Studies by solid state ^{2}H and ^{1}H NMR on waxy cornstarch have already shown that water was mobile in the starch matrix, despite the extremely high rigidity of starch molecules in the solid and semi-solid state (Li and others 1998).

In comparison to wheat starch and for similar concentrations (Figure 8), waxy cornstarch dispersions showed lower D_{rot} values at room temperature, suggesting starch-water interactions were favored. Compared to wheat starch, only slight changes occurred during the thermal treatment of waxy cornstarch. Up to 60 to 65 °C, D_{rot} increased slightly for

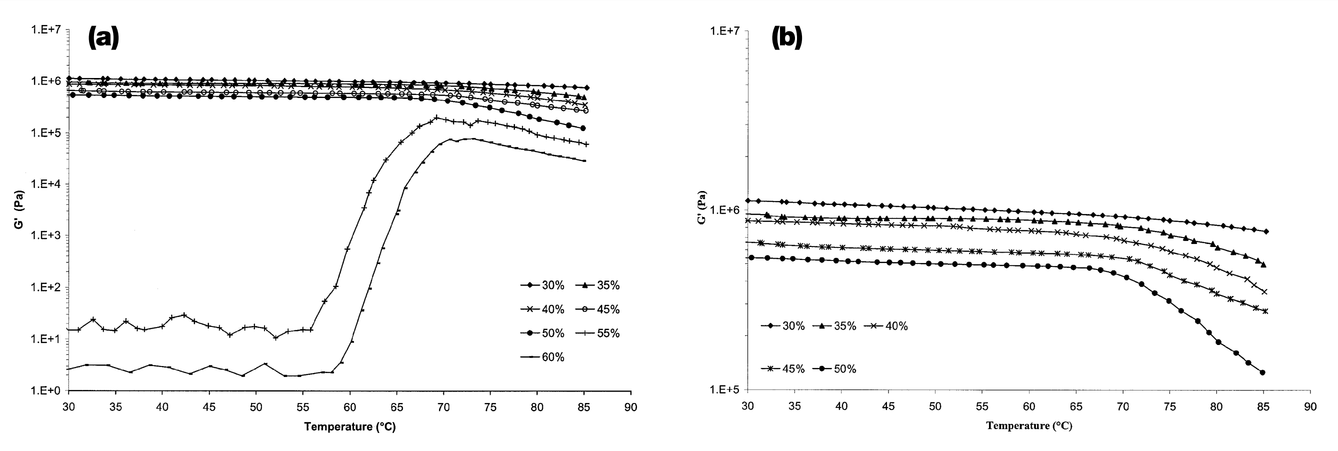

Figure 5—(a) Storage modulus changes for waxy starch dispersions at intermediate moisture contents (30 to 60% w/w, wb), as a function of temperature during heating. (b) Expansion of curves in Figure 5a.

dispersions having 30 and 40% moisture contents, was stable for 50% moisture content, and slightly decreased for 60% moisture content. From 60 to 65 to 85 °C, D_{rot} increased slightly for the lowest water contents (30 and 40%) and more sharply for 50 and 60% moisture contents.

During heating wheat starch dispersions with 50 and 60% moisture, a clear decrease in D_{rot} was observed from 47 to 50 °C to a minimum value at 57 to 60 °C (Figure 8). This decrease occurred in the same temperature range as does the *G'* increase and the onset of the endothermic events. Therefore, the D_{rot} decrease appeared to be related to the starch-water interactions that could be improved by amylopectin melting and granule swelling. However, this hypothesis seems still open to question. Indeed, if we carefully pay attention to the onset of the different phenomena, it seems that the decrease in probe mobility occurs slightly before the onset of starch melting (Figure 4b). Furthermore, waxy cornstarch dispersions with 50 and 60% moisture content, which also exhibit a similar melting process, did not show such a decrease in D_{rot}.

General discussion

Behavior at room temperature

Rolée and Le Meste (1999) showed that for wheat starch dispersions, the 45% water content seemed critical, since there was a radical change in the *G'* modulus of the starch preparation and of the thermomechanical behavior around this concentration. Beyond this critical volume fraction, granules are expected to be connected on a large scale, hence they act as a continuous phase. For waxy cornstarch, this radical change in modulus and thermomechanical behavior occurs at a higher moisture content (thus less concentrated suspensions), around 50 and 55% moisture. This observation is in agreement with the ESR results that suggested a higher affinity of waxy cornstarch for water at room temperature, in comparison to wheat starch. Thus, an improved swelling capacity at room temperature is expected for waxy cornstarch. The different values of the critical water content could also be partly explained by differences in the granules size distribution. Indeed, ϕ_m could be determined by a simple equation (Alberola and Mele 1996):

$$\phi_m = 1\text{-}0.47(d/D)^{0.2}$$

where d and D are respectively the lower and the upper limits of the size distribution of the particles. A previous study using laser-light diffraction (Rolée and Le Meste 1997) showed that wheat starch had a larger size distribution than waxy cornstarch. Using this relation and the published values of granule size distribution, ϕ_m could be estimated to be 0.73 for wheat starch and 0.66 for waxy cornstarch. The ϕ_m value calculated for wheat starch must be even higher because of the polydispersity of the wheat granules. Therefore, at room temperature, ϕ_m would be reached at a lower moisture content (higher granule concentration) for wheat than for waxy cornstarch.

