

# Thermomechanical Behavior of Concentrated Starch-Water Preparations

A. ROLEE<sup>1,2</sup> and M. LE MESTE<sup>1</sup>**ABSTRACT**

Cereal Chem. 74(5):581–588

The rheological behavior of concentrated starch preparations from various origins was studied by dynamic mechanical thermal analysis (DMTA). Four types of starch were used: wheat, potato, normal, and waxy corn adjusted to moisture contents in the 42–49% (w/w) range. The thermal treatments of the starch-water mixtures consisted of heating to 85°C and cooling to room temperature, both at a rate of 1°C/min. During heating, the storage modulus ( $E'$ ) appearance was first characterized by an increase with a maximum at  $\approx 70^\circ\text{C}$  (or potato starch at  $63^\circ\text{C}$ ) followed by a decrease to  $85^\circ\text{C}$ . During cooling, storage modulus increased steadily down to room temperature. The magnitude of these variations depended on the starch type. Despite some differences, all the loss tangent curves showed a decrease during heating from  $60\text{--}70^\circ\text{C}$  to  $85^\circ\text{C}$ ,

followed by a plateau during cooling. To propose an interpretation for the DMTA results, we measured, by laser-light diffraction, the influence of heating (up to the maximum  $E'$  peak) on the distribution of the granule sizes of the different starches. Moreover, differential scanning calorimetry (DSC) was used to measure the temperature range where the melting of starches ordered regions occurred. Partial melting enthalpies were plotted against temperature. The hypothesis of a relationship between swelling and an increase in rigidity during heating seemed to be confirmed by laser-light diffraction, whereas DSC indicated the decrease in rigidity was caused predominantly by order-disorder transitions. During cooling, amylose gelation plays a major role in the rigidity increase, but a contribution of amylopectin is not excluded.

Starch is one of the most important components responsible for the texture of baked cereal products. When starch-water preparations are heated, the changes in starch structure are usually called gelatinization. In the narrowest sense, gelatinization is characterized by the loss of crystalline order of native starch granules, but it generally includes granule swelling and polysaccharide (mainly amylose) leaching (Tester and Morrison 1990). It is now widely assumed that gelatinized starch preparations, which have not retrograded and have not been exposed to high temperatures, have rheological properties explained by the tight-packing of swollen and deformable granules (Evans and Haisman 1979). Another point of view, mainly based on microscopic observation, is that the rheological behavior of starch is mainly controlled by the organization of solubilized and entangled macromolecules leached out of the granules during gelatinization (Miller et al 1973). This proposition seems to be unsatisfactory for concentrated preparations (Evans and Lips 1992). Upon heating low concentration starch preparations much below a volume fraction ( $\phi$ ) of 0.7, which is the maximum volume fraction corresponding to close-packing of monodispersed spheres like Sephadex beads, the granules swell but don't occupy completely the available volume. Then, amylose leaches out of the granules and phase separation between amylopectin and amylose is nearly complete (Keetels 1995). The swollen granules, essentially composed of amylopectin, are embedded in an amylose matrix, which would play an important role in the rheological behavior of the composite. However, at high starch concentrations, the granules are only partially swollen after heating, and they occupy almost all the available volume. Furthermore, amylose and amylopectin are only partially separated, the swollen granules including consequently both amylose and amylopectin. The two key variables of the rheological behavior of concentrated starch preparations during a thermal treatment would be the volume occupied by the granules (closely related to swelling) and their deformability; the amylose continuous phase plays only a minor role (Keetels 1995).

The aim of this study was to examine the relationships between the modifications of the rheological behavior under low amplitude sinusoidal strains (storage modulus  $E'$  and  $\tan \delta$ ) and some structural changes of various concentrated starch preparations during a thermal treatment. Dynamic mechanical thermal analysis (DMTA) experiments were performed in parallel with an evaluation (by laser-light diffraction) of the influence of heating on the distribution of the granules sizes. Moreover, differential scanning calorimetry (DSC) was used to measure the temperature range where the ordered regions of starch melted. This work should permit a better understanding of the factors controlling the evolution of the rheological properties of bread dough during baking; indeed, the rheological behavior is expected to control the texture of baked products.

**MATERIALS AND METHODS****Samples**

Wheat starch was prepared from type 55 wheat flour by washing out with cold water then lyophilization. Potato starch used was Vivien Paille potato starch. Corn starches were obtained from Cerestar-France. The main characteristics of the starches are listed in Table I.

Preparations were made with starch and distilled water. Moisture contents were adjusted to be close to bread dough water content, as well as to reach a consistency allowing DMTA tension-compression experiments. The manual blending was continued until a homogeneous cohesive mixture was obtained.

**Moisture Contents**

A few grams of preparations were weighed, placed in an oven at  $105^\circ\text{C}$  for 5 hr and then in a dry atmosphere for 1 hr before being weighed again. Moisture contents are expressed in grams of water per 100 g of wet sample (% w/w) in Table I. Measurements were repeated twice and an average value was calculated.

**DMTA**

Analyses were made after a 1-hr rest in a covered bowl. The small amplitude oscillatory rheological measurement was performed with a viscoanalyzer (Metravib R.D.S, Limonest, France) between 40-mm diameter parallel plates. Samples were  $\approx 10$  mm high  $\times$  15 mm diameter. They were glued onto the plates with cyanoacrylate glue (Cyanolit) and coated with a silicone grease

<sup>1</sup>Laboratoire de Biochimie, 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. E-mail: arolee@u-bourgogne.fr

(Rhône-Poulenc) to prevent drying. The strain and frequency were set at 5  $\mu\text{m}$  and 5 Hz respectively, for all determinations. Strain sweep tests were performed at different temperatures. They confirmed that measurements were run in the linear range of viscoelasticity. Starch samples were heated to 85°C (1°C/min), then immediately cooled to room temperature (-1°C/min) during the 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.

