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Spatial variation of starch retrogradation in Arabic flat bread during storage

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Title: Spatial Variation of Starch Retrogradation in Arabic Flat Bread during Storage

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Research Highlights

- (i) Evaporative cooling keeps the inside of the bread within a few degrees of 100°C.
- (ii) A slight rise in internal temperature accompanies inflation.
- (iii) Different parts of the bread exhibit different rates of retrogradation during subsequent storage.
- (iv) This variation may be due to different local heating rates experienced by the different parts of the bread during baking.

Abstract

Samples from different radial positions of flat Arabic bread were analysed by differential scanning calorimetry (DSC) immediately after baking and after up to 3 days storage. This showed that whilst almost complete gelatinisation initially occurs, higher levels of subsequent retrogradation (typically 1.5 to 3 times) occurred in an area intermediate between the centre and outside of the pita bread (viewed from above). This coincided with the region with the highest moisture content (30% w.b.) immediately after processing, and which is likely to have heated at the slowest rate. A parallel study using DSC which subjected dough samples to a temperature profile similar to that found in baking also found that relatively low heating rates of 20 °C min⁻¹ produced slightly higher amounts of retrogradation (typically 5-25%) than higher heating rates of 200 °C min⁻¹. In each case moisture contents during storage were comparable between samples, thus suggesting that the local heating rate experienced during baking is a key parameter that can explain differences in subsequent retrogradation in different regions of the pita bread.

Keywords: Staling; pita bread; moisture content; gelatinisation; amylopectin; differential scanning calorimetry.

1. Introduction

Bread production is a major industry in almost every country of the world. There are many different types of bread in existence and ways in which industrial scale breadmaking can be achieved. In most Middle Eastern countries, Arabic flat bread or pita bread is the most popular form of bread. It characteristically consists of two layers, which form as a result of internal puffing during baking. It also differs from other types in that it has a lower protein content, higher surface area and higher crust/crumb ratio (Quail, 1996).

After baking and during storing, many inter-related changes occur in all types of breads leading to a stale flavour and a loss of consumer acceptance and saleability. Staling is a major concern for

breadmakers because it results in significant economic losses. It should however, not be confused with bread spoilage which is caused by microbial attack.

Investigations of factors governing bread staling have been the subject of numerous studies, mainly on pan bread. The most established mechanism for staling is the retrogradation of starch (Zobel and Kulp, 1996). Rapid associations of amylose molecules are believed to dominate starch retrogradation during the first hours after baking, and these are followed by slower amylopectin recrystallisations that dominate during subsequent days of storage. Starch retrogradation is affected by many factors such as storage temperature (Kelekci *et. al.*, 2003), amylose-to-amylopectin ratio (Ghiasi *et. al.*, 1984; Toufeili *et. al.*, 1993), and water content (Zelevnak and Hoseney, 1986; Liu and Thompson, 1998). Water migration and redistribution are thus important.

In contrast to pan bread, retrogradation in Arabic bread has been the subject of a relatively few investigations. Of these, both Quail *et. al.* (1990) and Toufeili *et. al.* (1993) used sensory evaluation data to track the consumer perception of bread quality over time. Toufeili *et. al.* (1993) also monitored the content of soluble starch over time to assess bread quality, a method also used by Faridi and Rubenthaler (1984). More recently, Sidhu and co-workers used Differential Scanning Calorimetry (DSC), X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) to study starch retrogradation in Arabic bread (Sidhu *et. al.*, 1997a,b). Gujral *et al.* (2008) also used DSC and texture analysis to study the staling of chapatti which is Indian flat bread. On the other hand, Abughoush *et. al.* (2008) used Near-Infra Red Spectroscopy (NIRS) as a non-destructive method.

An important feature that should be taken into account in baking studies is that differences in starch state and moisture content often exist between different parts of the bread. For example, it is well known that moisture content is much higher in the crumb of pan bread than the crust (Yasunaga *et al.*, 1968), and this is also the case for Arabic flat bread (Faridi and Rubenthaler, 1984). It is also known that differences in moisture content can result in different degrees of retrogradation during aging (Zelevnak and Hoseney, 1986; Liu and Thompson, 1998). However, sometimes this spatial variation factor has been overlooked. For example, Sidhu *et. al.* (1997b) analysed powdered freeze

dried samples of flat bread, which thus undoubtedly represented an ensemble average of the whole loaf.

