

# Effect of Moisture Content on Thermomechanical Behavior of Concentrated Wheat Starch-Water Preparations

A. Rolee<sup>1</sup> and M. LeMeste<sup>1,2</sup>

## ABSTRACT

Cereal Chem. 76(3):452–458

The rheological behavior of wheat starch preparations at intermediate moisture contents (25–60%, 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. Upon heating wheat starch preparations from 25 to 85°C, DMTA showed first a slight decrease in storage modulus ( $G'$ ) to 45–60°C, then an increase of the shear modulus (predominant effect of swelling) to 68–74°C, followed by a decrease (predominant effect of melting-softening) to 85°C. In this 25–85°C temperature range, the initial swelling and subsequent softening were less pronounced with decreasing moisture content. The 45% moisture content level appeared critical, since there was a radical change in the thermomechanical behavior below this concentration. DSC

showed that gelatinization did not appear as a single endotherm but as two endotherms. Whatever the moisture content, the melting started within a quite narrow temperature range, while the end of melting shifted progressively to higher temperatures as moisture content was decreased. ESR showed first a slight decrease in the water-soluble probe (Tempol) mobility as temperature was increased to 47–50°C, followed by a pronounced decrease to 57–60°C. Then, a progressive increase in probe mobility was observed to 85°C. These changes in probe mobility suggest some modifications of the kinetic and thermodynamic properties of the aqueous phase associated with changes in the starch physical state. For the lowest moisture contents, the probe mobility was quite stable during heating.

Observations on the water-dependent thermal stability of starch are of general interest, especially because many food systems exist under limited water conditions (Münzing 1991). The interaction of water with starch is an important phenomenon controlling the behavior of starch in various food processing operations such as baking of bread and cakes, extrusion of cereal-based products, and thickening and gelling of sauces and pie fillings (Biliaderis et al 1980). Indeed, the optimization of these food processing operations requires a thorough knowledge of the thermal and mechanical behavior of starch-water dispersions. Wheat starch was chosen for this investigation because of the widespread usage of wheat flour and starch in the food industry. Gelatinization of wheat starch is a hydrothermal event occurring when native starch granules are heated in excess water. It results in an irreversible order-disorder transition that can be evidenced by microscopy, X-ray diffractometry, differential scanning calorimetry (DSC), and many biochemical techniques (Garcia et al 1996). DSC is a particularly useful probe of this structural disordering, showing an endothermic melting process that is assumed to be directly related to the loss of crystalline order (Gidley and Cooke 1991). DSC studies have shown that ≈60% moisture content is required for complete gelatinization and ≈25% moisture content is required to initiate gelatinization (Lund 1984). In many starch-water systems with restricted water content, various additional endothermic DSC transitions have been reported, the nature of which still remains unclear. During a thermal treatment, the rheological behavior of such concentrated starch dispersions would be controlled by two key variables: the volume occupied by the granules (closely related to swelling), and their deformability (Keetels 1995, Gluck-Hirsch and Kokini 1997, Rolée and Le Meste 1997). Water would play a major role.

The aim of the present work was to understand the structural and physicochemical events underlying the rheological behavior of wheat starch dispersions at various intermediate water contents during a thermal treatment by using dynamic mechanical thermal analysis (DMTA) in combination with DSC and electron spin resonance (ESR) measurements. DMTA allows us to observe the

changes in the viscoelastic behavior of dispersed systems such as starch-water preparations. This behavior is related, at least partly, to the volume fraction of starch granules that depends on hydration and swelling during heating. The starch-water interactions involved in these events depend mainly on the physical and structural changes occurring during heating. Spin-probing ESR enabled us to investigate physical changes occurring in the liquid phase of hydrated starch, while DSC was used to understand the contribution of structural changes, such as crystals melting, to the rheological behavior.

## MATERIALS AND METHODS

### Sample Preparation

Wheat starch (Roquette Frères, Lestrem, France) was used for all investigations. Preparations were made with 18 g of starch (15.75 g of dry matter). Distilled water was added until moisture contents of 25, 30, 35, 40, 45, 50, 55, and 60% (wb, w/w) were obtained. Manual blending was continued until a homogeneous mixture was obtained, then the mixture was allowed to stand for at least 1 hr at room temperature in a closed environment. The more liquid-like samples (moisture contents >45%) were magnetically stirred.

### DSC

DSC assays were performed using a Perkin-Elmer DSC-7 instrument with a TAC/7 DX thermal analysis controller (Perkin Elmer, France) calibrated with azobenzene and indium in the positive temperature range. Portions of starch preparations (40–85 mg) were weighed and hermetically sealed in stainless steel DSC pans. The sample pans were heated from 25 to 160°C at a scanning rate of 10°C/min. An empty pan was used as the reference. All tests were performed at least in triplicate. The partial melting enthalpy was calculated from the onset of the endotherm to 85°C (1°C/step) to plot the curve representing the cumulative enthalpy values versus temperature. The average standard deviation was calculated to be 8%.

### DMTA

Small-amplitude oscillatory rheological measurements were performed with a viscoanalyzer (Metravib R.D.S, 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 <45%). For the more liquid-like samples, two different devices were used, depending on the range of temperature: annular pumping to 52–53°C, then annular shearing to 85°C. This change in device was necessary because during the thermal treatment, liquid-like samples became more rigid and annu-

<sup>1</sup> Laboratoire de Physicochimie et Propriétés Sensorielles des Aliments, Ecole Nationale Supérieure de Biologie Appliquée à la Nutrition et à l'Alimentation, 1 Esplanade Erasme, 21000 Dijon, France.

<sup>2</sup> Corresponding author. Phone: +33 3 80 39 66 55. Fax: +33 3 80 39 66 11. E-mail: mlemeste@u-bourgogne.fr

lar pumping was not efficient anymore. These different modes are shown in Fig. 1.

