



# Impact of visco-metric profile of composite dough matrices on starch digestibility and firming and retrogradation kinetics of breads thereof: Additive and interactive effects of non-wheat flours



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## ABSTRACT

The impact of wheat (WT) flour replacement up to 45% (weight basis) by incorporation of ternary blends of teff (T), green pea (GP) and buckwheat (BW) flours on the viscometric pasting and gelling profiles of quaternary blended dough matrices was investigated by applying cooking and cooling cycles to rapid viscoanalyser (RVA) canisters with highly hydrated samples (3.5:25, w:w). Viscometric cooking and cooling parameter trends related to suitable patterns for lower and slower starch hydrolysis, and lower and/or slower firming and starch retrogradation kinetics in blended breads mainly include higher viscosity values for peak viscosity, breakdown on cooking and viscosity of hot (95 °C) paste, but lower viscosity values after gelling (50 °C). These visco-metric requirements for achieving suitable textural and thermal features in blended breads, were met by adding T/GP/BW to replace 22.5% of WT flour in blended dough formulations. Larger WT flour replacement by 37.5% of the ternary mixture T/GP/BW (7.5/15/15) provided hydrated blends with higher values for viscosity of hot (95 °C) paste, and lower viscosity values after gelling (50 °C), in good accordance with poorer formation of rapidly digestible starch and total digestible starch, and more prominent formation of resistant starch and slowly digestible starch in breads, respectively.

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## 1. Introduction

Changes in the viscosity of highly hydrated starch-based systems such as doughs during baking are known to affect the viscoelastic behaviour, the texture, keepability and nutritional performance of finished bread (Collar, 2003; Roder et al., 2005; Waterschoot et al., 2015). Pasting performance of flours during cooking and cooling involves many processes such as swelling, deformation, fragmentation, and solubilisation that occur in a very

**Abbreviations:** BW, buckwheat;  $C_{\infty}$ , maximum starch hydrolysis extent; DS, digestible starch; GP, green pea;  $H_{90}$ , starch hydrolysis extent at 90 min;  $\Delta H_0$ , retrogradation enthalpy at 0 time;  $\Delta H_{\infty}$ , retrogradation enthalpy at  $\infty$ ;  $\Delta H_d$ , enthalpy of dissociation of amylose–lipid complex;  $\Delta H_g$ , gelatinization enthalpy;  $k$ , kinetic constant for starch hydrolysis;  $k_f$ , constant of proportion of firming kinetics;  $k_r$ , constant of proportion of retrogradation kinetics;  $n_f$ , Avrami exponent of firming kinetics;  $n_r$ , Avrami exponent of retrogradation kinetics;  $R$ , gelatinization temperature range; RDS, rapidly digestible starch; RS, resistant starch; RVA, rapid visco analyzer; SDS, slowly digestible starch; TDF, total dietary fibre; T, teff;  $T_{\infty}$ , crumb firmness at time  $\infty$ ;  $T_0$ , crumb firmness at time 0; TS, total starch; WT, wheat.

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complex media whose viscoelastic properties in the pasted and gelled states are governed primarily by the volume occupied by the swollen particles.

Starch is the major component controlling pasting properties of grain flours and subsequent impact on finished product performance, but visco-metric properties are also affected by other components in the system. Endosperm protein may restrict the starch granules from fully gelatinizing, thereby resulting in lower digestibility, and starch–protein interaction may occur during cooking or cooling that causes gelatinized sorghum starch to be in a less digestible state (Zhang and Hamaker, 2005). Inhibition of enzymic digestion of amylose by free fatty acids *in vitro* contributes to resistant starch formation (Crowe et al., 2000). The unusual high viscosity peak in the cooling stage of the rapid visco-analyzer (RVA) profile of stored whole grain sorghum flour was the result of starch interacting with liberated free fatty acids and flour protein (Zhang and Hamaker, 2005). Water-insoluble dietary fiber may cause disruption in the structure of amylopectin, resulting in a increase in the swelling power, so that, the disruption of the starch matrix and the uneven distribution of water within the matrix takes place due

to the competitive hydration tendency of the insoluble dietary fibers. This probably allow starch granules to rupture during heating, hence releasing higher levels of amylopectin into the system, finally giving rise to a highly porous structure of starch with disrupted amylopectin (Yildiz et al., 2013).