The VA2000 software package provided by Metravig R.D.S allowed calculation of rheological parameters including storage modulus ( $E'$ ) and loss tangent ( $\tan \delta$ ).

### Laser-Light Diffraction

Analyses were made on native and heated starch samples to estimate the size distribution and the swelling of the granules. To have conditions similar to those of DMTA experiments, the samples used were  $\approx 10$  mm high  $\times$  15 mm diameter. Heating was performed on samples coated with a silicone grease in the viscoanalyzer oven at 1°C/min. Samples were heated to 70°C for wheat,

corn, and waxy corn starches, and to 63°C for potato starch. They were then immediately dispersed manually in water before being poured in the waterbath of the particle-size analyzer. This apparatus allowed a brief sonication before each measurement to improve the starch granules dispersion. Analyses were done at room temperature. All tests were performed at least in triplicate.

Particle-size distributions were determined using a particle-size analyzer (Mastersizer S2-01, Malvern Instruments). The determination is based on the analysis of the forward light-scattering by the particles. The software package allowed diffraction patterns to be converted into particle-size distributions expressed in percentage of occupied volume, assuming that starch granules were spherical particles.

### DSC

DSC assays were made on a Perkin-Elmer DSC-7 instrument, calibrated with azobenzene and indium in the positive temperature range. Starch-water preparations (50–80 mg) were weighed and hermetically sealed in stainless steel DSC pans. After a 1-hr rest at room temperature, the sample pans were heated from 25 to

TABLE I  
Main Characteristics of Starch Samples

Starch Type	Amylose(%) <sup>a</sup>	Amylopectin(%) <sup>a</sup>	Density(g/cm <sup>3</sup> )	Initial Moisture Content (%) <sup>b</sup>	Granule Size ( $\mu\text{m}$ ) <sup>c</sup>	Starch Preparation	
						Moisture (%) <sup>c</sup>	$\phi_i$ <sup>d</sup>
Wheat	25	75	1.49	12.4	2–10/20–35	42	0.53
Potato	20	80	1.48	14.9	15–120	46	0.49
Normal corn	26	74	1.50	12.5	5–25	47	0.47
Waxy corn	1	99	1.50	12.2	5–25	49	0.44

<sup>a</sup> Percentages currently found in the literature for wheat and potato starch. Percentages given by Cerestar-France for normal and waxy corn starch.

<sup>b</sup> Moisture contents are expressed in grams of water per gram of wet sample (% w/w).

<sup>c</sup> Granule sizes currently found in the literature.

<sup>d</sup> Initial volume fractions were calculated as:  $\phi_i = 1 / (1 + d[r - (m_i/100)])$ , where  $d$  is starch density,  $r$  is water-to-starch mass ratio, and  $m_i$  is initial moisture content.