Finally, an influence of heating rate on the bread texture and shelf life of pan bread has been reported (Patel *et. al.*, 2005; Patel and Seetheraman, 2006). Both studies suggested that high heating rates would be likely to impact upon starch granule swelling, leaching of amylose and the reorganisation of amylose upon cooling. Moderate changes in heating rate (up to 10 °C min⁻¹) can affect DSC endotherms as reported by Donovan (1979) and Lelièvre and Liu (1994) but this can be an artefact of the technique (signal to noise and thermal lag effects) rather than due to changes in the sample. However, when heating rates were raised to 32 °C min⁻¹ by Wootton and Bamunuarachchi (1979) a significant decrease in enthalpy was observed. Different heating rates have been implicitly used in some studies of flat bread in which different oven temperatures are used (Faridi and Rubenthaler, 1984; Quail et al., 1990), however these have not included temperature information from within the bread and so an assessment of the impact of different rates is difficult. Thus, to our knowledge, no studies have been performed directly comparing heating rates at the heating rates typically encountered during the baking of Arabic flat bread.

In this study, two different pans (Aluminium and stainless steel) are used to evaluate the performance of each pan type and its effect on the enthalpy of starch gelatinisation (ΔH_g). Pan selection is considered a key factor influencing the accuracy of the measurements of starch thermal behaviour by DSC (Yu and Christie, 2001). A systematic analysis has been applied to investigate the spatial variation of moisture content and thermal response as measured by DSC in order to find out how different parts of the bread are affected during its processing. DSC was also used to simulate baking (following Fessas & Schiraldi, 2000) and employed to directly investigate the effect of heating rate on starch behaviour during and after thermal treatment, which may be a factor in the baking of pita breads.

2. Materials and methods

2.1. Dough preparation

Pita bread dough was prepared using the following amounts: white flour (100 g) (Kuwait Flour Mills and Bakeries Company, Kuwait), water (58 g), yeast (1 g), (Nevada Instant Yeast, Lesaffre Group, Turkey) and salt (1.5 g) (Saxa Table Salt, Premier Food Group, Spalding, UK). The protein content of the flour as given by the manufacturer was 8.5-10%. The ingredients were mixed for 4.5 minutes at speed 4 in a Kenwood mixer (Chef Classic, Model KM 400, Havant, UK). The mixture was placed in a plastic bowl lined with grease-proof paper, which was then placed in a humidity controlled cabinet (Gallenkamp Fitotron PG660, Weiss Technik, Loughborough, UK) for 60 minutes at 30 ± 1 °C and $70 \pm 2\%$ RH. The dough was then divided, rounded and allowed to rest for another 10 minutes in the same cabinet under similar conditions. Finally, dough balls were sheeted to a round shape of 2 mm thickness and 14 cm diameter, and allowed to rest for the final proof period of 30 minutes in open wooden boxes in the same cabinet under similar conditions. All surfaces which the dough contacted were lined with grease-proof paper to avoid sticking. After the final proof period the wooden boxes containing the samples were closed and quickly taken to the oven for baking.

Dough samples for “simulated DSC” experiments (see section 2.4) were prepared using the same ingredients and amounts as for the pita bread dough samples except that no yeast was used, to avoid possible problems from carbon dioxide generation in the DSC cell. The samples were mixed using the same method as for the pita dough samples and allowed to rest for 1 hour at 30 ± 1 °C and $70 \pm 2\%$ RH before loading into DSC pans.

2.2. Pita bread baking procedure

Pita dough sheets prepared following the method in section 2.1 were subsequently baked at an oven temperature of 600 ± 10 °C for 25 ± 1 seconds in a high temperature oven (maximum temperature 1100 °C, Carbolite Type BWF 11/13, Sheffield, UK). Sufficient time was allowed from when the

oven was first turned on to achieve steady temperatures before the pita bread dough samples were introduced. A type K thermocouple (1.5 mm diameter x 500 mm length, mineral insulated with pot seal and type 310 Stainless Steel sheath, TC Direct, Uxbridge, UK) was used to measure the temperature inside the dough during baking. A long thermocouple body was needed so it could be fed through from the outside to the centre of the oven, without requiring connections inside the oven. The thermocouple was placed in the centre of the baking tray in the oven with the tip angled upwards before placing the dough sample so that it penetrated the dough sheet when the dough was placed on to the tray. The oven was also instrumented with a thermocouple positioned at the upper left corner of the back wall. A photograph of the oven showing a pita bread at the end of a baking period is shown in Fig. 1. After baking, the loaf was removed, left to cool for about 5 minutes, placed in a zip-lock plastic bag and stored at room temperature.