**Plan shearing.** This device required two samples of the same size. Samples were 3 mm high  $\times$  15 mm in diameter or 4 mm high  $\times$  20 mm in diameter. They were vertically glued with cyanoacrylate glue (Amartron, England) on the outside and inside plates. The inside plates were connected to a sensor that regulated the amplitude and the frequency of the strain, whereas the outside plates were connected to a sensor that registered the stress.

**Annular pumping.** Several milliliters of sample were poured into a cylindrical cell. A piston was oscillating with small amplitude in the center of the cell, which was glued with cyanoacrylate glue onto the sensor registering the stress. The piston was screwed into the sensor that regulated the amplitude and frequency of the strain.

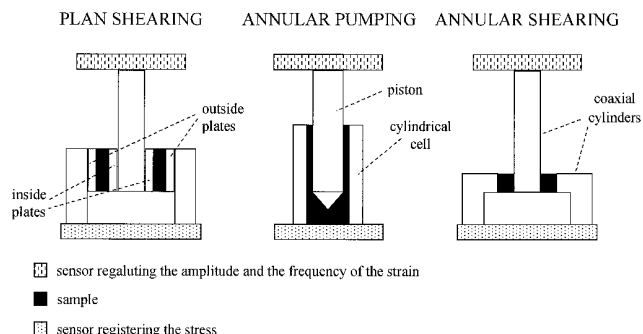
**Annular shearing.** This device consisted of coaxial cylinders connected to sensors. The gap between the two cylinders was 2 mm. The sample dispersion, poured into the cell in the liquid state before heating, was held in the annular space by capillary force.

Samples were coated with mineral oil (Nachet, France) for plan and annular shearing, or with silicone grease (Rhône Poulenc, France) for annular pumping, to prevent drying during the analysis. The strain and frequencies were set at 3  $\mu$ m and 5, 10, 20, or 40 Hz, respectively. Initially, strain sweep tests were performed at different temperatures. They confirmed that measurements were being run in the linear range of viscoelasticity. Starch samples were heated from 25 to 85°C (at 1.5°C/min) during the analysis. The highest temperature was 85°C, above which starch granules might be damaged (Tester and Morrison 1990). All tests were performed at least in triplicate.

The VA2000 software package provided by Metravig R.D.S allowed calculation of rheological parameters including storage modulus ( $E'$ ). The average standard deviation for all the tests was calculated to be 10.4%.

## ESR

Hydrated starch has no paramagnetic activity, so the spin-probing technique was employed, in which a compound with a nitroxide radical, possessing a stable free electron, is added to the system. The ESR spectra reflect the motion of the small paramagnetic probe, which depends on the probe size and on the solvent viscosity. The size and polarity of the probes influence their accessibility to micro-environments and their behavior in a network. A smaller probe may stay relatively mobile, whereas for steric reasons, a larger molecule may have a reduced mobility. The 4-hydroxy-2,2,6,6-tetramethylpiperidine *N*-oxyl (Tempol) radical was purchased from Aldrich Chemicals (Strasbourg, France). Because of its small size, this probe has the capability to diffuse into starch granules, so it can be dispersed in the aqueous phase inside and outside the granules. When preparing the samples, 300  $\mu$ L of a Tempol aqueous solution (2 mg/mL) were added to distilled water, then manually mixed with starch (final Tempol concentration:  $\approx 2.44 \times 10^{-7}$  mol/g of dry starch). Sealed capillary tubes containing aliquots of the samples



**Fig. 1.** Schematic cross sections of devices used for dynamic mechanical thermal analysis (DMTA).

were placed in 3-mm diameter ESR sample quartz tubes, and ESR spectra were collected using a Bruker EMX spectrometer (Bruker, France) with a nitrogen-flow temperature control. The operating frequency and center field were, respectively, at  $\approx 9.42$  GHz and 3,357 G. The spectra were recorded at a microwave power of 10 mW. Any saturation phenomenon was avoided. Scan rate, time constant, and modulation amplitude were adjusted so that distortion of the spectra was avoided. For all experiments, the temperature was varied stepwise every 2°C for 25–85°C. The sample was stabilized for 3 min before recording the spectra. All ESR experiments were made in triplicate. The average standard deviation for all the tests was calculated to be 8.8%.

The rotational correlation time ( $\tau_c$ ) was determined as:

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

deduced from the Freed and Fraenkel (1963) theory, where  $\Delta H_{I_{+1}}$  is the width of the  $I_{+1}$  line, and  $I_{+1}$  and  $I_{-1}$  are, respectively, the height of the lines  $I_{+1}$  and  $I_{-1}$  (Fig. 2). The conventional ESR method was used, allowing mobility measurements in the range  $10^{-11} < \tau_c < 10^{-7}$  sec. The rotational diffusion coefficient ( $D_{rot}$ ) was evaluated from the rotational correlation time ( $\tau_c$ ):

