

Water Binding Capacity of Rye Flours with the Addition of Native and Modified Arabinoxylan Preparations

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ABSTRACT

Despite a highly beneficial role of water soluble arabinoxylans, the information about the effect of their addition on the properties of rye dough is lacking. The aim of this study was to check the influence of their modification methods and properties on water binding capacity of rye flour and suggest some possible explanations for the action of various fractions of arabinoxylans. Three modifications of isolated arabinoxylans were carried out: enzymatic hydrolysis, cross-linking, and combination of both. The preparations used as additives differed in molecular characteristics of arabinoxylans, as well as their rheological behavior. The addition of all preparations at 1 and 2% levels to rye flour types 720 and 1,150 resulted in an increase of water absorption. The high water absorption of the two rye flour types with the same amount of arabinoxylan preparations was mainly related to structural properties of arabinoxylans, such as molecular mass and substitution ratio. Structural properties were responsible for rheological behavior of the samples, which allow prediction of the final water absorption of rye flour.

Keywords: Arabinoxylans, Cross-linking, Dough, Xylanase hydrolysis.

INTRODUCTION

Arabinoxylans are a group of non-starch polysaccharides, which are mainly produced from rye grain. Together with starch, they significantly influence properties of dough and bread made of rye flour, where gluten matrix is weak (Bushuk, 2001; Buksa *et al.*, 2010).

Some properties of arabinoxylans, such as water binding, cross-linking, and gel formation are crucial for establishing mechanical properties of the dough and, therefore, they are used as improvers, especially for wheat flour, where they are less abundant than in rye (Michniewicz *et al.*, 1991; Biliaderis *et al.*, 1995; Izydorczyk and Biliaderis, 1995; Vinkx and Delcour,

1996; Denli and Ercan, 2001; Goesaert *et al.*, 2005; Biliaderis and Izydorczyk, 2007).

The above mentioned properties of arabinoxylans depend, to a large extent, on their structure, i.e. size of molecules, branching characteristics controlled by arabinose/xylose (A/X), and mono- to disubstituted xylose ratios, distribution pattern of substituents, and especially location of ferulic acid. Rheological examination of the systems containing arabinoxylans usually includes determination of the flow behavior, which may be described e.g. by Ostwald–de Waele's power law model (by constants: n: Flow behavior index and K: Consistency index), and oscillatory rheometry, which allows to calculate storage (G') and loss (G'') moduli (Izydorczyk and Biliaderis, 1992; Cleemput *et al.*, 1993; Izydorczyk and

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Biliaderis, 1993; Biliaderis *et al.*, 1995; Izydorzyc and Biliaderis, 1995; Biliaderis and Izydorzyc, 2007).

The studies on water absorption of arabinoxylans have been done mainly in relation to wheat flour. Their effect on dough development and bread volume was checked for different amounts of preparations (soluble and insoluble) of varying origin (different cultivars of wheat and rye), characterized by a range of molecular masses (Michniewicz *et al.*, 1991; Cleemput *et al.*, 1993; Vanhamel *et al.*, 1993; Biliaderis *et al.*, 1995; Denli and Ercan, 2001). Linear increase of water absorption and dough development time was observed with rising addition level and molecular mass, and rye water soluble arabinoxylans proved to be especially efficient in increasing of these parameters (Delcour *et al.*, 1991; Denli and Ercan, 2001).

One of the ways to increase water binding capacity of the flour and bread volume is to cross-link its native arabinoxylans. The agents which could be used for this purpose include various oxidants, such as peroxidase–hydrogen peroxide system and laccase (Hoseney and Faubion, 1981; Buksa *et al.*, 2012b).

After cross-linking (peroxidase and hydrogen peroxide), rye water soluble arabinoxylans form weak gels, which is demonstrated by the changes of complex modulus with frequency. In their case, storage modulus G' doesn't depend on frequency and significantly exceeds loss modulus, which is frequency dependent (Dervilly-Pinnel *et al.*, 2001). In the case of wheat flour, the effect of cross-linking results in significant changes of dough rheology and bread volume (Vinkx and Delcour, 1996).

There are many possible applications of arabinoxylans in the food industry and one of them is bread improvement (Harris and Smith, 2006). Such preparations could be modified by enzymes, oxidative agents, and combination of both to achieve better results.

