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CHARACTERIZING IN SITU STARCH GELATINIZATION

Thermal and dynamic mechanical analysis of durum wheat dough

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Abstract

Data obtained by dynamic mechanical analysis and DSC analysis of durum wheat dough are presented and discussed. Doughs with water contents ranging from 45 to 55% (*w/w*) were subjected to sinusoidal shearing by means of a dynamic mechanical spectrometer (Rheometrics, RFS2) equipped with parallel plate geometry, 0.1 strain amplitude and 1 rad/min frequency. The tests were carried on in temperature sweep mode at a heating rate of 2°C min^{-1}.

Wheat samples with water contents in the range between 7.5 and 37.5% and doughs with 37.5% moisture content were mixed for different times and subjected to DSC analysis (Perkin-Elmer, DSC-7) at a heating rate of 20°C min^{-1}.

Dynamic mechanical analysis revealed that the relationship between the dynamic properties of the dough and the temperature was modified as the water content of the dough increased and was quite different from that for gluten.

A similar response was observed in the course of temperature scans made by means of DSC. These experimental findings suggest that the water-starch interaction in the presence of a protein matrix is affected by the availability of water and that the protein system is a competitor with respect to starch.

Keywords: DSC, gelatinization

Introduction

The production of bakery products starts from the dough preparation. This involves the mixing of raw materials, mostly wheat (or flour) and water, for a given time. During this operation, mechanical energy is supplied and water is uniformly dispersed in the mixture and adsorbed by the wheat constituents. The final result of this procedure is the unfolding of the protein complexes and their

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subsequent reorganization into a three-dimensional network [1]. Basically, it can be assumed that, during mixing, dough proteins held together by different kinds of bonds, intermolecular and intramolecular, give rise to a highly cross-linked macromolecular network, i.e. gluten, in which there are uniformly dispersed starch granules that will absorb part of the water and swell.

The next important step is the baking, where time and temperature are the main variables which affect the organoleptic characteristics and the quality of the finished products. The mechanism of formation of the structure of the products during baking is known to be associated with protein denaturation and starch gelatinization [2]. The gelatinization behaviour depends on the water content [3], but in the presence of proteins there is a competition for the available water [4]. The situation is even more complicated in the case of foods containing lipids, sugars and other constituents which may interact and interfere with proteins and starch [5].

In recent years, the use of advanced analytical techniques such as differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) has allowed an extensive clarification of the interactions which develop among the dough constituents [5–12]. The basic approach followed was to recognize the chemical, biochemical and chemo-physical phenomena that influence the various functional constituents of dough in the presence of water, with the aim of clarifying the role of the raw materials and selected technological variables.

If one considers the large differences in size and properties of the samples used for these two types of analyses, it is not surprising that the information derived from one kind of experimental technique does not always agree completely with that derived from the other. It must also be noted that DSC and DMA have been used together in a single investigation only rarely.

In the present study, DSC and DMA were performed in parallel to characterize the main interactions of starch, gluten proteins and water during the main stages in the technological process of dough-based products.

Materials and methods

Durum semolina wheat provided by CO.RI.AL. S.C.p.A., Foggia, Italy, was used. Where not specified samples were prepared just prior to each test by mixing wheat and water in different ratios for a given time by means of a Brabender Farinograph. In a few cases, the time between mixing and analysis was longer.

The gluten was extracted from the dough by washing it with a phosphate-buffered solution at *pH* 6.8, according to the stepping procedure recommended by AACC; the gluten was then weighed into DSC sample pans and subjected to analysis.

The gluten was divided into two fractions by extraction into alcoholic solution (70%, *w/w*) for 18 h. The alcohol-soluble phase was concentrated under reduced pressure at 25°C.

DSC analysis

A Perkin-Elmer DSC-7 instrument was used. Calibration was performed at 20°C min^{-1} via the melting point of indium. Sample scans started at 10°C and ended at 150°C, at a scanning rate equal to that used to perform calibration. The sample pans were then cooled immediately (200°C min^{-1}) to 25°C (load temperature). A second scan was performed to determine the baseline. As reference, 4.8 mg aluminum was used in a sample pan. Since heating was extended to 150°C, special sample pans for volatile compounds were used to avoid evaporation. The thermal data obtained in each scan were elaborated by means of a computer program (Peakfit, Jandel Software) which provides data smoothing by FFT filtering and deconvolution of the peaks with respect to a baseline, under the hypothesis that the peak shape can be described by a Gaussian curve [12].

Dynamic mechanical analysis (DMA)

DMA was performed with a dynamic mechanical spectrometer (Rheometrics, RFS2) equipped with parallel plates (5 cm diameter) operating in temperature sweep mode. The sample thickness was 2 mm.