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

## RESULTS

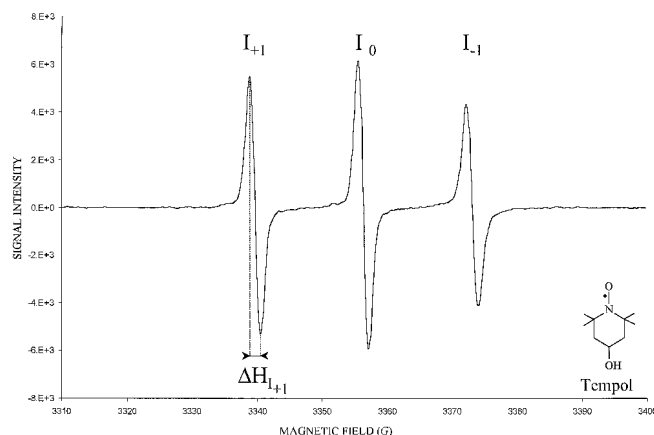
### Melting of Ordered Regions

All DSC thermograms are displayed in Fig. 3. Starch-water preparations showed three endothermic peaks. The first and second transitions formed a biphasic endotherm made up of a main peak and a trailing shoulder:  $G$  and  $M_1$ , respectively, according to Donovan (1979). When the water content decreased from 60 to 25% moisture content, the  $G$  peak area decreased progressively, while  $M_1$  peak area increased and became predominant at a water content of 40%. The first peak ( $G$ ) disappeared at 25 and 30% moisture content. Furthermore, whereas  $G$  remained located in the same temperature range,  $M_1$  shifted to higher temperatures when the moisture content decreased (Fig. 3). Similar observations have already been reported for wheat starch (Eliasson 1980, Ghiasi et al 1982). A shift to higher temperatures was also observed for the third transition ( $M_2$ ) when the moisture content decreased.

Partial melting enthalpy to 85°C is displayed in Fig. 4. The higher the moisture content, the faster and more pronounced was the melting of starch-ordered zones in the temperature range considered.

### Viscoelastic Behavior of Starch-Water Preparations

The observed changes in moduli were not frequency-dependent in the frequency range considered. Thus, only the 5 Hz results are



**Fig. 2.** Typical electron spin resonance (ESR) spectrum of a nitroxide free radical (Tempol).

shown and discussed. Storage modulus ( $G'$ ) versus temperature was plotted for all moisture content levels (Fig. 5A). Because the scale used for  $G'$  in Fig. 5A was very large, the curves plotted for moisture contents <40% were very close. Therefore, this part of the graph was expanded (Fig. 5B).

The initial storage modulus ( $G'_i = G'$  at 25°C) increased as moisture content decreased. For dispersions with 50–60% moisture content,  $G'_i$  was very low (1–10 Pa), whereas  $G'_i$  was very high for dispersions with 25–45% moisture content ( $2 \times 10^5 - 2 \times 10^6$  Pa). Because of a lack of sensitivity, a major shortcoming of the annular pumping device was the difficulty in accurately measuring storage modulus at the lowest starch concentrations in the low temperature range.

Upon heating, the storage modulus  $G'$  decreased slightly to 45–60°C. For samples with 50, 55, and 60% moisture content,  $G'$  increased very strongly at 50–55°C and reached a maximum value at 68–70°C, then decreased slightly to 85°C. The lower the moisture content, the higher was the maximum value of  $G'$ . The dispersions with the highest  $G'_i$  (moisture content of 25–40%) did not show important viscoelastic changes (Fig. 5A) during heating. However, for the dispersions at 30–40% moisture content, an expansion of the corresponding curves (Fig. 5B) revealed that  $G'$  increased from 60–63°C to a maximum value of  $\approx 74^\circ\text{C}$ , followed by a decrease until the end of heating. For the lowest moisture content (25%), no  $G'$  increase was observed.

Another interesting feature appeared to be the influence of moisture content on the onset of the  $G'$  increase. Figure 6 illustrates the relationship between the moisture content and the temperatures of onset of the  $G'$  increase and of maximum  $G'$ . As moisture content decreased, maximum  $G'$  was shifted toward slightly higher temperatures. Moreover, for dispersions with moisture contents in the 45–60% range, the lower the moisture content, the lower was the temperature of onset of the  $G'$  increase. A 15°C jump in the temperature corresponding to the onset of the  $G'$  increase was observed between 45 and 40% moisture content.

### Motional Behavior of Tempol in Starch-Water Dispersions

For all the moisture contents in the temperature range studied using ESR, three line spectra similar to those of the probe in water were obtained. This behavior is generally interpreted in terms of isotropic motion (Biliaderis 1986). However, lineshape changes occurred during the thermal treatment, manifested primarily in changes in the peak width and height ratios. The calculated rotational diffusion coefficients ( $D_{\text{rot}}$ ) for starch-water systems (Fig. 7) were lower than the values for the probe in water (not shown). For 50 and 60% moisture contents, a slight decrease in  $D_{\text{rot}}$  of the water-soluble probe was observed from 25 to 47–50°C, followed by a pronounced decrease to 57–60°C. Then an increase in  $D_{\text{rot}}$  was evidenced from  $\approx 60$  to 85°C. For the lower moisture contents (30 and 40%), only a reduced increase in  $D_{\text{rot}}$  was observed from  $\approx 70$  to 85°C.

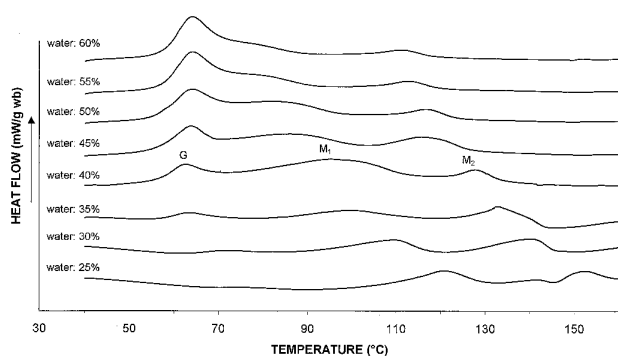


Fig. 3. Differential scanning calorimetry thermograms of wheat starch preparations at intermediate moisture contents (wb, w/w).  $G$ ,  $M_1$ , and  $M_2$  indicate the three successive endothermic peaks.

### Loss of Ordered Regions

DSC curves were strongly affected by the mass fraction of water. The behavior of the starch-water dispersions is in agreement with previous findings on different starches (Donovan 1979, Eliasson 1980, Keetels 1995, Garcia et al 1997, Rolée and Le Meste 1997). The typical biphasic gelatinization endotherm was observed for moisture contents at 35–60%. When the moisture content decreased, the  $G$  peak area decreased progressively and became almost imperceptible at moisture contents of 25 and 30%; this could be explained by an insufficient amount of material involved in this endothermic phenomenon (Garcia et al 1996). The third transition was attributed to the melting of amylose-lipid complexes (Kugimiya et al 1980).

