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STRUCTURE AND PROPERTIES OF BREAD DOUGH AND CRUMB

Calorimetric, rheological and mechanical investigations on the effects produced by hydrocolloids, pentosans and soluble proteins

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Abstract

The effects of hydrocolloids (guar and locust bean gums), soluble pentosans, and whey proteins on staling of bread crumb were investigated by means of DSC, rheometry, and image analyis. One current hypothesis, that these ingredients would behave as "water binders" and, at least the former two, as anti-staling agents, was indeed confirmed, although this action might be indirect. All the samples considered showed an exothermic DSC peak preceding the endotherm of the amylopectin fusion. According to a previous work, this signal was attributed to a water-dependent cross-linking process that would involve next-neighbouring polymer chains.

To check the effect produced by molecular modifications that were expected to increase the water uptake of these ingredients, doughs containing added succinylated pentosans and whey proteins, and a polycarboxylate polymer, PEMULEN TR-1, were examined. These modifications enhanced starch retrogradation and yielded a firmer crumb. It was tentatively concluded that some direct interaction between these modified molecules and the crumb polymers might have taken place.

In line with the food polymer science approach, the use of Time-Temperature-Transformation (TTT) diagrams is also discussed.

Keywords: bread crumb, bread dough, DSC, hydrocolloid, mechanical properties, pentosans, protein

Introduction

Bread dough is an intermediate-viscosity system that contains a gluten network with a subambient, DSC-determined [1] glass transition temperature, T_g. At this stage, starch granules compete with other dough ingredients for the available water [2], those with a surfactant character tending to occupy interfacial regions between less and more hydrophilic environments [3]. Baking induces starch gelatinization, extension of cross-linking within the gluten network [4] and, possibly, between this and other non-gluten polymers [5].

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The T_g of the baked crumb is just below room temperature [6]. After a few-day shelf life at room temperature, the crumb resembles a rigid sponge that can be compared to a cured thermoset polymer [7]. Crumb staling can thus be thought of as the result of a cure-like process that takes place at room temperature ($T_{cure}=T_{room}$) and mainly involves gelatinized starch (although gluten/starch interactions have also been postulated [5, 8, 9]), which undergoes amylopectin retrogradation and formation of a more rigid, amorphous starch matrix within the mesh-like gluten network.

In a previous work [10], a model has been proposed to describe the role of mobile water in the mechanism of formation of the bread-crumb structure, which depends on the number and kind of cross-links formed between nearest-neighbouring biopolymer chains. These links can be either direct, such as hydrogen bonds between functional groups of next-neighbouring chains, or mediated by interstitial water molecules bridging interchain gaps. Mobile water molecules would be displaced along polymer chains and would act as interchain zip-sliders moving from some embryonic structure [10]. An exothermic effect (as in curing of a thermoset polymer) has actually been observed [10] in the 15–30°C range of DSC traces for staled crumb samples. The final crumb structure has therefore been referred to as the result of a water-dependent process.

In terms of an overall picture, bread crumb can be viewed as a composite material containing two main components, namely a gluten network and starch glue, with different T_gs, and the structural changes in a bakery product can be suggested to result from the curing of a gluten network, which occurs mainly at high baking temperatures, and the curing of an amorphous starch matrix, which continues to progress during storage at room temperature. This naive picture requires improvement, by including the effects of non-starch and non-gluten ingredients.

Since water insertion between nearest-neighbouring chains should be affected by water-holding compounds, the addition of gums, pentosans, or proteins is expected to significantly modify the structure of bread crumb. This is why a number of studies have been previously reported, in which the actions of non-starch and non-gluten ingredients are often explained as the result of a competition for the available water [11–13].

Because of their possible anti-staling effect, such ingredients are of interest to food scientists and bread producers [14–17]. Among others, hydrocolloids of natural origin [water-soluble gums] have received special attention, because they may contribute to a "healthier" image of products. According to Christianson *et al.* [3], hydrocolloids affect starch gelatinization and retrogradation in bakery products, since they can interact with either gluten or starch.

It should be noted, however, that the specific effects of hydrocolloids added to a food recipe, i.e. increase of viscosity [18], thickening, emulsifying, water-holding [19, 20], with resulting modification of the sensory quality of the final product [3, 17, 20], may depend on many factors, such as temperature, concentration, ionic strength, etc. [18, 21].

Another class of polysaccharides that has received special attention is that of water-soluble and water-insoluble pentosans [14, 22], which can absorb up to ten times their own weight of water. Possibly because of differences in purity of the ingredients used, some disagreements still exist among various workers [e.g. 11, 22–24] about the functional role(s) of soluble (mainly arabinoxylans) and insoluble (mainly arabinogalactans) pentosans. Nonetheless, it appears to be established that, although they would not significantly affect starch gelatinization, water-soluble pentosans can limit starch retrogradation [14] and interfere with the gluten network in a dough [24], since a detrimental, post-baking collapse of structure is observed in products with added pentosan [22].

The present work was undertaken to observe the effects produced on the structure of bread crumb by non-starch and non-gluten ingredients, either of natural origin, such as guar and locust bean gums and rye-flour water-soluble pentosans, or of synthetic preparation, such as succinylated pentosans and proteins and polycarboxylate polymers having a surfactant character. Calorimetric, rheological, and image-analysis investigations were carried out to characterize the final product and identify the main action(s) of these ingredients.

Materials and Methods

Bread Preparation

Lab-scale bread was produced, using a conventional baker's yeast fermentation process. The raw materials used were: soft wheat patent flour (water content, 14.45% d.b.; total protein, 12.37% w.b.) obtained from a commercial source (Molini di Vigevano, Vigevano, Italy) and stored at 4 °C; compressed baker's yeast (*S. cerevisiae*) ("Vinal", Gist-Brocades, Casteggio, Italy); guar gum TH-225 (Cisalpina S.p.A., Bergamo, Italy, moisture content, 6.55% d.m.); and locust-bean gum LN-2 (Cisalpina S.p.A., Bergamo, Italy, moisture content, 8.78% d.m.j.).

Native pentosans were extracted from rye flour according to the following procedure [25]: following the thermal denaturation of soluble proteins, pentosans were collected as an ethanol precipitate (45–75% w/w), powdered and dried under vacuum. From this product, a succinylated derivative was obtained by reaction with succinic anhydride (1:0.5 w/w) at basic *pH* [10–11] in the presence of 0.5% sodium borohydride; emisuccinate group content was quantitated by titrimetry and found to be 1.26 meq g^{-1}. As a protein additive, a concentrated whey protein (GLOBULAL 70A, MEGGLE) was used; the succinylated derivative was obtained, as described above, at neutral *pH* (7–8)]; the total carboxyl group content was found to be 2.2 meq g^{-1}. As a highly carboxylated additive (15 meq g^{-1} of carboxyl group content), PEMULEN TR-1 (Goodrich) was used.

The dough recipes considered are shown in Table 1.