Because of highly beneficial role of water soluble arabinoxylans (Harris and Smith, 2006), the aim of the present study was to check the effect of their modification methods and properties on water binding capacity of rye flour and suggest some possible explanations for the action of various fractions of arabinoxylans. Comparison of these effects with molecular properties of arabinoxylans should extend the knowledge about mechanism of their action, and allow the establishment of indices important for describing their quality. Studies on the influence of varying water soluble arabinoxylans on rye dough and bread were not yet done.

MATERIALS AND METHODS

Materials used in this study consisted of arabinoxylan preparations, described in detail in the previous research work (Buksa *et al.*, 2012b). The samples were obtained from rye grain of Amilo variety (Plant Breeding Company Danko, Poland) by laboratory method: natural (LP AX) and modified by means of enzymatic hydrolysis with xylanase (LP HYD), oxidative cross-linking with peroxidase and hydrogen peroxide (LP CR) and hydrolysis followed by cross-linking (LP HCR) that were isolated and modified as described and characterized according to Buksa *et al.* (2012c).

For isolation of water soluble arabinoxylans, 100 g of milled rye wholemeal was pretreated for inactivation of grain enzymes with 500 mL 80% (v/v) EtOH at 90°C for 2 hours, the ethanol solution was removed and the precipitate dried at 40°C (20 hours), followed by extraction with water (2 L) at room temperature for 6 hours. Afterwards, the suspension was centrifuged. The clear supernatant was boiled and cooled to 37°C. The solution was incubated with 50 U α -amylase from saliva at 37°C for 2 hours, and boiled to inactivate the enzyme. The solution was filtered under vacuum through cellite

bed. The clear filtrate was poured in 4 times volume of ethanol/acetone solution (1:1). The precipitate centrifuged was frozen and stored for further processing within 2 weeks.

Laboratory Preparation of Arabinoxylans

In order to obtain unmodified preparation of arabinoxylans (LP AX), 15 g of frozen precipitate was thawed and dissolved in 40 mL de-ionized water by intensive stirring at 50°C for 6 hours. Dissolved arabinoxylans were poured in 4 times volume of ethanol/acetone solution (1:1). The precipitated arabinoxylans were centrifuged, washed with 20 mL of ethanol/acetone solution (2 times), and only with 20 mL of acetone (2 times). Finally, the precipitate was dried at 50°C for 2 hours.

Modification of Isolated Arabinoxylans

Enzymatic Hydrolysis

Frozen precipitate was thawed and dissolved in de-ionized water by intensive stirring at 50°C for 6 hours. After cooling of the solution to 30°C, xylanase (375 FXU/g arabinoxylan) was added and incubated at 37°C for 30 minutes. The supernatant was then boiled, centrifuged, and poured in 4 times volume of ethanol/acetone solution (1:1). Cleaning procedure was the same as for unmodified arabinoxylans.

Cross-linking by Peroxidase Treatment:

Frozen precipitate was thawed and dissolved in de-ionized water by intensive stirring at 50°C for 6 hours. After cooling of the solution to 25°C, H₂O₂ (1 μg g⁻¹ of arabinoxylans) and peroxidase (5 U g⁻¹ arabinoxylans) was added to react for 15 minutes. The process was stopped by pouring the solution in 4 times volume of ethanol/acetone solution (1:1). Cleaning

procedure was the same as for unmodified arabinoxylans.

Combination of Enzymatic Hydrolysis and Cross-linking:

After enzymatic hydrolysis (see above), inactivation of enzyme by autoclaving (at 120°C for 15 minutes) and cooling to 25°C, the cross-linking reaction was performed. Details of isolation and modification were as described for hydrolyzed and cross-linked arabinoxylans, and cleaning procedure was the same as for unmodified arabinoxylans.

The studies on the influence of arabinoxylans on water absorption were done with commercial rye flours type 720 (CF720) and type 1150 (CF1150) (PZZ Kraków, Poland) of low enzymatic activity, 5.8 (CF720) and 10.3% (CF1150) protein content, 4.5 (CF720) and 5.3% (CF1150) of total pentosans content (Bukša *et al.*, 2012a).

Molecular Mass Analysis

The distribution of molecular masses of the arabinoxylan samples was determined with GPC chromatographic system: combination of Sephacryl S-200 and S-500 gels from Healthcare; eluent: 0.032% Na₂CO₃; flow rate: 0.35 mL min⁻¹ (peristaltic pump); injected volume (1 mL of sample); with fraction analysis according to Bukša *et al.* (2012c). The molecular mass distribution, average parameters M_n , M_w and M_w/M_n (Dispersity: Đ) were calculated with the software program CPC win (a.h.group, Graz, Austria).

