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# Significance of thermal transitions on starch digestibility and firming kinetics of restricted water mixed flour bread matrices

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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 thermal profiles of quaternary blended dough matrices have been investigated by simulating baking, cooling, and storage in differential scanning calorimeter (DSC) pans. Endothermal transitions related to suitable patterns for low and slow starch hydrolysis, softer crumb and retarded firming kinetics in blended breads include delayed temperatures for starch gelatinization, and for the dissociation of amylose–lipid complex. In addition, (a) higher stability for the amylose–lipid inclusion complex, (b) lower energy for starch gelatinization, (c) lower limiting melting enthalpy and (d) slower rate for amylopectin retrogradation meet thermal requirements for achieving suitable textural and starch digestibility features in blended breads, fulfilled by adding T/GP/BW to replace 45% of WT flour in blended dough formulations.



## 1. Introduction

Bread that explicits both a multicomponent and multiphase nature, can be viewed as a composite material where amylose amylopectin, and protein form separate phases due to thermodynamic immiscibility of the polymers in presence of surrounding ingredients (Hug-Iten, Escher, & Conde-Petit, 2003). The final structure of bread crumb described as a porous material with flexible elastic cell walls, is the result of a water-dependent thermal process related to the number and type of cross-links formed between the nearest neighboring chains of biopolymers (protein network and starch) present in the dough (Biliaderis, Page, Maurice, & Juliano, 1986). Starch gelatinization and protein coagulation induce bread crumb formation. After cooling, the higher final water content of the crumb (35–45%) is responsible for the rubbery behavior, which gives structural mobility and smooth bread crumb behavior, and explains the sensitiveness of starch to retrograde during storage (Cuq, Abecassis, & Guilbert, 2003).

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 & Copeland, 2013). The gelatinization degree of starch in baked products depends primarily on the water availability and the amount of heating (Shin, Kim, Ha, Lee, & Moon, 2005). Products (white bread, sugar cookies, pie crust, angel food cake, cake doughnuts and cinnamon rolls) can range from essentially completely gelatinized (97%) to almost native-like conditions (4%) (Lineback & Wongsrikasem, 1980). Other factors influencing gelatinization account for other components in the food matrix competing for water (e.g. sugar and proteins), heat transfer, the presence of lipid/starch complexes or other types of complexes, and they are usually negatively associated with extent of swelling, probably due to increased hydrophobicity. Modifications of water availability by the presence in dough matrices of hydrocolloids (Santos, Rosell, & Collar, 2008), low molecular weight dextrins (Miyazaki, Maeda, & Morita, 2004), blended starches of different sources (Waterschoot, Gomand, Fierens, & Delcour, 2014) and high damaged starch flours retrogradation (León, Barrera, Pérez, Ribotta, & Rosell, 2006) among other factors changed the thermal behavior of flour-water mixtures during gelatinization and retrogradation. Mechanisms involved relate restriction of enzyme-substrate contact, interference as a physical barrier to prevent amylopectin chain association during storage, and a viscosity effect that affects mobility within the stored

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**Abbreviations and symbols**

| | |
|---|---|
| $C_\infty$ | maximum starch hydrolysis extent |
| DS | digestible starch |
| $H_{90}$ | starch hydrolysis extent at 90 min |
| $\Delta H_0$ | retrogradation enthalpy at 0 time |
| $\Delta H_\infty$ | retrogradation enthalpy at $\infty$ |
| $\Delta H_d$ | entalpy of dissociation of amylose–lipid complex |
| $\Delta H_g$ | gelatinization entalpy |
| $k$ | 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 |
| SDS | slowly digestible starch |
| $t_{1/2f}$ | half-life for firming |
| $t_{1/2r}$ | half-life for retrogradation |
| TDF | total dietary fibre |
| $T_e$ | end temperature |
| $T_o$ | onset temperature |
| $T_p$ | peak temperature |
| TS | total starch |

system (Khanna & Tester, 2006). All these factors may limit the gelatinization degree constraining the swelling and breakdown of the starch granule structure, thus resulting in less digestible starch (Llorca et al., 2007). In general, any process or condition where the water availability or thermal energy is limited could generate the same effect, this is a lower degree of gelatinization encompassing a lower amorphous structure, and thus a lesser amount of digestible starch (Parada & Aguilera, 2011). In addition, granule size and surface characteristics (for example, pores, grooves or furrows, and surface-associated proteins and lipids), starch damage, amylose content, fine structure of amylopectin, degree of crystallinity and phosphorus content, can all affect digestibility (Wang & Copeland, 2013).

Main studies focused on the effects of gelatinization and retrogradation at higher water content on starch digestibility, but there is scarce information on the effect of retrogradation at low water content on starch digestibility (Wang & Copeland, 2013). The amount of gelatinization, swelling and hydrolysis are intimately controlled by the water content of the system and the temperature, and moderated by the botanical origin and composition of starches in limiting water conditions. According to Tester and Sommerville (2000), gelatinization, swelling and hydrolysis are restricted where crystalline order is retained within starch granules. However, when the water content and temperature profile become sufficient to allow gelatinisation and starch hydrolysis by α-amylase to proceed, swelling may be constrained because starch ability to hydrate and expand is hindered as a consequence of the complex composition, particularly in starch blends of different botanical origin.

Starch retrogradation involves reassociation of starch component molecules into a partially crystalline, ordered structure. Amylopectin recrystallization requires several days. Because firming of bread also develops over several days, most staling models view the changes in amylopectin as the primary cause for crumb firming (Zobel & Kulp, 1996). The slow crystallization of amylopectin was referred to as a nucleation-limited growth process, which occurred above the glass transition in a mobile, viscoelastic, fringed-micelle network (Roos, 1995). Staling involves hardening of the crumb that is a complex phenomenon in which multiple mechanisms operate, all of them involving amylopectin retrogradation as the main player (Gray & BeMiller, 2003). Water plays a critical role in bread staling. When the retrogradation of amylopectin occurs, water molecules are incorporated into the crystallites and the distribution of water is shifted from gluten to starch/amylopectin, thereby changing the nature of the gluten network (Gray and BeMiller, 2003). Besides the molecular order of starch, water also plays an important role in crumb firmness due to its plasticizing effect on the crumb network (Hug-Iten et al., 2003).

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, Jiménez, Conte, & Fadda, 2014). Blended flours of different starch nature are expected to modify the mechanism of water mobility in bread crumb, and concomitantly its thermal properties during gelatinization and ageing due to water restrictions for swelling, gelatinization and starch hydrolysis. Starch digestibility kinetics and crumb firming evolution during storage of blended breads are both water-dependent processes. Thermal transitions of multicomponent bread matrices baked at restricted water conditions are not well known, and the possible relationships between thermal properties, textural behaviour and the susceptibility of starch to enzymatic digestion in those heterogeneous matrices lack.

This paper is aimed (a) at investigating the thermal transitions that occur during starch gelatinization and retrogradation in complex grain flour matrices with restricted 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 transition phases and (c) at exploring the relationships between thermal properties and starch digestibility and firming 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. Protein, dietary fibre and fat contents (% flour, dry basis) were 14.13%, 2.19%, 1.56 (WT); 25.12%, 14.56%, 1.27 (GP); 19.71%, 13.52%, 3.44% (BW), and 13.05%, 12.19%, 5.06% (T), respectively.

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 10000 a maltogenic thermostable α-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: three experimental factors (T, GP and BW flours) at two levels, coded 0 (7.5% wheat flour replacement) and 1 (15% wheat flour replacement), and five error