2.3 Moisture analysis

Bread samples were kept at room temperature (for 0, 1 or 24 hours) and analysed for wet basis moisture content gravimetrically by following AACC 44-40 method (AACC, 2000). Approximately 2 g of sample was removed by tearing from a complete cross section of the upper layer and placed in an aluminium dish before drying in an oven for 24 hours at 100 ± 2 °C. To assess the possible spatial variation of moisture (and the thermal behaviour of starch), the upper layer of bread was divided into three zones based on the radial distance from the centre. The outermost zone (radius > 4 cm) was named “Zone A”, the intermediate radius zone ($4 \text{ cm} > \text{radius} > 2 \text{ cm}$) was named “Zone B” and the central zone (radius < 2 cm) was named “Zone C”. Reported moisture contents for each zone are the average of ten measurements (from five separate baked bread samples, with two measurements taken from each zone of each bread sample).

2.4 DSC analysis

A DSC model TA Q10 (TA Instruments, Newcastle, DE) was utilised to determine the peak temperature (T_p), enthalpy of starch gelatinisation (ΔH_g) of unbaked dough samples, and the enthalpy of starch retrogradation (ΔH_r) of baked bread samples after storage for various periods at room temperature (20 °C). Two types of pans were used in the study: Aluminium pans (Al pan) and high pressure stainless steel pans (HPP). Sample masses were 20-25 mg for Al pans and 50-60 mg for HPP. Sample and empty reference pans were placed in the DSC microfurnace and, after an initial isothermal hold of 2 minutes, heated from 20 to 160 °C at a rate of 3 °C min⁻¹. All measurements were performed in duplicate from different bread samples, which were scanned without water addition or any other treatment. The starch retrogradation enthalpy was taken as an average calculation of the area enclosed by a straight line and the amylopectin endotherm curve in the region of 50-80 °C.

Three different types of experiment were performed using DSC (all measurements made in duplicate):

1. Scanning of unbaked dough using the above method – to measure the gelatinisation enthalpy.
2. Scanning of baked bread samples after storing the whole bread sample in sealed packaging at 20 °C for 1 hour, 1 day, 2 days and 3 days after baking. Samples of crumb were taken from the inside of the upper layer (i.e. from not the exterior crust) from zones A, B and C.
3. “Simulated baking” studies whereby samples in HPP were heated in a DSC from 30 to 105 °C at scan rates of 10, 20 or 200 °C min⁻¹. The pans were then either rescanned immediately at 3 °C min⁻¹ to assess the residual enthalpy or stored for up to 7 days at 4 °C which is regarded as the optimum temperature for retrogradation (Seetharaman *et. al.*, 2002). The aim was to assess what effect the initial heating rate would have on the subsequent retrogradation of the starch.

2.5. Statistical Analysis

Analyses were performed to evaluate whether changes in sample location and storage time had a statistically significant effect (above that caused by sample on sample variation), following a similar methodology to that used by Rasmussen and Hansen (2001). Data were analysed by either one-way or two-way analysis of variance (ANOVA) followed by paired comparisons (*t*-tests) of the means when the ANOVA analysis indicated significant differences. A 95% confidence level ($P < 0.05$) was used throughout to determine significance, but cases where a 0.1% confidence interval ($P < 0.001$) was also exceeded are also noted. All bar charts show mean values with error bars denoting standard deviations.

3. Results and discussions

3.1. Temperature measurement inside the dough sheet during baking

The measurement of the temperature inside the bread loaf while baking was difficult due to the high oven temperature, short baking time and the thermocouple type used to monitor the temperature profile of the dough during baking. Unlike pan bread, where thermocouples can easily follow temperatures during the baking process (León *et. al.*, 1997), no literature data were found regarding temperatures in Arabic flat bread. Quail (1996) attributed the scarcity in such information to the difficulty of monitoring the dough baking conditions under extremely high oven temperatures.

Results depicted in Fig. 2 show an initially high temperature as the thermocouple was fixed to the baking tray inside the hot oven before the dough was introduced. Introducing the dough (at 4 s) then cools the thermocouple, which stabilises at around 89 °C by 22 s. During this time the bread warms from room temperature to approximately the recorded thermocouple temperature, giving an average apparent heating rate of ~3 °C/s. Once the thermocouple temperature has stabilised then the thermocouple temperature will also (for the first time) reflect the bread temperature. The temperature then encounters a small step change to 100.4 °C before slowly rising to 103.4 °C at which point the pita bread is removed from the oven. During pita bread baking a crust forms which

prevents steam escaping from the dough and leads to the well known phenomenon of pita bread inflation due to the internal generation of steam. It can be surmised that the initial trapping of steam caused by the formation of the crust produces the step change in temperature from 88.6 to 100.4 °C as steam pervades the interior structure. As the pressure slowly increases inside the pita (which is now effectively a pressurised vessel) this then leads to a boiling point rise of the water. Assuming water is exhibiting its full saturated vapour pressure the internal pressure rise can be estimated to be 0.11 bar (values interpolated from steam tables from Haywood, 1972), and this drives the puffing/inflation of the bread.