To avoid rapid drying during the test, the exposed edges of the sample were covered with a thin layer of baseline. Samples with different moisture contents were subjected to a sinusoidal shearing of 0.1 strain amplitude and 1 rad/sec frequency and heated at a rate of 2°C min^{-1}. Data were elaborated by means of a computer program (Rhios V3.0.1, Rheometric Inc, USA) which provides dynamic properties, G', G'' and tan δ, where G' is the storage modulus, representative of the energy stored in the sample in any cycle, G'' is the loss modulus, a measure of the energy lost in any cycle, and their ratio G''/G', tan δ, is representative of the relative viscous and elastic contribution to the complex dynamic modulus.

Results and discussion

During the mixing operation, the dispersion of water and its absorption from the wheat constituents occur. At the same time, mechanical stresses cause the physical modification of proteins and structural changes to starch granules. The phenomena interfere with and influence one another.

In order to differentiate the effects due to water dispersion and absorption from those due to the mechanical energy provided during mixing, we first in-

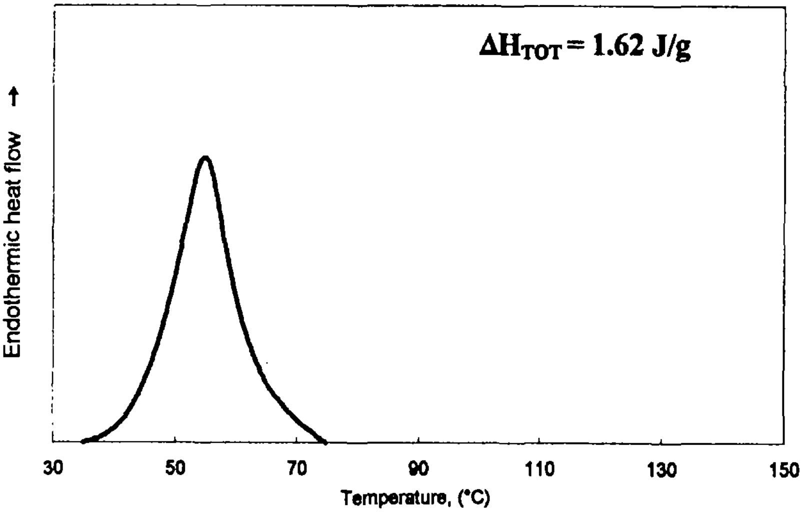

Fig. 1 DSC curve of wheat with 13% (w/w) moisture content

vestigated the thermal response of the wheat/water system on variation of the water content, and next that of the wheat/water system on variation of the mixing energy.

Figure 1 shows the DSC response of wheat with a moisture content of 13% (*w*/*w*). The DSC curve exhibits a single endothermic transition in the temperature range from 35 to 75°C, with the peak located at 55–60°C. This corresponds to an irreversible event, because it disappeared when the sample was subjected to a second scan. The total energy released was 1.62 J g^{-1}, evaluated (like the other values reported here) as the arithmetic mean of 5 independent runs performed under the same experimental conditions.

Figure 2 illustrates the DSC responses of wheat with different moisture contents of from 7.8 to 37.5% (*w*/*w*).

To obtain samples with moisture contents less than that of the starting wheat, the wheat was dehydrated at room temperature in a dryer containing silica gel for 24 h. Samples with moisture contents higher than that of the starting wheat were prepared by weighing wheat directly in the sample pans and then adding water with a syringe from the top until the desired weight was reached.

The sample pans were closed and left at rest to equilibrate at room temperature. Preliminary tests indicated that the energy released during the thermal scan varied with the length of the equilibration period as the water distribution is a time-dependent phenomenon. However, it was found that 2 h was sufficient for equilibrium to be reached.

The DSC curve of dehydrated wheat presents a single transition, corresponding to that exhibited by the original wheat. However, the energy released is much lower, at about 0.40 J g^{-1}.

