

Effect of Small and Large Wheat Starch Granules on Thermomechanical Behavior of Starch

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ABSTRACT

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The physicochemical properties of small- and large-granule wheat starches were investigated to reveal whether gelatinization properties and rheological behavior differ between size classes of wheat starch. All samples contained 60% water (w/w, wb). The starch granule size and shape were examined by scanning electron microscopy in the separated A- and B-type granule populations and in the whole wheat starch granule population. Differential scanning calorimetry (DSC) and electron spin resonance (ESR) analyses were performed in parallel with rheological measurements using dynamic mechanical thermal analysis (DMTA) to relate the viscoelastic changes to modifications in dynamic properties of

aqueous solutions and structural disorganization of starch. The small (B-type) granules had slightly higher gelatinization temperature and lower gelatinization enthalpy than did the large (A-type) granules. Also, B-type granules had higher enthalpy for the amylose-lipid complex transition. Moreover, our results suggested that small granules have higher affinity for water at room temperature. It seems that there is a less ordered arrangement of the polysaccharide chains in the smaller granules when compared with the larger ones. These differences in functional properties of small and large granules suggested that the granule size distribution is an important parameter in the baking process.

Starch constitutes the major component of wheat flour and serves as a multifunctional ingredient for the food industry. Previous investigations of granule size distribution of wheat starch have reported a bimodal distribution (Soulaka and Morrison 1985; Morrison and Scott 1986; Rolée and Le Meste 1997). Mature wheat (*Triticum aestivum* L.) endosperm contains two types of starch granules: large (10–35 μm) A-type and small (1–10 μm) B-type. Biosynthesis occurs at two different stages of kernel development. No satisfactory explanation has yet emerged from biosynthesis studies with respect to the origin of this dual population (Buléon et al 1998). Such a bimodal size distribution is characteristic of wheat starch as well as rye, oat, and barley starches (Eliasson and Larsson 1993; Buléon et al 1998). However, Raeker et al (1998) reported that wheat starch shows a trimodal rather than bimodal distribution. This may be because accuracy of granule size distribution is dependent on both starch isolation methods and size-determination techniques. According to these authors, a good isolation method should prevent loss of small granules and a good particle size determination technique should allow one to use a large sample size and measure all the particles in the sample.

A-type starch granules contribute to >70% of the total weight and \approx 3–5% of the total granules of endosperm starch, whereas B-type starch granules account for >90% of the total granule number but <30% of the total weight of starch in wheat endosperm (Morrison and Scott 1986; Eliasson and Larsson 1993; Raeker et al 1998; Peng et al 1999). The two types of starch granules reportedly differ in their chemical and physical properties and also have different end uses. The lipid content was found to be higher in the small wheat starch granules (Soulaka and Morrison 1985a; Raeker et al 1998), while higher lipid contents in small barley starch granules have been reported by Myllärinen et al (1998). Many reports claim that the amylose content is higher in the large granules (Peng et al 1999; Takeda et al 1999), whereas others have found the same amylose content in both small and large granules (Evers et al 1974; Myllärinen et al 1998). The smaller granules gelatinize at higher temperatures than the larger ones (Eliasson and Karlsson 1983; Myllärinen et al 1998). Eliasson and Karlsson (1983) claimed that the gelatinization enthalpy was independent of the particle size distribution. However, Peng et al (1999) found that the A-type starch granules had

higher gelatinization enthalpies than the B-type starch granules. The dissociation enthalpy of the amylose-lipid complex of the small granules was higher than for the large granules (Eliasson and Karlsson 1983; Myllärinen et al 1998). Finally, differences have also been observed concerning hydration and enzyme susceptibility (Meredith 1981), as well as crystallinity and swelling properties (Wong and Lelievre 1982) of small and large granules.

These differences result in the two starch granule types being used differently, both in food and nonfood uses. For example, starch with predominantly B-type granules (\approx 2 μm in diameter, or similar in size to the lipid micelle) can be used as a fat substitute (Daniel and Whistler 1990), while starch with a high percentage of A-type starch granules has applications in the manufacture of biodegradable plastic films and carbonless copy paper (Peng et al 1999). Lim et al (1992) reported a linear correlation between film thickness and particle size, and an inverse linear correlation between film tensile strength and particle size. Moreover, the proportion of small granules is important for the baking performance of a wheat flour. Kulp (1973) noted a lower baking potential for small granules compared with regular starch. Soulaka and Morrison (1985b) performed baking experiments with mixtures of A- and B-type granules from different wheat starches. These authors showed that the percentage of B-type granules in the starch has an appreciable effect on loaf volume. The optimum proportion of B-type granules for baking was 25–35%, by weight. In a similar way, Stoddard (1999) reported that the small (B-type) starch granules have a particular impact on the processing quality of the wheat for two reasons. First, the higher surface-to-volume ratio of the B-type granules has been associated with a higher rate of water absorption than that of A-type granules, affecting the mixing of the dough and the baking properties of the final goods. Thus, bread made with an enhanced proportion of B-type granules was lower in volume than normal, while enhancement of A-type granules led to reduced water absorption but no change in volume. Second, smaller granules do not precipitate from aqueous suspension as rapidly as larger granules. In any rapid industrial process, such as the manufacture of starch and gluten from flour, they may be carried away in the supernatant. They are, thus, not only a wasted resource for the manufacturer, but they make it necessary to treat the effluent.

The previous findings suggest that granule size distribution of wheat starch is an important characteristic that can influence chemical composition and physical properties, which in turn affect functionality. Despite claims of the importance of starch granule size, there are no sufficient studies for conclusions concerning their effect on thermomechanical behavior of starch-based products, and contradictory results have been published on the respective properties of A-

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and B-type granules. Accordingly, this investigation was undertaken to reveal whether gelatinization properties and rheological behavior, as measured by DSC and DMTA, differ between size classes of wheat starch. Electron spin resonance was used in parallel to evaluate the physical changes occurring in the liquid phase of hydrated starch.