Liu et al (1991) and Chinachoti (1994) emphasized that the literature on gelatinization contained a number of conflicting results. Several interpretations have been suggested for the state change responsible for this biphasic profile:

By observing molecular order using X-ray diffraction, Maurice et al (1985) reported only minor crystallinity changes after the first thermal event (first DSC peak [ $G$ ]). It has been suggested that the characteristic biphasic endotherm could represent a combination of a glass transition of water-plasticized amorphous regions responsible for a change in heat capacity and located at the leading edge of the first peak, thus permitting the following nonequilibrium melting of microcrystallites of the partially crystalline amylopectin (Maurice et al 1985, Russell 1987, Slade and Levine 1988, Slade et al 1996). Biliaderis et al (1986) agreed with this hypothesis but added that a DSC thermal curve was not representative of the initial crystalline profile. Instead, it would reflect the composite thermal effect of several processes that may occur simultaneously during heating: melting, annealing, and crystallization. The water, acting as a plasticizer, would decrease the glass transition temperature of the amorphous parts of the granule and, hence, facilitate the melting or reorganization of the starch crystallites and of amylose-lipid complexes, thus occurring at lower temperatures (Slade and Levine 1988).

However, according to DSC results, Zeleznak and Hosney (1987) postulated that the glass transition occurred at a temperature well below the starch melting temperature. Furthermore, X-ray diffraction experiments by Liu et al (1991) suggested that melting accounted for both DSC transitions ( $G$  and  $M_1$ ) and that the thermal expansion observed by thermomechanical methods was due to the increasing amount of amorphous starch rather than to a glass transition followed by a melting.

The biphasic profile observed in conditions of reduced hydration might be better explained by other interpretations, taking into account the heterogeneous distribution of water in the sample.

Donovan (1979) postulated that the first peak reflects stripping of polymer chains from the surface of the crystallites, facilitated

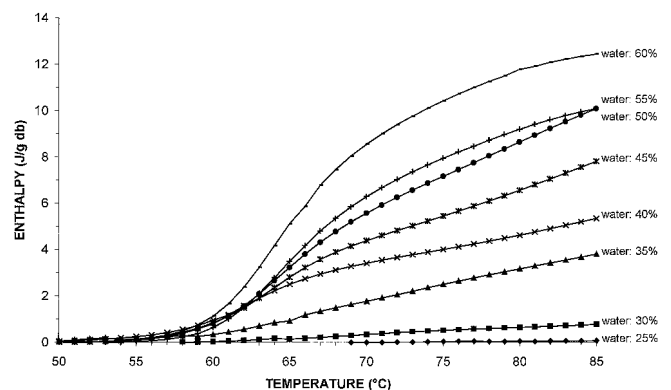


Fig. 4. Partial melting enthalpy as a function of temperature for wheat starch preparations (moisture content, wb, w/w).

by the destabilizing action of hydration and swelling of the amorphous regions. This phenomenon would occur first in regions with relatively high concentrations of water. As these localized concentrations of water decreased, the remaining less hydrated crystallites would undergo melting at higher temperatures, giving rise to the second peak.

Whereas this hypothesis focuses attention at the crystallite level, Evans and Haisman (1982) proposed a similar interpretation considering the granule level. They suggested that the successive endothermic peaks would correspond to melting transitions of crystalline materials with different stabilities due to the heterogeneous moisture distribution within the sample. Granules with the least perfect crystallites gelatinize cooperatively, and consequently, the effective water concentration available for the remaining ungelatinized granules is reduced, due to the interactions between water and the disordered polysaccharide chains. More recently, Beleia et al (1996) focused attention on the distribution of water at the granule level.

In agreement with the above hypothesis, and according to Garcia et al (1996), two processes would be involved in the second DSC peak ( $M_2$ ): the melting of remaining less hydrated crystallites and the redistribution of water molecules induced by the melting. The melting-dissolution process for starch would be dependent on the nature of the crystalline organization of the granules as well as on the heating rate and amount of available water (Garcia et al 1996). Under these conditions, the melting-dissociation process would also be dependent on the redistribution of the available water from one area to another and thus on the time required to assure redistribution of the water toward the crystals undergoing the melting process (Liu and Lelièvre 1992, Garcia et al 1996).

$^{13}\text{C}$  nuclear magnetic resonance (NMR) results showed that the level of helical order is often significantly greater than the extent of crystalline order as determined by X-ray diffraction, therefore suggesting that starch granules contain double-helical chains that are not involved in extended crystalline arrays (Gidley and Cooke 1991). Thus, the gelatinization enthalpy would reflect both crystalline order and the level of amylopectin double-helical order (Cooke and Gidley 1992). In fact, starch gelatinization appears to be a very complex series of events. Donovan (1979), Evans and Haisman (1982), and Biliaderis et al (1986) suggested that the enthalpy associated with gelatinization is the result of multiple thermal processes occurring within the same time frame. The gelatinization endotherm would essentially represent 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 complex molecules (Kugimiya et al 1980). The loss of crystallinity may be equivalent to an enthalpy change only in the absence of diluent (Liu et al 1991).

Thus, further information obtained from complementary methods is necessary to propose a better description of the events associated with starch gelatinization.

### Swelling of Granules and Viscoelastic Behavior

The swelling power of starch is controlled by water-holding capacity. Hydrogen bonds stabilizing the structure of the double helices in crystallites are broken during gelatinization and are replaced by hydrogen bonds between starch and water. Thus, swelling is regulated by the crystallinity of starch (Tester and Karkalas 1996). The destruction of steric constraints leads to a higher segmental flexibility of the amorphous chains and hence a higher swelling power.