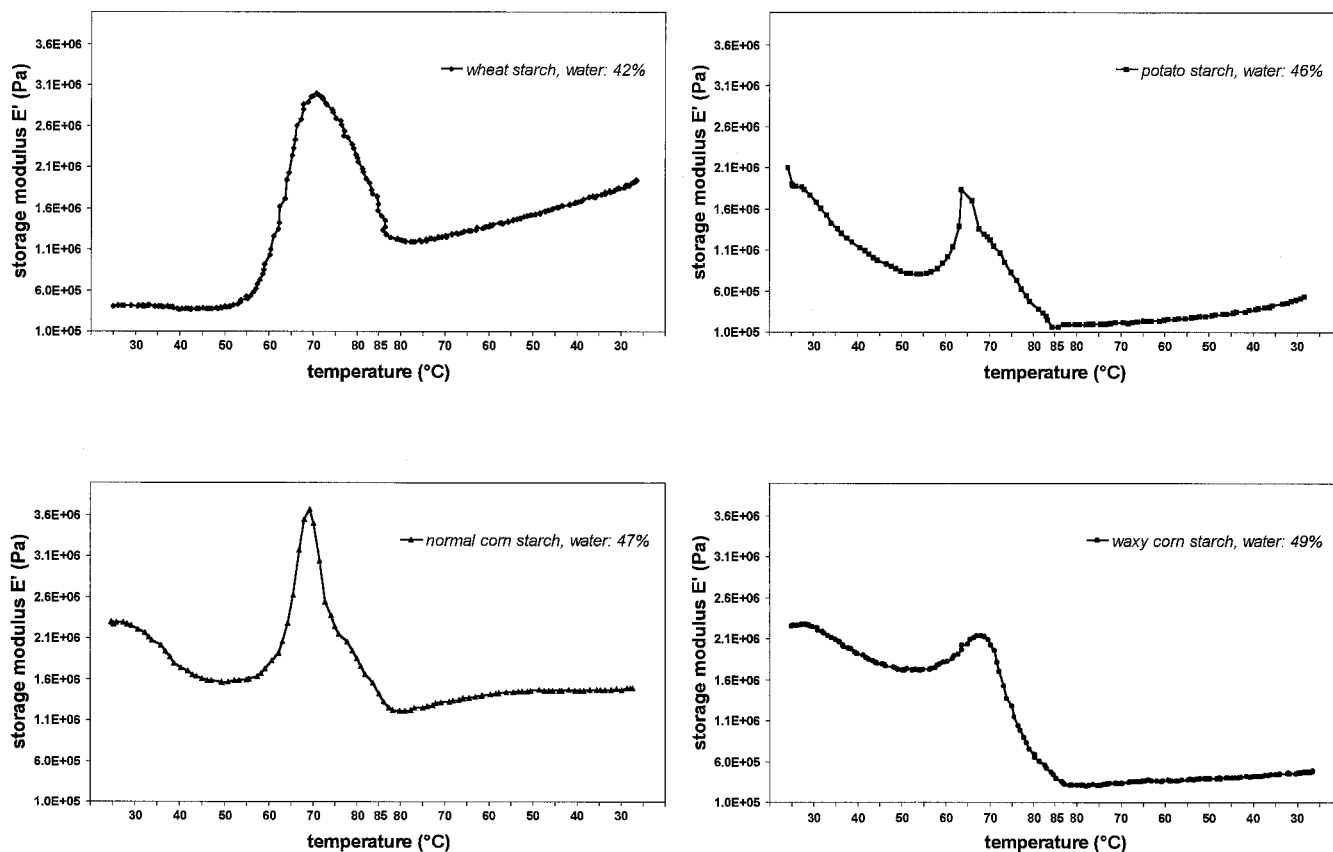


Fig. 1. Storage modulus changes for concentrated starch preparations (moisture contents expressed on a wet basis) as a function of temperature during a heating and cooling cycle.

125°C (135°C for wheat starch) at a scanning rate of 5 or 10°C/min. An empty pan was used as the reference. All tests were performed at least in triplicate. For each endotherm, the melting enthalpy  $\Delta H$  (J/g of dry sample) and the initial, 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.

## RESULTS

### Viscoelastic Behavior of Starch-Water Preparations

Viscoelastic properties were measured by DMTA in the tension-compression mode.

*Wheat starch.*  $E'$  decreased slightly up to 50°C. Rigidity increased strongly from 50 to 70°C, and decreased up to 85°C (end

of heating). During cooling,  $E'$  increased almost linearly (Fig. 1). When the sample was held for 5–10 min at 85°C, a slightly more pronounced decrease of rigidity was observed, but the slopes remained identical during cooling (results not shown). The loss tangent remained constant to 60°C, then dropped until the end of heating. During cooling, the loss tangent was stable, then increased very slightly from 50°C to room temperature (Fig. 2). This behavior was similar to that described for shear measurements on less concentrated preparations (Svegmark and Hermansson 1991, Lii et al 1995).

*Potato starch.*  $E'$  decreased up to 54°C. The rigidity increased strongly from 54 to 63°C, then decreased up to 85°C. The rigidity increase during cooling was less pronounced than for wheat starch (Fig. 1). The loss tangent curve (Fig. 2) showed an increase with a maximum at 50°C, then a decrease, very pronounced from 65°C to the end of heating. A very slight increase was observed during cooling.

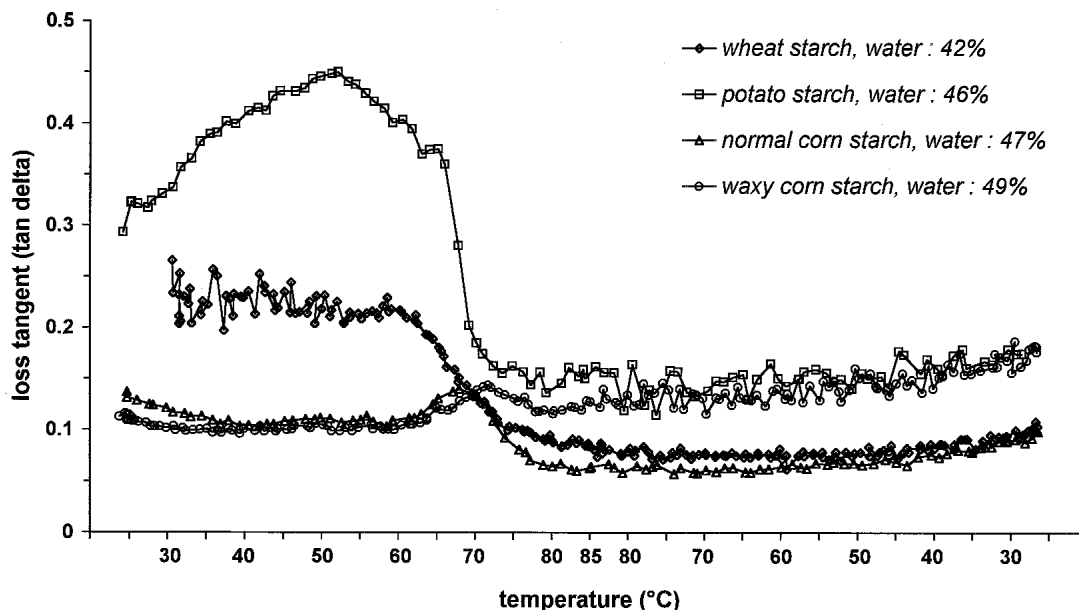


Fig. 2. Loss tangent of concentrated starch preparations (moisture contents expressed on a wet basis) as a function of temperature during a heating and cooling cycle.