MATERIALS AND METHODS

Sample Preparation

Whole wheat starch granules (normal) and segregated small (A-type) and large (B-type) starch granules from wheat were supplied by Roquette Frères (Lestrem, France). Preparations were made with starch and distilled water. Moisture content was adjusted to 60% (wb, w/w). A blend of A- and B-type wheat starch granules at a ratio of 30:70 (small to large granules, by weight), which is close to the composition of normal wheat starch, was also examined. The samples were blended manually until a homogeneous mixture was obtained and left resting overnight (under magnetic stirring) at room temperature in a closed environment before measurements. All tests in this study were performed at least in triplicate. Mean and standard deviation values were calculated.

Environmental Scanning Electron Microscopy (ESEM)

A- and B-type wheat starch granules, as well as normal wheat starch, were examined by environmental scanning electron microscopy (ESEM). The starch was sprinkled on double-sided adhesive tape, mounted on aluminum stubs, and examined in a Philips XL30-ESEM at an accelerating potential of 12 kV at 5°C.

Differential Scanning Calorimetry (DSC)

The differential scanning calorimetry (DSC) measurements were made with a Perkin-Elmer DSC-7 calibrated with azobenzene and indium in the positive temperature range. Starch-based preparations (60–85 mg) were weighed in stainless steel DSC pans, which were then hermetically sealed. Samples were heated from 25 to 165°C at a rate of 10°C/min. An empty pan was used as the reference. Pans were reweighed at the end of the run to ensure that water was not lost during heating. For each endotherm, the overall gelatinization enthalpy ΔH (J/g) and onset T_o , peak G , and end T_e temperatures (°C) were reported. Moreover, the partial melting enthalpy was calculated from the onset of the endotherm to 85°C (1°C/step) to plot the curve representing the cumulated enthalpy values versus temperature. The average standard deviation for the enthalpy determination was 2%.

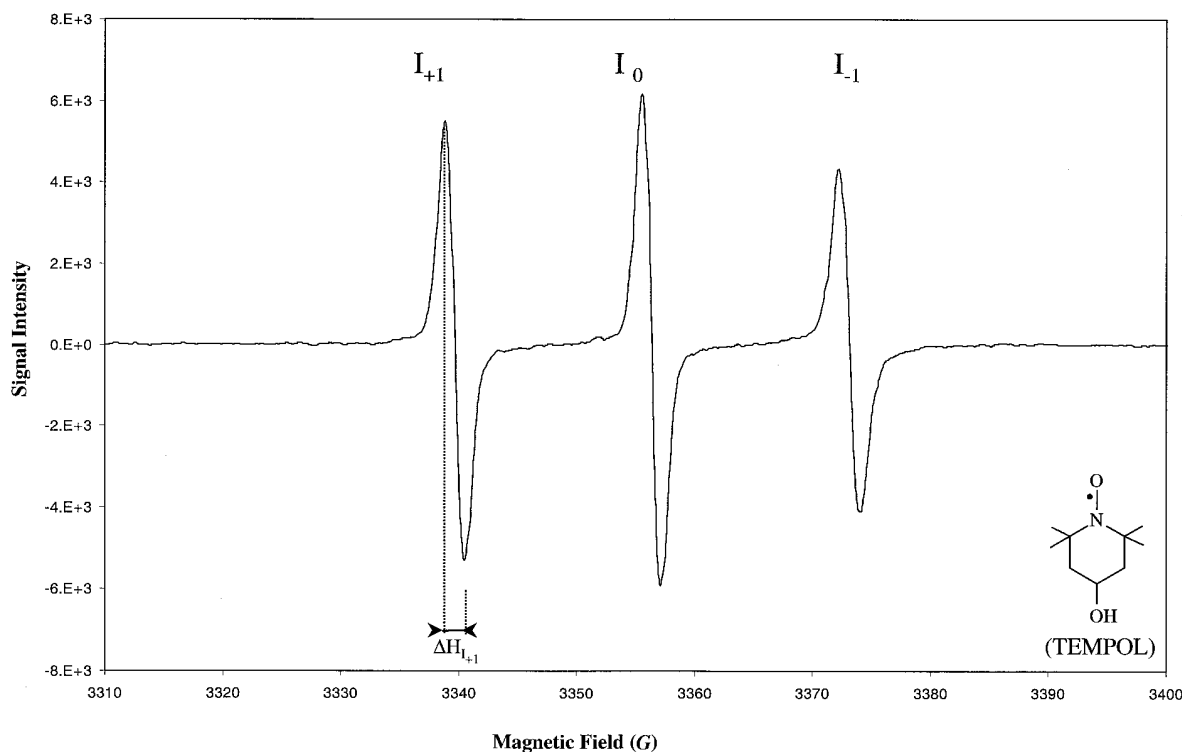
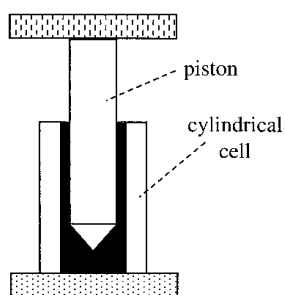


Fig. 1. Typical electron spin resonance (ESR) spectrum of a nitroxide free radical (TEMPOL).

ANNULAR PUMPING



- sensor regulating the amplitude and the frequency of the strain
- sample
- sensor registering the stress

ANNULAR SHEARING

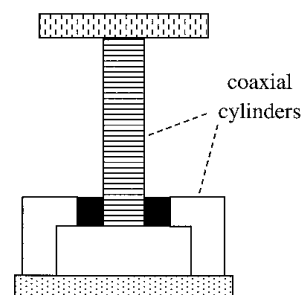


Fig. 2. Schematic cross-sections of dynamic mechanical thermal analysis (DMTA) devices.