Table 1 Dough recipes. The content of each ingredient is given in parts by weight

Ingredients	Reference dough	+ guar gum	+ locust bean	+ pentosans	+ proteins	+ surfactants
Flour	100	99	99	100	100	100
Water(*)	56.6	58.8	59.3	60	60	60
NaCl	1	1	1	1	1	1
Yeast	3.75	3.75	3.75	3.75	3.75	3.75
Guar gum		1				
Locust bean gum			1			
Pentosans (**)				0.4		
Whey proteins (**)					0.4	
PEMULEN-TRI						0.4

(*) The water content of each dough was adjusted so as to attain 500 Brabender units in farinograph (Brabender OHG, Duisberg, Germany) 15-minute tests with 63-rpm mixing speed at 30°C, according to a standard procedure (AACC Official Method 54-21, 1987).

(**) Representing either underivatized or succinylated compound.

Preliminary tests showed that the higher the gum concentration, the higher the amount of water needed to reach the conventional 500 B.U. dough-consistency level. To keep the water content close to that of the reference dough, the hydrocolloid /flour ratio was accordingly limited to 1% (w/w). As for pentosan or protein (either native or succinylated) addition, the best performance was found for a 0.4% (w/w) content, which gave doughs with rheological properties comparable to those of the reference dough.

Ingredients were mixed with a spiral-arm mixer for 12 min and then allowed to rest for 10 min. 200 g loaves were then formed and proofed at 30°C and 70% relative humidity for 60 min in a climatic cell (Heraeus Vötsch HC0020, Balingen, Germany). The loaves were baked for 25 min at 225°C in a forced convection oven (Moretti, mod. Mikro, Marotta, Italy). Baked loaves were allowed to cool to room temperature (in 120 min), wrapped in a polyethylene bag (VC 999 05 Export, Inanem Mescineg), and stored in a constant-temperature chamber (Hereaus) at 20°C.

Physical and chemical characterizations

Moisture content of the bread crumb was determined by drying 3 g samples for 12 h at 105°C. Results (average of 3 replicates) were expressed as g H_2O/g d.m.

The apparent specific weight of bread was measured by rapeseed displacement 2 h after baking. The reported results are averages of 5 replicates.

Image analysis

Air-cell shape of the bread crumb was evaluated by computerized image analysis (Ansel software) of photographs of crumb slices (1 cm thick). The digital image had a resolution of 400 dpi (pixel per inch), at 256-gray-intensity-units full scale. Files of the converted images were analyzed with software for graphic elaboration (Pstyler). This allowed visualization of the borders of the pores and definition of the gaussian distribution of color gray (which is correlated with the pore depth). Finally, a specific calculation routine (Table Curve software, Jandel Scientific, Erkrath, Germany) allowed the pore-size distribution to be fit with Gaussian functions; area and curve width are proportional to number and size of the pores, respectively.

Rheometry and dynamometry

Dynamic thermomechanical analyses of doughs were performed using a VOR Bohlin rheometer (Bohlin Reologi AB, Lund, Sweden), equipped with parallel plates (3-cm diameter) and a device for control of the temperature-scanning rate. The rheometer was interfaced to a PC for data recording. 1-mm-thick samples were prepared just before each test; doughs were mixed in the farinograph bowl to attain the optimum dough consistency, and tested after 5 min of relaxation. To avoid rapid drying during the test, the exposed edges of the specimen were covered with a thin layer of vaseline. Temperature-sweep tests were performed in the 30–90 °C range, with a 4 °C min^{-1} heating rate, at 2.5% strain amplitude and 1 Hz frequency.

Large-deformation tests by uniaxial compression were carried out on bread crumb using an Instron UTM (mod. 4301, Instron Ltd., High Wycombe, United Kingdom). The dynamometer was equipped with a 10 Kg loading cell and operated with a crossbar speed of 20 mm/min. Five replicates of a cylindrical crumb sample (about 30 mm high and 25 mm diameter) for each bread tipology were taken from the central zone of the loaf core. Crumb samples were allowed to rest for one minute and then compressed 40% between parallel plates, using a plane circular surface (80 mm diameter) plunger. The dynamometer was interfaced with a PC for data recording (software "Instron series IX, Automated Materials Testing System"). Force-deformation curves were formatted as ASCII files and analyzed with Table Curve software. A mathematical routine allowed removal of the dead shift of the plunger from the overall displacement (expressed as stress *vs.* Henky deformation) and calculation of the elastic modulus in the linear region of the trace [26].

Thermal analyses

DSC investigations of doughs were carried out with a differential scanning calorimeter Setaram DSC92, using 40 mg samples sealed in aluminum pans.

The reference cell was empty. Runs from 20 to 100°C were carried out at 4°C min^{-1} heating rate. Other thermal analyses on 40 mg bread crumb samples were carried out with a Mettler DSC 20. The reference cell contained aluminum slices to counterbalance, as much as possible, the sample heat capacity. Runs covered the temperature range 10 to 80°C; the lower end of this range was attained by use of a liquid nitrogen holder positioned over the DSC furnace. Data in the −10 to +10°C range were nonetheless discarded because of the initial drift of the record. The traces (three replicates for each sample) were converted into ASCII format, for processing (baseline assessment, trace smoothing, and trace deconvolution) according to a previous work [27]. Heating–cooling–heating cycles between −5 and 35°C were performed, on 20 mg bread crumb samples sealed in aluminum pans, with a Perkin Elmer DSC 6 (which was better able to follow this kind of temperature program) at 4°C min^{-1} heating rate.

Results and discussion

Breads and doughs with added gums

Preliminary tests revealed that addition of hydrocolloids modified the rheological properties of the dough; i.e. addition of guar gum weakened the dough, which subsequently collapsed, whereas the opposite occurred after addition of locust bean gum.

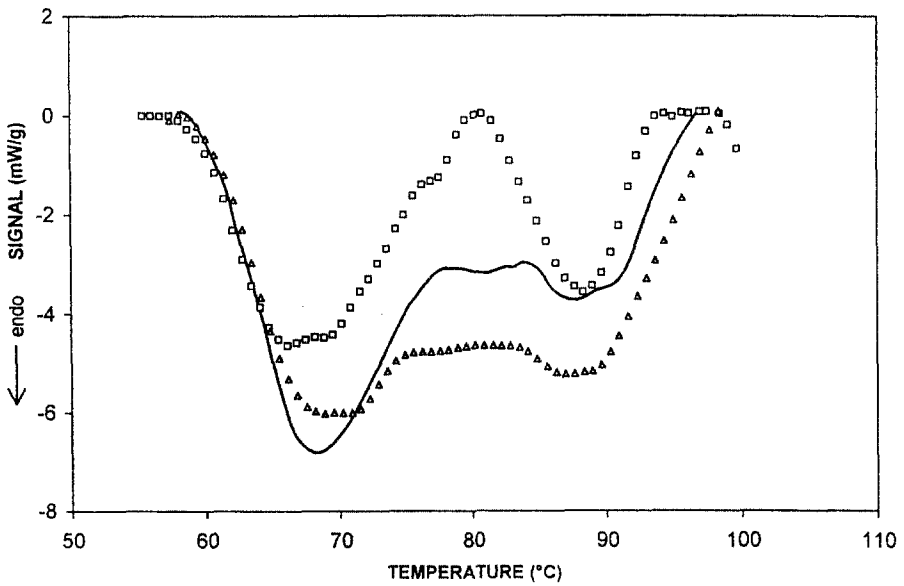

Fig. 1 DSC traces (4°C min^{-1} heating rate) of reference dough (–), dough with 1% guar gum added (□), and dough with 1% locust bean gum added (△). Each trace is the average of three replicates

Machined doughs are complex matrices, in which gluten behaves as a thermosetting biopolymer, while starch granules act as fillers within the protein network. These granules undergo gelatinization when heated above their own T_g. Fig. 1 shows DSC traces smoothed according to the method of Riva and Schiraldi [25], each being the average of three replicates.