The extent of gelatinization and retrogradation are major determinants of the susceptibility of starch to enzymatic digestion and its functional properties for food processing such as stickiness, ability to absorb water and ageing (Wang and Copeland, 2013). In starch blends, gelatinization occurs mostly independently in excess water, while at intermediate water content more non-additive behaviour is recorded. Pasting, rheological, and textural properties show primarily non-additive effects while retrogradation of starch blends occurs mainly in an additive way (Waterschoot et al., 2015). Interactive effects have been attributed to large differences in granule size and swelling power between the starches in a blend leading to uneven moisture distribution during heating of the starch suspension. This results in a different behaviour of the blend than what would be expected based on the behaviour of the individual starches (Waterschoot et al., 2015).

In blended flour matrices, high wheat flour replacement by non-gluten forming flours from cereals, pseudocereals and legumes, particularly associated mixtures of teff, buckwheat and green pea, have proven to provide technologically viable and acceptable sensory rated multigrain breads with superior nutritional value compared to the 100% wheat flour counterparts (Collar et al., 2014a). Thermal transitions of multicomponent bread matrices baked at restricted water conditions have recently been described (Collar et al., 2015), and some relationships between thermal properties, textural behaviour and the susceptibility of starch to enzymatic digestion in those heterogeneous matrices defined.

This paper is aimed a) at investigating the visco-metric changes that occur during starch gelatinization, pasting and gelling in complex grain flour matrices with unrestricted water availability, b) at knowing the impact of non-breadmaking whole grains (teff, green pea and buckwheat flours), highly replacing wheat-based matrices on the viscometric profiles, and c) at exploring the relationships between visco-metric properties and starch digestibility and firming and retrogradation kinetics of technologically viable and sensorially accepted multigrain bread matrices.

## 2. Materials and methods

### 2.1. Materials

Commercial flours from refined common wheat *Triticum aestivum* (WT), and whole teff *Eragrostis tef* (T), green pea *Pisum sativum* (GP), and buckwheat *Fagopyrum esculentum* (BW) were purchased from the Spanish market. Proximate chemical and nutritional composition of flours (Table 1) were determined following the ICC methods (ICC, 2014). Refined WT (70% extraction rate) of  $356 \times 10^{-4}$  J energy of deformation W, 0.64 curve configuration

ratio P/L, 95% Gluten Index, 62% water absorption in Brabender Farinograph, was used. Ireks Vollsauer sour dough was from Ireks (Spain); Novamyl 10,000 a maltogenic thermostable  $\alpha$ -amylase of 10,000 Maltogenase Units (MANU) of activity, from Novozymes (Denmark); and calcium propionate, from Sigma–Aldrich (USA).