Electron Spin Resonance (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 (Fig. 1) reflect the motion of the small paramagnetic probe that depends on the probe size and on the solvent viscosity. We used 4-hydroxy-2, 2, 6, 6-tetramethyl-piperidinyloxy (TEMPOL) radical (Aldrich Chemicals, Strasbourg, France). Samples were prepared by adding 300 μL of a TEMPOL aqueous solution (2 mg/mL) to distilled water before manual mixing with starch (approximate final TEMPOL concentration 2.4×10^{-7} mol/g of dry starch). Because of the small size (MW = 172.2 g/mol), the probe was assumed to be able to diffuse inside the starch granules so it can be dispersed in the aqueous phase inside and outside the granules. Sealed capillary tubes containing the samples were placed in 3-mm diameter ESR sample quartz tubes. ESR spectra were recorded using a spectrometer (EMX, Bruker, France) equipped with a nitrogen gas flow variable temperature controller. The operating microwave frequency was 9.42 GHz and center magnetic field was 3,357 G. The microwave power was 10 mW. Any saturation phenomenon was avoided. The scan rate, time constant, and modulation amplitude were adjusted so that distortion of the spectra was avoided. For all experiments, the temperature was varied stepwise 2°C at $25\text{--}85^\circ\text{C}$ during heating and subsequent cooling; samples were allowed to reach temperature equilibrium (1 min) before recording the spectra. The rotational correlation time (τ_c) of the paramagnetic radical (representing the time during which the molecule remains in a given orientation) was determined as:

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

deduced from the Freed and Fraenkel (1963) theory, where I_{+1} and I_{-1} are the peak-to-peak height of the lines, and $\Delta H_{I_{+1}}$ is the width

of the I_{+2} line (Fig. 1). The conventional ESR method was used, allowing mobility measurements at $10^{-11} < \tau_c < 10^{-7}$ sec. The rotational diffusion coefficient (D_{rot}) representing probe mobility, was evaluated from the rotational correlation time (τ_c) (Nordio 1976):

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

Average standard deviation for all the tests was 14.3%.

Dynamic Mechanical Thermal Analysis (DMTA)

The small amplitude oscillatory rheological measurements were performed with a viscoanalyzer (Metravib R.D.S., Limonest, France) equipped with a thermocontrol unit. Two different solicitation modes were used for this study: annular pumping and annular shearing. These modes are shown in Fig. 2.

Annular Pumping

The annular pumping mode is used for samples with liquid-like behavior. A few milliliters of sample are poured into a cylindrical tube with a piston in the center ($\varnothing = 9$ mm) oscillating with a small amplitude. The tube was glued with cyanoacrylate glue (Eco-Fast, X-ERGON, UK) 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

As the liquid-like samples became more rigid during the thermal treatment, annular pumping was no longer efficient (no reliable modulus as a result of slippage). So annular shearing was used at $52\text{--}85^\circ\text{C}$ as well as for cooling. This device consisted of coaxial cylinders connected to the sensors with a 2-mm gap between the two cylinders. The starch dispersion, poured in the cell in the liquid state before heating, was held in the annular space by capillary force.