3.2. Moisture content

The moisture analysis results presented in Fig. 3 show heterogeneity in the distribution of moisture across the bread loaf immediately after baking. The intermediate zone B has a higher moisture content than the other zones ($P < 0.001$). The explanation for the outer zone A being drier than zone B is most likely caused by it being closest to the side walls of the oven (where the heater elements are positioned, see Fig. 1) and directly facing the wall during puffing. An explanation for the central zone C being drier than zone B is less apparent, as it does not appear to receive more radiant heat. One possible explanation is that the central region may puff first, and the separation of the layers means that the top layer is insulated to some extent from the bottom layer (which receives all its heat via the top layer). Thus if less heat is transmitted to the bottom layer then there is more heat available for evaporation of water from the top layer. This explanation would require further verification in future studies.

Thus when analysing studying pita bread baking (whether in a laboratory or industrial context), attention should be paid to the position of radiant heaters and the strong likelihood of a variation in radiant heat flux incident upon different parts of the bread, and the role that changes to the bread shape during puffing play in heat transfer.

After storing the bread for 24 hours, the moisture contents for all 3 zones were found to be almost the same ($P > 0.05$), indicating an almost complete equilibration. No significant change was recorded in the moisture content on the fourth day of storage ($P > 0.05$), which was expected as the bread loaf was packaged in a sealed plastic bag. The moisture content of commercial Arabic flat bread produced in Kuwait is 28.5% (Sidhu *et. al.*, 1997a), which is comparable to the results presented here.

The results obtained in this study are in agreement with moisture distribution results reported by Faridi and Rubenthaler (1984) relating to their work on Balady bread. Similarly, the described results corroborate the results of moisture studies on Arabic flat bread carried out by Sidhu *et. al.* (1997a) who reported an insignificant moisture loss after a storage period lasting four days due to use of effective plastic packaging. In contrast, Shaikh *et. al.* (2007) found a decrease in moisture content in Chapatti (Indian single-layered flat bread) stored at room temperature although it was kept packaged in sealed plastic bag. However, the reduction in moisture content was examined over a longer storage period of one month.

These researchers also recorded a decrease from 32% to 24% on the fourth day of storage at room temperature, while no significant decrease was reported for the same samples stored in a refrigerator. These results also match the data reported by Piazza and Masi (1995) on moisture redistribution in pan bread from the crumb to the crust.

3.3. Thermal Analysis

3.3.1 Unbaked dough samples

Fig. 4 compares DSC gelatinisation endotherms of dough samples using the two different types of pans (Al pan & HPP). Results from both types of pan showed three peaks. According to previous reports (Donovan, 1979; Lelièvre and Liu, 1994), the first peak can be attributed to amylopectin gelatinisation using the available water, whereas the second peak is due to melting of remaining crystallites. The third peak is believed to be melting of amylose-lipid complexes (Biliaderis *et. al.*,

1985). As the peaks overlap it is difficult to deconvolute the individual peak enthalpies, however the combined enthalpies of the first two peaks attributed to amylopectin gelatinisation were 4.7 and 7.4 Jg⁻¹ for Al pans and HPP, respectively. The peak temperatures in their corresponding endotherms were also similar.

Above 130 °C differences can be seen between the endotherms from the two pan types and this is attributed to the bursting of Al pans (which are not as mechanically strong as HPP) and subsequent leaking of water vapour. Some Al pans (endotherms not shown) also appeared to leak at temperatures as low as 90 °C. Even low leaking temperatures have been reported by Yu and Christie (2001) for this type of pan. HPP ultimately leaked at a significantly higher temperature of 200 °C (thermogram not shown). The leaking may affect the thermal contact between the pan and the furnace, but more likely it induces further vaporisation of water which consequently affects the measured heat flow to the pan (Schiraldi *et. al.*, 1996). It is very possible that the “Peak III” enthalpy values reported by Sidhu *et. al.* (1997b) from experiments using Aluminium pans are in fact due to water evaporation, as the reported enthalpies were large (40 Jg⁻¹) and the peak temperatures were consistently close to 100 °C.