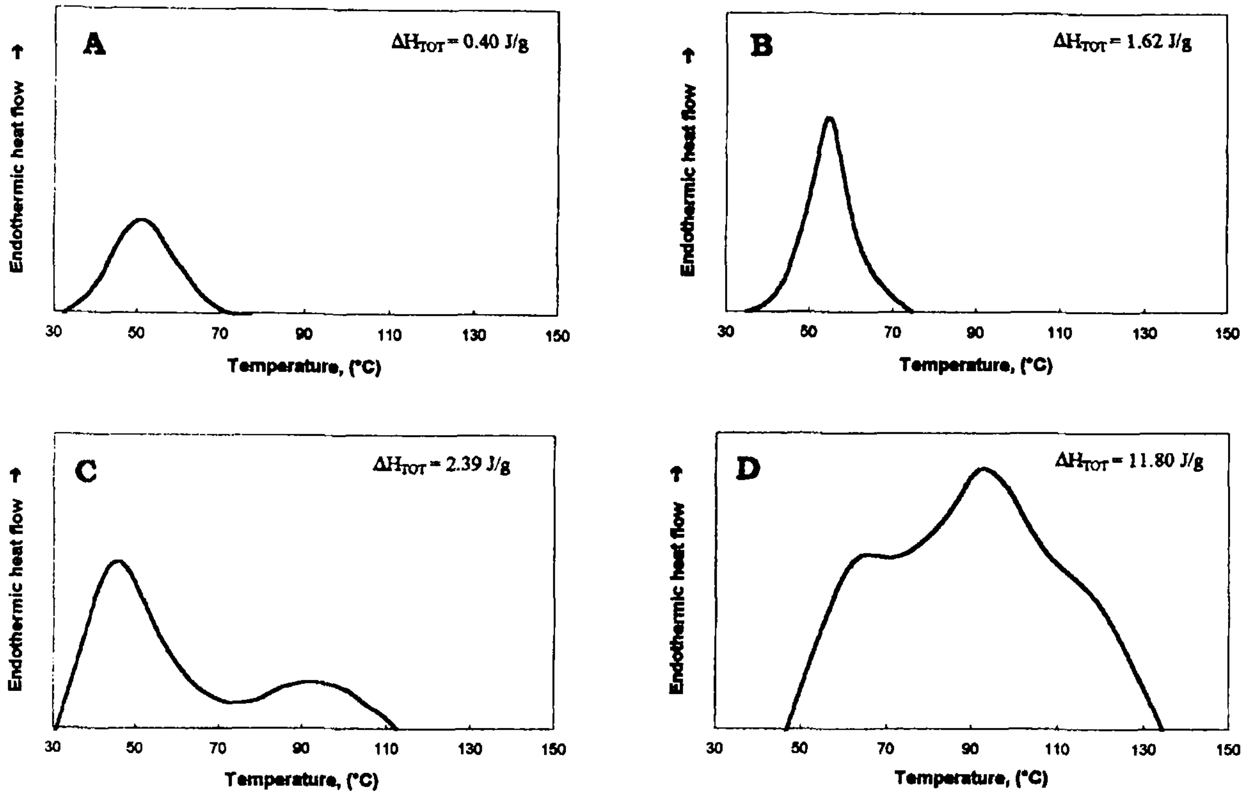

Fig. 2 DSC curves of wheat with increasing moisture content (w/w): (A) dehydrated wheat, 7.8%; (B) wheat, 13%; (C) hydrated wheat, 17.5%; (D) hydrated wheat, 37.5%

The DSC curves of moist samples exhibit a progressive variation of the shape, the position and the number of endothermic transitions.

Wheat containing 17.5% (*w*/*w*) moisture yields a DSC curve characterized by two transitions. The first has a shape, amplitude and location similar to those of the transition given by the original wheat.

A second endothermic transition, smaller than the first, develops at higher temperature (70–110°C).

As the moisture content further increases, from 17.5 to 37.5% (*w*/*w*), a third peak can be detected at a temperature close to 120°C. Moreover, the energy per gram released in the course of the thermal scan is much larger.

Figure 3 shows the dependence of the total energy released from the samples with variation of the moisture content. Enthalpy is not a linear function of water content. A reduction of 40% with respect to the original moisture content results in an enthalpy decrease of almost 75%.

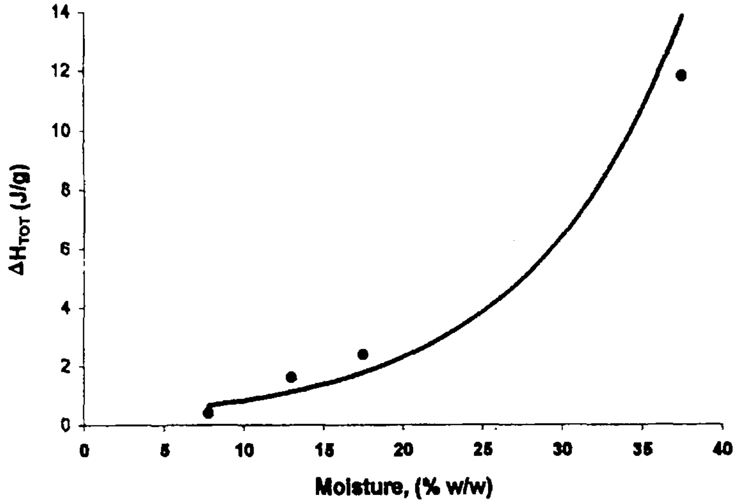

Fig. 3 Influence of moisture content of wheat on the total energy released in DSC scans from 30 to 150°C

Moreover, when the moisture content is increased 3-fold, the enthalpy increases more than 7-fold.