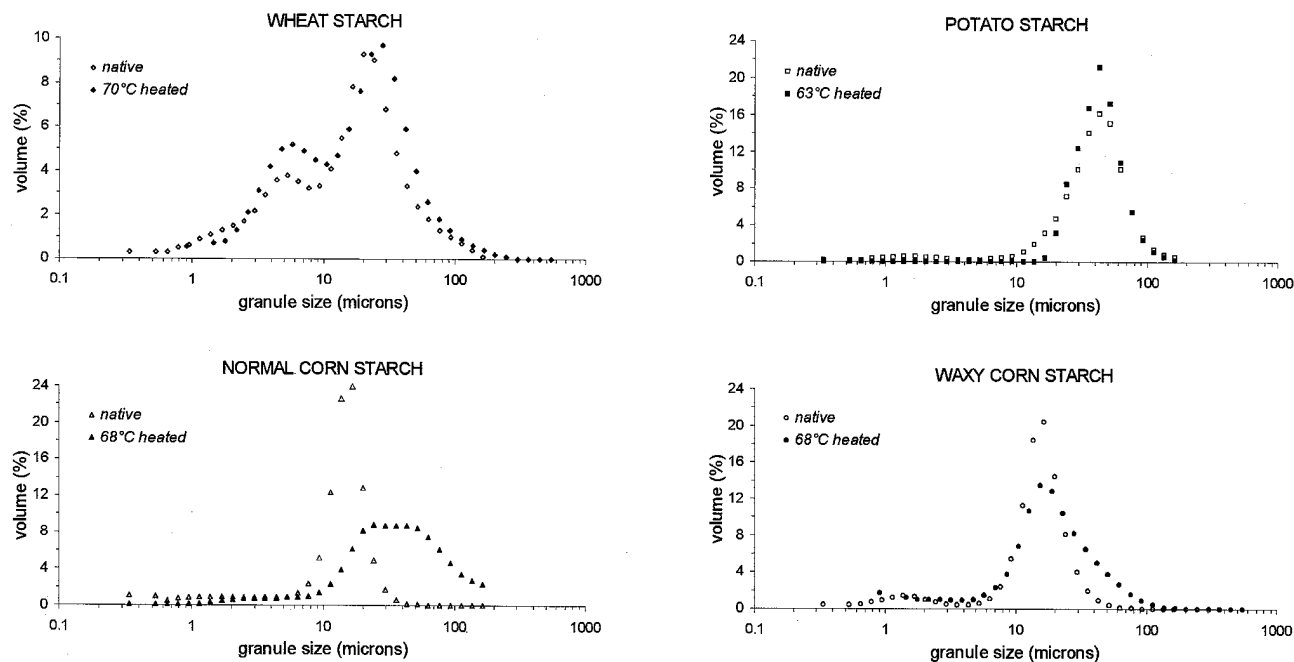


Fig. 3. Volume frequency distributions of native and heated starch preparations granule size. Moisture contents are given in Table I.

*Normal corn and waxy corn starches.* These two types were characterized by a decrease of  $E'$  from 25 to 54°C, then an increase, slight for waxy corn starch and more pronounced for normal corn, with a maximum at 68°C. Then, the rigidity decreased up to 85°C (end of heating). During cooling, the increase of  $E'$  was lower for waxy corn than for normal corn (Fig. 1). The loss tangent curves were quite identical up to 70°C, showing a small peak at this temperature (Fig. 2). Until the end of heating, the loss tangent decreased, but only very slightly, for waxy corn starch. During cooling,  $\tan \delta$  was quite stable despite a slight increase for normal corn starch.

### Size and Swelling Studied by Laser-Light Diffraction

*Wheat starch.* For native starch, Figure 3 showed polydispersed granules (two populations), as described in the literature (Galliard and Bowler 1987; C. C. Maningat and P. A. Seib, unpublished): granules of small sizes with diameters varying from 0.5 to 10  $\mu\text{m}$  (mean value: 5  $\mu\text{m}$ ) and larger granules with diameters >10  $\mu\text{m}$  (mean value: 20  $\mu\text{m}$ ). The abnormal high values of diameters (>100  $\mu\text{m}$ ) in the particle-size distribution could be explained by aggregates when wheat starch-water blends were prepared.

Heating to 70°C, the temperature at maximum rigidity (Fig. 1), induced an increase in the granule size. Most of the granules with very small sizes disappeared; they all reached a diameter >2  $\mu\text{m}$ . For the largest granules, the peak maximum was shifted toward  $\approx 25 \mu\text{m}$ .

*Potato starch.* For native starch, Figure 3 showed monodispersed granules (one population), whose diameters varied from 10 to >100  $\mu\text{m}$ , the majority being centered at  $\approx 40 \mu\text{m}$ .

After heating to 63°C, the temperature at maximum rigidity (Fig. 1), swelling affected mainly the smallest granules ( $\varnothing < 60 \mu\text{m}$ ) with no significant changes observed in the largest ones.

*Normal corn starch.* For native starch, Fig. 3 showed monodispersed granules whose diameters varied from 5 to 40  $\mu\text{m}$ , the majority being centered at  $\approx 14\text{--}15 \mu\text{m}$ .

After heating to 68°C, the results showed clearly an important change of the distribution toward larger diameters, from 10  $\mu\text{m}$  to >100  $\mu\text{m}$  with the majority of granules being centered at  $\approx 35 \mu\text{m}$ .

*Waxy corn starch.* For native starch, Fig. 3 showed monodispersed granules as described in the literature with diameters varied from 5 to 50  $\mu\text{m}$ , centered at 14–15  $\mu\text{m}$ .

After heating to 68°C, the results showed a slight shift of the distribution toward larger diameters (to 100  $\mu\text{m}$ ). In comparison with normal corn starch, swelling was clearly less important, the majority of granules being centered at 18  $\mu\text{m}$  only.

### Melting of Ordered Regions Studied by DSC

Results are summarized in Table II. All curves are displayed in Figure 4. Wheat and normal corn showed respectively two endotherms. The first one was assigned to amylopectin double helices dissociation and crystals melting, whereas the second one was attributed to amylose-lipid complexes melting. Potato and waxy corn starches showed only the first endotherm. The first endotherm for all preparations was a biphasic endotherm as it was made up of a main peak and a shoulder.

Partial melting enthalpy increased until 85°C (Fig. 5). In comparison with normal and waxy corn, the melting of wheat starch ordered zones began at a lower temperature and the partial melting enthalpy reached at 85°C was lower too. Thus, normal and waxy corn ordered zones melted faster. The melting of potato starch ordered zones was faster and much more pronounced up to 85°C than for all the other starches we studied.