Below ϕ_m, the modulus of the suspensions of both type of starch is similar and controlled by the continuous phase. Above ϕ_m the modulus of the suspensions is controlled by the rigidity of the granules acting as a continuous phase. The main difference in the rheological behavior of the suspensions obtained with the 2 starches can be at least partly attributed to the hydration properties (or granule concentration), and swelling capacity, allowing the granule volume fractions ϕ to get close to their respective ϕ_m.

Thermomechanical behavior

For the highest moisture contents studied, the increase in rigidity observed by DMTA occurred at a lower temperature for wheat starch than for waxy cornstarch (Figure 5 and 6). As previously, the increase was attributed to the fact that the granule volume fraction gets close to ϕ_m, as a consequence of the heat-induced swelling. As ϕ_m would be higher for wheat starch granules than for the other starch, the DMTA results suggest that granule swelling upon heating started at a lower temperature for wheat starch. DSC results, showing that wheat starch crystallites start melting at a lower temperature, are in agreement with this proposition. These structural changes have been described as being accompanied by a redistribution of water within the material. Indeed the amorphous domains are expected to exhibit a higher affinity for water than the crystalline zones. NMR spectroscopic studies have shown that water molecules in starch are highly mobile even at low water contents, thus they can diffuse

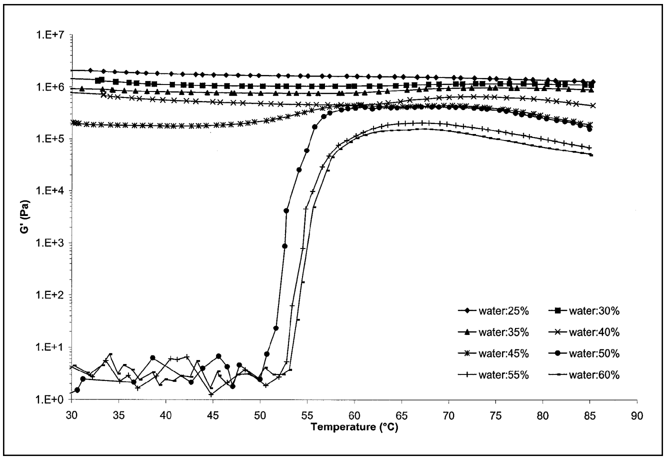

Figure 6—Storage modulus changes for wheat starch dispersions at intermediate moisture contents (25 to 60% w/w, wb), as a function of temperature during heating (Rolée and Le Meste 1999).

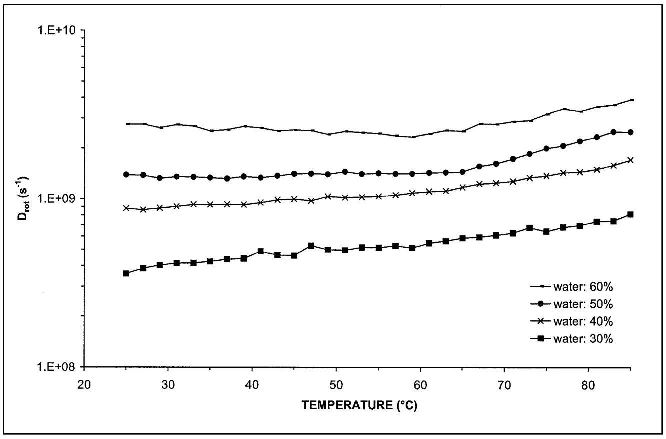

Figure 7—Rotational diffusion coefficient of spin probe (TEMPOL) dispersed in the aqueous phase of waxy cornstarch dispersions at intermediate moisture contents (w/w, wb), as a function of temperature.

rather rapidly into the starch samples. As a result, water can be heterogeneous with respect to mobility, depending on its partitioning among domains, such as in a gel phase, in dissolved starch (solution domains), in crystalline domains, or in the granular amorphous regions. Changing the initial water content and temperature could thus greatly influence the balance or the distribution of the water within different phases or domains (Li and others 1996). The decrease in the rotational diffusivity of the water soluble probes dispersed in the high moisture wheat starch dispersions in the same temperature range as the onset of melting, has been attributed to the improved starch-water interactions associated with melting (Rolée and Le Meste 1999). However, the ESR results obtained for waxy cornstarch seem to exclude the latter hypothesis. Indeed, in that case starch melting was not associated to a decrease in D_{rot}.