Structural Analysis

To determine the substitution ratio (SR) of monosubstituted xylose to 2,3-disubstituted xylose residues in arabinoxylans molecules, ¹H NMR analysis was performed. The analysis was done using Mercury-VX 300 MHz (Varian Inc, Palo Alto, USA),



according to Hoffman *et al.* (1992) and Izydorczyk and Biliaderis (1993). Each sample (approx. 15-20 mg) was mixed with 0.8 mL D₂O, shaken and simultaneously heated in a dryer (70 °C). The decanted solution was incubated in a measuring cell at 50°C for 10 minutes, and the ¹H NMR analysis was performed at 300 MHz. Acetone was used as a standard (δ = 2.23 ppm). Calculations were done with VnmrJ 1.1D software (Varian Inc, Palo Alto, USA). Peak assignments were done on the basis of literature data (Hoffman *et al.*, 1992; Izydorczyk and Biliaderis, 1993).

Rheological Properties of the Samples

Rheological measurements were carried out with 5% aqueous solutions of the samples. The dissolving was performed for 4 hours at 40°C at intensive stirring (600 rpm). The obtained solutions were taken for further analysis, which started approximately 5 hours after the beginning of dissolving. Rheological characterization was carried out in both steady and dynamic conditions, using a rheometer Rheostress RS 1 in controlled stress mode and Haake RheoWin software (Gebrueder Haake GmbH, Karlsruhe, Germany). The sample was held for 10 minutes in a rheometer in order to stabilize the system, then, the oscillatory measurements were performed. Oscillatory tests were performed in controlled deformation mode, in the range from 0.1 to 10 Hz, with a constant strain of 5%, which was checked to be in the linear viscoelastic region (LVR). Determination of flow curves was performed in controlled rate mode, at 25°C, using the measuring system CP 60/2 (Steffe, 1996; Schramm, 1998).

Water Absorption of Flour with the Addition of Arabinoxylans

Water absorption of flour with the addition of arabinoxylans was checked by preparing the dough from 50 g flour, one gram

Saccharomyces cerevisiae yeast (Saf-instant, Lesaffre, France, Product Code: 3 267793000007), 2 g baking acid (Bionat, Poland) to obtain acidity of the dough (pH= 4.4), and 1 g salt. Part of the dough was exchanged with 1 or 2% of the preparations obtained by laboratory method (LP). The addition of water was set so as the final consistency was 150 FU (Farinographic Units) as measured by the Farinograf E (Brabender, Germany).

Statistical Analysis

To establish the statistical differences between means, the analysis of variance (ANOVA) was performed and the least significant difference (LSD), at significance level of 0.05, was calculated. Additionally, Principal Component Analysis was applied to evaluate the selected data using Statistica version 9.0 software (StatSoft, Inc., Tulsa, OK, USA).

RESULTS AND DISCUSSION

All AX preparations, according to results presented in Buksa *et al.* (2012c), were composed of approximately 70% of arabinoxylan and 16% of protein. A/X ratio, calculated from arabinose (A) and xylose (X) content determined by HPLC/RI after hydrolysis of arabinoxylans, was 0.7, and the applied modifications of LP did not have any considerable effect on A/X ratios (Buksa *et al.*, 2012c). Arabinoxylans in the preparations, according to results presented in Buksa *et al.* (2012c), differed in molecular mass as presented in Table 1.

¹H NMR allowed to determine the substitution ratio (SR) of mono- (in the majority substitution 3-Xyl) to disubstituted (2,3-Xyl) xylose (Table 2). This index for LP preparation varied between 2.8 to 4.2 and was similar to that calculated from data by Dervilly-Pinel *et al.* (2001) (SR= 3.9). The observed tendency was that the values of mono- to disubstituted xylose were higher in

Table 1. Characteristics of molecular parameters of arabinoxylans (Buksa *et al.*, 2012c).

	LP AX ^a	LP HYD ^b	LP HCR ^c	LP CR ^d
$M_n \times 10^3$ (g mol ⁻¹)	14.2 ^c	1.8 ^b	1.6 ^a	51.6 ^d
$M_w \times 10^4$ (g mol ⁻¹)	40.0 ^c	15.0 ^a	18.7 ^b	76.9 ^d
\bar{D}	28.1 ^b	85.9 ^c	116.6 ^d	14.9 ^a

^a Laboratory preparation of arabinoxylans; ^b Laboratory preparation, hydrolyzed; ^c Laboratory preparation, modified by hydrolysis and following cross-linking; ^d Laboratory preparation, cross-linked. Means in the same line followed by the same letter are not significantly different ($P < 0.05$).

