NIR measurements of the development of crystallinity in stored bread crumb

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Differential scanning calorimetry and near infrared (NIR) reflectance spectroscopy have been used to follow the development of crystallinity in stored bread. Using each technique, changes in measured properties were apparent which, when fitted by first-order exponential equations, gave calculated rate constants of similar magnitude. It is postulated that each technique is giving complementary information about the changes taking place in the amylopectin fraction of the bread crumb.

Ageing of bread has generated research interest for many years. It is a phenomenon involving starch which is a polysaccharide made up of two components, amylose and amylopectin. Both are polymers of glucose but amylose is linear while amylopectin has a branched structure. In the starch granule, the amylose and amylopectin are intermingled but when the linear segments of amylopectin align they become ordered into crystallites. During the baking of bread, an order to disorder transition occurs in which the starch granules present in the flour swell and some of the amylose diffuses out of the granule destroying the crystalline structure. This process is essentially reversed during the ageing of bread as crystallinity slowly redevelops in the amylopectin fraction [1]. This crystallinity is responsible for the increase in firmness in the bread

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crumb during ageing which is the most obvious manifestation of the phenomenon commonly referred to as staling.

The progress of bread staling has been followed by differential scanning calorimetry (DSC) [2]. The principle is based on the well-known fact that stale bread can be refreshed by heating. The amount of heat required to disorder the amylopectin crystallites once more can be estimated from the DSC endotherm area and plotting endotherm area against storage time of bread gives rise to progress curves from which kinetic parameters can be calculated. The disadvantages of DSC are that it is experimentally difficult to perform and it is invasive.

NIR spectroscopy, in contrast, is simple and with the use of fibre optic probes can be non-invasive so as to allow remote in situ investigation of foods. NIR is generally used for the compositional analysis of foods following calibration against a reference chemical method. However, in this application, first reported in 1991 [3] and re-interpreted in 1997 [4], NIR has been used as a research technique in its own right.

Materials and methods

Test baking

Doughs were mixed accordingly to the recipe in table I on a laboratory-scale double Z-blade mixer operating at 300 cycles min^{-1} and controlled work input to an energy expenditure of 11 Wh kg^{-1} in the mixer. Dough temperatures were controlled at 30.5 ± 1 ºC by adjusting water temperature. Immediately after mixing, the doughs were hand-scaled at 0.908 kg, re-moulded into a spherical shape using a conical moulder, rested for 6 minutes at 20 ºC and re-moulded into a Sorensen moulder. The dough pieces were placed in greased bread pans and proved at 43 ºC at 80% relative humidity until the dough reached a height of 120 mm. Baking was then carried out in a Bone gas-fired reel oven set at 244 ºC for 30 minutes without steam injection. After baking, loaves were allowed to cool for 2 hours, sealed immediately in two polyethylene bags, and stored in a constant temperature environment of 21 ± 2 ºC pending measurement.

Table I. Experimental bread recipe.

Ingredients	*Mass (relative to flour mass)*
Flour	100.0%
Water	59.6%
Yeast	2.1%
Salt	1.8%
Fat	0.7%
Calcium propionate	2000 mg kg^{-1}
Potassium bromate	45 mg kg^{-1}
Ascorbic acid	30 mg kg^{-1}

DSC measurements

Two measurements were taken daily on samples removed from a single loaf. Samples were removed from the central portion of each loaf using a cork borer of 3.5 mm internal diameter. The resulting cores were compressed to form plugs. 10 mg samples were sliced from the middle of these plugs and placed into tared DuPont DSC pans which were hermetically sealed using a press. Pan and sample were reweighed and DSC scans were carried out (5 – 130 ºC, 10 ºC/min) using the Perkin-Elmer DSC-2 differential scanning calorimeter fitted with a subambient accessory, calibrated and operated as described in [5].

NIR spectroscopy

Each loaf was sliced to a thickness of 10 mm using a commercial bread slicer and circular subsamples of 60 mm diameter were taken from the centre of each slice by means of a pastry cutter. The NIR instrument was used as a Pacific Scientific Mk 1 6350 Research Composition Analyzer (the predecessor to the NIRSystems Model 6500 and no longer in production) that was allowed a 1 hour warm-up time before use. Each crumb sample was placed in a sample holder that held it between a spring-loaded back plate and a glass window. The sample holder was then placed in the instrument in a fixed orientation for measurement of the NIR spectrum.

The data were recorded as log $1/R$, where R is the relative relectance, at 2 nm intervals in the range 10 100 – 2500 nm. R is defined as P_S/P_O where P_s is the power of radiation reflected from the sample and P_O the power of radiation reflected from a ceramic standard measured prior to each sample. Each spectrum (including that of the ceramic standard) was recorded as an average of 50 scans taken over a period of 30 s. Spectra were measured on each of six separate slices per loaf and averaged. The mean spectra were subjected to a multiplicative scatter correction as described in [6] and to a second derivative transformation using a segment size of 10 nm and 10 nm gap between segments.