Granule swelling corresponds to an increase in the volume fraction occupied by the dispersed phase (granules), which should generate changes in the rheological behavior of the dispersion, consistent with the empirical equation of Eilers and van Dijk (Ferry 1980):

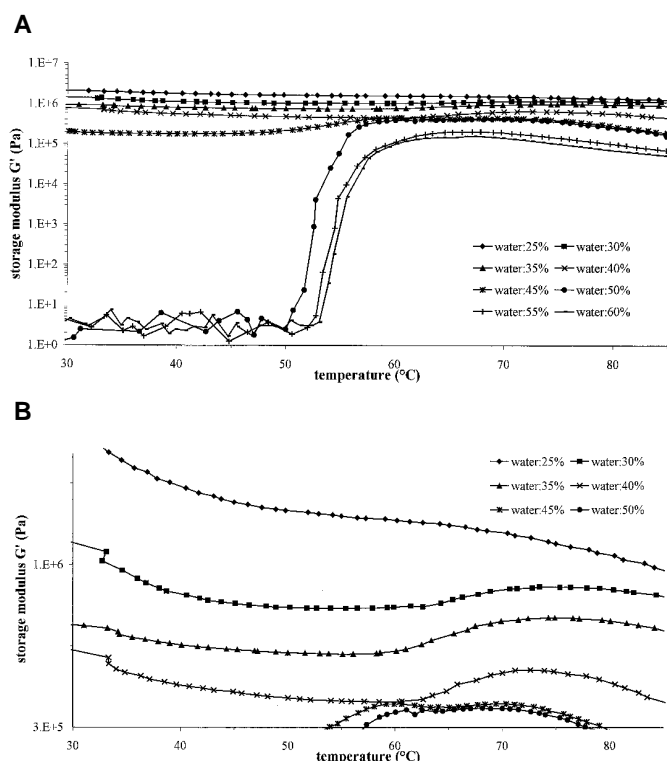
$$\frac{G_e}{G_{e0}} = \left[ 1 + \frac{1.25 \phi}{1 - \frac{\phi}{\phi_m}} \right]^2$$

where  $G_{e0}$  is the modulus of the continuous phase (without filler), and  $\phi_m$  is the maximum volume fraction corresponding to close-packing. Below close-packing ( $\phi_m$ ), the shear modulus is expected to be independent of the particle size and to increase with the volume fraction  $\phi$  of the filler.

For dispersions with 50, 55, and 60% moisture content, a strong increase in  $G'$  was observed from 50–55°C to 68–70°C, where a maximum value was reached (Fig. 5A). In such dispersions, it has already been shown that an increase in volume fraction of starch granules was responsible for an increased rigidity (Bagley and Christianson 1982, Doublier et al 1987, Rolée and Le Meste 1997).

The starch granules may be considered as dispersed fillers. So the increase in modulus  $G'$  observed between 50–55°C and 68–70°C, for dispersions with 50 to 60% moisture content could be attributed to the dominant effect of the progressive swelling of starch granules during gelatinization. The granules progressively fill the available sample volume until they touch each other (corresponding to close-packing for rigid-particle fillers). Moreover, in parallel to the change in volume fraction occupied by the granules, the granules become more hydrated, less crystalline, and thus less rigid and more deformable. Once granules are interacting,  $G'$  would still increase and reach its maximum value since swollen granules could deform and eventually reach a volume fraction equal to unity (Evans and Lips 1992, Lii et al 1996). When granules are in contact,  $G'$  would then be sensitive to the intrinsic softness of the granules. Softness may be closely related to the swollen state and the remaining ordered zones.

In their studies on rheological behavior of concentrated dispersions of soft spheres, Fridrikh et al (1996) considered a critical concentration ( $C^*$ ), defined as a concentration where the volume is filled by particles with the same size and shape as in a diluted dispersion. The volume fraction is equal to the volume fraction at close-packing for rigid particles ( $\phi \approx 0.7$ ). In other words, the concentration  $C^*$  corresponds to a maximum packing of soft but still non-deformed particles. At  $\geq C^*$ , the particles touch each other, and the system forms a gel with a crystal-like package of the particles,



**Fig. 5.** Storage modulus changes for wheat starch dispersions at intermediate moisture contents (wb, w/w) as a function of temperature during heating. **A**, all curves; **B**, expansion of curves in A.

as observed with hard spheres. Therefore, the storage modulus appears to be dependent on the individual rigidity of the particles. For native wheat starch,  $C^*$  had a 40–45% moisture content range.

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 decrease (Lii et al 1996). DSC results (Fig. 4) showed evidence of melting or dissociation of ordered zones in this temperature range.

Dispersions of 25–40% moisture exhibited a high initial modulus at 25°C ( $G' \approx 10^6$  Pa), explained by the tight packing of compressed granules. Upon heating to 85°C, only slight viscoelastic changes were observed (Fig. 5B). This is in agreement with DSC results showing only a limited melting in the temperature range considered. For the sample with 25% moisture content, no melting and no increase in  $G'$  were observed in the temperature range considered. This confirms the previous suggestion that melting induces the disappearance of steric constraints controlling the swelling and, thus, the increase in rigidity. Because the initial concentrations of these dispersions were  $>C^*$ ,  $G'$  would be sensitive to the softness of the granules within the whole heating range. This could explain the very limited  $G'$  increase and the high onset temperature for the  $G'$  increase when compared to that for the less concentrated dispersions.  $G'$  decreased slightly to 85°C, for the same reasons as dispersions with 50–60% moisture contents.

