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Thermogravimetric analysis of water release from wheat flour and wheat bran suspensions

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ABSTRACT

Bran is hygroscopic and competes actively for water with other key components in baked cereal products like starch and gluten. Thermogravimetric analysis (TGA) of flour–water mixtures enriched with bran at different incorporation levels was performed to characterise the release of compartmentalised water. TGA investigations showed that the presence of bran increased compartmentalised water, with the measurement of an increase of total water loss from 58.30 ± 1.93% for flour only systems to 71.80 ± 0.37% in formulations comprising 25% w/w bran. Deconvolution of TGA profiles showed an alteration of the distribution of free and bound water, and its interaction with starch and gluten, within the formulations. TGA profiles showed that water release from bran-enriched flour is a prolonged event with respect to the release from non-enriched flour, which suggests the possibility that bran may interrupt the normal characteristic processes of texture formation that occur in non-enriched products.

1. Introduction

Baking involves a process of an irreversible series of heat induced chemical, physiological and biochemical changes (Chang, 2006) and is normally the final stage of processing a cereal end product (i.e. bread, cookies etc.). During baking, the three main ingredients: water, starch and gluten, interact to transform the product from a foam-like structure (dough) to a sponge-like, porous structured end product (e.g. bread) (Hug-Iten et al., 1999). During this transformation, the product undergoes a series of changes that start with; (1) the formation of a viscoelastic gluten network during mixing at room temperature, (2) the gelatinisation of starch during the early stages of baking, (3) the coagulation of the gluten network during the latter stages of baking, and (4) the gelation and crystallization of starch during cooling. These processes are all governed by water.

Water, in the presence of heat, establishes a high vapour pressure gradient within dough and becomes the main driving force for the chemical and physical changes, i.e. acting as a plasticiser on proteins and a solubiliser of the starch component. Both the starch and the gluten compete actively for the available water (Grinberg and Tolstoguzov, 1997) and retain the captured water in different ways. Starch being a polysaccharide, holds onto this water through hydrogen bonding between the amylose and amylopectin branches and inter amylopectin helices (Orlowska et al., 2009). These helices have an ability to form junction zones in which large amounts of water can be stored (Chaplin, 2003). Gluten protein on the other hand favours the formation of covalent disulfide bonds via the cysteine groups of the glutenin. In addition it forms hydrogen bonds via the glutamine residues (Belton et al., 1998). These will bind water tightly and will resist the removal of this water for an extended period of time (Durchschlag and Zipper, 2001).

Bran is viewed mostly as a milling by-product of the wheat milling industry (Dexter and Wood, 1996; Antoine et al., 2004) and consists mainly of the dead outer layers of the wheat kernel. However, incorporation of cereal bran and use of wholegrain flours in commercial food products are driven by their widely reported and recognised health benefits for humans. However, this poses technological challenges. Bran incorporation increases the mass of the end product due to the additional water needs, decreases loaf height and cookie spread, darkens colour and decreases sensory acceptance of the end product by the consumer (Vratanina and Zabik, 1978; Krishnan et al., 1987; Chen et al., 1988; Sievert et al., 1990; Park et al., 1997; Zhang and Moore, 1997; Abdul-Hamid and Luan, 2000; Lang and Jebba, 2003; Ragaee and Abdel-Aal, 2006; Seyer and Gélinas, 2009). Bran tends to be highly hygroscopic and on addition to a formulation results in an extra water need, which needs to be added in order to compensate. On the other hand bran has a low affinity for water (Robertson and Eastwood, 1981) and this results in it releasing most of its absorbed water when placed under stress (mechanical, gravimetrical or heat), hence causing its undesirable side effects.

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Thermogravimetric analysis (TGA) of flour–water mixtures have been undertaken by previous researchers (Fessas and Schiraldi, 2001, 2004; Lodi and Vodovotz, 2008; Orlowska et al., 2009). They have shown how water is held within a simple water–flour mixture and through the deconvolution of peaks, they could discriminate different water fractions during baking. Fessas and Schiraldi (2001) showed through the first derivative of the TGA mass loss curve (DTG), that water in both the starch fraction and the gluten fraction could be discriminated. The water in the gluten trace showed two peaks, with the first early peak (at low T), attributed to the mobile water (free water), and the second peak identified was attributed to the tightly bound water (at high T) (Durchschlag and Zipper, 2001). Starch on the other hand only showed a single early large peak (greatly overlapping the first low temperature peak of the gluten), which shows that water associated with the polysaccharides are held by weak bonding. This weak bonding largely comprises of the polysaccharides' hydrogen bonds, but also includes its ability to form junction zones (Chaplin, 2003). This is one of the reasons that the starch peak, shown in the TGA mass loss curve (Fessas and Schiraldi, 2001) is larger than that of the gluten peak. Further investigation by Orlowska et al. (2009) using NMR and TGA, showed that within the single peak of a wheat starch–water suspension, free and bound water phases do exist, but overlap each other and as a result show as one peak in the TGA.

The aim of this study was to investigate the effect of the addition of wheat bran, to a flour–water mixture, on how water is distributed between the different components (bran, starch and gluten), and the release of water at baking temperatures.