### 2.2. Methods

#### 2.2.1. Bread making of wheat and wheat-based blended flours

Doughs and breads were prepared from WT as control, and wheat-based blended flours (T, GP, BW) by WT replacement from 22.5% up to 45%, and incorporation of ternary blends of T, GP and BW flours according to a Multilevel Factorial Design (Statgraphics Centurion XV, version 15.2.11, Statpoint Technologies, Inc. Warrenton, Virginia, USA) with the following attributes: 3 experimental factors (T, GP and BW flours) at 2 levels, coded 0 (7.5% wheat flour replacement) and 1 (15% wheat flour replacement), and 5 error degrees of freedom. Levels of wheat flour replacement were chosen after performing preliminary trials to set the range of non-wheat flours to be incorporated in associated blends to the formulations in such a way that significant enhancement of bread nutritional properties was achieved without notable deterioration of sensory attributes (Collar et al., 2014a). The model resulted in 8 randomized runs in 1 block. A 3 digit bread sample code was set referring to low (0) and high (1) wheat flour replacement by T (1st digit), GP (2nd digit), and BW (3rd digit) flours in sample formulation, as it follows: 010, 001, 011, 000, 111, 101, 100, 110. Blended flours, water, commercial compressed yeast, salt, margarine, sugar, commercial sour dough, milk powder, Novamyl 10,000, and calcium propionate were mixed, and used to make control and blended breads according to the quantitative formulations and breadmaking procedure described earlier (Collar et al., 2014a). Bread samples were stored in co-extruded polypropylene bags and stored for 1, 3, 6, and 8 days at 25 °C until performance of firming kinetics studies.

#### 2.2.2. Dough measurements

**2.2.2.1. Visco-metric properties.** The pasting profiles (gelatinization, pasting, and setback properties) were obtained with a Rapid Visco Analyser (RVA-4, Newport Scientific, Warriewood, Australia) using ICC standard method 162. Freeze-dried composite dough blends and individual flours (3.5 g, 14% moisture basis) were transferred into canisters and  $\approx 25 \pm 0.1$  mL of distilled water were added (corrected to compensate for 14% moisture basis). Three replicates were made per sample. The slurry was heated to 50 °C and stirred at 160 rpm for 10 s for thorough dispersion. The slurry was held at 50 °C for up to 1 min, and then heated to 95 °C over 3 min 42 s and held at 95 °C for 2 min 30 s, and finally cooled to 50 °C over 3 min 48 s, and held at 50 °C for 2 min. The pasting temperature (°C) (when viscosity first increases by at least 25 mPa.s over a 20-s period), peak time (when peak viscosity occurred), peak viscosity (maximum hot paste viscosity), holding strength or trough viscosity (minimum hot paste viscosity), breakdown (peak viscosity

**Table 1**

Proximate chemical and nutritional composition<sup>a</sup> of flours (per 100 g flour, d.b.).

| Flours    | Protein <sup>1</sup> (g) | Total dietary fibre (g) | Insoluble dietary fibre (g) | Soluble dietary fibre (g) | Fat (g)      | Ash (g)      | *DC (g) | Moisture (g)  |
|-----------|--------------------------|-------------------------|-----------------------------|---------------------------|--------------|--------------|---------|---------------|
| Wheat     | 14.13 ± 0.05b            | 2.19 ± 0.12a            | 1.20 ± 0.09a                | 0.99 ± 0.25a              | 1.56 ± 0.09a | 0.63 ± 0.09a | 81.70   | 14.32 ± 0.10c |
| Green pea | 25.12 ± 0.04d            | 14.56 ± 0.95d           | 8.50 ± 0.15d                | 6.05 ± 0.27c              | 1.27 ± 0.15b | 2.58 ± 0.12c | 56.63   | 8.17 ± 0.09a  |
| Buckwheat | 19.71 ± 0.06c            | 13.52 ± 0.38c           | 6.58 ± 0.25b                | 6.93 ± 0.36d              | 3.44 ± 0.18c | 2.05 ± 0.19b | 61.16   | 11.70 ± 0.18b |
| Teff      | 13.05 ± 0.02a            | 12.19 ± 0.49b           | 7.40 ± 0.36c                | 4.80 ± 0.30b              | 5.06 ± 0.09d | 2.21 ± 0.09b | 66.97   | 11.90 ± 0.09b |

<sup>(a)</sup>Mean values ± standard deviation. Within columns, values (mean of three replicates) with the same following letter do not differ significantly from each other ( $p > 0.05$ ).

<sup>(\*)</sup>DC: digestible carbohydrates calculated by indirect determination: DC = 100 - [Moisture + Protein + Fat + Ash + Dietary Fibre].

<sup>(1)</sup>Conversion Factor from N to protein = 6.25.

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