



# Starch–gluten interactions during gelatinization and its functionality in dough like model systems



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## ABSTRACT

Gluten–starch interactions are of specific importance during processing of cereal-based products. They become especially relevant during heating because of heat-induced changes within these biopolymers. A comprehensive characterization of the interactions during heating of the starch–gluten model dough based on its mechanical behavior taking into account its raw material ratios and dough adapted water additions has yet to be achieved. Thus, the macrostructural characteristics with varying starch–gluten ratios (92:8, 89:11, 86:14, 83:17, 80:20) in combination with different water additions (57.77, 60.78, 63.78, 65.58, 69.11 g water 100 g<sup>-1</sup> blend) was analyzed in dynamic oscillatory study during heating from 30 to 98 °C. The delayed gelatinization onset (+7 °C) with increasing gluten content could be referred to a barrier effect of gluten around the starch granules with a hindered diffusion of water into the granules, since a competitive hydration was not significantly detectable. The decreased gelatinization intensity (–67%) due to an increased gluten content showed a negligible effect of the barrier effect and a more competitive hydration between gluten and starch. A further reason can be weakening zones in the leached amylose network and a hindered granule–granule interaction. Moreover, a simple possibility to identify the gelatinization onset in oscillatory tests by the derivative of the loss factor was defined.

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## 1. Introduction

Interactions between biopolymers such as polysaccharides and proteins are of direct relevance to the macroscopic properties of many food matrices. They influence its functionality expressed by the rheological behavior, the stability, the texture, and the structure (Doublier, Garnier, Renard, & Sanchez, 2000; de Kruif & Tuinier, 2001). For this reason the interactions between polysaccharides and proteins have been studied in different fields of science and research for identifying functional properties (Considine et al., 2011; Koksel & Scanlon, 2012; Matignon et al., 2014; Navickis, Anderson, Bagley, & Jasberg, 1982; Petrofsky & Hoseney, 1995; Rosell & Foegeding, 2007; Ryan & Brewer, 2005). Among food matrices in particular, dough is a complex matrix of different, closely associated components. Induced by mechanical or thermal energy input, its polymers can be cross-linked creating the macroscopic structure through inter- and intramolecular forces. The matrix of (wheat) dough mainly consist of starch granules,

(gluten) proteins, lipids and arabinoxylans. The properties of these components shows a great variety due to its different growing, harvesting, and processing treatments, resulting in varying functionalities. Interactions between the components, which in consequence become visible in the viscoelastic characteristics, can be evaluated by macroscopic examination in dynamic oscillation measurements (Rosell & Foegeding, 2007). For a systematic analysis of different interactions model dough systems containing starch and gluten can be used. Thus the complexity of the real systems is reduced and relations between specific components can be analyzed. Dynamic rheological measurements of these kinds of model dough systems made with only starch and gluten already show that starch does not only act as an inert filler but interacts with gluten and is active in determining the viscoelastic behavior of systems (Champenoi, Rao, & Walker, 1998; Miller & Hoseney, 1999; Petrofsky & Hoseney, 1995). Therefore, it is assumed, that not only the functionality of the single ingredients but rather the interactions between them influence the behavior of the matrix.

The functionality of starch becomes specially dominant during the heating process (Jekle & Becker, 2012). Interactions between these polymers could also be rearranged. During heating the gelatinization of starch and the denaturation of gluten occurs due

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to heat-induced conformational changes. The endothermic changes during the gelatinization of starch in the presence of gluten were already comprehensively investigated by Differential Scanning Calorimetry analyses (Delcour et al., 2000; Eliasson, 1983; Homer, Kelly, & Day, 2014; Mohamed & Rayas-Duarte, 2003). Furthermore, mechanical analyses of starch protein mixtures during heating were already conducted to investigate the interactions of starch and protein or gluten during heating: starch and meat protein during heating (Li & Yeh, 2003), starch and soy protein during heating (Li, Yeh, & Fan, 2007), gluten in already gelatinized starch gels (Lindahl & Eliasson, 1986), starch and gluten without a continuous recording of the changes due to the temperature (Yang, Song, & Zheng, 2011), starch and gluten (with different strength) mixtures (Chen, Deng, Wu, Tian, & Xie, 2010), and starch and gluten mixtures as dispersions in excess of water (Champenois et al., 1998). The last study was especially comprehensive in regard to the interactions. Since the high water content in this study varies from a typical dough system, a direct transfer of knowledge to dough based systems is hindered (Schirmer, Zeller, Krause, Jekle, & Becker, 2014). It is known that in starch–gluten systems the hydration properties play a major role (Mohamed & Rayas-Duarte, 2003). However, since the water levels of the mentioned studies were fixed or even in excess water, this could be a limitation for some interpretations of interactions of starch–gluten model systems in low water systems.

From the mentioned studies above two main interactions between starch and gluten during heating are derived: a) a competitive hydration between the polymers during their structural changes, and b) a diffusion barrier by the gluten proteins located on the starch granule surface and thus a changed diffusion of water into the starch granules. In order to enable an elucidation of the interaction between starch and gluten a comprehensive characterization using a full factorial design of the macrostructural changes during heating of starch–gluten model dough was conducted in this study. In the course of this, the raw-material ratios in wheat and dough adapted (and thus low) water additions were taken into account. In order to differentiate between the two main interactions different gluten and water additions were used in a full factorial design and in a dynamic mechanical thermal analysis (DMTA) the rheological properties complex shear modulus and loss factor were continuously examined during the heating and the following gelatinization. Since there is still no simple mathematical definition of the onset of starch gelatinization in rheological measurements, a further aim of this analysis was to define a quantitative determination of the start gelatinization temperature.

