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Characterization of rheological properties of rye arabinoxylans in buckwheat model systems

Denisse Bender [a], Renata Nemeth [b], Giada Cavazzi [c], Fanni Turoczi [b], Eszter Schall [b], Stefano D'Amico [a], Kitti Török [b], Mara Lucisano [c], Sandor Tömösközi [b], Regine Schoenlechner [a, *]

[a] Department of Food Science and Technology, BOKU- University of Natural Resources and Life Sciences, Muthgasse 18, 1190, Vienna, Austria
[b] Department of Applied Biotechnology and Food Science, Budapest University of Technology and Economics, Műegyetem Rkp.3, 1111, Budapest, Hungary
[c] Department of Food and Nutritional Sciences, University of Milan, Via Celoria 2, 20133, Milan, Italy

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ABSTRACT

The aim of this investigation was to study the rheological properties (gelation profile, mixing and pasting properties) of two rye arabinoxylans (AXs) (water-extracted (WEAXs), calcium hydroxide-extracted (CEAXs)) in buckwheat model systems using wholemeal and white flour. To promote gelation in these systems, pyranose 2-oxidase (POx) was added. AX characterization in solution showed a higher gelation profile for the CEAXs (G': 0.48 Pa, G'': 0.25 Pa) compared with the WEAXs (G': 0.21 Pa, G'': 0.14 Pa), probably due to differences in chemical and structural properties. In buckwheat batter systems, highest rheological properties were achieved when POx was added to the control flours (for wholemeal flour: G': 40.1 kPa, G'': 8.6 kPa; for white flour: G': 18.7 kPa, G'': 1.4 kPa), whereas most AX concentrations improved these properties to a lower degree. Nearly all wholemeal flour systems reached higher viscoelastic properties when containing CEAXs (G': 20.0–35.1 kPa; G'': 4.2–6.7 kPa), while WEAXs improved the majority of these properties in systems made with white flour (G': 10.4–12.7 kPa; G'': 2.2–2.3 kPa). No additional effect was seen in the batter viscoelasticity when POx was combined with these AXs. Pasting and mixing properties of the flour systems were mostly reduced by the addition of AXs, while the presence of POx displayed little or no further effect. These observations indicate that AXs could be applied as natural structure-forming agents in GF bread, when used in the right amount.

1. Introduction

Water soluble arabinoxylans have a significant effect on the baking properties of bread, especially during mixing and dough development, as they enhance the viscosity of the dough, due to their high water-binding capacity (Buksa et al., 2014). They also possess outstanding gelling properties, mainly attributed to the formation of covalent di-FA and tri-FA linkages and weak hydrogen interactions. Its gelling properties closely depend on the AX structure such as molecular size, distribution pattern of arabinose residues, molecular weight, branching degree and amount and location of ferulic acid (FA) residues in the polymer (Izydorczyk & Biliaderis, 1992). Due to the action of oxidizing agents, which are naturally present in the dough and air oxygen during mixing, some crosslinking between AXs and/or AXs and proteins occur. Cross-linking can be further supported by the addition of oxidative agents such as hydrogen peroxide, enzymes with oxidizing potential or a combination of both (Bagdi, Tömösközi, & Nyström, 2016, 2017).

Application of oxidases has shown to improve dough handling properties and stability during bread-making in gluten containing systems. From the group of oxidases, glucose oxidase (E.C. 1.1.3.4) (GO) has been most commonly used. A less common alternative,

Abbreviations: AX, arabinoxylan; CEAX, calcium hydroxide-extracted arabinoxylan; FA, ferulic acid; FC, final consistency; FV, final viscosity; GF, gluten-free; GO, glucose oxidase; Mw, molecular weight; PC, peak consistency; PT, peak through; PV, peak viscosity; POx, pyranose-2-oxidase; WEAX, water-extracted arabinoxylan; WHC, water holding capacity.

* Corresponding author.
E-mail addresses: denisse.bender@boku.ac.at (D. Bender), nemeth.renata@mail.bme.hu (R. Nemeth), giada.cavazzi@unimi.it (G. Cavazzi), turoczi.fanni27@gmail.com (F. Turoczi), s.eszter@mail.bme.hu (E. Schall), stefano.damico@boku.ac.at (S. D'Amico), ktorok@mail.bme.hu (K. Török), mara.lucisano@unimi.it (M. Lucisano), tomoskozi@mail.bme.hu (S. Tömösközi), regine.schoenlechner@boku.ac.at (R. Schoenlechner).

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which was found to have similar effects as GO, is POx (E.C. 1.1.3.10), although its application in food is still rare (Decamps et al., 2012). Its specificity towards glucose has made POx more favorable for application in comparison to GO, because it is able to oxidize α-D- and β-D-glucose, while GO specificity is only limited to β-D-glucose (Giffhorn, 2000). This enzyme catalyzes the oxidation of C_2 and C_3 of mono- and disaccharides in the presence of oxygen to the corresponding dicarbonyl derivatives and H_2O_2. When used in breadmaking, it can not only generate AX crosslinking, but is also able to promote di-tyrosin and tyrosin-ferulic acid crosslinks and increase water binding capacity (Boeriu et al., 2004; Mattinen et al., 2005).