The 45% moisture content dispersion appeared to be close to a critical concentration. On one hand, these dispersions had a high initial  $G'_i$  ( $2 \times 10^5$  Pa), close to the  $G'_i$  of the more concentrated dispersions. On the other hand, Fig. 6 shows clearly that the onset of the  $G'$  increase occurred at a temperature close to those for the less concentrated dispersions. At 45% moisture content, starch granules would be at a concentration close to (but below)  $\phi_m$  before heating, generating a high initial modulus  $G'_i$ . The space left for swelling was small, and consequently during heating,  $G'$  increased by one decade only.

In the absence of melting, the hydration of the amorphous regions would result in a limited swelling of the granules. This might cause a tearing effect in the crystalline zones, breaking some of the secondary bonds stabilizing the crystalline regions. DMTA results (onset of swelling) suggest that at  $<45\%$  moisture content, this mechanical stressing of the secondary bonds would be lower, and thus the thermal energy necessary to initiate gelatinization would be higher. Note that the 45% moisture content appears to be a critical concentration for other properties. Indeed, Mendes Da Silva et al (1996) measured the degree of gelatinization of wheat starch in starch-water systems, using the ratio between the protons in the liquid phase and those in the solid phase, as determined by pulsed-proton NMR. Those authors investigated the kinetics of gelatinization versus moisture content. Based on the assumption that the gelatinization kinetics followed a first-order reaction, the minimum activation energy for gelatinization (deduced from NMR results) occurred at 45% moisture content. Mendes Da Silva et al (1996) suggested that

the process would be affected by other kinds of energy besides that caused by the increase of temperature. At 45% moisture content the hydration sites in the amorphous zones might be saturated, and the resulting increase in volume would contribute to destabilizing the crystalline regions. At lower moisture contents, the thermal energy required to initiate the gelatinization process would be higher since the mechanical stress resulting from the increase in volume might not be sufficient to break hydrogen bonds. This interpretation is in agreement with our results. At  $>45\%$  moisture content, additional energy would be necessary to break the interchain hydrogen bonds and the subsequent increase in the number of hydrated sites, causing an increase in the activation energy (Mendes Da Silva et al 1996).

For dispersions of 45–60% moisture content, the lower the moisture content (i.e., the more concentrated the starch dispersion or the higher the initial value of  $\phi$ ), the faster the preparation would reach a volume fraction  $\phi$  close to  $\phi_m$  during heating due to granule hydration and swelling. Consequently, during heating, the starch granules of less-concentrated dispersions reach close-packing at higher temperatures and hence  $G'$  also increases at higher temperatures (Fig. 6).

### Probe Mobility and Starch-Water Interactions

To detect any change in the properties of the water phase within starch dispersions, ESR was used to measure the rotational mobility of a water-soluble spin probe (Tempol). The rotational diffusivity of a probe dispersed in a homogeneous liquid medium is described by the modified Debye-Stokes-Einstein equation:

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

where  $k$  is the Boltzmann constant,  $T$  is the absolute temperature,  $\eta$  is the viscosity of the medium,  $r$  is the radius of the diffusing molecule, and  $C$  is the coupling parameter representing the amount of solvent that is dragged with the molecule when it moves (Kowert and Kivelson 1976).

In homogeneous solutions,  $\eta$  is the macroscopic viscosity of the solution. In heterogeneous systems such as concentrated starch-water dispersions, the relevant parameter for probe mobility would be the viscosity of the diffusion medium (i.e., aqueous phase). This viscosity results from the interactions between water and the starch molecules and, as such, is expected to be sensitive to starch structural disorganization.

At room temperature, the rotational diffusion coefficients ( $D_{\text{rot}}$ ) for the starch-water systems (Fig. 7) were lower than the values for the probe in water. Biliaderis and Vaughan (1987) obtained similar results with another water-soluble probe (Tempo). The observed slower motion in the presence of starch suggests that the probe molecules experienced an environment of higher viscosity. When a starch-water dispersion is prepared, the starch granules absorb water from the system, starch molecules become more hydrated, and the granules swell reversibly to some extent. Considering that because of its small size (MW = 172), the probe can diffuse inside the granule, it would thus partition between the aqueous phase

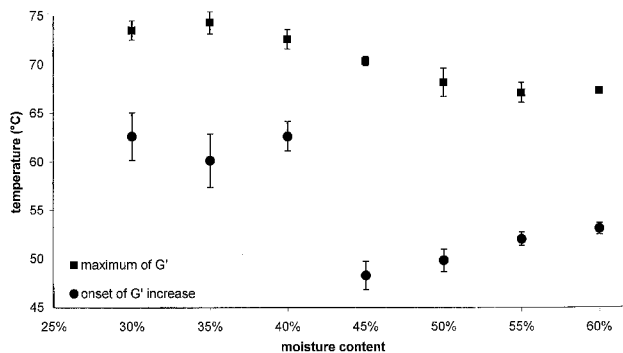


Fig. 6. Temperatures of maximum  $G'$  and onset of  $G'$  increase for wheat starch preparations as a function of moisture content (w/w, wb).