The most important observation to emerge from this set of experiments is that, as the water content increases, different phenomena occur. The fact that water may interact with starch in different ways as its amount increases is well known [13]. Data reported in the literature [14] indicate that the endothermic peak of gelatinization of wheat starch is located at 59°C; this suggests that the transition we observe could be associated with this phenomenon. However, the presence of proteins does not allow any conclusion at this time since the transitions observed could be associated with phenomena involving proteins, despite

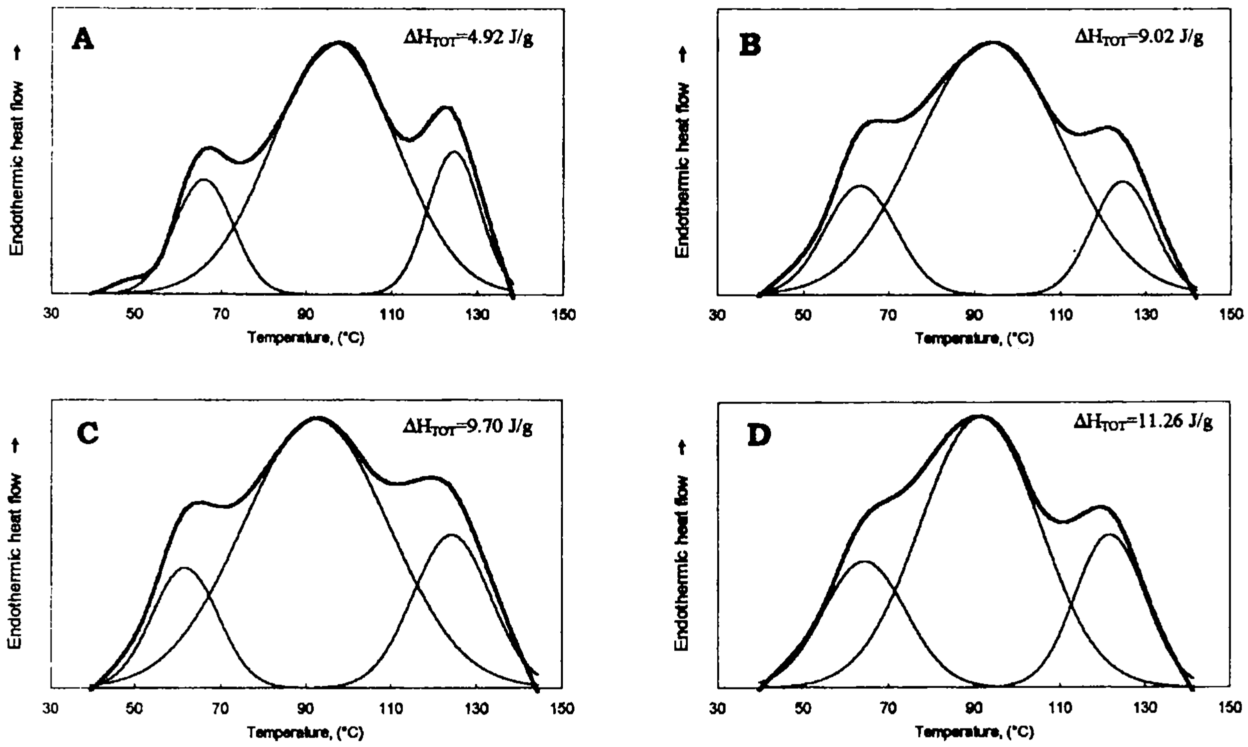

Fig. 4 DSC curves of dough mixed in a Brabender unit for different times: (A) 1 min; (B) 3 min; (C) 5 min; (D) 15 min

their relative amount being much less than that of starch. In fact, according to Lund [14] the latent heat of gelatinization of wheat starch is 10 J g^{-1}, which is appreciably larger than that for a sample with a moisture content less than 37.5%. If the transitions observed were mainly associated with starch gelatinization, we should expect a linear dependence of the latent heat of gelatinization on the water content below 37.5%.

Figure 4 shows DSC curves of wheat-water mixture containing 37.5% (*w/w*) water mixed in a Brabender unit from times varying from 1 to 15 min.

