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# CALORIMETRIC AND RHEOLOGICAL PROPERTIES OF WHEAT FLOUR SUSPENSIONS AND DOUGHS
## Effects of wheat types and milling procedure

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## Abstract

Three types of wheat were submitted to two different milling procedures, giving rise to six flours which differed by some physico-chemical characteristics such as particle size, level of damaged starch and protein content. Differential scanning calorimetry was used for monitoring heat-induced structural changes in flour aqueous dispersions 80% water and in doughs 45% water. Differences between the thermal behaviour of the flour dispersions and doughs were explained mainly by differences in protein content. This result was confirmed after partial substitution of flour by gluten. Dynamic mechanical analysis performed at 20°C on the flour doughs indicated, as expected, a linear increase in the elastic modulus with increasing protein content. The results did not bring any evidence that, under these experimental conditions, starch damage might affect gluten hydration.

**Keywords:** DSC, gelatinisation, gluten, rheology, starch damage, wheat flour

## Introduction

Wheat flour is composed by carbohydrates (70 to 80%, of which starch is the major component), proteins (8 to 15%), fat (2 to 3%) and water (10 to 12%). When used for bread preparation, wheat flour is firstly mixed with water in presence of air, to form a dough (water 45% w.b.). Generally, flour doughs are considered as viscoelastic liquids, with elastic properties attributed to the non-covalently bound gluten network, but depending also on other flour components (starch granules, polysaccharides..), which in addition may compete for available water [1]. For many years, the structural modifications (gelatinisation, melting of crystallites and of amylose-lipid complexes) have been studied under the effect of water and temperature by differential scanning calorimetry (DSC) [2–5]. These structural transitions which concern mainly the starch granule and its components (amylose, amylopectine and lipids) have been studied in various conditions such as different proportions of water or gluten [6–10]. Other studies considered the effect of starch granule size or of degree of damaged starch. Stevens and Elton [2] observed that

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the gelatinisation temperature was higher for smaller starch granules (mean diameter 10 μm, compared to 20–35 μm), and Tester [11] observed that, while the heat of starch gelatinisation did not depend on starch particle size, it seemed to decrease with the level of starch damage for various botanical origins. On the other hand, Wannenberger and Eliasson [12] observed an increase in the peak temperature and in the enthalpy change with the degree of damage of rice starch. This last result, which does not agree with the previous one, was explained by differences in protein composition of the various starch samples. In another study, Eliasson [13] observed an increase in temperature and a decrease in heat of starch gelatinisation at an intermediate water content (47% w.b.), as the proportion of gluten was increased. However, Erdogdu *et al.* [14] observed a reverse trend when water content was in excess, and Chevalier and Colonna [10] showed no evidence that proteins affect starch gelatinisation or melting at moisture contents in the range 15 to 40% (w.b.).

In the present work, we first determined some physicochemical characteristics of flours which were obtained from three wheat types prepared by two milling procedures and containing different proportions of proteins. Then, we used DSC to study heat-induced structural changes of flours at two different moisture contents (approx. 80 and 45%, w.b.), and dynamic viscoelastic measurements to characterize the corresponding wheat flour doughs.

## Materials and methods

We used three types of wheat (Levis, CWRS and Dinghy). The wheat hardness index was determined spectrophotometrically in near-infrared region, following the procedure described by Mahaut [15] and usually applied in cereal industry to compare the hardness index of wheats.

Grinding of wheat grains was done with a laboratory roller mill (Chopin–Dubois), following two separated steps. The objective of the first step, which is carried out in the break system of the mill, was to remove the bran and germ from endosperm. The objective of the second step was to reduce the endosperm to flour fineness. The flours issued from these two steps were collected separately. In the present study, flour collected from the first milling procedure is named ‘grinding flour’, and that obtained from the second step is named ‘reduction flour’.

Total dry matter of the 6 flours were determined by heating at 103°C up to a constant mass, and their protein content was evaluated by Kjeldhal method. The iodometric method (Rapid FT-Chopin) was applied for evaluation of apparent damaged starch, and light scattering (Master Sizer, Malvern-Orsay/France) was used to obtain the size distribution of flour particles when dispersed in ethanol, from which the mean diameter, $D_{0.5}$ was calculated. Scanning Electron Microscopy (SEM) images of the six flour powders were also obtained (Jeol model JSM-2500).