2. Materials and methods

2.1. Materials

Both wheat bran (wheatings) and wheat flour samples (Claire, a UK soft wheat variety) were kindly supplied by Premier Foods, Rank Hovis (UK).

2.2. Methods

2.2.1. Hydration

Flour, bran and flour–bran suspensions were produced by the addition of 1 g of either flour, bran or flour–bran mixture, to 15 mL of distilled water and left over night to allow them to become fully hydrated (18 h). After soaking the suspensions were drained under gravity and 20 mg used for TGA analysis.

2.2.2. Thermal gravimetric analyzer (TGA)

Using a TGA Q50 (TA instruments, Crawley, West Sussex, UK) the sample was heated in a aluminium pan from room temperature (±25 °C) to 120 °C, using a heating profile of 5 °C per minute and run in triplicate.

The resulting TGA trace of mass loss (%) (derived from mass loss over temperature (°C)) was then analysed for its first derivative (Derivative Thermogravimetry (DTG) (%/°C)) and its second derivative (2nd DTG (%/°C^2)) using Universal Analysis Software V 4.7A (TA Instruments, Crawley, West Sussex, UK) with subsequent deconvolution of peaks using PeakFit V 4.12 (Systat Software, San Jose, CA, USA).

Mass loss experiments were performed on 100% flour, and 100% bran samples. Additional experiments were conducted with samples in which the bran–flour ratio was altered from 100% flour to 100% bran on a gradient scale by mass which decreased 5% for flour and increased 5% for bran, up to 75% flour–25% bran mixture, followed by 50–50% flour–bran mixture, and then continued from 25% flour–75% bran to 100% bran.

For the mass loss traces, the DTG and 2nd DTG were calculated and the deconvolution of peaks under the DTG was determined in order to establish their different water types (i.e. free, bound, etc.), with the 2nd DTG used to identify specific water loss events and used to check the validity of the deconvoluted peaks.

2.2.3. Statistical analysis

The TGA experiments were performed and analysed in duplicate. Statistical investigations were performed using SPSS V.17.0.2 (Chicago, Illinois, USA).

3. Results

3.1. Derivative thermogravimetry (DTG)

Fig. 1 shows the first derivative DTG plots derived from the raw TGA data of %mass loss vs. temperature. The DTG plots are only shown for selected flour/bran mixtures for clarity. Examination of the DTG plots reveal that the flour rich mixtures exhibit two distinct features with the initial peak attributed to starch and a secondary shoulder (at approximately 80–90 degrees Celsius (labelled A in Fig. 1)) attributed to gluten, as described by Fessas and Schiraldi (2001). A gradual shift occurs in the gluten shoulder (A), in conjunction with the addition of bran to the mixture. Whilst still being visible in the flour 50–bran 50% mixture, the gluten shoulder (A) is absent in the bran rich mixtures (bran 100%). The introduction of bran not only forces the gluten shoulder (A) to shift towards a lower temperature, but on further increase of the bran (up to 100%), an increase in peak height (B), as well as a shift of the complete peak to a higher temperature range was observed.

To calculate the amount of water lost associated with each peak (gluten and starch peaks in the bran poor mixtures and bran peak in bran rich mixtures), the maximum peak heights were calculated using the DTG and overlaid onto the TGA signal (Table 1). This showed that an increase of bran resulted in an increase of total water loss (%), from 58.30 ± 1.93% in the presence of flour (100%) to 75.64 ± 1.34% bran (100%). Mass loss of the starch peak, which shifts towards the bran peak, also increased from 68.96 ± 0.60% to 76.65 ± 1.20%. The gluten peak was unchanged by the addition of bran until 50% bran was added, above which the gluten peak could no longer be detected.

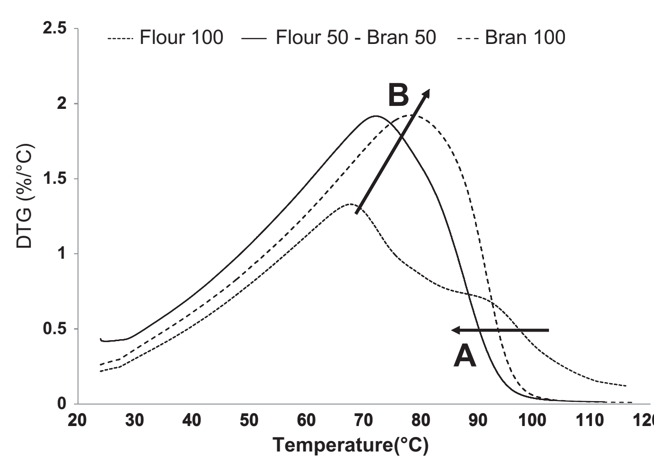

Fig. 1. DTG of 100% flour, 50% flour/bran and 100% bran. The replacement of 50% of flour with 50% bran has a profound effect on the peak shape, with an increase in peak height (B) as a transition occurs away from the starch and into the bran, and a shift to the left (A) of the gluten shoulder, as a result of bran dilution on both the starch and flour components. Extra additional incorporation of bran, above 25% does not have such a dramatic effect.