All the curves are similar. Three different transitions occur, evidenced by fitting the thermal response with Gaussian curves. Even the peak location appears independent of the mechanical energy supplied, while the amount of energy released varies to a great extent.

Figure 5 depicts the total enthalpy released on variation of the mixing time. The diagram also indicates, for comparison (full symbol), the energy corresponding to the original wheat (13% moisture). On increase of the mixing time, the energy increases, approaching a constant value of ca. 12 J g^{-1}.

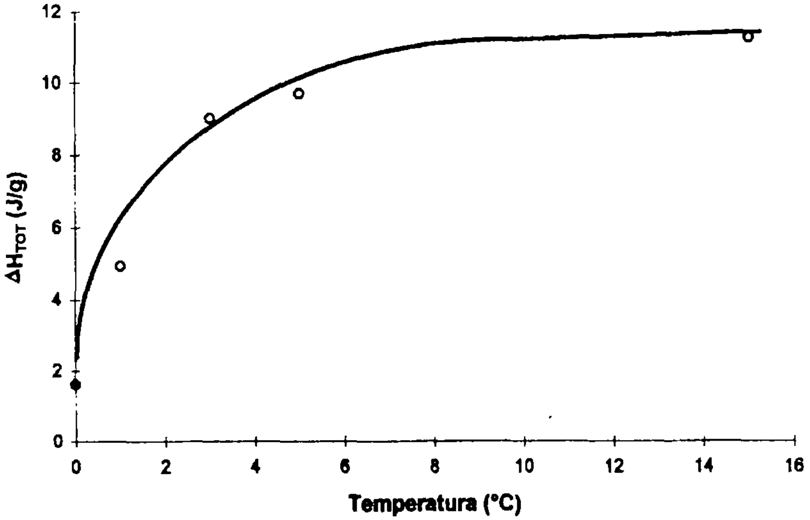

Fig. 5 Influence of the length of the mixing stage on the total energy released in DSC scans from 30 to 150°C

This value is the same as evaluated for wheat rehydrated and left to equilibrate for 2 h. The farinogram in Fig. 6 reveals that the time at which ΔH reaches its maximum does not clash with the time necessary to reach the maximum of the farinogram, occurring in 5 min, which corresponds to dough development, i.e. the maximum exposure of the active sites of the proteins.

These observations indicate that curve variations resulting from variation of the mixing time can be attributed mainly to water distribution into the mass, and they are almost independent of the energy provided by the mixer.

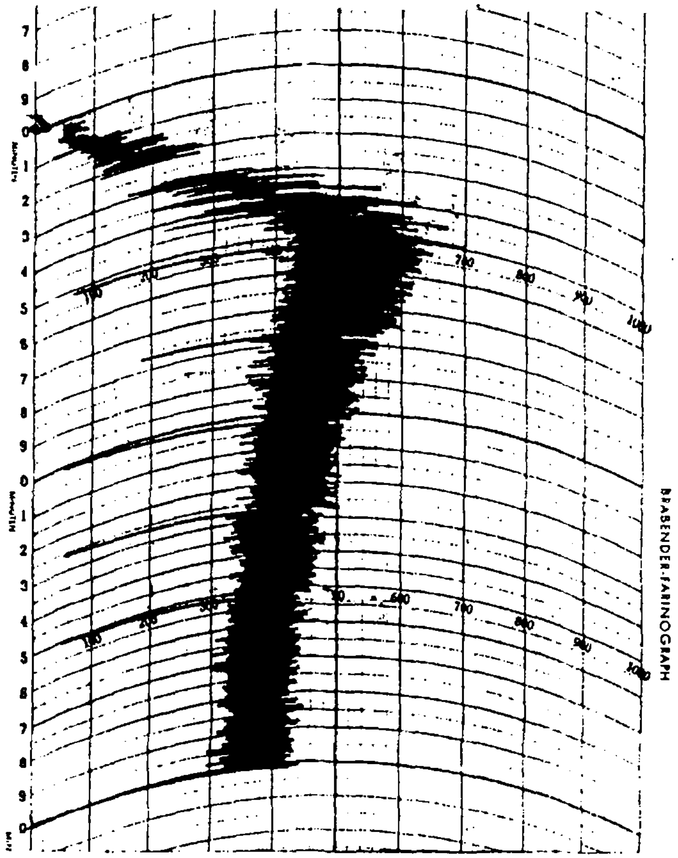

Fig. 6 Farinogram of wheat-water mixture containing 37.5% (w/w) moisture

As the gelatinization endotherm of wheat starch requires 10 J g^{-1} the additional energy measured for a sample with a moisture content of 37.5% should be ascribed to other water-wheat component interactions, probably those involving proteins.