The overall endothermic signal was spread over the 55–95°C temperature range and indicated the following changes in the overall enthalpy on gum addition: $\Delta_{gel}H = 1.99$, 1.27 and 2.49 J g^{-1} for reference, guar- and locust bean-added dough, respectively.

Were the model of Biliaderis *et al.* [28] accepted, starch gelatinization should progress through glass transition, "fusion" of partially crystalline regions, and finally "fusion" of more extended amylopectin crystals. However,

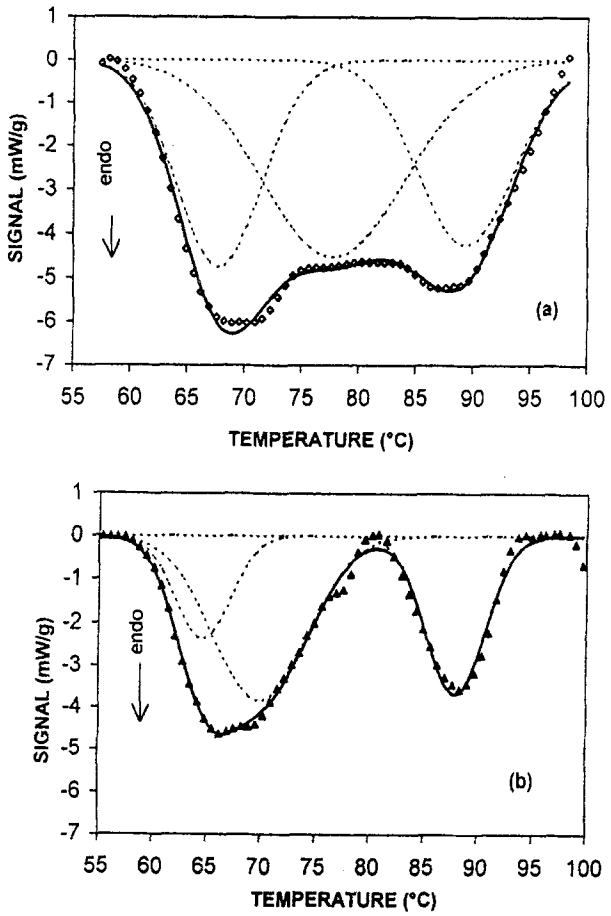

Fig 2 Deconvolution, into three gaussian components, of the DSC trace obtained from dough with added locust bean (a) or guar (b) gum. The continuous line corresponds to the sum of the three gaussian functions (dotted lines) that fit the experimental trace

the T_g-related shift in the baseline of the DSC trace is concealed by the endothermic effect of the early "fusion", when enough water is available. For this reason, a naive treatment of the experimental data [29] can be expedient: the DSC trace can be subjected to deconvolution [27] into pseudotransition gaussian peaks. In the present case, three peaks were used to describe the whole gelatinization signal: the cases of locust bean- and guar-added doughs are shown in Fig. 2.

The first two peaks can be related to early transformations promoted by the available water, including the glass transition, while the third mainly concerns "fusion" of more extended crystalline regions [28].

According to this analysis, hydrocolloid addition resulted in differences in the sequence and breadth of the single transitions within the temperature range investigated. In no case were the endothermic events completely separated, except for the guar-added dough, for which the third component appeared rather well resolved (Fig. 2b). The first endothermic signal was smaller in guar-added doughs.

In aqueous solutions, guar and locust bean gums exist in a conformation that allows aggregation with eventual formation of thermoreversible gels [30, 31]. When heated above their own gel $\Leftrightarrow$ sol transition temperature, hydrocolloid molecules bind much solvation water, part of which is released upon cooling back to the gel state. Such water release depends on molecular structure, being more likely for more branched polymers, such as guar gum (whose *D*-mannan backbone contains a larger number of *D*-galactose side-chains), than for more linear molecules, such as locust bean gum. Formation of these gels is therefore expected to occur within the freshly prepared dough. If the gel $\Leftrightarrow$ sol transition temperature of the added gum is above the starch T_g, enough water is available to sustain gelatinization, and no significant modification is therefore expected on gum addition. This is the case for locust bean gum (Fig. 2a), whose gel $\Leftrightarrow$ sol transition occurs in the 65–80°C range with an endothermic effect of 0.6 J g^{-1} [32]: deconvolution of the relevant DSC trace accordingly shows broad and largely overlapped components. If the gum forms a sol phase below the starch T_g, the available water is reduced, and starch gelatinization takes place, with a neat separation between the "fusion" of partially crystalline regions and that of extended crystals. This is the case for guar gum (Fig. 2b), whose gel $\Leftrightarrow$ sol transition occurs in the 15–25°C range with an endothermic effect of 0.2 J g^{-1} [32]: deconvolution of the relevant DSC trace accordingly shows a smaller first component (that includes the heat capacity drop accompanying glass transition) and a well-resolved third component that mainly corresponds to the "fusion" of extended amylopectin crystals.

Starch gelatinization in these gum-added doughs was also investigated by determination of G' (storage modulus), G'' (loss modulus) and tanδ (G''/G' ratio), in the course of temperature-sweep tests carried out at 2.5 % strain amplitude

and 1 Hz frequency in the 30–90°C range. Under these conditions, the response is independent of stress/strain intensity and amplitude [33, 34]. The same 4°C min^{-1} heating rate as for DSC measurements was chosen. The experimental data are shown in Fig. 3.