3.3.2 Baked bread

An example endotherm (HPP) for a fresh bread sample is shown in Fig. 5. The sample was taken from the crumb in Zone C but identical endotherms were found for samples from Zones A and B. The endotherm suggest almost complete starch gelatinisation during the 25 seconds of baking as is evidenced by the lack of a peak in the range of 50-80 °C. A small peak was recorded at temperature ~ 100 °C. The detected peak at 120 °C can be attributed to the melting of amylose-lipid complexes which tend to reform rapidly upon cooling. Amylose is important in setting the primary structure of bread (Seetharaman *et. al.*, 2002) and this peak was consistently present during the storage period without a significant change. This is in agreement with previously published results (Biliaderis *et. al.*, 1985; Gudmundsson, 1994; Fessas and Schiraldi, 2000; Hug-Iten *et. al.*, 2003).

The thermograms from each of the three zones over 3 days of storage showed bimodal endotherms with peak temperatures approximately around 62 and 98 °C. However only the first peak appears to grow over time, indicating that retrogradation (probably of amylopectin) continues on the second day after baking. The second peak remains more or less unchanged. Similar peaks were reported by other researchers (Zobel and Kulp, 1996; Sidhu *et. al.*, 1997b). It was also observed that the temperature ($T_p = 62$ °C) corresponding to the first peak is lower than the temperature of the first gelatinisation peak shown in Fig. 4 ($T_p = 69$ °C). A similar result was reported by León *et. al.* (1997).

These results were expected based on previous studies; a rapid gelation of amylose after baking, and a slower amylopectin recrystallisation which is expected to govern the retrogradation process during further days of storage, although the second peak attributed to amylopectin was not reported previously in studies on starch retrogradation in pan bread or buns.

Fig. 6 shows the enthalpy values (the first peak in the range of 50-80 °C) of bread samples during storage. These results not only show an increase in the value of ΔH_r for all samples over time ($P < 0.001$), but they also show that the increases occur at different rates. The rate of increase over 3 days storage was found to be highest in the intermediate zone B at $0.223 \text{ J g}^{-1} \text{ day}^{-1}$ ($P < 0.001$) followed by the central zone C ($0.170 \text{ J g}^{-1} \text{ day}^{-1}$, $P < 0.001$), with the outer zone A ($0.080 \text{ J g}^{-1} \text{ day}^{-1}$, $P < 0.001$) having the lowest increase. Multiple linear regression analysis confirmed that there was a clear positive correlation of enthalpy with starting moisture content (regression slope was $+ 3.6 \pm 0.48 \text{ J g}^{-1}$ per unit increase in moisture content). It had been reported previously that the moisture content is an important factor affecting the retrogradation of starch (Lelièvre, 1974; Donovan, 1979; Zeleznak and Hosney, 1986; Lelièvre and Liu, 1994; Fukuoka *et. al.*, 2002). This might be attributed to the difference in moisture content of these zones or to the different exposure to heat.

3.3.3 "Simulated baking" in DSC

Three different heating rates 10, 20 and 200 °C min⁻¹ were selected in this study, whereby samples were heated to 105 °C and held for 30 seconds in the DSC, followed by a rescan. The lower rates of 10 and 20 °C min⁻¹ represent typical heating rates when baking pan bread and buns. León and his co-workers had reported a heating rate of 11.7 °C min⁻¹ to simulate the baking of pan bread crumb (León *et. al.* 1997). However, flat bread must be baked at much higher heating rates to achieve an acceptable product (Faridi and Rubenthaler, 1984; Quail *et.al.*, 1990). For example, Quail *et al.* (1990) baked Arabic flat bread in 21 seconds, giving an apparent heating rate of 200 °C min⁻¹. Very similar rates are reported in this study (see section 3.1). For this simulated baking study, a heating rate of 200 °C min⁻¹ was selected as the fastest rate, being the maximum nominal heating rate that can be achieved by DSC.