10 g of flour dough were prepared by mixing flour and added water for 3 min in a micro-kneader (National TMCO, INC. Lincoln-Nebraska/USA). The total water content of flour doughs was adjusted to 45% (w.b.). In a series of experiments we substituted a part of flour powder by an equivalent mass proportion of vital wheat

gluten (Roquette, France), containing 12% water (w.b.). Characteristic temperatures (peak temperatures, $T_p$) and total heat of structural modifications ($\Delta_{cal}H$) of the 6 wheat flours were determined by DSC (μ-DSC Setaram-France). We used samples (600 to 700 mg) of either dispersions in distilled water (85 to 80% water) of flour powders, or the corresponding doughs (water 45% w.b.) which were heated at 0.5°C min$^{-1}$ from 20 to 120°C [16]. The peak temperatures correspond to the peak deviations of the heat flow signal, and $\Delta_{cal}H$ values were determined from the area under the heating curve by using a straight baseline drawn from the beginning to the end of the heat flow deviations. Viscoelastic properties of flour doughs were evaluated at 20°C, after 1 h rest. We used a stress controlled rheometer (Carri-Med CSL 100) with a cone-plate geometry (4 cm diameter, 4° angle). The measurements were made at a frequency of 1 Hz, and in the quasi-linear domain (0.2% amplitude) [17].

## Results and discussion

### *Flour characterization*

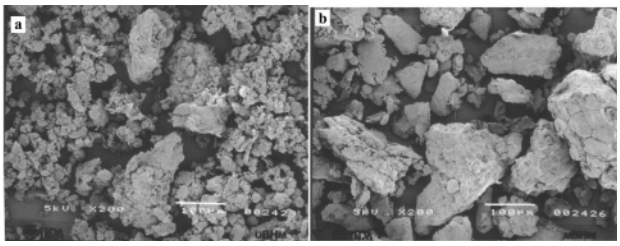
Some physico-chemical characteristics of 6 flours used in the present study are shown in Table 1. Levis and CWRS wheat grains presented the higher values of hardness index (94 and 78, respectively), which means that the endosperm of these grains is physically hard. Dinghy wheat presented the lowest hardness index (index 6), which means that this grain variety is soft and, consequently, more friable.

**Table 1** Physico-chemical characteristics of wheat flours (for definition of milling procedures, see text)

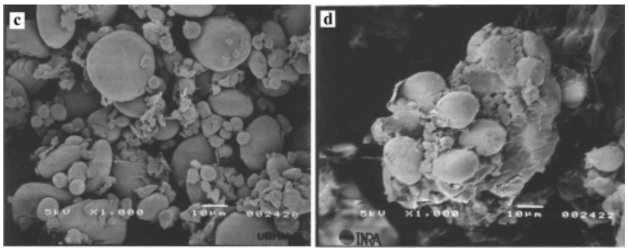
| Wheat variety | Hardness index/% | Milling procedure | Water content (w.b.)/% | Protein (w.b.)/% | Index of damaged starch (UCD) | $D_{0.5}$/μm |
|---|---|---|---|---|---|---|
| Levis | 94 | grinding | 12.2 | 14.8 | 21.2 | 93.7 |
| | | reduction | 13.9 | 12.6 | 13.8 | 135.2 |
| CWRS | 78 | grinding | 11.6 | 14.9 | 17.9 | 96.7 |
| | | reduction | 13.4 | 14.5 | 11.4 | 120.3 |
| Dinghy | 6 | grinding | 13.4 | 7.2 | 12.6 | 45.2 |
| | | reduction | 13.6 | 8.2 | 14.0 | 69.8 |

The trend of damaged starch index evaluated for flours obtained by grinding seems to follow the grain hardness, indicating starch damage by mechanical treatment. This result is in agreement with Viot [18], who observed that damaged starch is much higher for wheat variety with hard and glass-like endosperm. Values in Table 1 indicated also that the hard wheats (Levis and CWRS) contain more proteins than the soft wheat Dinghy.