Samples of doughs of maximum consistency were collected directly from the Brabender mixer and tested after 5 min rest times. The observed trends of G', G'' and tanδ with temperature were all similar for the three types of dough. While the temperature remained below the onset of starch gelatinization, the material strength decreased slightly, with increasing temperature, just as for a non-reacting system. Above this threshold temperature, the behaviour reversed, as expected because of the formation of a starch gel (with swelling of starch

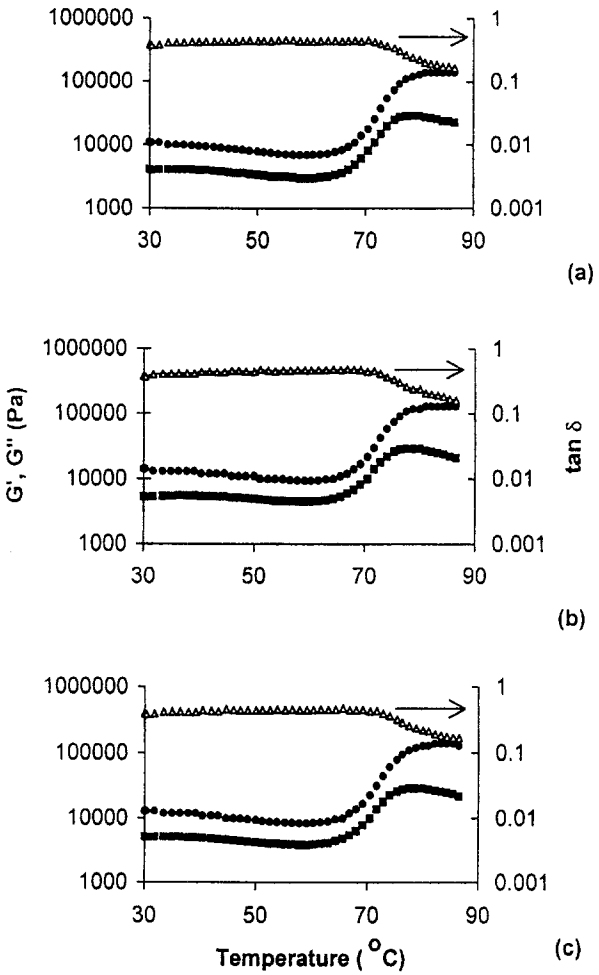

Fig. 3 G' (•), G'' (■) and tanδ (▲) as functions of temperature, recorded at 4°C min^{-1} heating rate, for reference (a), guar-added (b), and locust bean gum-added (c) doughs

granules) and the thermosetting of the gluten network. Above 75–80°C, G' reached a constant level, while G'' went through a broad maximum.

The effects of gum addition were better revealed by the trends in the rheological parameters scaled to their starting values, namely G''_t/G''_o and G''_t/G''_o. Figure 4 shows the relevant data. Reference and gum-added doughs showed the same behaviour up to 75°C, thus well above the starch T_g, but just around the onset of the third component of starch gelatinization (Fig. 2), when even the crystalline regions of starch undergo "fusion" and bind water. Reference doughs attained larger G' and G'' values, suggesting a more extended thermosetting of the structure. The lower G' and G'' found for either gum-added dough can be tentatively explained by the reduced availability of water that governs the mechanism of cross-link formation [10]; at this temperature, the stable phase is indeed a sol that traps large amounts of solvating water.

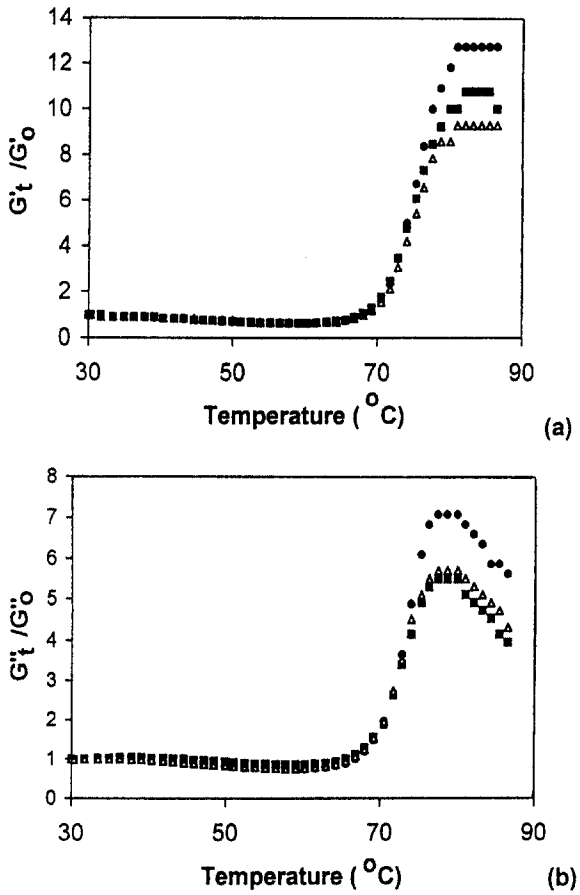

Fig. 4 Scaled G' (a) and G'' (b), as function of temperature, for reference (•), guar-added (■), and locust bean gum-added (Δ) doughs. Only above 75°C did significant differences appear

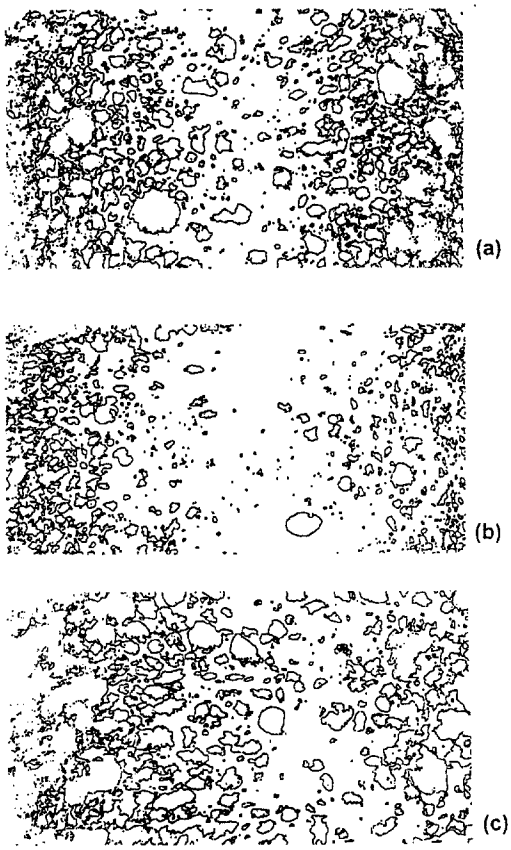

Fig. 5 Image analysis of pore contours in the central slice of bread loaves prepared from reference (a), guar- (b), and locust bean gum-added (c) doughs

Freshly baked and aged (up to 20 h at 20°C) breads were examined to study the early staling of the products. The apparent densities of the loaves were statistically (95% confidence level) different, i.e. 1.46, 1.56 and 1.29 g ml^{-1} for reference, guar- and locust bean-added breads, respectively. The digital images (Fig. 5) of the central slice of three loaves, prepared from reference and either gum-added doughs, revealed that the guar-added bread was the most continuous, i. e. had the smallest pores.

According to the gaussian distribution of the gray tones (Fig. 6), guar-added bread crumb showed the highest pore homogeneity, with the highest frequency in the brightest zone, which indicates many small and shallow pores.