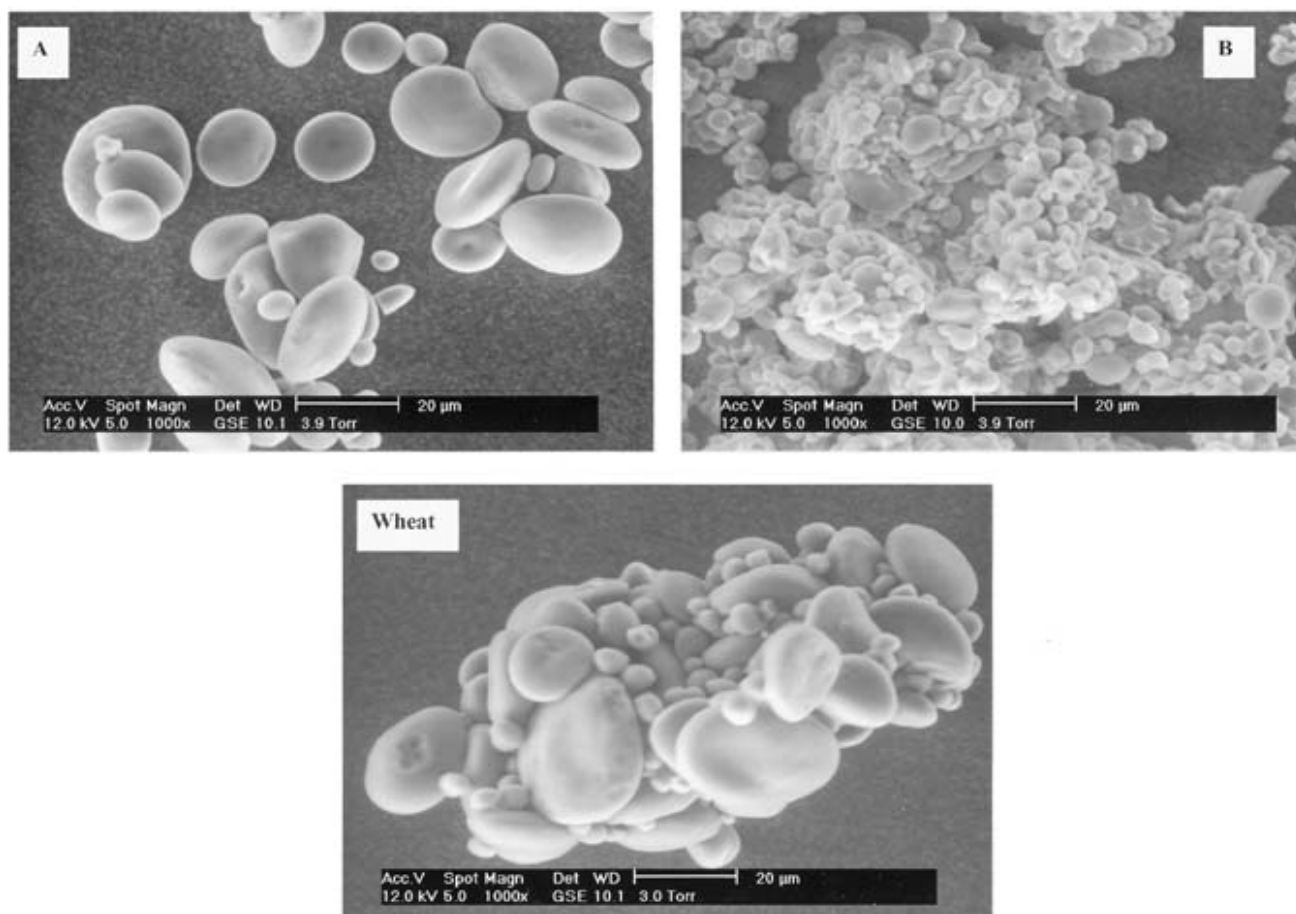


Fig. 3. Scanning electron microscopy (SEM) of large (A) and small (B) granule starches from wheat and normal starch (**wheat**). Bar = 20 μm .

To prevent drying during analysis, samples were coated with a mineral oil (Nachet, France). The strain and frequencies were set at 3 μm and 5, 10, 20, and 40 Hz, respectively. Measurements were made in the linear region of viscoelasticity, where the amplitudes of stress and strain are proportional. Starch samples were heated from 25 to 85°C (1.5°C/min), then immediately cooled (-1.5°C/min) to room temperature during analysis. VA2000 software provided by Metravib R.D.S. allowed calculation of rheological parameters including storage modulus (G'). Average standard deviation for all tests was 10.4%.

RESULTS

Scanning Electron Microscopy

Micrographs of small (B-type) and large (A-type) wheat granules and normal wheat starch granules observed with ESEM are shown in Fig. 3. The B- and A-type granules were oval to round in shape with diameter ranges of 4–6 and 12–24 μm , respectively. Normal wheat starch clearly showed two granule populations. The surface of the granules at 2,000 \times magnification (not shown) appeared to be smooth and showed no evidence of damaged starch. The B-type granules appeared to be more irregular than the A-type; they were also more highly agglomerated. This trend of B-type granules to agglomerate was also confirmed by granulometric measurements with a particle size analyzer (Coulter counter LS130) using the dry powder module to avoid granule swelling (not shown). We observe in Fig. 3 that B-type granules can be found mixed with A-type granules, which means that the granules from the wheat were not perfectly separated.

Melting of Ordered Regions Studied by DSC

The DSC thermograms of the wheat starch and the A- and B-type granules are shown in Fig. 4. The corresponding transition temperatures and enthalpies are given in Table I. The two endothermic transitions previously described for wheat starch with sufficient water present (Rolée and Le Meste 1999) were observed for all samples. The first one (G) was assigned to amylopectin double helices dissociation and crystals melting; the second one (M_c) was attributed to amylose-lipid complexes melting. The shape of the endotherms was characteristic of the size distribution of the starch

granules. The gelatinization endotherm (G) looks narrower for A-type granules and looks broader for the B-type granules. The shape of the endotherm of the normal wheat starch was somewhere in between. These observations are in good agreement with the results of Eliasson and Karlsson (1983). The gelatinization peak temperature of the B-type starch granules was 64.6°C, which was 4.5°C higher than that of the A-type granules. The gelatinization interval was slightly broader for the A-type granules (41.2°C) than for the B-type (38.7°C), but both intervals were narrower when compared with normal wheat (50.2°C). The peak temperature of the second transition (M_c) was not significantly affected by particle size. The gelatinization enthalpy of B-type granules (8.12 J/g) was lower than that of A-type granules (11.06 J/g). Various investigators (Eliasson and Karlsson 1983; Soulaka and Morrison 1985a; Peng et al 1999; Tang et al 2000) have reported similar findings concerning enthalpy of gelatinization of B- and A-type starch granules of the same cultivar. The dissociation enthalpy of the amylose-lipid complex of the B-type granules (1.70 J/g) was higher than for the A-type (0.99 J/g). This is consistent with observations of Eliasson and Karlsson (1983) on wheat starch granules and Myllärinen et al (1998) on barley starch granules. Cumulated enthalpy values of all samples up to 85°C are shown in Fig. 5. The melting of wheat starch and A-type ordered zones was faster and more pronounced at $\leq 85^\circ\text{C}$ than for B-type granules.

Motional Behavior of TEMPOL in Starch-Water Dispersions 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; Chiotelli et al 2000). In our 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 phase of the suspension. The rotational diffusivity of the probe is inversely proportional to microscopic viscosity (η) of the aqueous phase surrounding the probe, approximated by the modified Debye-Stoke-Einstein equation:

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

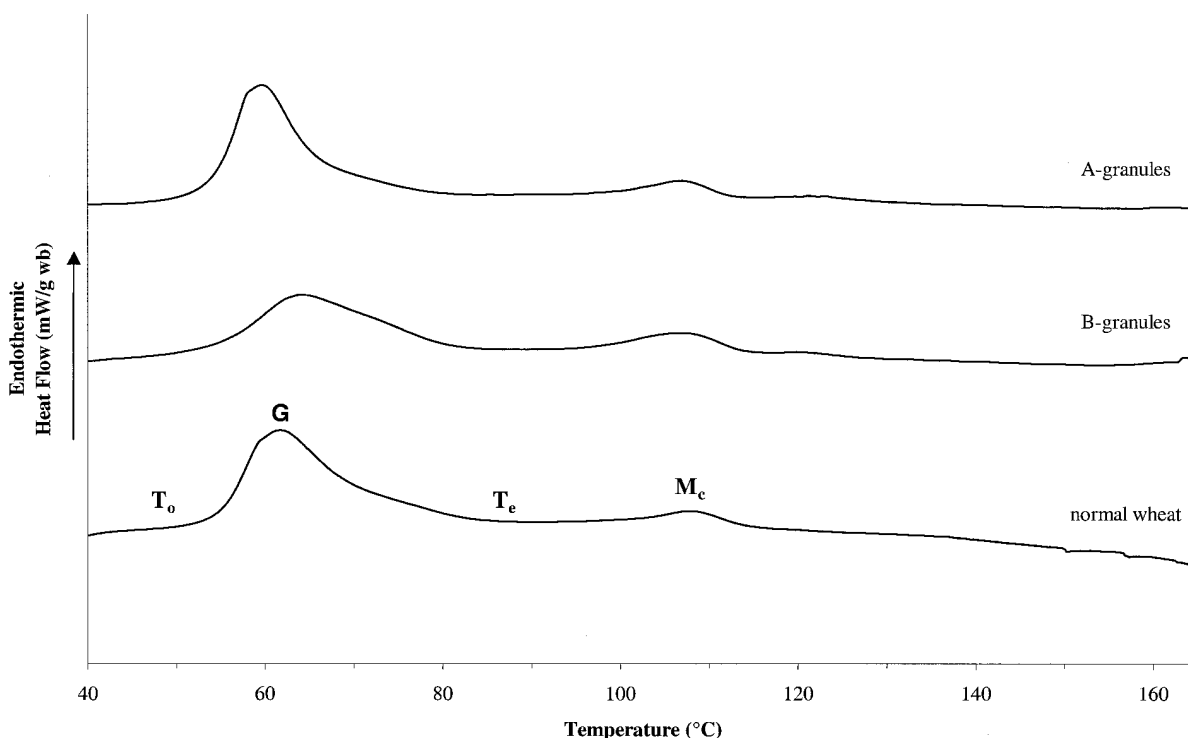


Fig. 4. Differential scanning calorimetry thermograms of wheat starch, B-type and A-type granule dispersions (60% wb, w/w). T_o (onset), G (peak), and T_e (end) gelatinization temperatures (°C)

where k = Boltzmann's constant, T = absolute temperature, r = radius of the diffusing molecule, and C = coupling parameter representing the amount of solvent dragged with the molecule when it moves (Kowert and Kivelson 1976).

For all samples and over the temperature range studied, three line spectra, similar to those of probes in water, were obtained (not shown). These spectra represent rapid isotropic motions (low-viscosity aqueous environment). However, the calculated rotational diffusion coefficients (Fig. 6) were lower than the values for the probe in water, suggesting a higher viscosity of the probe environment in the starch preparations (Rolée and Le Meste 1999; Chiotelli et al 2000). Only one probe population was observed (i.e., probes inside and outside of the granules could not be distinguished). This also demonstrates the absence of any direct interaction between the spin probe and the starch.

Compared with wheat starch, B-type dispersion showed a lower D_{rot} value at room temperature, while A-type dispersion had a much higher probe mobility. During heating, a slight decrease in D_{rot} was observed at 25–47°C for normal wheat starch and A-type granule dispersions, followed by a more pronounced decrease at ≤57°C. Above the temperature of minimum mobility, D_{rot} gradually increased to 85°C. In contrast, D_{rot} was almost constant for B-type dispersion at ≤57°C, and then it increased sharply. Upon cooling, the probe mobility decreased monotonically with decreasing temperature for all samples. By the end of the cooling stage, the mobility of the water in the dispersions was the same for all preparations, regardless the initial mobility in the sample.

Viscoelastic Behavior of Starch-Water Preparations

Changes in the storage modulus (G') of the wheat starch systems as a function of temperature are shown in Fig. 7A. The observed

changes in G' were not frequency dependent in the frequency range considered. Thus, only the 5 Hz results are shown and discussed. The initial storage modulus ($G'_i = G'$ at 30°C) was higher for the B-type granules than for all other samples. During heating, G' of normal wheat, and blended (30:70) B- and A-type granules increased very strongly from ≈54°C and reached a maximum value at ≈66°C, then decreased slightly up to 85°C. This increase in rigidity occurred at a lower temperature (≈50°C) for B-type granules. More precisely, G' of B-type granules increased in two stages during heating: slightly from ambient temperature to ≈50°C, then more strongly to a G'_{max} value of the same order (10^5 Pa) as for the other samples. During cooling, G' remained almost constant, and it was somewhat higher for the B-type granules. The blend (30:70) of B- and A-type granules showed rheological behavior during heating and cooling that was similar to normal wheat starch and A-type granules.

DISCUSSION

Loss of Ordered Regions

DSC curves were affected by the size distribution of the wheat starch granules. B-type granules gelatinized at slightly higher temperatures than A-type granules and normal wheat starch, but needed a lower enthalpy (Table I). This lower total enthalpy value for the gelatinization of B-type granules suggests a lower percentage of organized arrangements in B-type granules than in A-type or a lower stability of the crystals. Actually, the X-ray diffraction patterns of the B- and A-type granule wheat starches (not shown) suggest that A-type granules are somewhat more crystalline than B-type. Vasanthan and Bhatti (1996) obtained similar results on barley starches. These authors reported that the A-type granule starches had higher percentage of relative intensities (PRI) of major peaks in the X-ray dif-

TABLE I
Differential Scanning Calorimetry Data of Gelatinization of Starch Samples^{a,b}

Starch Granule	Melting Endotherm ^c				Amylose-Lipid Complex Endotherm ^d	
	T_0	G	T_e	ΔH_G	M_c	ΔH_{Mc}
Normal wheat	44.62 ± 0.58	62.24 ± 0.10	94.85 ± 1.52	14.32 ± 0.48	111.51 ± 0.69	2.53 ± 0.94
A-type	45.93 ± 0.00	60.15 ± 0.73	87.17 ± 0.69	11.06 ± 0.20	107.33 ± 0.63	0.99 ± 0.09
B-type	50.33 ± 0.00	64.61 ± 0.51	89.03 ± 0.00	8.12 ± 0.08	107.25 ± 0.51	1.70 ± 0.04

^a Mean ± standard deviation values of three separate measurements.