Although the importance of AX in rye bread baking has been widely established (Buksa, Nowotna, & Ziobro, 2016), only few information about the potential application of AXs in GF bread have been reported (Ayala-Soto, Serna-Saldívar, & Welti-Chanes, 2017). Since AXs play an essential role in structure formation and bread production of rye, they could potentially be used to improve the physical quality of GF breads by imitating a rye-bread like network in a GF matrix. For this purpose, fundamental knowledge and understanding of AX functional properties is essential before application in these GF products. So far, previous studies (Bender et al., 2017) could not fully explain the rheological behavior and functionality of differently extracted rye bran AXs in solution. Therefore, the aim of this investigation was to thoroughly study the gelling properties of two previously extracted rye AXs (WEAX, CEAX), first in solution and later in GF batter model systems using wholemeal and white buckwheat flour. Gelation was promoted by the addition of POx and evaluated by rheological means. To understand their behavior in different systems, AXs were characterized in more detail in regards to their chemical and structural properties (i.e. ash content, other monosaccharides (galactose, mannose, glucose), water-holding capacity and molecular weight range), which has partially been carried out previously (Bender et al., 2017). The best performing AX was selected to further evaluate its influence on the mixing and pasting properties of GF model systems.

2. Material and methods

2.1. Materials

Buckwheat grains from Caj. Strobl Naturmühle GmbH (Linz, Austria) were used for flour production. Rye bran flour from Good Mills Austria GmbH (Schwechat, Austria) was used for AX isolation. POx was recombinantly expressed in *Phanerochaete chrysosporium* and purified as described by Spadiut, Posch, Ludwig, Haltrich, and Peterbauer (2010). All used chemicals and reagents were of analytical grade and purchased from Sigma-Aldrich (Steinheim, Germany).

2.2. Flour production

Whole meal flour was produced in a pin mill (Fa. Pallmann Maschinenfabrik, PXL 18, Zweibrücken, Germany) producing flour with particle size of 250 μm. As for the white flour production a FQC-109 type laboratory mill (Metefém, Hungary) was used. The flour was then sieved on a 250 μm standard sieve (ISO 3310–1:2016) using an AS200 type laboratory sieve (Retsch, Germany).

2.3. Arabinoxylan isolation

AXs were isolated from rye bran using two different solvents (water, calcium hydroxide), following the procedure described by Bender et al. (2017). These were selected from the previous study, due to their promising physicochemical properties for application in GF bread.

2.4. Analytical methods

2.4.1. Chemical composition

Chemical composition of AXs was carried out by standard methods. Dry matter was determined according to ICC-standard method No. 110/1. Crude protein content was carried out by the ISO-standard method No. 16634 using a FP-528 instrument (Leco, Saint Joseph, USA). A general conversion factor of 6.25 was applied to calculate the protein content. Ash content of the samples was quantified by muffle furnace method (ISO, 2007). Ferulic acid of AXs was analyzed as reported by Mattila, Pihlava, and Hellström (2005). Monosaccharide composition was determined by gas chromatography with a pre-column derivatization according to Bender et al. (2017). The AX content was calculated as the sum of arabinose and xylose fractions. All analyses were performed in triplicate, except for monosaccharide composition, which was performed in duplicate.

2.4.2. Gluten

Gluten content of AXs was determined by a competitive Enzyme Linked Immunosorbent Assay (ELISA), using the R5 antibody (Ridascreen® Gliadin competitive, R-Biopharm, Darmstadt, Germany) following the manufacturer's instructions (R-Biopharm, 2007). Gliadin concentrations were firstly calculated using Microplate Manager 6.0 (Bio-Rad, Tokyo, Japan) computer software with a Logit-Log fit and then converted into gluten concentration, by multiplying the gliadin content by a factor of two (Codex Alimentarius, 2008). Gluten quantification was performed in duplicate measurements.

2.4.3. Water holding capacity

The water-holding capacity (WHC) of the AXs was measured in triplicate measurements following the official AACC method No. 56–30 with some modifications. 250 mg of AX was dissolved in 25 ml of distilled water and stirred for 1 h. The samples were centrifuged twice at 2000 g for 10 min and the supernatant was discarded. Afterwards the centrifuge tubes were inverted to drain for 10 min and the weight of the remaining sample was recorded.

2.4.4. Determination of molecular weight

Molecular size distribution of AXs was performed by SE-HPLC using a Flexar HPLC System (Perkin Elmer, USA) with RI detection mode, following the method of Bagdi, Tömösközi, and Nyström (2017). A Shodex, OH pak 10 μm SB-804HQ 200 A column (300 mm × 8 mm) was used for separation of carbohydrates in the range of 10–1000 kDa by elution with 0.3 g/L NaCl (0.3 ml/min at 38 °C). To calculate molecular weights, sample peak retention times were compared to a standard curve created of the logarithmic molecular weight of pullulan standards with a range of 5.900–708.000 kDa (Shodex Standard Kit P-82, Japan). Since the obtained sample peaks were very wide, only a molecular weight interval was specified. This provided more representative information about the AX size distribution.

2.5. Rheological properties of arabinoxylans

2.5.1. Basic rheology: oscillation measurements

Gelation of different AXsin the presence of POx were characterized in solution and simplified batter systems at 25 °C and 35 °C, respectively, using a Kinexus Rheometer pro+ (KNX 2001; Malvern Instruments GmbH, Herrenberg, Germany). First, a strain sweep test was performed at the corresponding temperature with a shear strain of 0.001–100% and a constant frequency of 1 Hz to identify