We cannot advance any hypothesis about the development of these interactions with temperature and whether they interfere with each other. For this purpose, samples rich in gluten were prepared by using an appropriate procedure to wash dough prepared from the original wheat.

Figure 7 compares the DSC curves of dough mixed for 15 min containing 37.5% moisture and the gluten extracted from the same dough. The largest transition in the curve of the dough, i.e. that with the peak located close to 90°C, almost disappears, suggesting that the other two transition, at temperatures below and above 70°C, must be attributed to phenomena which involve proteins and water.

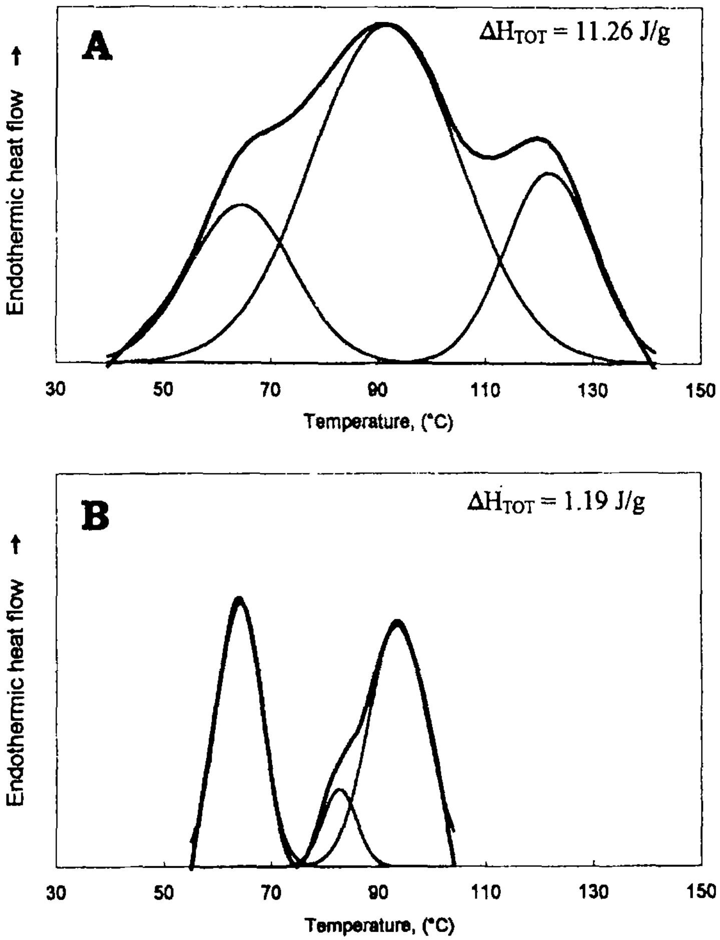

Fig. 7 Comparison between DSC scans of: (A) dough containing 37.5% (w/w) moisture, mixed for 15 min in a Brabender unit and (B) gluten extracted from the same dough

Figure 8 shows the DSC responses of the alcohol-insoluble and alcohol-soluble protein fractions: both fractions display the transition at low temperature, while the soluble fraction is responsible for the high-temperature one.

The energy released by those transitions is quite low as compared to that corresponding to starch (10 J g^{-1}), but of the same order of magnitude as that measured for samples with moisture contents equal to or less than 17.5%.

It can be concluded that there is a strong competition between proteins and starch with respect to the available water. As water is added to wheat, it is kept preferentially by the proteins, and only when the moisture content of the mixture reaches 35–37% does it become available to the starch; additionally, the gelatinization peak is shifted along the temperature axis by more than 30°C.