^b Moisture content 60% (w/w, wb).

^c T_0 , G , and T_e = initial, peak, and end temperatures (°C), respectively; ΔH_G = gelatinization enthalpy (J/g of dry starch).

^d M_c = amylose-lipid complex peak temperature (°C); ΔH_{Mc} = enthalpy of amylose-lipid complex transition.

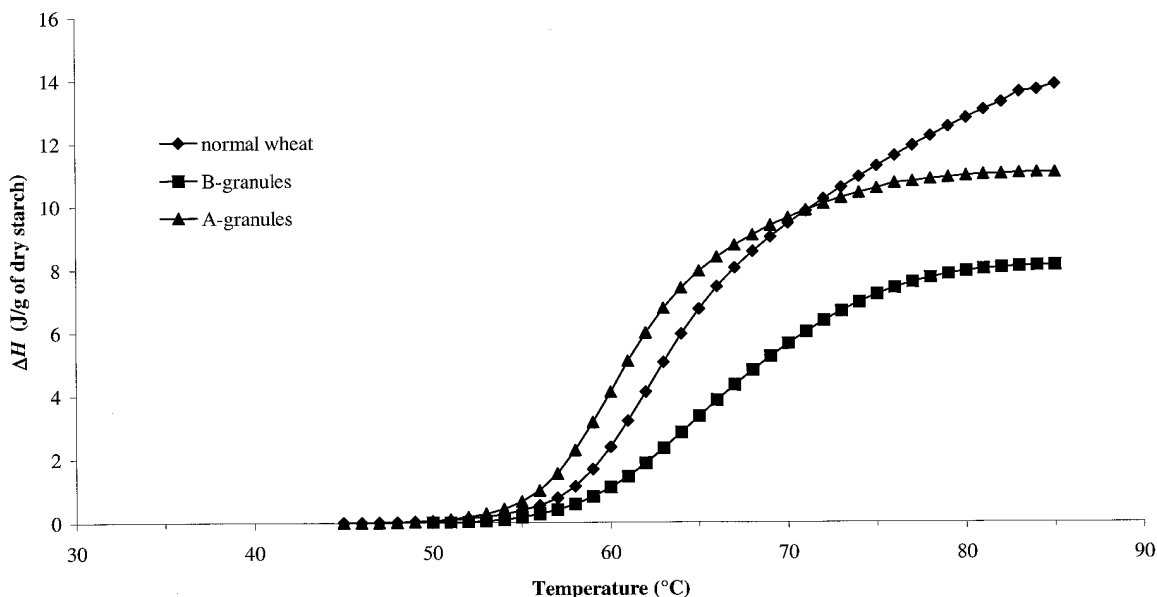


Fig. 5. Partial melting enthalpy as a function of temperature for wheat starch, B-type, and A-type granule dispersions (60% wb, w/w).

fraction patterns of barley starches. Higher PRI of starch indicates higher degree of crystallinity. Nevertheless, the crystalline material in B-type granules seem to have somewhat greater stability (more perfect crystallites) than in A-type granules because its melting transition starts at slightly higher temperature and with a slower rate (Fig. 5). The enthalpy of the second endothermic transition was greater for the B-type granules. As this transition is due to the amylose-lipid complex, the greater ΔH_{Mc} value of the B-type granules could be explained as in Soulaka and Morrison (1985a) and Raeker et al (1998) by the greater lipid content in the B-type wheat granules. The better stability of amylopectin observed in B-type granules may be related to the amylose-lipid complex formation during heating, which would obstruct the gelatinization process (Buléon et al 1998). Moreover, 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 amylose-lipid complexes (Kugimiya et al 1980), the greater amount of internal lipids in B-type granules (as well as better hydration) may generate a lower endothermic energy (enthalpy underestimation).

Probe Mobility and Starch-Water Interactions

The water-soluble probe (TEMPOL) used in this study is sensitive to changes in the dynamic properties of the water phase associated with the temperature-induced starch structural transformations. We assume that a decrease in probe mobility reflects an increase in the “microviscosity” of the aqueous phase, which corresponds to improved starch-water interactions (Rolée and Le Meste 1999; Chiotelli et al 2000; Rolée et al, *in press*).

At room temperature, B-type granule preparations exhibited lower probe mobility than did A-type and normal wheat starch granules, suggesting favored starch-water interactions in B-type granules. Since A-type granules seem to be slightly more crystalline than B-type granules (X-ray diffraction results), water would migrate less freely into the A-type granule starch molecules, which could explain the higher initial probe mobility. During heating, we can distinguish three stages of probe mobility for A-type granules and normal wheat starches. First, the decrease of D_{rot} from 25 to 47°C reflects the progressive hydration and reorganization of the amorphous regions, which is improved by increasing temperature (thermal agitation). Then, from 47 to 57°C, the more pronounced decrease in probe mobility indicates a higher rate of starch hydration and swelling. This must be due to some structural modifications, most likely concerning the less ordered regions (helices dissociation, amylose solubilization, etc.), thus improving starch-water interactions (the starch-chains become more flexible and more accessible to water). Finally, from 57 to 85°C, the progressive increase in D_{rot} can be attributed to the melting of the crystalline zones (revealed by DSC, Fig. 5) and the long-range order destruction; the dominant effect on probes is increased overall molecular mobility at higher temperatures. On the other hand, B-type granules containing less

ordered arrangements exhibit a higher affinity for water and are more hydrated at room temperature, showing no significant modification in starch-water interactions on heating. The more pronounced increase in probe mobility at >57°C for these granules could be related to higher lipid content. If complex formation occurs during heating, then less amylose would be free to dissolve in water and decrease probe mobility.