## 2. Materials and methods

### 2.1. Materials

Wheat starch and gluten was kindly provided by Kröner Stärke, Ibbenbüren, Germany. Starch had a moisture content of  $11.24 \pm 0.50\%$  ( $n = 2$ ), protein content of  $0.24\%$  ( $n = 1$ ) in the dry mass, and amylose content of  $22.18 \pm 0.13\%$  ( $n = 2$ ). Gluten had a moisture content of  $6.44 \pm 0.39\%$  ( $n = 2$ ) and protein content of  $82.36\%$  ( $n = 1$ ) in the dry mass. Moisture content was analyzed following ICC 110/1 and protein content following the Kjeldahl Method (EBC) (Anger, 2006). For the amylose content the colourimetric method of the Amylose/Amylopectin Assay Kit by Megazyme International Ireland, Bray, Ireland was used.

### 2.2. Sample preparation and experimental design

In total, 25 starch–gluten model dough systems (each 5.0 g) were prepared, based on five different starch–gluten ratio and five

different distilled water levels in a full factorial design. The following starch–gluten ratios were used: 92:8, 89:11, 86:14, 83:17, and 80:20. The starch–gluten blend with the ratio of 86:14 reflects a realistic composition of starch and gluten in wheat flour (Goesaert et al., 2005). The other starch to gluten ratios are based in the narrow range below and above 14% gluten content. The amount of distilled water added to each starch–gluten blend was 57.77, 60.78, 63.78, 65.58, and 69.11 g  $100 \text{ g}^{-1}$  of total sample weight (based on 14% blend moisture content). The used water additions are derived from the solvent retention capacity (SRC) of the materials in accordance with AACC method 56-11 (AACCIInternational, 2000): The SRC of starch–gluten blends with the ratio 86:14 and 80:20 was determined to define the model dough adapted water addition and revealed a water absorption of  $63.78 \pm 1.46\%$  ( $n = 4$ ) and  $57.77 \pm 2.28\%$  ( $n = 4$ ), respectively. The further water additions correspond to the water absorption of wheat starch ( $69.11 \pm 1.09\%$  ( $n = 4$ )) and for comparison of wheat flour type 550 obtained from Rosenmühle, Landshut, Germany ( $65.58 \pm 0.11\%$  ( $n = 4$ )). The water addition of 60.78% corresponds to the mean of 57.77% and 63.78%. The water levels were chosen to enable a water addition comparable to the production of bakery products. Another reason was the quite equal distribution of the water levels for the experimental design. The model dough was mixed for 3 min in a Glutomatic system, which was specially modified for the sample preparation (Döring, Nuber, Stukenborg, Jekle, & Becker, 2015). Since mixing has a distinct effect on gelatinization properties (Mohamed & Rayas-Duarte, 2003) this mixing procedure and time was chosen for a standardization of the preparation. For the mixing, the metal sieve insert of the Glutomatic wash chamber was replaced with a metal insert without sieving functionality. Furthermore, the automatic washing after the mixing phase was deactivated.

### 2.3. Dynamic mechanical thermal analysis (DMTA) with oscillatory measurements

Dynamic mechanical thermal analysis (DMTA) with oscillatory measurements was performed with an AR-G2 rheometer (TA instruments, New Castle, USA; software Rheology Advantage 5.7.2.0) using a Smart Swap Peltier plate temperature system with a 40 mm plate–plate geometry and a gap of 2000  $\mu\text{m}$ . After placing the dough between the plates and adjusting the gap, the excess dough was trimmed with a spatula and the edges were coated with paraffin to prevent drying. The initial temperature was maintained at 30 °C for all tests. The oscillation was carried out within the linear viscoelastic region of the sample at a constant strain amplitude (0.1% strain) as well as a constant frequency of 1 Hz. Equilibrium time before the test was set to 2 min, based on equilibrium in time sweep tests in pre-trials. After a oscillatory time sweep for 1 min at the initial temperature a heating step simulating the baking process from 30 °C to 98 °C with a temperature ramp of  $4.25 \text{ }^\circ\text{C}/\text{min}^{-1}$  was performed. This heating rate was found in preliminary tests to be a realistic increase in temperature in dough during baking process. At the end of the heating step the temperature of 98 °C was held for 3 min. The loss factor  $\tan \delta$  and the complex shear modulus  $|G^*|$  were recorded. The DMTA was performed with all combinations (in total 25) of the in 2.2 described starch–gluten ratios and water addition levels. Analyses were performed in triplicate.

### 2.4. Determination of starch start gelatinization temperature

The gelatinization process of starch can be easily monitored by the course of the dynamic moduli. During this process the complex shear modulus  $|G^*|$  and the loss factor  $\tan \delta$  show a pronounced maximum at different temperatures. While the maximum of  $|G^*|$  is characteristic for the maximal structural hardening, the maximum

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