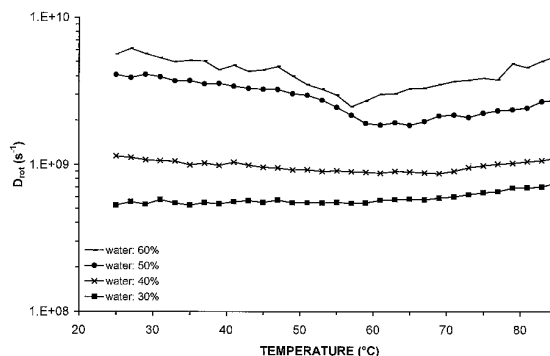


Fig. 7. Rotational diffusion coefficient of spin probe (Tempol) dispersed in the aqueous phase of wheat starch dispersions at intermediate moisture contents (wb, w/w) as a function of temperature.

entrapped within the granule and the surrounding aqueous phase. The recorded average motional mobility of the probe would thus be decreased due to the expected reduced mobility of water molecules involved in the starch-water interactions. Steric constraints could also decrease the probe mobility but this hypothesis seems unlikely since ESR spectra did not reveal any anisotropic or strongly restricted motion. This interpretation seems to be confirmed by the clear decrease in  $D_{rot}$  observed from 47–50°C to a minimum value at 57–60°C for dispersions with 50 and 60% moisture content. This decrease occurs in the same temperature range as the  $G'$  increase and the onset of the endothermic events. Therefore, the  $D_{rot}$  decrease appears to be closely related to modifications in the starch-water interactions induced by melting and to the subsequent increased swelling. The limited melting and swelling in dispersions with 30 and 40% moisture contents would explain why such a  $D_{rot}$  decrease was not observed. For all moisture contents, the increase in  $D_{rot}$  observed from 60–70°C to 85°C would reflect mainly the temperature effect on probe, starch and water mobilities.

The rotational diffusivity of probe molecules is thus expected to reflect the influence of starch and temperature on the structure and dynamics of water molecules in the solvent phase within the dispersion. It might be particularly sensitive to the disruption of low energy starch-starch interactions (melting) and to the subsequent increase in starch-water hydrogen bonding. This interpretation seems to be in agreement with NMR measurements, as well as dielectric relaxation spectra of water associated with macromolecules. These measurements distinguish water molecules where mobility is reduced due to interactions with the biopolymers and have thus a relaxation time  $\approx 10^{-9}$  sec from bulk-like water with a relaxation time of  $\approx 2 \times 10^{-11}$  sec (Biliaderis and Vaughan 1987). Indeed, Lim et al (1992) reported NMR results, for  $^{17}\text{O}$  water in starch-water preparations, which are quite in agreement with our interpretation. For 70% moisture content, they observed a decrease of the  $^{17}\text{O}$  water mobility from  $\approx 49^\circ\text{C}$  to a minimum value at  $53^\circ\text{C}$  and then a gradual increase to  $87^\circ\text{C}$ .

Moreover, it is known that some starch components, such as amylose, may dissolve in the aqueous phase during gelatinization, and hence contribute to the increase in the viscosity of this aqueous phase and reduction in water, and thus of probe mobilities.

## CONCLUSIONS

Starch gelatinization is a very complex phenomenon. It could be concluded from our results that the dissociation or melting of the crystalline regions appeared to be responsible for the extensive swelling of the starch granules during heating. At intermediate water contents, DMTA results suggested that swelling would occur in the range of temperature corresponding to the first endothermic DSC peak. In the same range of temperature, the ESR results suggested an increase in the starch-water interactions and leaching of soluble starch molecules. The increase in volume fraction generated an increase in storage modulus, when  $\phi$  reached a volume fraction close to  $\phi_m$ . The 45% moisture content level seemed critical because there was a 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 at 25–60%, the storage modulus  $G'$  would be closely related to the rigidity and the deformability of the granules once the volume fraction had reached  $\phi_m$ .

Melting is expected to control both 1) water redistribution, granules hydration, and thus swelling; and 2) granule deformability and the subsequent changes in the rheological properties of the dispersion as soon as  $\phi$  gets close to  $\phi_m$ .

A similar study is currently in progress on waxy corn starch. A comparison with the results obtained for wheat starch should permit us to estimate the influence of leaching of soluble components such

as amylose on the thermomechanical behavior and on the properties of the aqueous phase. Furthermore, the effect of sucrose on these properties is also being studied with water-sucrose-starch blends to evaluate the influence of the properties of the aqueous phase on the gelatinization process.

## ACKNOWLEDGMENTS

The study was conducted with financial support from the Commission of the European Communities, Agriculture and Fisheries (FAIR) specific RTD programme, CT96-1085: Enhancement of Quality of Food and Related Systems by Control of Molecular Mobility. It does not necessarily reflect its views and in no way anticipates the Commission's future policy in this area. We greatly appreciate the help from Patrick Calboo (University of Wageningen).