We noticed that at the temperature corresponding to the onset of endothermic events, probe mobility has approximately the same value in three different preparations (Fig. 6). This suggests that for melting to occur, a similar starch hydration state must be reached in all starch preparations. These observations are in agreement with previous results on starch-sucrose preparations (Chiotelli et al 2000).

During cooling, D_{rot} constantly decreased, indicating an increasing viscosity of the probe environment. This must be due to starch gelation. Such a reorganization of the starch network could generate a slowdown of probe motion by strengthening the biopolymer matrix. We noticed that the Arrhenius plot of the evolution of probe correlation time as a function of temperature (not shown) demonstrated a non-Arrhenius-like evolution, suggesting that several phenomena take place during the thermal treatment of starch involving not only temperature but also structural modifications.

Swelling of Granules and Viscoelastic Behavior

DMTA measurements showed that B-type granule dispersions exhibited higher initial modulus and increased rigidity during heating at lower temperature compared with the other samples. This means that despite the similar volume fraction (ϕ) of all samples (same moisture content), the dispersion of B-type granules with 60% water would have an initial volume fraction (ϕ_i) closer to ϕ_m (maximum volume fraction corresponding to close-packing). To verify whether B- and A-type granules have different ϕ_m values, we used the equation of Alberola and Mele (1996), which permits an approximate determination of ϕ_m for unimodal suspensions of particles assimilated to spheres:

$$\phi_m = 1 - 0.47 \times (d/D)^{0.2} \quad (4)$$

where d and D are, respectively, the lower and the upper bounds of the size distribution of the granules (i.e. 8,400 and 42,300 μm for A-type granules, and 1,670 and 13,300 μm for B-type granules determined particle size analysis). No significant difference in ϕ_m was found between B- and A-type granules. Moreover, microscopic and granulometric measurements indicate that B-type granules exhibit a tendency to form large aggregates. Thus, the higher ϕ_i of B-type granules is most likely due to higher affinity for water of these granules, which swell rapidly in water already at room temperature. B-type granules also appeared to be less crystalline than A-type granules (X-ray diffraction data). Thus, a less ordered arrangement of the polysaccharide chains in B-type granules (higher proportion of amorphous zones more accessible to water) could explain earlier hydration and swelling compared with A-type granules. These

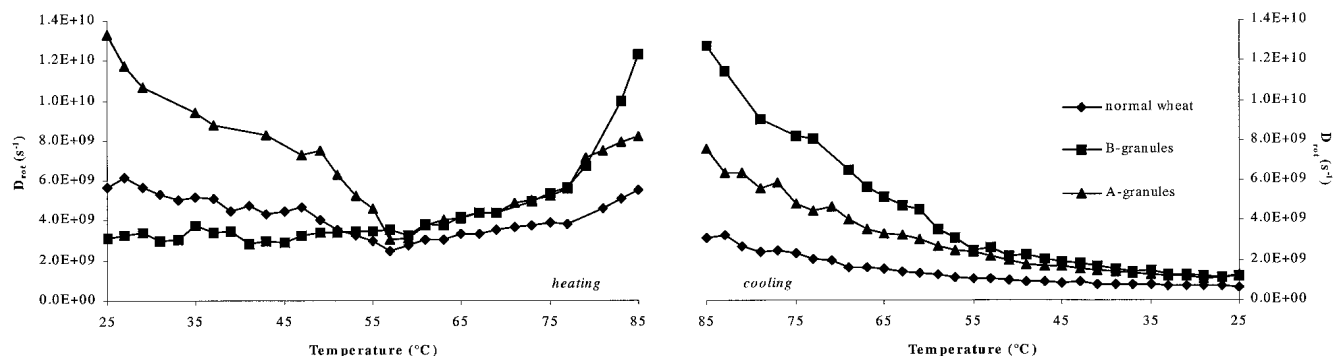


Fig. 6. Rotational diffusion coefficient D_{rot} of spin probe (TEMPOL) dispersed in aqueous phase of wheat starch, B-type, and A-type granule dispersions (60% wb, w/w) as a function of temperature during heating and cooling.

observations are in good agreement with the DSC results, which showed slightly higher total enthalpy for the (more crystalline) A-type granules (11.06 J/g of dry starch) than for the B-type granules (8.12 J/g of dry starch), and with the ESR results, showing lower probe mobility for the B-type granules at the beginning of the heating cycle. Another cause for this higher water absorption of B-type granules could be greater surface area/g of B-type granule sample, which has been estimated at 0.70 m²/g for B-type granules and 0.25 m²/g for A-type granules in wheat starch (Morrison and Scott 1986).

During heating, G' increased very strongly from $\approx 54^\circ\text{C}$ and reached a maximum value at $\approx 66^\circ\text{C}$, before decreasing slightly to 85°C (Fig. 7A). In such dispersions with quite high moisture contents, an increase in volume fraction of starch granules (because of granule swelling) is responsible for this rigidity increase during heating (Rolée and Le Meste 1997; Rolée and Le Meste 1999; Chiotelli et al 2000). The dominant effect of the progressive swelling of starch granules, subsequent to the crystallite melting in this temperature range, led to a maximum occupancy of the available space by the swollen granules. Heating above the G' max provides energy to break down the residual crystalline structure of starch, causing G' to drop (Lii et al 1996). DSC results (Fig. 5) showed evidence of melting-dissociation of ordered zones in this temperature range. During cooling, G' increased only slightly. An increase in the elastic behavior of starch dispersions when temperature decreases after heating has been

reported by others (Doublrier 1987; Champenois et al 1998; Chiotelli et al 2000) and attributed to gelation of leached amylose. An expansion of the curves in Fig. 7A revealed a less pronounced modulus decrease for B-type granules on heating above G' max than for the other samples (Fig. 7B). It seems that swollen B-type granules are somewhat less deformable than A-type granules. This fact, in addition to a lower amylose solubilization in B-type granules due to complexation with lipids, could also explain the slightly higher modulus (on cooling) of these granules in comparison with A-type granules and the absence of rigidity increase during cooling (Fig. 7A).