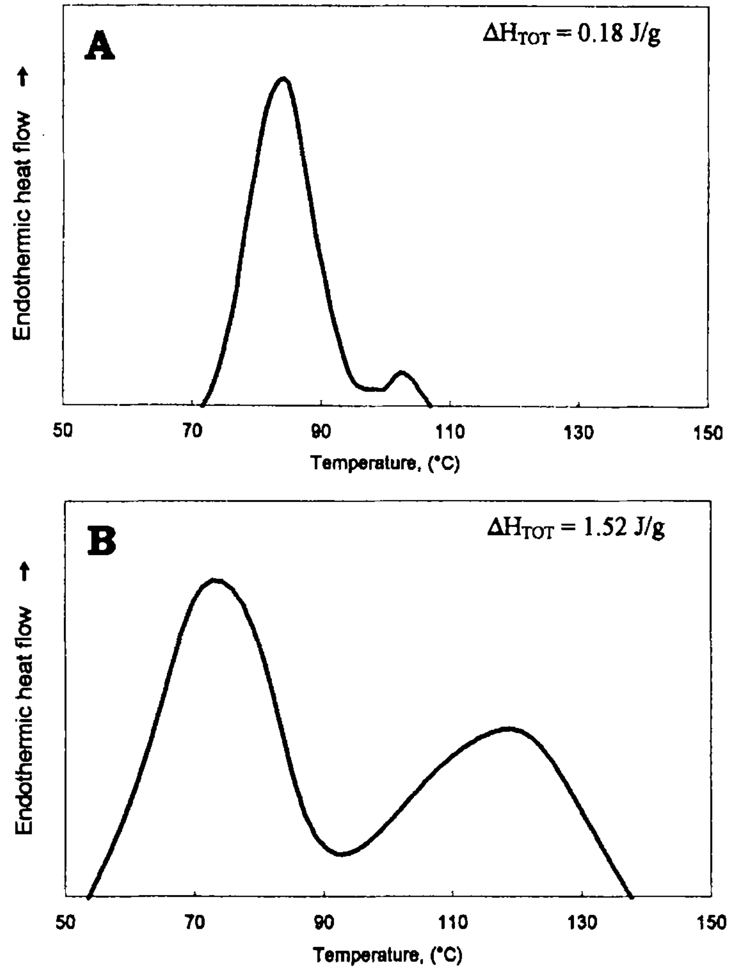

Fig. 8 DSC curves of: (A) alcohol insoluble protein fraction and (B) alcohol soluble protein fraction

Additional evidence of this competition between proteins and starch with respect to water results from dynamic mechanical analysis in temperature sweep mode.

Figure 9 shows the evolution of the elastic component of the dynamic modulus, *G′*, for increasing temperature of gluten and dough with moisture contents of from 45.8 to 54.4%. With increasing temperature, the curve for gluten first diminishes, exhibiting a broad minimum, and then increases. Up to 40–45°C, the behaviour is reversible [15]; it next becomes irreversible, suggesting that water and gluten proteins form permanent bonds. The shape of the curves for dough is quite different. The curves all diminish up to 40–50°C. As the tem-

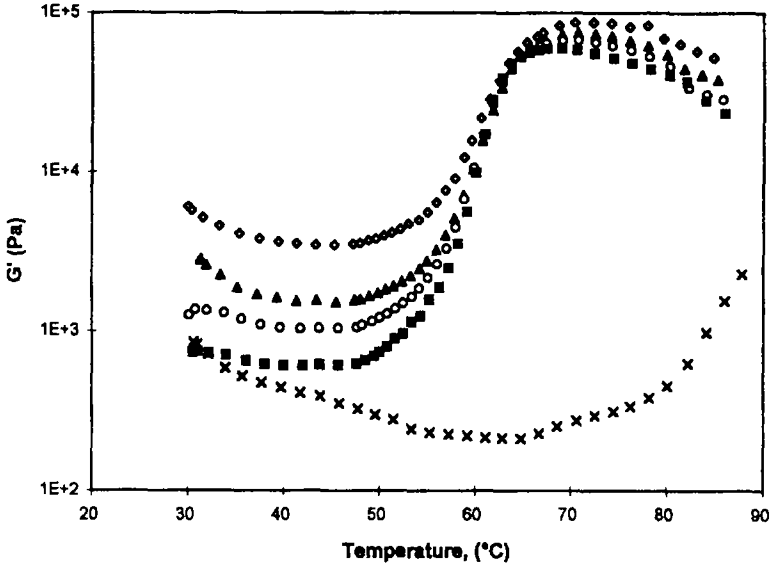

Fig. 9 Storage modulus, G', with varying temperature of gluten (×) and dough with different moisture content (w/w): (◊) 45.8%; (▲) 49.1%; (o) 51.1%; (■) 54.4%