Uniaxial compression tests allowed mechanical characterization of bread-crumb samples. The values of elastic modulus, obtained from the linear region of the stress/strain curve (in the 2–8% deformation range), where bread shows an elastic behaviour, were 0.695, 0.663, and 0.531 g mm^{-2} for reference, guar-

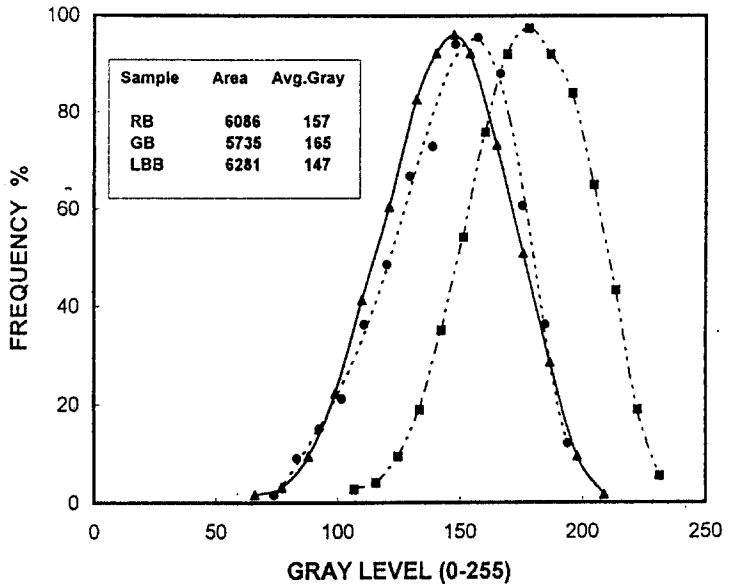

Fig. 6 Statistical distribution of gray intensity of pores in the image of the central slice of bread loaves prepared from reference (•), guar- (■), and locust bean-added (▲) breads, indicated as RB, GB, and LLB in the insert, where the underlying area and the average (i.e. the median value) gray level are tabulated

and locust bean-added bread, respectively. According to the Duncan test, locust bean-added bread was statistically (95% confidence) different from the other two, although the small difference could be explained as the result of the different water content, i.e. 0.89 *vs.* 0.85 g H_2O/g d.m. for the former *vs.* the others, attained in the post-baking phase, in which remarkable water losses occurred, i.e. 2.32, 3.25 and 3.80% for reference, guar- and locust bean-added breads, respectively.

Since water acts as a plasticizer [2], it reduces the network T_g, i.e. softens the structure (lower elastic modulus of the locust bean-added bread), and enhances the rate of phase transitions (effect on starch retrogradation). Thus, some retarding effect on bread staling was accordingly expected.

Figure 7 shows the DSC traces of crumb samples from fresh bread (0 storage time).

According to various workers [35–37], the extent of starch retrogradation can be quantitatively assessed from the enthalpy change associated with the melting of amylopectin crystals in the 35–70°C range. The findings of the present work were 1.1, 0.2 and 0.1 J g^{-1} (d.m.) for reference, guar gum- and locust bean gum-added breads, respectively; thus, gum addition reduced starch retrogradation to a larger extent than was expected from the small differences in water content: accordingly, it seemed reasonable to speculate about some direct effect of the gum on the nucleation of amylopectin crystals.

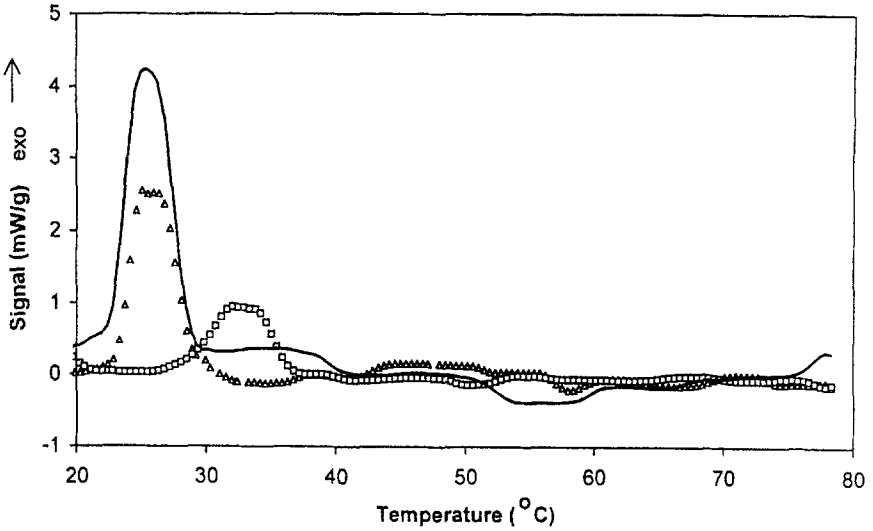

Fig. 7 DSC traces (2°C min^{-1} heating rate) for crumb samples of reference (–), guar- (□), and locust bean- added (△) breads at zero storage time

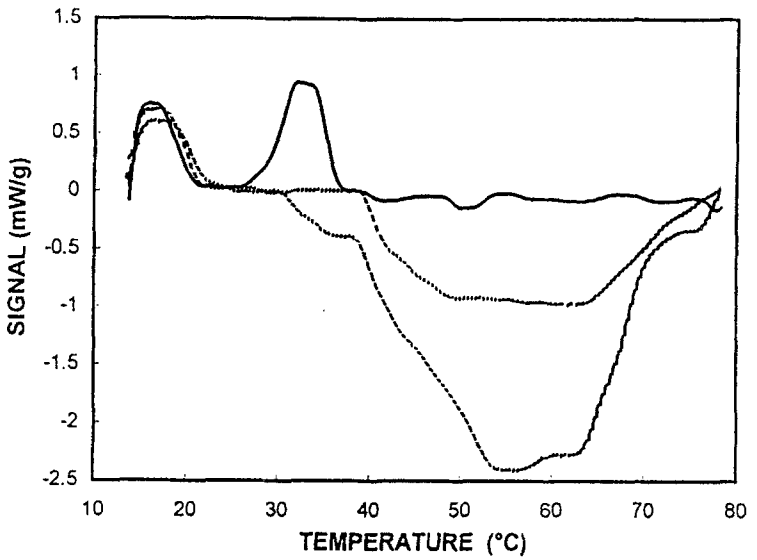

Fig. 8 DSC traces (2°C min^{-1} heating rate) of guar-added bread sample after 0 (–), 5 (upper dotted line) and 20 (lower dotted line) hours of storage at room temperature. Upward peaks correspond to exothermic effects

In a previous work [10] concerning bread staling, exothermic and partially reversible DSC signals were observed in the 15–30°C range, which were attrib-

Table 2 Exo- and endothermic effects in stale bread crumb

Time/	$\Delta_{exo}H$/J (g d. m.)$^{-1}$			$\Delta_{endo}H$/J (g d. m.)$^{-1}$		
h	RB	GB	LBB	RB	GB	LBB
0	1.4	0.6	1.0	0.2	0.2	0.1
2	1.7	0.3	1.3	1.2	0.4	0.8
5	0.1	0.3	1.8	1.2	1.5	0.8
12	1.2	0.3	0.7	1.4	2.1	1.2
20	0.5	0.3	1.4	1.9	3.3	2.2

RB, GB and LBB represent reference, guar- and locust bean gum-added bread.

uted to the solvation of water-binding sites along starch (and non-starch) polymer chains. The intensity of these thermal events was found to go through a broad maximum after about 10 h of aging at room temperature. In the present work, analogous signals were found in the DSC traces of gum-added bread-crumb samples. Figure 8 shows the case of guar-added bread aged for 0, 5 and 20 h at room temperature. Table 2 shows the enthalpy changes associated with the exothermic and endothermic DSC signals.