The particle size distributions were monomodal for CWRS and Levis flours, and bimodal for flours obtained from Dinghy, in agreement with previous results, [19]. The mean diameter $D_{0.5}$ is lower for Dinghy flours than for Levis and CWRS ones (Table 1),



**Figs 1** a – b Scanning electron microscopic images of Levis (right) and Dinghy (left) reduction flours (×200)



**Figs 1** c – d Scanning electron microscopic images of Levis (right) and Dinghy (left) grinding flours (×1000)

with a slight effect of the milling steps (simple grinding seems to give flours having a lower particle size than reduction flours). Images (Fig. 1) obtained by SEM confirmed this observation. Images shown on Figs 1a and 1b were obtained from Dinghy and Levis reduction flours, and Figs 1c and 1d from the corresponding grinding flours. From these images, it appears clearly that starch granules in Levis flours are embedded in a protein network, whereas for Dinghy flours many starch granules appeared to be isolated.

*Calorimetric parameters*

Examples of curves obtained from dispersions of flour and gluten (approx. 80% water) are shown on Fig. 2. The shape of the calorimetric signal observed after a first heating scan of a flour dispersion (Fig. 2a), is characteristic of heat-induced structural modifications in starch granules when in presence of a high volume fraction of water [9]. It presents a major transition peak (P1) around 60°C, accompanied by a minor peak (P2) around 90°C. In the DSC signal obtained in the second heating curve (Fig. 2b), only the minor transition peak was observed. The main peak P1, irreversible, corresponds to starch granules gelatinisation (breaking of the granule, destruction of crystalline structures, and partial dispersion of amylose in the continuous aqueous phase). The minor peak is attributed to the melting of the amylose-lipid complex [20]. The curve (Fig. 2c) obtained from a gluten dispersion in water (less than 80% water) shows two very small endothermic peaks located close to 60 and 84°C. The first one may be attributed to gelatinisation of residual starch and not to the gluten itself [21].

The calorimetric parameters of water dispersion of the 6 flours are reported in Table 2. They indicated that temperature of peak P1, and heat of reactions between 20 and

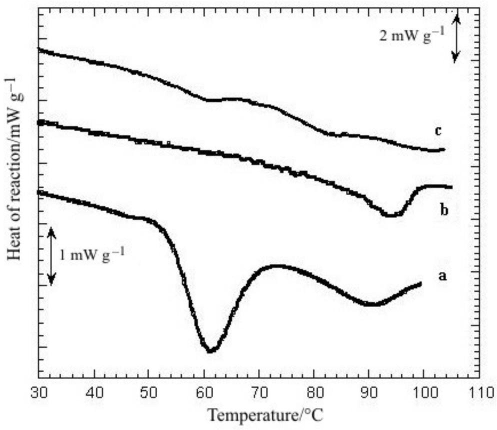



**Fig. 2** Examples of curves obtained from water dispersions of flour (a – first heating scan, b – second heating scan), or gluten (c – first heating scan), (μ-DSC Setaram, 0.5°C min$^{-1}$, from 20 to 120°C, endothermic heat flow downward)

110°C, are the highest for CWRS grinding flour. Following Stevens and Elton [2], and Tester [11], this effect could be in relation with its low particle size or with its high level of damage starch. However, we did not observe similar effects on the values obtained with the two other flours. It seems interesting to note that the relation between these characteristics and calorimetric parameters were in agreement with the hypothesis of Stevens and Elton [2], and Tester [11] only in the case of CWRS flour where the milling procedure did not have a significant effect on the flour protein content. The calorimetric parameters shown in Table 2, where the total heat of reaction ($\Delta_{cal}H$) was calculated on the basis of all solid components of wheat flour, except protein (in J g$^{-1}$ NP, per g of non-protein solids), indicated that $\Delta_{cal}H$ is the smallest for Dinghy grinding flour having the lowest protein content.