CONCLUSIONS

The thermomechanical behavior of separated large (A-type) and small (B-type) starch granules from wheat was investigated. Accordingly, it seems that A- and B-type starch granules have significantly different gelatinization and rheological properties, indicating that they may have distinct applications in food and nonfood industries.

The B-type granules showed slightly higher gelatinization temperature and lower gelatinization enthalpy than that of the A-type granules. Moreover, B-type granules exhibited higher enthalpy values for the amylose-lipid complex transition, indicating that the amylose-lipid complex formation is facilitated in B-type granules. ESR and

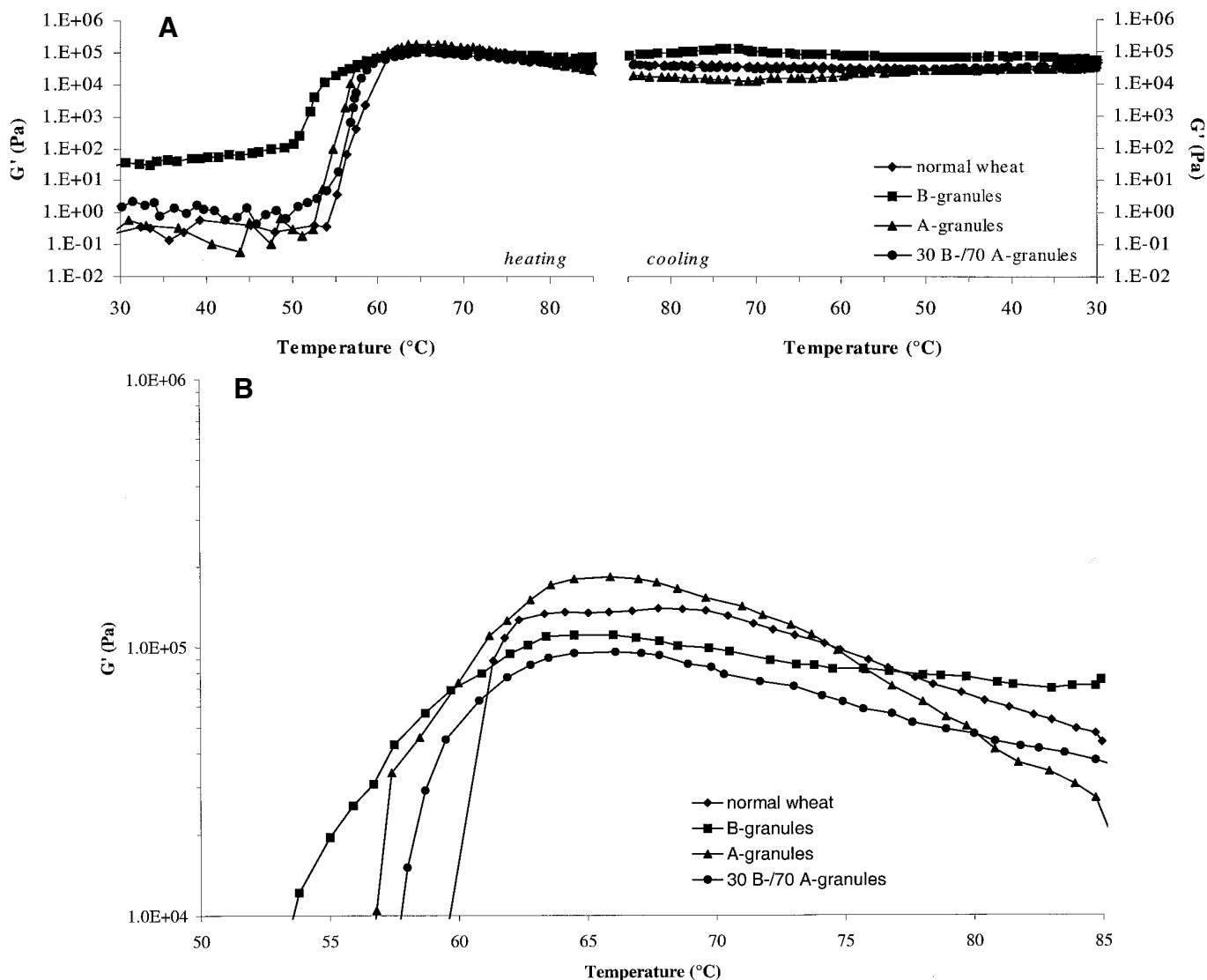


Fig. 7. A, Storage modulus (G') changes as a function of temperature during heating and cooling of wheat starch, B-type and A-type granule preparations (60% wb, w/w). B, Expansion of curves.

DMTA results suggested that B-type granules have a higher affinity for water at room temperature. Considered with DSC measurements, there seems to be a less ordered arrangement of the polysaccharide chains in the B-type granules compared with the A-type. This higher hydration property of B-type granules before heat treatment could be used, for example, to avoid syneresis in several milk products or to stabilize the structure of low-fat products.

These results suggested that the starch granules have different characteristics in the different fractions and, thereby, display different functional properties.

These differences may be important in processes such as baking, thus the knowledge of the particle size distribution should be essential.

Further studies are needed to elucidate the mechanism and the factors controlling the biosynthesis of starch granules, and their influence on the technological properties of starch.

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