According to the observed $\Delta_{endo}H$ *vs.* time trend, the rate of starch retrogradation in the reference bread was faster during the first 2–3 h of staling, then progressed at a slower rate later on (Fig. 9); this confirmed the retarding action of the gums in the early phase of starch retrogradation.

It was mentioned earlier that gum gels are thermally reversible and ripen during storage. As a consequence, the endothermic event observed in gum-

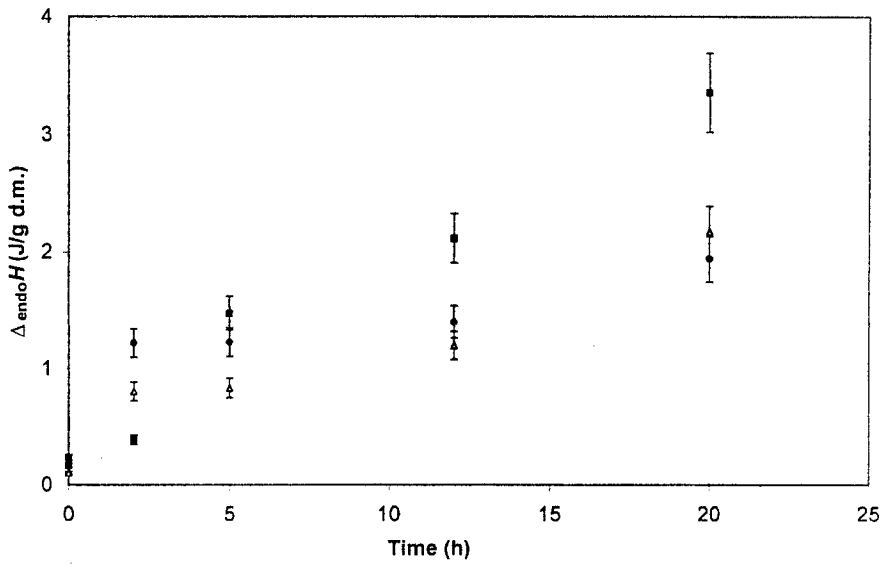

Fig. 9 Trend of endothermic peak enthalpy *vs.* time for reference (•), guar- (■), and locust bean-added (▵) bread-crumb samples

added breads could comprise two contributions, namely the melting of amylopectin and the gel-to-sol transition of the gums. The functional role of hydrocolloids as "anti-staling" agents can thus be defined only by relating calorimetric evaluations of starch modifications with other investigations, such as of changes in moisture content and rheological properties, which were considered in the present work.

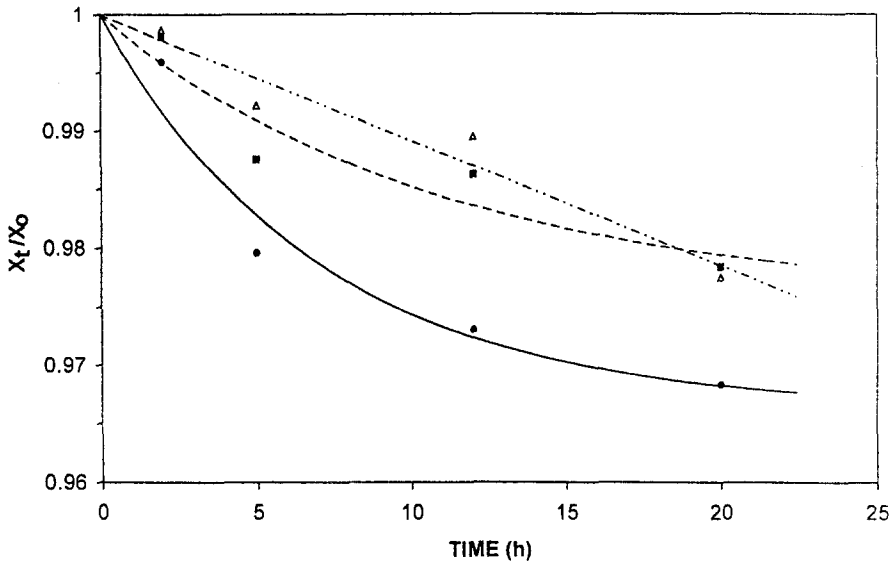

Fig. 10 Water loss as a function of storage time for reference (•), guar-added (■), and locust bean-added (▵) bread samples. Absolute humidity values are scaled with respect to the initial values

Figure 10 shows the water loss during bread storage at room temperature; the values are normalized with respect to the initial value (X_t/X_o). It was thus possible to qualitatively verify that hydrocolloid addition affects dehydration kinetics; in the reference bread, the rate of water loss was actually the highest at every storage time. No significant differences were observed between gum-added breads, although their moisture contents remained high throughout the storage period.

Figure 11 shows the change of the elastic modulus of the crumb during storage as a function of the moisture content. These rheological data are the average values of six replicates: they were statistically different (95% level) from one to another bread type at any storage time. Once again, these data suggested that bread consistency would depend on the hydration of the matrix. The same E value was in fact reached for different water contents (especially for locust bean added bread), thus confirming that part of the added water might play a functional role other than plasticizing. As previously argued, water might be involved in the sol ⇔ gel transition of the gums.