**Table 2** Calorimetric parameters of heat-induced structural changes in wheat flour dispersions (approx. 80% water). $\Delta_{cal}H$ (J g$^{-1}$ NP) is the total heat of reactions occurring in the temperature range 20 to 120°C, and calculated relatively to the mass of non-protein (NP) dry-matter

| Wheat variety | Milling procedure | $T_p$/°C | | $\Delta_{cal}H$/J g$^{-1}$ NP |
|---|---|---|---|---|
| | | P1 | P2 | |
| Levis | grinding | 59.1 | 89.1 | 14.0 |
| | reduction | 58.9 | 89.4 | 15.0 |
| CWRS | grinding | 62.0 | 90.4 | 16.2 |
| | reduction | 61.3 | 91.0 | 14.7 |
| Dinghy | grinding | 59.5 | 91.5 | 13.4 |
| | reduction | 59.9 | 90.0 | 14.5 |

The calorimetric signals obtained for doughs (45% water) showed the presence of three transition peaks (Fig. 3), instead of two peaks observed for the corresponding flour dispersions (Fig. 2a). For doughs in comparison with flour dispersions, the temperatures corresponding to peak P1 and the heats of reactions ($\Delta_{cal}H$), expressed in J $g^{-1}$ NP, are higher by approx. 1.5 to 3°C, and 3 to 4 J $g^{-1}$, respectively (Tables 2 and 3). On the other hand, while the temperature of peak P2 observed in the curves of flour dispersions is located around 89–91°C, for doughs peak P3 is located around 102–106°C. The appearance of P2 in the case of dough (total water content 45% w.b.) and the increase in transition peak temperatures and in total heats of reaction, in comparison with the corresponding flour dispersions (more than 80% water), are in fair agreement with previous results [3, 4, 22–24]. This effect of water content has been attributed to various mechanisms. At a low volume fraction of water, hydration of amorphous structures of starch granules being incomplete, higher temperatures and heats of reaction are needed for the fusion of crystallites [3, 4, 22]. On the other hand, P1 could be due to gelatinisation of starch granules containing the less stable crystallites, while the additional peak P2 observed for dough could be associated with granules containing more stable crystallites [23]. Following Colonna and Mercier [24], the fusion of crystallites could also be followed by a transition corresponding to he-

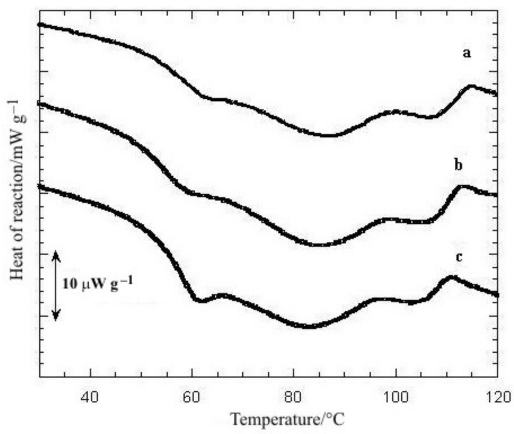



**Fig. 3** Examples of curves obtained from dough prepared from milling flours; a – CWRS, b – Levis and c – Dinghy. (μ-DSC Setaram, 0.5°C $min^{-1}$, from 10 to120°C, endothermic heat flow downward)

lix-coil structural changes of polysaccharides, which cannot occur simultaneously at reduced volume fraction of water.