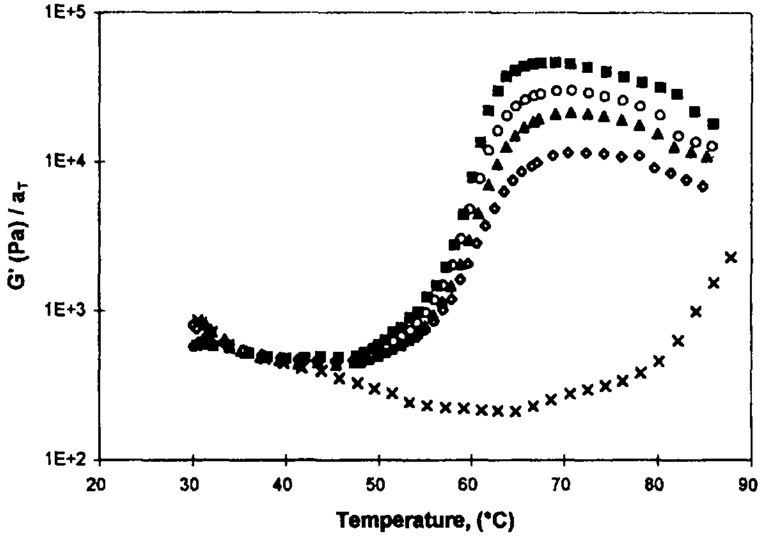

Fig. 10 Curves of storage modulus, G', of dough with different moisture content shifted along the vertical axis and superimposed to the curve of gluten. Symbols as in Fig. 9

perature is further increased, they suddenly increase, reaching a maximum value close to 70°C, and then decrease. As expected, the lower the water content of the dough, the greater its consistency.

In order to demonstrate the differences between the rheological responses of gluten and dough, and of dough with various moisture contents, the curves for dough in Fig. 9 were shifted along the vertical axis so as to superimpose them on the first portion of the curve for gluten. From Fig. 10, it is evident that the difference between the curves for dough and gluten can be attributed to starch-water interactions, and that these interactions increase as the water content in the mixture increases.

In Fig. 11, the area under the gluten curve and each of the curves for dough, measured in arbitrary units, is plotted against the moisture content of the dough.

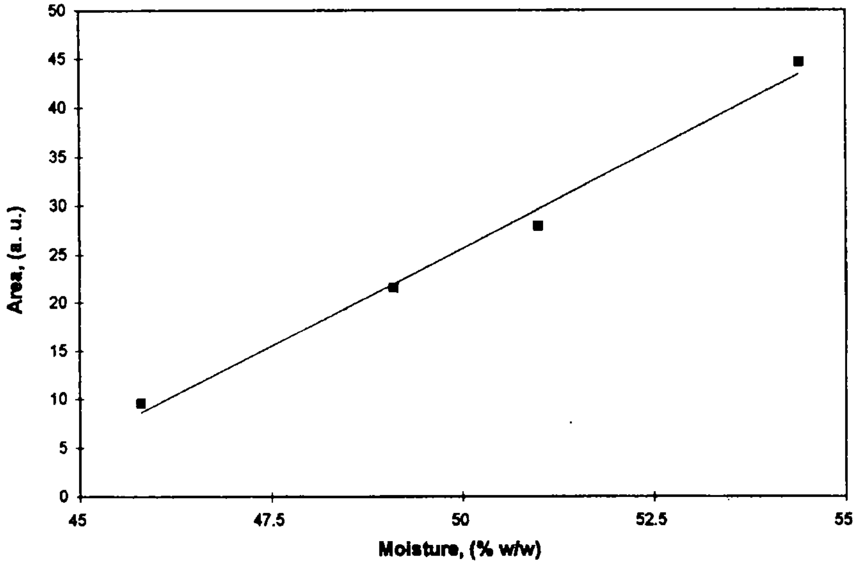

Fig. 11 Effect of moisture content of dough on the area between each curve and that relative to gluten given in arbitrary units

The experimental data fit a straight line that intercepts the horizontal axis at a moisture content close to 39%. Consequently, in dough containing less than 39% of moisture, the interaction between starch and water is negligible from a rheological point of view.

Since the true correlation of the data in Fig. 11 is probably not linear and we are comparing results from two sets of experiments involving quite different analytical techniques, the agreement of the information provided by DSC and DMA is more than satisfactory.

Conclusions

The interactions which take place between water and starch and proteins when a dough is heated are strongly dependent on the amount of available water. From a thermodynamic point of view, the mixing operation promotes the dispersion of the water molecules in the wheat mass, as does allowing the system to equilibrate for an appropriate time. Of course, mixing is indispensible from a rheological point of view, in order to obtain protein unfolding and the formation of a continuous network.

DSC tests and DMA used jointly demonstrate that water interacts preferentially with proteins, and only when its amount is greater than 30–35% can interactions with starch take place. During heating, proteins react first and then,if the amount of water is greater than the above-mentioned limit, starch reacts. It is interesting that part of the alcohol-soluble protein fraction reacts at a temperature well above 100°C. This would imply that a proportion of the gluten proteins do not take part in the settling process of dough during baking, which to a large extent occurs at a temperature below 100°C. Work is in progress to elucidate this aspect.

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