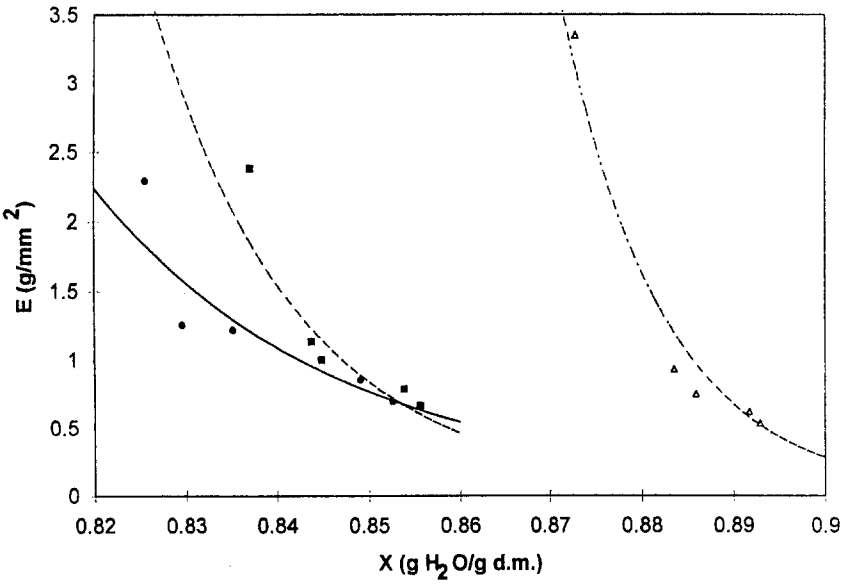

Fig. 11 Elastic modulus of reference (•), guar-added (■), and locust bean-added (△) bread-crumb samples *vs.* moisture content

Breads with added pentosans, protein, or PEMULEN TR-1

The above ingredients were added in moderate amounts, in order to keep the studied systems as close as possible to real conditions attainable by the use of naturally pentosan- or protein-rich cereal flours. In this context, data from other workers [e.g. 11, 22] who dealt with 1–2% pentosan addition, should be considered as much more viscous systems. In view of the expected action of pentosans and proteins as water "binders", succinylated substitutes were also believed to enhance this effect.

It is noteworthy that while native and succinylated pentosan-added breads scarcely differed from one another in their water aftinity, succinylated proteins increased the retention of water more than did underivatized proteins.

PEMULEN TR-1-added breads retained less water than did the reference bread. None of these ingredients appeared to affect starch gelatinization at the water contents studied here; however, significant differences were observed in breads.

As expected [22, 24], addition of water-soluble pentosans led to larger loaf volumes, whereas neither succinylated pentosans nor proteins produced detectable effects. The action of pentosans is believed [14] to depend on a direct interaction with the gluten network, which would undergo a moderate post-baking collapse. Accordingly, addition of succinyl groups would limit this effect.

In these modified breads, two exothermic signals appeared in the relevant DSC traces (Fig. 12), even after 5 days of storage at room temperature. In the

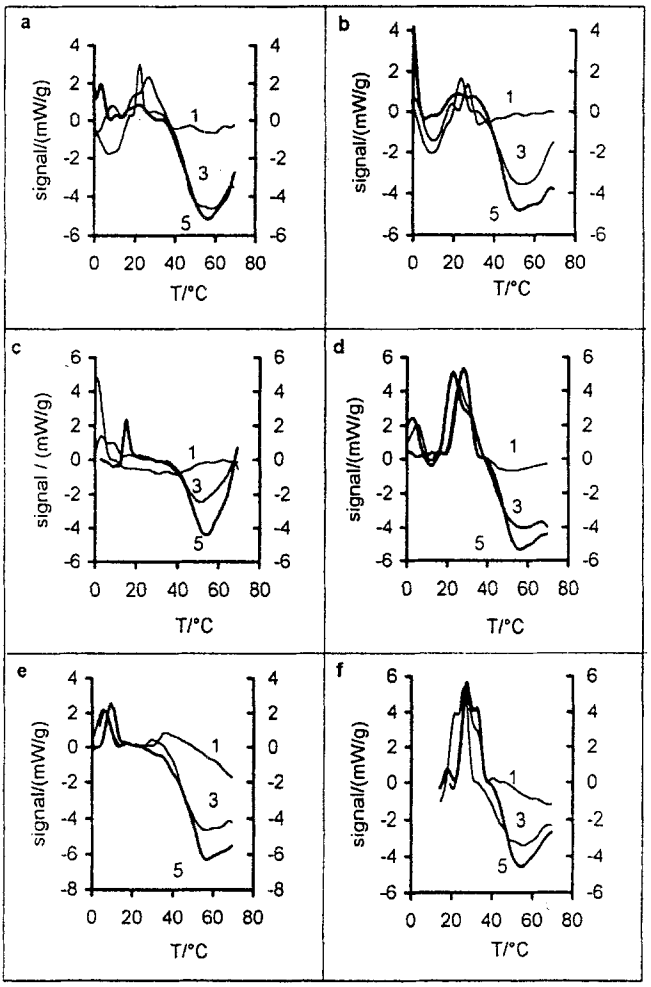

Fig. 12 Exothermic(upward) and endothermic (downward) signals in DSC traces for stale bread-crumb samples: (a) reference, (b) PEMULEN TR-1-, (c) pentosan-, (d) succinylated pentosan, (e) whey protein-, and (f) succinylated whey protein-added breads. 1, 3 and 5 stay for days of ageing

pentosan-added breads, the appearance of these signals was delayed with respect to the reference bread, in that the signals were rather faint after 1 day of storage, but larger for a 5 day-staled crumb. Table 3 lists the values of the exothermic effects, calculated from the relevant overall areas and the temperature range in which the signals appeared.

The fact that these exotherms were significantly larger for breads with added succinylated compounds could correspond to an enhancement of the underlying process. In a previous work [10], it was observed that the exothermic effect

Table 3 Exo- and endothermic effects in stale bread crumb

Aging	$\Delta_{endo}H$/J (g d. m.)$^{-1}$					
days	RB	PB	SPB	PrB	SPrB	TB
1	0.4	0.9	0.4	0.5	0.6	0.3
3	3.0	1.3	3.3	3.4	1.5	2.7
5	3.3	2.9	3.8	4.4	2.9	3.6

Aging	$\Delta_{exo}H$/J (g d. m.)$^{-1}$					
days	RB	PB	SPB	PrB	SPrB	TB
1	1.2	0.9	0.5	0.5	1.3	0.2
3	0.7	0.4	1.2	0.4	1.9	0.3
5	0.2	1.4	1.2	0.4	1.6	0.4

RB, PB, SPB, PrB, SPrB and TB represent reference, pentosan-, succinylated pentosan-, whey protein-, succinylated whey protein- and PEMULEN TR-1-added bread.

tended to disappear with aging of the bread, although the same occurred when the bread sample was heated to 35°C. In a heating-cooling-heating cycle, the exotherm changed into an endotherm on cooling and reappeared as an exotherm on reheating over the same temperature range. This reversibility was maximized after 8–10 h of storage at room temperature; on cooling, the endotherms disappeared, and on-reheating, the exotherms were hardly detectable in samples stored for more than 1 day. Such behaviour was explained [10] as a result of a three-step mechanism, i.e. solvation of binding sites, diffusion of water molecules along the polymer chains, and cross-link formation between next-neighbour chains. Water molecules would keep chains close one another, so as to promote formation of direct hydrogen bonds between sites on different chains, thus acting like a zip slider. Formally, the model was described [10] as coexisting "water-binding" equilibria, coupled with an irreversible network formation.