Besides this effect of water content on the shape of curves and on the calorimetric parameters, we observed, for both doughs and flour dispersions, that the higher peak temperatures were obtained with the flours from CWRS having the higher protein content. In addition, the total heats of reactions ($\Delta_{cal}H$ in J $g^{-1}$ NP), calculated on the basis of non protein dry matter, are the lowest for Dinghy which has the lowest protein content. To explain this trend we performed DSC experiments on dispersions (approx 80% water) and doughs (water 45% w.b.) where parts of wheat flours were substituted by gluten. Our results showed a slight increase in peak temperatures with increasing gluten content, as previously observed by Eliasson [13] for mixtures of starch/gluten at 47% water content and in the temperature range 40–100°C. The total heat of reactions occurring in the temperature range between 20 and 120°C decreased slightly for samples where flour was substituted by gluten. The values of $\Delta_{cal}H$ (in J $g^{-1}$ NP), calculated on the basis of all solid components, except protein, increase with gluten adding, as shown in Fig. 4. The total heats of reaction in gluten dispersions (approx. 80% water) were also calculated from the area under the peak between 40 and 100°C (Fig. 1c). This value being lower than 0.5 J $g^{-1}$, it represents a negligible endothermic contribution to the total heat of reactions observed for wheat flour dispersions or doughs. Consequently the trend in $\Delta_{cal}H$ values, calculated on the basis of non-protein content (Fig. 4) cannot be explained by an endothermic effect due to added gluten. Previous results [13] obtained by DSC on starch/gluten mixtures (water 47% w.b.) indicated a decrease in the heat of starch gelatinisation, as a function of gluten/starch mass ratio up to 0.4. $\Delta_{cal}H$ was calculated from the first DSC peak (attributed by the author to starch gelatinisation) and on the basis of starch content (in J $g^{-1}$ starch). The author explained the observed increase in $T_p$ and the trend in $\Delta_{cal}H$ values, just opposite to the results shown in Fig. 4, by a possible water transfer from gluten to starch during heating. Chevalier and Colonna [10] explained the increase in $T_p$ of gelatinisation by a possible transfer to starch of water released from hydrophilic components other than proteins. The increase in $\Delta_{cal}H$ (in J $g^{-1}$ NP) found in the present study in presence of more than 80% water cannot be explained by a lack of available water for starch gelatinisation in presence of gluten, and it could indicate that in doughs (45% water) gelatinisation of starch does not deprive gluten of its water upon heating, as recently suggested by Sevenou *et al.* [25].

**Table 3** Calorimetric parameters of heat-induced structural changes in wheat flour doughs, $\Delta_{cal}H$ (J $g^{-1}$ NP) is the total heat of reactions occurring in the temperature range 20 to 120°C, and calculated relatively to the unit mass of all solid components, except proteins (NP, non protein content)

| Wheat variaty | Milling procedure | $T_p$/°C | | | $\Delta_{cal}H$/J $g^{-1}$ NP |
|---|---|---|---|---|---|
| | | P1 | P2 | P3 | |
| Levis | grinding | 60.5 | 81.1 | 102.2 | 19.9 |
| | reduction | 60.1 | 83.8 | 102.0 | 20.6 |
| CWRS | grinding | 64.2 | 83.0 | 104.7 | 18.3 |
| | reduction | 64.5 | 85.4 | 106.1 | 20.7 |
| Dinghy | grinding | 61.3 | 80.9 | 103.0 | 17.3 |
| | reduction | 61.5 | 81.1 | 103.0 | 17.6 |

We have also examined if some relationships could be established between *G*' and *G*'', the 'elastic' and 'viscous' elastic modulus of doughs (45% water content, 1 Hz), and mean flour particle size (Fig. 5a) or starch damage (Fig. 5b). In both cases, no definite trend is observed. If there is any effect, it is of second order compared to the one due to protein content: Fig. 6 shows that it is positively correlated with *G*' and *G*", as generally

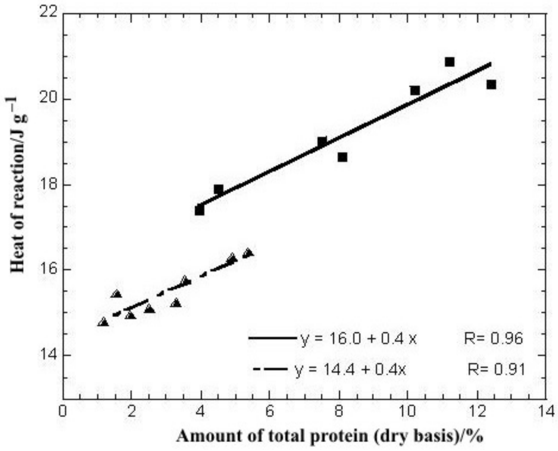



**Fig. 4** Effect of partial substitution of gluten, at various mass ratios (dry basis), on the total heat of reaction ($\Delta_{cal}H$ in J g$^{-1}$ NP) relative to non protein dry matter content. Flour dispersions (triangles) and doughs (squares)