TABLE II  
Differential Scanning Calorimetry Data of Starch Samples Gelatinization<sup>a-c</sup>

Starch Type	Melting Endotherm				Amylose-Lipid Complexes Endotherm			
	$T_i$	$T_p$	$T_e$	$\Delta H \pm SD$	$T_i$	$T_p$	$T_e$	$\Delta H \pm SD$
Wheat	56.7	72.0	112.0	10.46 $\pm$ 0.54	116.9	130.8	143.8	0.96 $\pm$ 0.05
Potato	62.1	72.9	98.5	16.19 $\pm$ 0.56				
Normal corn	63.4	79.6	106.0	10.40 $\pm$ 0.21	106.5	119.4	128.5	1.03 $\pm$ 0.06
Waxy corn	64.0	81.7	107.3	14.92 $\pm$ 0.12				

<sup>a</sup> Values are means of at least three determinations.

<sup>b</sup>  $T_i$ ,  $T_p$ , and  $T_e$  = initial (when curve deviates from baseline), peak maximum, and end (of endothermic peak) temperatures (°C).  $\Delta H$  = gelatinization enthalpy (J/g of dry matter).

<sup>c</sup> Moisture contents are given in Table I.

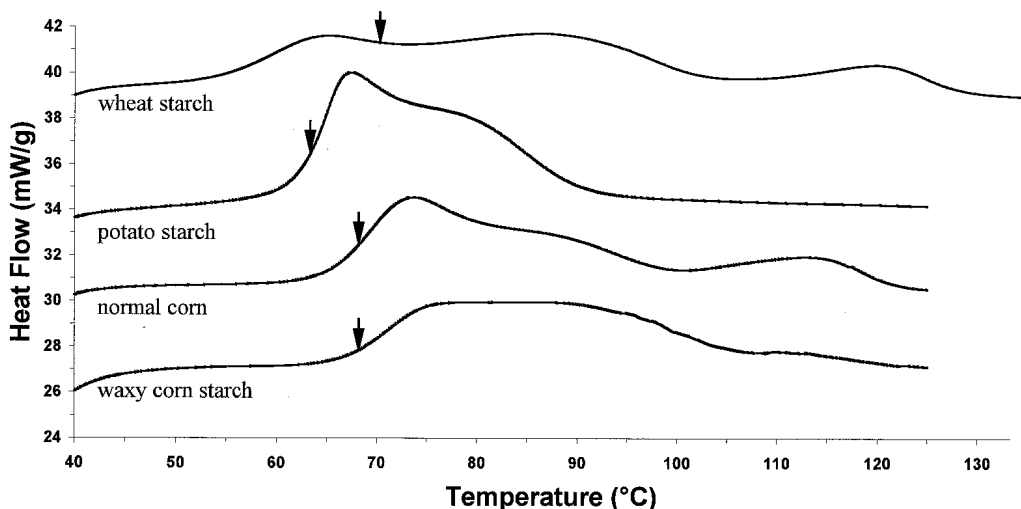


Fig. 4. Differential scanning calorimetry thermograms of concentrated starch preparations: wheat (42% w/w water), potato (46% w/w water), normal corn (47% w/w water), waxy corn (49% w/w water). Arrows indicate temperature at maximum rigidity.

## DISCUSSION

### Order-Disorder Transition

To study changes in the ordered arrangement within starch granules during heating, DSC proved to be one of the most effective methods. Previous studies (Donovan 1979, Biliaderis et al 1980, Eliasson 1980, Ghiasi et al 1982) have already shown the major role played by the water-starch ratio. An endothermic peak was present at  $\approx 60^\circ\text{C}$  at high moisture contents ( $>65\%$  w/w), the position of the peak and the enthalpy varied slightly with the starch type (Stevens and Elton 1971, Wootton and Bamunuarachchi 1979, Kugimiya et al 1980, Russel 1987). For lower moisture contents, the endotherm decreased and developed a trailing shoulder. This shoulder shifted progressively to higher temperatures when moisture content decreased, and at very low moisture contents ( $<35\%$ , w/w), only the second endotherm is present. In our case, moisture contents were ranged from 42 to 49%. In the 50–100°C range, we observed indeed two successive, but not separated endothermic peaks, which we named a biphasic endotherm. The presence of a third endothermic peak was observed only for starches containing both amylose and lipids; it has been attributed to the dissociation of amylose-lipid complexes (Kugimiya et al 1980).

The gelatinization endotherms of the different starches have been attributed to amylopectin crystals melting (Tester and Morrison 1990). Several explanations have been suggested for the state change responsible for their biphasic profile. According to Evans and Haisman (1982), the granules could enclose crystalline zones with different stabilities. Thus, the most hydrated crystals would melt first, allowing water uptake by granules. The remaining less hydrated crystals (the most stable ones) would melt at a higher temperature, depending on water availability and therefore on sample moisture content (Evans and Haisman 1982). The predominant role of the distribution of water in the biphasic behavior was reinforced by other studies (Liu and Lelievre 1992). According to Tester and Morrison (1990), the crystalline order in the native granules would be due to "clusters" of double helix made up with amylopectin adjacent chains. The "clusters" dissociation could be responsible for the first part of the endotherm (the loss of birefringence examined by optical microscopy would happen at this moment). The second part of the endotherm would be explained by the dissociation and the disappearance of the double helices (Tester and Morrison 1990). However, Gidley and Cooke (1991) inferred from their results that, for waxy maize starch, loss of

crystalline and molecular order were not experimentally resolvable events during gelatinization (i.e., hypotheses invoking melting of noncrystalline molecular order before crystalline order loss or those invoking loss of crystal register before molecular order loss did not appear to be appropriate). The biphasic profile also suggested simply the image of melting and reorganization processes happening simultaneously during heating (Biliaderis et al 1986, Biliaderis 1992). Other authors proposed that this characteristic biphasic endotherm could represent a combination of glass transition, of water-plasticized amorphous regions, followed by nonequilibrium melting, of microcrystallites of the partially crystalline glassy amylopectin (Slade and Levine 1988, Slade et al 1996).