Figure 13 shows the DSC traces obtained from a heating–cooling–heating cycle, between –5 and 35°C, for a one-day-aged crumb sample. The exotherm appeared in the first heating run, whereas no signal was present either on cooling or reheating. Thus in this case the process is not reversible.

The underlying structural changes take place in the course of shelf life at 20°C; when the samples are cooled to –5°C, the process is quenched, to start again on reheating. The longer the storage, the smaller the signal observed.

With regard to bread firming, elastic modulus determinations showed that native soluble pentosans improved product quality (lesser firmness) more than did the succinylated pentosans, whereas both protein- (either native or succinylated), and PEMULEN TR-1-added breads were firmer than the reference bread. It is noteworthy that within a family of additives, the increase in carboxyl content corresponded to a greater firmness of the crumb at any aging time; we speculate that the succinyl groups could enhance the possibilities of interaction

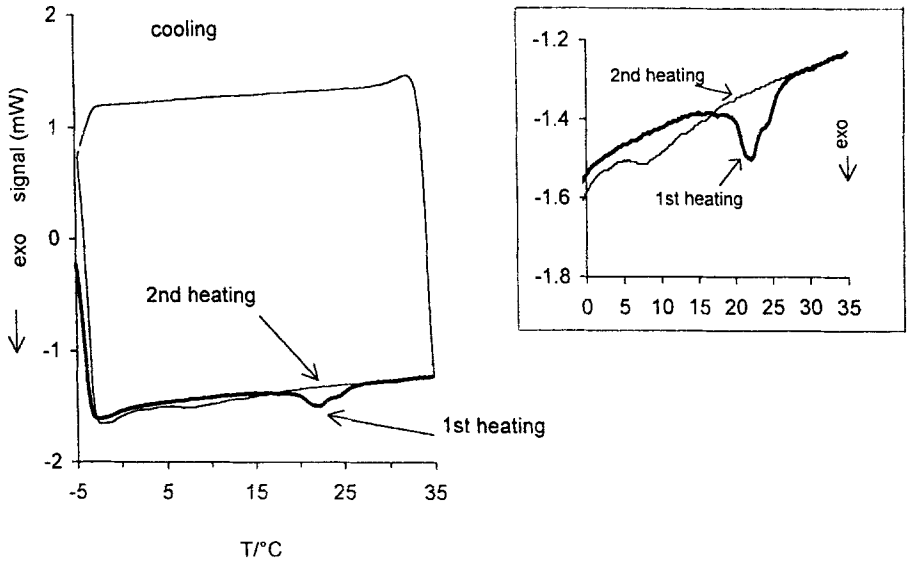

Fig. 13 DSC trace for a heating–cooling–heating cycle for pentosan-added bread crumb after 1 day of storage at room temperature

between the gluten network and starch polymers, possibly by formation of stronger bonds. This hypothesis is in line with the tentative interpretation of the exothermic DSC signals observed, which were in fact larger for breads with succinylated additive. In the case of pentosan-added breads, another explanation can be suggested; as a side effect of pentosan purification, a significant increase of the ferulic acid fraction (from 0.02 to 0.12% w/w in the present work) would enhance the cross-linking of these compounds with the gluten fibers so as to impose a reduced gluten-to-starch water diffusion and thus limit starch retrogradation. Succinylation (carried out at basic *pH*) should reduce the content of ferulic acid and therefore allow a greater gluten-to-starch water transfer, with subsequent enhancement of starch crystal formation.

Conclusions

The present work is part of a program of research devoted to the characterization of bakery products by means of physical and physicochemical investigations, including image analysis to quantitatively describe the air cells.

With regard to the staling of bread crumb, the experimental results reported here have shown that, for the concentration of hydrocolloids investigated, no clear anti-staling role of guar and locust bean gums could be established, although locust bean was found to improve the quality of the fresh bread. These gums act essentially through their water-holding properties, their role strictly

depending on the changes in their physicochemical state produced by the heat (baking) treatment. Because the gel structure of a polysaccharide in water is thermally reversible, further investigations are needed to separate the polysaccharide contribution from the starch and protein transformations that take place in the course of baking and aging.

The addition of soluble pentosans improved the quality of aged crumb, possibly because of their strong hydrophilic action. Some interaction with gluten and starch could be suggested for succinylated pentosans, since, at any bread age, the relevant crumb, although softer than that of the reference bread, was firmer than that formed in the presence of underivatized pentosans. In line with this hypothesis, the effect of polycarboxylated PEMULEN TR-1 could also be described. With regard to whey proteins, interactions with gluten and starch seem possible, inasmuch as the addition of whey proteins produced a firmer crumb, in spite of the expected water-trapping effect, which should *per se* imply a softening effect.

A more extended investigation is certainly necessary to fully characterize these systems. For example, it would be interesting to establish a state diagram, as defined by Slade and Levine [2], to clearly identify the intermediate viscosity states, above T_g, in which chemical and physical transformations can progress in a reasonable time span. Such an approach has been proven to be useful to describe simple aqueous binary mixtures of sugars, polysaccharides, and proteins [7], but its application to real food systems, such as doughs and bakery products, is unlikely to be straightforward in all cases. Even if the state diagram of the aqueous binary mixtures involving every "water-binding" ingredient in a dough were known, the overall effect of several ingredients would be difficult to predict, since many of these ingredients, if not all, compete simultaneously for the available water and modify the extent of starch-water and gluten-water interactions, while others interfere with the development of the gluten network and/or the starch-gluten "interface" [3].

One should also remember that when a polymer, such as gluten, undergoes extended cross-linking in the course of heat treatment, just like thermoset polymers during curing, it evolves progressively toward higher T_g states [38–40], in which the extent of the effect of water can be different from that observed in the initial system; that is to say, the state diagram of gluten changes in the course of the baking process. A state diagram should therefore be determined at various stages of baking to account for the effects of water and non-gluten ingredients on structure development. Generally, whenever formation of a polymer network is involved, a TTT (Temperature, Time Transformation) diagram [39, 40] can be used to correlate the viscosity-related molecular mobility with structure development, which can be tentatively referred to as the degree of cross-link extension [41, 42]. As the network continues to cross-link, its T_g increases and eventually attains the temperature of cure, T_c, at this point, any further network

formation becomes hindered [43]. Once cooled to room temperature, the system becomes glass-like. This advanced polymer-science approach has been previously discussed [7], but has not yet been widely applied to real, complex foods, possibly because of the experimental difficulties involved. When applied, useful information has indeed been obtained [2, 7, 44].

Our group is at present engaged in an effort to define such a TTT diagram for a simple-recipe dough, in order to define the "ideal" thermal history that should be followed to tailor the desired final structure of the baked product. The present work is part of this project, although it does not yet include a TTT diagram, because many difficulties still remain to be overcome. According to the picture presented thus far, the crumb-relevant TTT diagram should account for at least two coexisting polymers that evolve almost independently of one another. This gives rise to the question: where should the stages of the overall process, i.e. from dough to stale bread crumb, be positioned on the TTT diagram?

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