Thermograms from the immediate rescans of samples are shown in Fig. 7. All three samples show amylose-lipid melting occurring at just over 115 °C, but there appears to be an indication of incomplete gelatinisation in the endotherms immediately preceding the amylose-lipid complex peak, the apparent area of which increases with heating rate. Some of this is due to thermal lag in the DSC as the measured pan temperature only reaches 97.6 °C at the end of the isothermal period in the case of the 200 °C min⁻¹ heating rate, whereas 103.5 °C was reached in the case of the 20 °C min⁻¹ heating rate. When held in storage over 3 days, however, a significant endotherm appeared in the temperature range between 50 and 80 °C (see Fig. 8(a) and (b)), which became larger (although at a slower rate of increase) over the rest of the storage period. The enthalpy values are shown in Fig. 9 and are much larger than those observed for conventionally baked pita bread (Fig. 6) ($P < 0.001$). This may be due to the lower storage temperature and also the higher moisture content within the DSC pans (assumed to be the same as the initial dough moisture content). Fig 9. shows a small but significant effect of prior heating rate on retrogradation enthalpy values, although the effect is only truly significant after 3 days storage. Over longer storage periods the retrogradation rate slows and

the differences between the enthalpies of the two types of sample are greatly reduced (such that the error bars overlap).

4. Conclusions

Despite the high oven temperatures used, thermocouple data indicate that temperatures inside the pocket of Arabic flat bread during baking do not rise more than a few degrees Celsius above the normal boiling point of water. However, this is enough to provide sufficient generation of steam and with a high enough internal pressure to drive the characteristic puffing that occurs in successful pita bread baking. Although after baking it would be expected that differences in moisture content will occur between the crust and crumb (interior) parts of Arabic flat bread, this study has also shown that there are noticeable variations in moisture content across the bread which is likely to arise in part from the different intensities of radiant heat reaching different parts of the bread. We thus recommend that the location of sampling should always be recorded when taking samples from pita bread for analysis. In this case it appears that a region halfway from the centre to the edge of the pita bread (zone B) retained the most amount of moisture. After one hour of storage the moisture gradients had largely disappeared, but the intermediate zone then also produced the most retrogradation as measured by DSC over 3 days of storage at room temperature. This is presumably not a storage moisture content effect (which was almost the same for all parts of the bread during storage) but may be linked to the lower heating rate or evaporation rate during processing. When compared with retrogradation studies of samples heated at different rates in a DSC to simulate baking it was found that slightly higher amounts of retrogradation were found in the samples heated at lower heating rates (but higher overall heat exposure). So it would appear that the only conclusion that would be consistent across both baking and simulated baking studies is that higher heating rates during processing reduce the amount of subsequent retrogradation. Heating rate has previously been found to influence starch granule swelling which is a kinetically constrained process (Patel &

Seetharaman, 2006), and may thus help to explain this observation. Further work is necessary to deepen our understanding of this effect.

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Figures

Fig. 1. Photograph of the oven used in experiments showing Arabic flat bread just before removal, and thermocouple positions. The heating elements are situated at the sides.

Fig. 2. Temperature/time profile for an initially exposed thermocouple that is subsequently positioned within a pita dough sample of 2 mm thickness during baking for 25 ± 5 s (oven temperature $600 \pm 10^{\circ}\text{C}$).

Fig. 3. Moisture contents at different positions in the upper layer of baked bread after storing in sealed packaging for 0, 1 and 24 h (A= outer zone, B=intermediate zone and C=centre zone).

Fig. 4. Comparison of DSC gelatinisation endotherms of dough using a high pressure pan (HPP) and aluminium pan (Al), both at a scanning rate of $3^{\circ}\text{C min}^{-1}$. Both endotherms show the presence of three peaks.

Fig. 5. DSC thermogram (HPP) of fresh bread crumb showing the melting of amylose-lipid complexes.

Fig. 6. DSC peak enthalpy values (in temperature range 50-80°C) for bread crumb stored in HPP at room temperature (20°C) for 1, 2 and 3 days, where A=outer zone, B=intermediate zone and C=centre zone.

Fig. 7. DSC thermograms (HPP) from rescans at 3 °C min⁻¹ of dough samples previously heated from 30 to 105°C at heating rates of 10, 20 and 200 °C min⁻¹.

(a)

(b)

Fig. 8. DSC thermograms from rescans at $3\text{ }^{\circ}\text{C min}^{-1}$ of dough samples previously heated from 30 to 105°C (HPP) at heating rates of (a) $20^{\circ}\text{C min}^{-1}$ and (b) $200^{\circ}\text{C min}^{-1}$, and then stored at 4°C for 1, 3, 5 and 7 days.

Fig. 9. DSC peak enthalpy values (in temperature range 50-80 °C) for dough samples previously heated from 30 to 105°C (HPP) at different heating rates (20 and 200 °C min⁻¹) and then stored at 4°C for 1, 3, 5 and 7 days.