Another hypothesis relies on an increase in starch-water interactions not directly related to melting and swelling of starch granules. This could well be the reason why ESR results for wheat and waxy cornstarches are different. A high inherent amylose content has been reported to enhance the rigidity of starch granular structures (Lii and others 1996). It can, thus, be suggested that amylose could prevent the penetration of water molecules into some sites of starch. The presence of amylose in wheat starch would then explain the higher D_{rot} at room temperature and during heating up to 50 °C. Eliasson (1986) and Tester and Morrison (1990) reported results showing that amylose could leach out from temperatures as low as 50 °C for wheat starch. When the amylose leaching starts it may open up more sites for hydration in domains that water molecules were not able to reach before. New starch-water interactions could then form, that can be evidenced by the clear decrease in probe mobility from 50 °C to a minimum value at approximately 60 °C for wheat starch dispersions with 50 and 60% moisture contents (Figure 8). Lower moisture contents should not allow amylose solubilization and leaching out and hence no further D_{rot} decrease was observed. Since waxy maize starch contains only a little proportion of amylose (about 1%), water could absorb more freely onto the starch molecules, whatever the temperature, inducing a lower probe mobility, than for wheat starch, with no clear decrease during heating as no amylose can leach out.

The decrease in probe mobility could also be attributed to a structural reorganization. Hydrothermal treatments, such as storage performed at a certain moisture level during a certain period of time at a temperature above the glass transition temperature but below the gelatinization temperature, are known to cause physical modifications, such as the development of new crystals in the amorphous regions, or crystallite growth or perfection of already-existing crystals. Such hydrothermal treatments are called «annealing» when storage is in excess of water, while the term «heat moisture treatment» is used when low moisture levels are applied. Storage in the gelatinization temperature range can also lead to structural reorganization. Recrystallization or polymorphic transition processes, which entails melting followed by renewed crystallization, have been reported (Yost and Hoseney 1986; Zobel and others 1988). However, this phenomenon is more noticeable at higher temperatures, perhaps because at lower temperatures, the presence of the greater number of crystallites tends to constrain the amorphous regions into conformations that are incompatible with crystal formation (Liu and others 1991). Although no storage was performed, the slow heating of the samples during our experiments could have caused crystal improvement and/or more orderly arrangements between chains segments in amorphous regions. This strengthening of the biopolymer matrix could generate a decrease in D_{rot}. However, it must be noticed that waxy cornstarch did not show the D_{rot} decrease around the onset of melting. This could be due to the presence of apparently more stable crystals in native waxy cornstarch as suggested by DSC results.

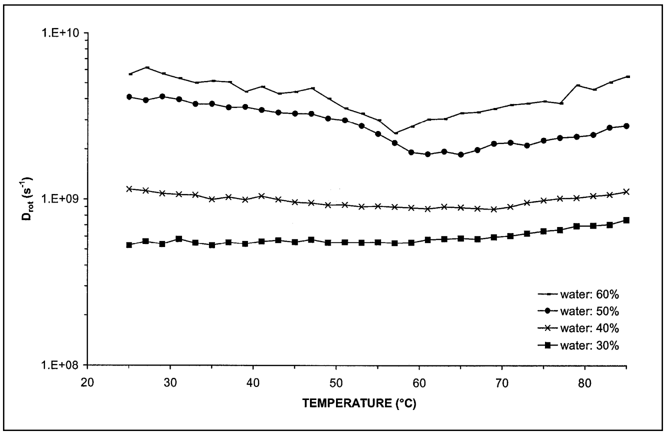

Figure 8—Rotational diffusion coefficient of spin probe (TEMPOL) dispersed in the aqueous phase of wheat starch dispersions at intermediate moisture contents (w/w, wb), as a function of temperature (Rolée and Le Meste 1999).

Conclusions

DMTA RESULTS EVIDENCED A CRITICAL MOISTURE CONTENT (approximately 45%) for wheat starch that delimited a radical change in the rheological behavior. This critical water content was between 50 and 55% for waxy cornstarch. These critical water contents were interpreted as corresponding to the concentrations where the volume fractions occupied by the partly hydrated starch granules get close to their respective close-packing volume fraction ϕ_m. For less concentrated dispersions, this critical volume fraction is reached upon heating, through the swelling subsequent to the melting process.

Whatever the moisture content from 30 to 60%, the storage modulus G' appears closely related to the rigidity of the granules once the volume fraction had reached ϕ_m and to the viscosity of the continuous aqueous phase when $\phi < \phi_m$. Differences in the rheological behaviors of wheat and waxy cornstarches have been partly attributed to the polydispersion and size distribution of the granules, but also to differences in the accessibility of water to starch hydration sites attributed to the presence or not of amylose.

DSC results suggested that amylose could affect the enthalpy of melting of ordered regions in wheat starch. Low values of enthalpy found for the melting of wheat starch, compared with waxy cornstarch, could be explained, at least partly, by an underestimation of the enthalpy of melting, due to the concomitant exothermic formation of amylose-lipid complexes.

At the highest moisture contents studied, leaching out of amylose occur during the heating process of non-waxy starches. The decrease in probe mobility observed in the range 50 to 60 °C for wheat starch was attributed to either a structural reorganization, or more probably to starch-water interactions which should form when amylose starts to leach out, opening up more sites of hydration in domains where water molecules were not able to reach before. In preventing the penetration of water into some regions of the granules, up to 50 °C, the presence of amylose could well explain why wheat starch reaches the close-packing volume fraction, at room temperature, at a lower moisture content (that is, critical moisture content) than waxy cornstarch.

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