### Granule Swelling

Granules size evaluations were made at ambient temperature on native and on heated starch preparations. The preparations were heated to a temperature which generated maximal rigidity in DMTA (Fig. 1).

Several facts were noteworthy. Up to  $70^\circ\text{C}$ , the small wheat starch granules swelled, whereas the larger ones varied slightly. This could be explained either by the fact that wheat starch granules have undergone a two-stage swelling: from 60 to  $80^\circ\text{C}$  then from 80 to  $85^\circ\text{C}$  (Williams and Bowler 1982), or most likely by the lack of available volume at such concentrations (42% moisture content). Indeed, at high concentrations, the larger granules are nearly close-packed, but the smaller ones have more available volume to swell between the large ones. For potato starch, up to  $63^\circ\text{C}$ , swelling occurred only in the granules with diameters  $<60\ \mu\text{m}$ . For normal corn starch, a marked swelling happened by heating the preparation up to  $68^\circ\text{C}$ . However, though native waxy corn starch and native normal corn starch had similar granule sizes and similar moisture contents, waxy corn starch granules surprisingly showed only a limited swelling. It has been shown that waxy corn starch swells much more than normal corn starch in excess of water (Navarro et al 1996). The same observations were noted on waxy and normal barley starch, and it was concluded that swelling could be a property of amylopectin (Tester and Morrison 1990). The results we obtained for normal and waxy corn starches did not agree with that observation. Higher concentrations may explain this disagreement, in a way still unknown.

For each starch type, granule swelling means an increase in the volume fraction of the dispersed phase (granules), which should generate changes in the rheological behavior.

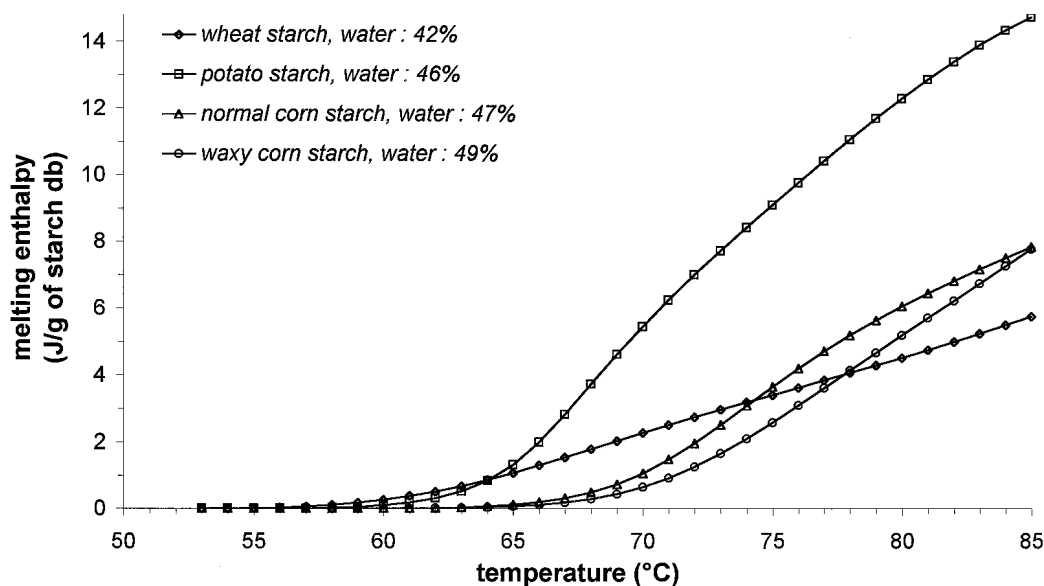


Fig. 5. Partial melting enthalpy as a function of temperature for concentrated starch preparations (moisture contents expressed on a wet basis).

### Modification of Rheological Behavior During Heating

The DMTA curves showed a common general behavior for all starches studied here. The rigidity increase observed from 50–54°C to 63–70°C could be attributed to the progressive swelling of starch granules that begin to fill the sample volume still available. The granules can be considered as dispersed fillers with an initial volume fraction  $\phi$  on the order of 0.5 (Table I) in a continuous amorphous phase made up of an aqueous solution of amylose. As starch concentrations were high, the diffusion of amylose out of the granules during heating should be limited and, consequently, the continuous phase was limited to a thin layer enveloping the granules. Therefore, the properties of the matrix between swollen granules are expected to be of less importance for the small deformation properties (Keetels 1995). The rigidity increase should depend mainly on filler (granules) content and size.

Below close-packing, the shear modulus appears to be independent of the particle size and increases with volume fraction  $\phi$  of filler in accordance with an 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. The value for  $\phi_m$  may be between 0.70 and 0.80 for spherical particles (Ferry 1980, Evans and Lips 1992). The same relation can be stated for Young's modulus  $E_e$ . Theoretical curves are presented in Figure 6.  $E_e/E_{e0}$  versus  $\phi$  is plotted for different maximum volume fractions  $\phi_m$  (0.70, 0.75, and 0.80). Figure 6 shows clearly that an increase in volume fraction of starch is responsible for increased rigidity of the composite, especially near close-packing.