## LITERATURE CITED

- Bagley, E. B., and Christianson, D. D. 1982. Swelling capacity of starch and its relationship to suspension viscosity—Effect of cooking time, temperature and concentration. *J. Texture Stud.* 13:115-126.
- Beleia, A., Miller, R. A., and Hosney, R. C. 1996. Starch gelatinization in sugar solutions. *Starch/Staerke* 48:259-262.
- Biliaderis, C. G., Maurice, T. J., and Vose, J. R. 1980. Starch gelatinization phenomena studied by differential scanning calorimetry. *J. Food Sci.* 45:1669-1680.
- Biliaderis, C. G., Page, C. M., Maurice, T. J., and Juliano, B. O. 1986. Thermal characterization of rice starches: A polymeric approach to phase transitions of granular starch. *J. Agric. Food Chem.* 34:6-14.
- Biliaderis, C. G., and Vaughan, D. J. 1987. Electron spin resonance studies of starch-water-probe interactions. *Carbohydr. Polym.* 7:51-70.
- Chinachoti, P. 1994. Probing molecular and structural thermal events in cereal-based products. *Thermochim. Acta* 246:357-369.
- Cooke, D., and Gidley, M. J. 1992. Loss of crystalline and molecular order during starch gelatinization: Origin of the enthalpic transition. *Carbohydr. Res.* 227:103-112.
- Donovan, J. W. 1979. Phase transitions of the starch-water system. *Biopolymers* 18:263-275.
- Doublier, J. L., Llamas, G., and Le Meur, M. 1987. A rheological investigation of cereal starch pastes and gels. Effect of pasting procedures. *Carbohydr. Polym.* 7:251-275.
- Eliasson, A. C. 1980. Effect of water content on the gelatinization of wheat starch. *Starch/Staerke* 32:270-272.
- Evans, I. D., and Haisman, D. R. 1982. The effect of solutes on the gelatinization temperature range of potato starch. *Starch/Staerke* 34:224-231.
- Evans, I. D., and Lips, A. 1992. Viscoelasticity of gelatinized starch suspensions. *J. Texture Stud.* 23:69-86.
- Ferry, J. D. 1980. Cross-linked polymers and composite systems. Pages 404-436 in: *Viscoelastic Properties of Polymers*, 3rd ed. J. D. Ferry, ed. John Wiley and Sons: New York.
- Freed, J. H., and Fraenkel, J. 1963. Theory of line width in electron spin resonance spectra. *J. Chem. Phys.* 39:326-348.
- Fridrikh, S., Raquois, C., Tassin, J. F., and Rezaiguia, S. 1996. Rheological behavior of concentrated suspensions of soft spheres. *J. Chim. Phys.-Chim. Biol.* 93:941-959.
- Garcia, V., Colonna, P., Lourdin, D., Buleon, A., Bizot, H., and Ollivon, M. 1996. Thermal transitions of cassava starch at intermediate water contents. *J. Thermal Anal.* 47:1213-1228.
- Garcia, V., Colonna, P., Bouchet, B., and Gallant, D. J. 1997. Structural changes of cassava starch granules after heating at intermediate water contents. *Starch/Staerke* 49:171-179.
- Ghiasi, K., Hosney, R. C., and Varriano-Marston, E. 1982. Gelatinization of wheat starch. III. Comparison by differential scanning calorimetry and light microscopy. *Cereal Chem.* 59:258-262.
- Gidley, M. J., and Cooke, D. 1991. Aspects of molecular organization and ultrastructure in starch granules. *Biochem. Soc. Trans.* 19:551-555.
- Gluck-Hirsch, J. B., and Kokini, J. L. 1997. Determination of the molecular weight between crosslinks of waxy maize starches using the theory of rubber elasticity. *J. Rheol.* 41:129-139.
- Keetels, C. J. A. M., and Van Vliet, T. 1993. Mechanical properties of concentrated starch systems during heating, cooling, and storage. Pages 266-271 in: *Food Colloids and Polymers: Stability and Mechanical*

- Properties. E. Dickinson, and P. Walstra, eds. R. Soc. Chem.: Cambridge.
- Kowert, B., and Kivelson, D. 1976. ESR linewidths in solution. VIII. Two component diamagnetic solvents. *J. Chem. Phys.* 64:5206-5217.
- Kugimiya, M., Donovan, J. W. , and Wong, R. Y. 1980. Phase transitions of amylose-lipid complexes in starches: A calorimetric study. *Starch/Staerke* 32:265-270.
- Lii, C. Y., Tsai, M. L., and Tseng, K. H. 1996. Effect of amylose content on the rheological property of rice starch. *Cereal Chem.* 73:415-420.
- Lim, H., Setser, C. S., Paukstelis, J. V. , and Sobczynska, D. 1992. <sup>17</sup>O nuclear magnetic resonance studies on wheat starch-sucrose-water interactions with increasing temperature. *Cereal Chem.* 69:382-386.
- Liu, H., Lelievre, J., and Ayoung-Chee, W. 1991. A study of starch gelatinization using differential scanning calorimetry, X-ray, and birefringence measurements. *Carbohydr. Res.* 210:79-87.
- Liu, H., and Lelievre, J. 1992. Differential scanning calorimetric and rheological study of the gelatinization of starch granules embedded in a gel matrix. *Cereal Chem.* 69:597-599.
- Lund, D. 1984. Influence of time, temperature, moisture, ingredients, and processing conditions on starch gelatinization. *Crit. Rev. Food Sci. Nutr.* 20:249-273.
- Maurice, T. J., Slade, L., Sirett, R. R. , and Page, C. M. 1985. Polysaccharide-water interactions—Thermal behavior of rice starch. Pages 211-227 in: *Properties of Water in Foods*. D. Simatos and J. L. Multon, eds. Martinus Nijhoff: Dordrecht.
- Mendes da Silva, C. E., Ciacco, C. F., Barberis, G. E., Solano, W. M. R., and Rettori, C. 1996. Starch gelatinization measured by pulsed nuclear magnetic resonance. *Cereal Chem.* 73:297-301.
- Münzing, K. 1991. DSC studies of starch in cereal and cereal products. *Thermochim. Acta* 193:441-448.
- Rolee, A., and Le Meste, M., 1997. Thermomechanical behavior of concentrated starch-water preparations. *Cereal Chem.* 74:581-588.
- Russell, P. L. 1987. Gelatinisation of starches of different amylose/ amylopectin content. A study by differential scanning calorimetry. *J. Cereal Sci.* 6:133-145.
- Slade, L., and Levine, H. 1988. Non-equilibrium melting of native granular starch: I. Temperature location of the glass transition associated with gelatinization of A-type cereal starches. *Carbohydr. Polym.* 8:183-208.
- Slade, L., Levine, H., Wang, M., and Ievolella, J. 1996. DSC analysis of starch thermal properties related to functionality in low-moisture baked goods. *J. Thermal Anal.* 47:1299-1314.
- Tester, R. F., and Morrison, W. R. 1990. Swelling and gelatinization of cereal starches. I. Effects of amylopectin, amylose, and lipids. *Cereal Chem.* 67:551-557.
- Tester, R. F., and Karkalas, J. 1996. Swelling and gelatinization of oat starches. *Cereal Chem.* 73:271-277.
- Zelezna, K. J., and Hoseney, R. C. 1987. The glass transition in starch. *Cereal Chem.* 64:121-124.

[Received October 26, 1998. Accepted February 26, 1999.]