Data treatment

Experimental data from the DSC and NIR measurements were analysed separately by fitting an Avrami equation to each data set and comparing the fits statistically [2,7].

Result and discussion

The rate constant for DSC (Tab. II) was found to be consistent with, although at the upper end of, the range of published data [2,7].

The log $1/R$ spectra obtained on day 1 and day 14 of storage showed a general decrease in log $1/R$ with storage time over the whole range of wavelengths scanned. This suggests an increase in scattering of NIR radiation as the crumb structure changes during staling as a result of the physical manifestation of the development of crystallinity in the amylopectin of the bread crumb.

The use of NIR to measure wheat kernel texture (hardness) by virtue of its effect on scattering is well-known and it is therefore reasonable to follow the progress of bread

Table II. Calculated kinetic parameters from physical measurements of bread during storage.

Technique	*Rate constant* $K \times 10^3$ (h^{-1})
DSC	16.06
Log 1/*R* 1934 nm	16.31
d^2 Log 1/*R* / $d\lambda^2$ 1465 nm	15.29
d^2 Log 1/*R* / $d\lambda^2$ 1414 nm	14.16

ageing in an analogous manner. Wheat hardness has been measured using wavelengths at which constituents of the samples absorb or at spectral minima or both. In the present work, progress curves could be obtained by plotting log 1/*R* at any one wavelength against bread storage time but use of data at 1934 nm resulted in a rate constant (Tab. II) which was in closest agreement with that obtained by DSC. This wavelength corresponds to an absorption band due to water so, to confirm that the observed effect was due to scattering and not to changes in crumb moisture content, the log 1/*R* data were subjected to a multiplicative scatter correction and re-analysed. There was now virtually no trend in the data at 1934 nm with bread storage time, although there was still some residual effect corresponding to about 5% of the original variability. The scatter correction is known to remove most (but not all) of the variability in the log 1/*R* data due to scatter and enable a high correlation to be obtained between log 1/*R* at 1934 nm and moisture content [6]. Therefore, this result confirms that the effect was due to scatter.

NIR spectroscopy provides another, more direct, approach to the study of the disorder to order transition in the starch fraction. Since carbohydrate polymers such as starch are extensively hydrogen bonded, both intramolecularly and to solvent water, changes in the hydrogen bonding network of the system may be reflected in the NIR spectra. Second derivative data at 1412 and 1466 nm have been assigned to water in foods in different states of hydrogen bonding [4,8]. Second derivative transformation of the log 1/*R* data allows deconvolution of overlapping absorption bands and some degree of scatter correction so would be expected to reveal absorption phenomena not readily apparent in the log 1/*R* spectra. Substraction of the second derivative spectra of extreme samples may be used to display the absorption features which vary most in the spectra. In this experiment, absorption maxima and minima at 1414 nm and 1465 nm were observed in the difference spectrum of bread stored at 0 and 12 days (Fig. 1). Plotting the second derivatives of log 1/*R* at these wavelengths against bread storage time resulted in progress curves which gave very similar calculated rate constants to those obtained from DSC measurements (Tab. II).

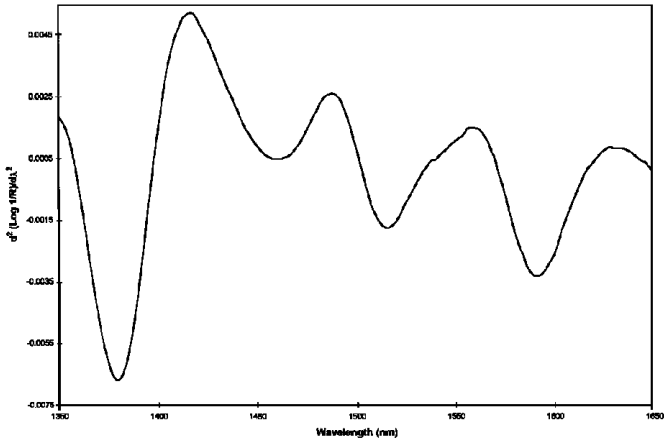

Figure 1. Difference spectrum for stored and fresh bread.

These results indicate that NIR data may be used to follow the progress of bread ageing by means of either scattering or absorption phenomena, resulting in calculated kinetic parameters which are similar to each other and to that established by DSC.

Conclusion

The progress of bread ageing can be followed by NIR reflectance spectroscopy. The rate constants calculated from log 1/*R* at 1934 nm and second derivative at 1414 and 1465 nm were all very close in magnitude to each other and to that obtained from DSC data. The results may be interpreted in terms of development of crystallinity in the amylopectin fraction of the bread crumb.

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