As swollen starch granules are deformable particles (Evans and Haisman 1979, Evans and Lips 1992, Steeneken 1989), volume

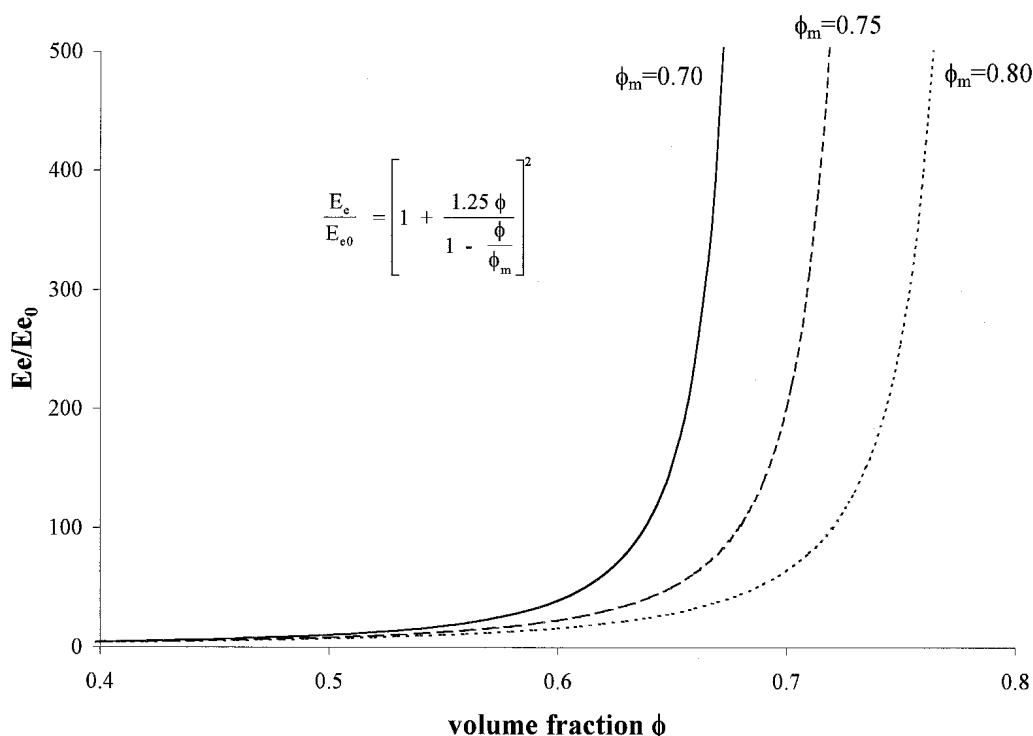
fractions can reach higher values than close-packing volume fraction (Evans and Lips 1992). However, the Young's modulus does increase; its evolution is still unclear, though a few studies were made (Evans and Lips 1992, Doublier et al 1987, Gluck-Hirsch and Kokini 1997).

Thus, a marked swelling of small wheat starch granules and normal corn starch would explain the great increase of storage modulus from 50 to 70°C and from 54 to 68°C, respectively. In the same way, the swelling of the smallest potato starch granules would generate the rigidity increase from 54 to 63°C. The limited swelling or the high deformability of waxy corn starch granules would be responsible for the low rigidity increase from 54 to 68°C (Fig. 1).

The rigidity decrease up to 85°C was assumed to be the consequence of the increase in the granule deformability. This increase was in a temperature range associated with the second part of the endotherm and was expected to result from double-helix dissociation, according to Tester and Morrison interpretation (1990), or from the melting of the more stable amylopectin crystals, according to Evans and Haisman (1982). In both cases, granule deformability would depend on the degree of amylopectin cross-linking. According to polymer sciences, the melting temperature is always higher than the glass transition for semicrystalline polymers (Sperling 1986). The Young's modulus value in the rubbery plateau for cross-linked polymers could be described by the following relation (Sperling 1986, Matsuoka 1992):

$$E = 3 \rho RT/M_e$$

with  $\rho$  being the density,  $R$  the universal gas constant,  $T$  the temperature and  $M_e$  the molecular weight of polymer segments between the entanglement points. The crystalline regions of the granules tend to behave like physical cross-links, tying the chains together (Sperling 1986). The melting of crystalline zones means a decrease of entanglement points and consequently a pronounced increase of  $M_e$ , generating a decrease of  $E$ .



**Fig. 6.** Theoretical Young's modulus changes of a noninteracting rigid-particle filler dispersion as a function of volume fraction  $\phi$ . Curves for three assumed maximum volume fractions ( $\phi_m$ ) are plotted.

The graph displaying the partial melting enthalpy increases (Fig. 5) shows that melting of the ordered zones begins at a temperature lower than those at which the storage modulus start to decrease, and slightly higher than those at which the storage modulus begin to increase. This implies that granules swelling would not only result from the melting of ordered regions (i.e., amylopectin crystals) as observed by DSC. It seems likely that the native amorphous phase could be at the origin of an uptake of water responsible for the initial swelling, generating the initial increase in  $E'$ . Other authors also reported that the initial increase in storage modulus was caused by the starch granules swelling progressively and finally becoming close packed (Eliasson 1986, Keetels and van Vliet 1994, Lii et al 1995). Melting of ordered zones would allow both a deformability increase and further uptake of water, thus further swelling. This uptake would also contribute to the increase of deformability, that is why it is reported that granular rigidity is inversely proportional to the degree of swelling (Lii et al 1996).

The behavior of the curve  $E' = f(T)$  from  $\approx 50^\circ\text{C}$  to  $85^\circ\text{C}$  (increase then decrease in  $E'$ ) would be the result of both granule swelling and ordered regions melting. The rheological property of rice starch also depended mainly on the interaction among the close-packed granules and their rigidity during the heating process (Lii et al 1996). The storage modulus increase would be caused by a dominant effect of the increase of volume fraction, while the storage modulus decrease would be due to a dominant effect of the deformability increase.