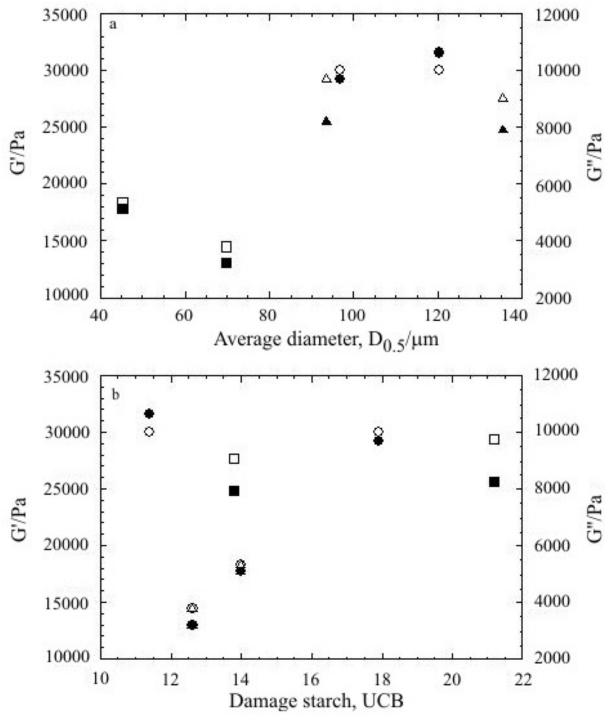



**Fig. 5** Elastic (*G*', full symbols) and viscous (*G*", open symbols) modulus of dough *vs.* mean diameters, $D_{0.5}$ (a), and *vs.* damaged starch in UCB units (b)

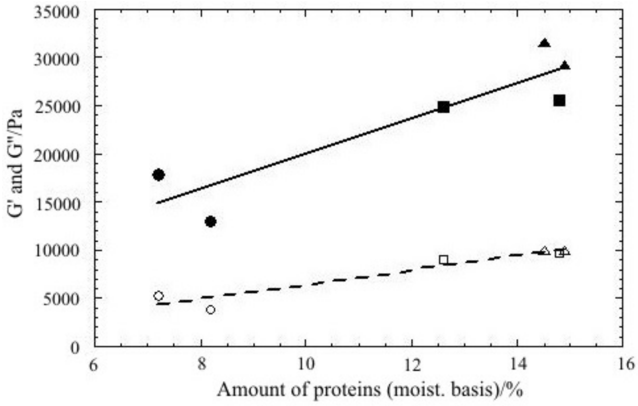



**Fig. 6** Relationship between elastic ($G$', plain symbols) and viscous ($G$", open symbols) modulus of dough and flour protein content (wet basis)

observed. Previous studies indicated that some rheological characteristics, consistency during mixing [18] or dough resistance to biaxial extension evaluated with the Chopin Alveograph [26], could partly depend on starch damage. It was concluded that flour having a high level of damaged starch absorb more water during mixing, but release it during rest or during the fermentation step, reflecting water redistribution between flour constituents. Our rheological measurements having been done following 1 h rest, it may be assumed that, in these conditions and at lab temperature, water hydration of gluten is not significantly modified by damaged starch.

## Conclusions

In this study, we used three types of wheat having different hardness indexes, submitted to two different milling procedures. The calorimetric and rheological behaviours observed for dough were discussed in terms of particle size, level of damaged starch and protein content of flours. Our results showed that these flours gave values of calorimetric parameters higher at intermediate water content (45% w.b.) than in excess of water which seem to depend on their protein contents. These results were confirmed by performing DSC experiments on flour dispersions and doughs, where wheat flour was partially substituted by gluten between 0 and 23% (w.b.). More investigations are needed, first to confirm this result and then to examine if this effect could be attributed to starch-gluten interactions.

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