The  $\tan \delta$  decreases observed from  $60\text{--}70^\circ\text{C}$  to  $85^\circ\text{C}$  means that samples behave in a more solid-like manner with increasing temperature. This could partly be a consequence of gelation beginning with local reordering of amylose molecules. The behavior of 30%, w/w, dry matter potato and wheat starch suspensions has been studied (Keetels and van Vliet 1994, Keetels 1995). A similar decrease in  $\tan \delta$  was described and was taken to the evidence of an elastic gel formation (at least partly). Lii et al (1996) also suggested that indica rice (Kaoshiung Sen 7) starch with high storage modulus ( $G' > 5,000$  dyne/cm<sup>2</sup>) and low  $\tan \delta$  ( $< 0.2$ ) showed gelling behavior during heating at sufficient concentrations.

#### Modification of Rheological Behavior During Cooling

During heating, some amylose molecules leach out of the granules in the embedding aqueous phase. This leaching is explained both by the amylose-amylopectin incompatibility and by the higher mobility of amylose. However, at high concentrations, swollen granules fill almost the whole volume, and, thus, amylose leaching is more difficult. The amylose-amylopectin separation would happen mainly inside the granules, forming amylopectin-rich and amylose-rich zones (Keetels 1995). Only a thin amylose layer surrounds the granules, and high concentrations of amylose molecules favor their reorganization during cooling, forming a hardening gel between the granules. The rigidity increase of waxy corn starch (1% amylose) was indeed very low. However, potato starch (20% amylose) showed a low rigidity increase too. The large granule size or the high molecular weight of its amylose might not facilitate amylose leaching.

The role played by amylopectin in short-term hardening has not been demonstrated yet. However, we have not excluded the possibility that amylose-amylopectin entanglements could form inside the granules and consequently modify rigidity.

#### CONCLUSION

Our results suggest that the rheological behavior of starch-water preparations during thermal treatment is controlled by changes in both the volume fraction of the starch granules and deformability of the granules from hydration and loss of long-range order.

To estimate the respective contributions of these modifications, experiments are currently in progress on starch-water preparations

with different moisture contents. Moreover, experiments are being conducted to study the relationship between swelling and loss of long range order within starch granules.

#### ACKNOWLEDGMENTS

We wish to thank Gaele Roudaut and Dominique Champion for many valuable suggestions during the course of this investigation. We also appreciate technical assistance of Bernadette Rollin.

#### LITERATURE CITED

- 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. 1992. Structures and phase transitions of starch in food systems. *Food Technol.* 46:98-109.
- 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.
- Eliasson, A. C. 1986. Viscoelastic behavior during the gelatinization of starch. I. Comparison of wheat, maize, potato and waxy-barley starches. *J. Texture Stud.* 17:253-265.
- Evans, I. D., and Haisman, D. R. 1979. Rheology of gelatinized starch suspensions. *J. Texture Stud.* 10:347-370.
- Evans, I. D., and Haisman, D. R. 1982. The effects 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*. J. D. Ferry, 3rd ed. John Wiley and Sons: New York.
- Galliard, T., and Bowler, P. 1987. Gelation and retrogradation of concentrated starch gels. In: *Starch: Properties and Potential*. T. Galliard, ed. John Wiley and Sons: New York.
- Ghiassi, K., Hoseney, 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. 1994. Morphology and composition of starch. Pages 271-280 in: *Gums and Stabilizers for the Food Industry 7*. G. O. Phillips, P. A. Williams, and D. J. Wedlock, eds. IRL Press: Oxford.
- Keetels, C. J. A. M. 1995. Retrogradation of concentrated starch systems; mechanism and consequences for product properties. PhD thesis. Wageningen Agricultural University: Wageningen, The Netherlands.
- 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., Shao, Y. Y., and Tseng, K. H. 1995. Gelation mechanism and rheological properties of rice starch. *Cereal Chem.* 72:393-400.
- 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.
- 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.
- Matsuoka, S. 1992. The molten state. Pages 143-197 in: *Relaxation Phenomena in Polymers*. S. Matsuoka, ed. Carl Hanser Verlag: Munich.
- Miller, B. S., Derby, R. I., and Trimbo, H. B. 1973. A pictorial explanation for the increase in viscosity of a heated wheat starch-water suspension. *Cereal Chem.* 50:271-280.

- Navarro, A. S., Martino, M. N., and Zaritzky, N. E. 1996. Modelling of rheological behaviour in starch-lipid systems. *Lebensm. Wiss. Technol.* 29:632-639.
- Russel, 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.
- Sperling, L. H. 1986. Glass-rubber transition behavior. Pages 224-295 in: *Introduction to Physical Polymer Science*. L. H. Sperling, ed. John Wiley and Sons: New York.
- Steeneken, P. A. M. 1989. Rheological properties of aqueous suspensions of swollen starch granules. *Carbohydr. Polym.* 11:23-42.
- Stevens, D. J., and Elton, G. A. H. 1971. Thermal properties of the starch/water system. I. Measurement of heat of gelatinisation by differential scanning calorimetry. *Stärke* 23:8-11.
- Svegmark, K., and Hermansson, A. M. 1991. Changes induced by shear and gel formation in the viscoelastic behaviour of potato, wheat and maize starch dispersions. *Carbohydr. Polym.* 15:151-169.
- 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.
- Williams, M. R., and Bowler, P. 1982. Starch gelatinization: A morphological study of Triticum and other starches. *Starch/Stärke* 34:221-223.
- Wootton, M., and Bamuniarachchi, A. 1979. Application of differential scanning calorimetry to starch gelatinization. I. Commercial native and modified starches. *Starch/Stärke* 31:201-204.

[Received December 23, 1996. Accepted May 29, 1996.]