Table 2. Structural characteristics of arabinoxylan preparations obtained by ¹H NMR (Hoffman *et al.*, 1992; Izydorczyk and Biliaderis, 1993).

Preparation	Monosubstituted xylose (%) 5.53 ppm	Disubstituted xylose (%) 5.42 ppm+5.36 ppm	Substitution ratio (SR) ^e
LP AX ^a	73.5 ^a	26.5 ^b	2.8 ^a
LP HYD ^b	76.3 ^a	23.7 ^b	3.2 ^a
LP HCR ^c	80.0 ^b	20.0 ^a	4.0 ^b
LP CR ^d	80.6 ^b	19.4 ^a	4.2 ^b

^a Laboratory preparation of arabinoxylans; ^b Laboratory preparation, hydrolyzed; ^c Laboratory preparation, modified by hydrolysis and following cross-linking; ^d Laboratory preparation, cross-linked. ^e Chemical shifts (δ in ppm), $SR = [(2\text{-Xyl}) + (3\text{-Xyl})] / (2,3\text{-Xyl})$.

the case of cross-linked and hydrolyzed/cross-linked than the unmodified and hydrolyzed arabinoxylans (Table 2), indicating that cross-linking affected the solubility of arabinoxylans, if we assume that modifications did not change substitution ratio (as was earlier described in the section on Materials). It is possible that the part of arabinoxylans close to ferulic acid bridges (which were formed as a result of cross-linking) gave only background noise, while the ¹H NMR signal was measured only for the molecules which were completely dissolved (Toole *et al.*, 2009).

High ratios of mono- to di-substituted xylose at $A/X < 1$ demonstrate that water soluble arabinoxylans probably contain multiple araban branches as bran arabinoxylans may be present in preparation (Ebringerova *et al.*, 1990; Izydorczyk and Biliaderis, 1995; Biliaderis and Izydorczyk, 2007).

As it is known from the characteristics of the preparations, which was described in detail in a previous paper (Buksa *et al.*, 2012c), the average molecular mass of arabinoxylans was the largest for cross-

linked, and the smallest for the hydrolyzed arabinoxylans. M_w values of preparation LP HCR were larger compared to LP HYD, but smaller than the LP CR, which means that the product was partially cross-linked (Buksa *et al.*, 2012c). To study rheological properties of arabinoxylan preparations, flow curves were registered, which were then used to calculate power law parameters i.e. n and K . Additionally, oscillatory measurements were applied to determine complex modulus and phase tangent (G' , G'' and $\tan \delta$). The results are presented in Table 3 and in the Figures 1 and 2.

K and n parameters in Ostwald-de Weale Equation $\tau = K \cdot (\dot{\gamma})^n$ depended on the modification type. Cross-linked samples displayed the highest value of the flow consistency index: K ($Pa \cdot s^n$), while the lowest were calculated for hydrolyzed and hydrolyzed/cross-linked arabinoxylans. On the other hand, the flow behavior index n (dimensionless) was the lowest for cross-linked samples and the highest for LP HYD and LP HCR preparations.

Water solutions of all analyzed samples exhibited non-Newtonian, pseudoplastic



Table 3. Results of rheological measurements conducted at 25°C in 5 % aqueous solutions of arabinoxylan preparations.

Preparatio n	Ostwald de Waele Equation parameters		Oscillatory measurements
	K (Pa·s ⁿ)	n (-)	tan δ at 1 Hz
LP AX ^a	12.13 ± 1.03 ^b	0.524 ± 0.004 ^b	1.502 ± 0.098 ^b
LP HYD ^b	0.49 ± 0.04 ^a	0.669 ± 0.013 ^c	2.364 ± 0.018 ^d
LP HCR ^c	0.38 ± 0.02 ^a	0.676 ± 0.006 ^c	1.963 ± 0.021 ^c
LP CR ^a	228.30 ± 40.73 ^c	0.149 ± 0.000 ^a	0.534 ± 0.032 ^a

^a Laboratory preparation of arabinoxylans; ^b Laboratory preparation, hydrolyzed; ^c Laboratory preparation, modified by hydrolysis and following cross-linking; ^d Laboratory preparation, cross-linked. Means in the same line followed by the same letter are not significantly different (P < 0.05).

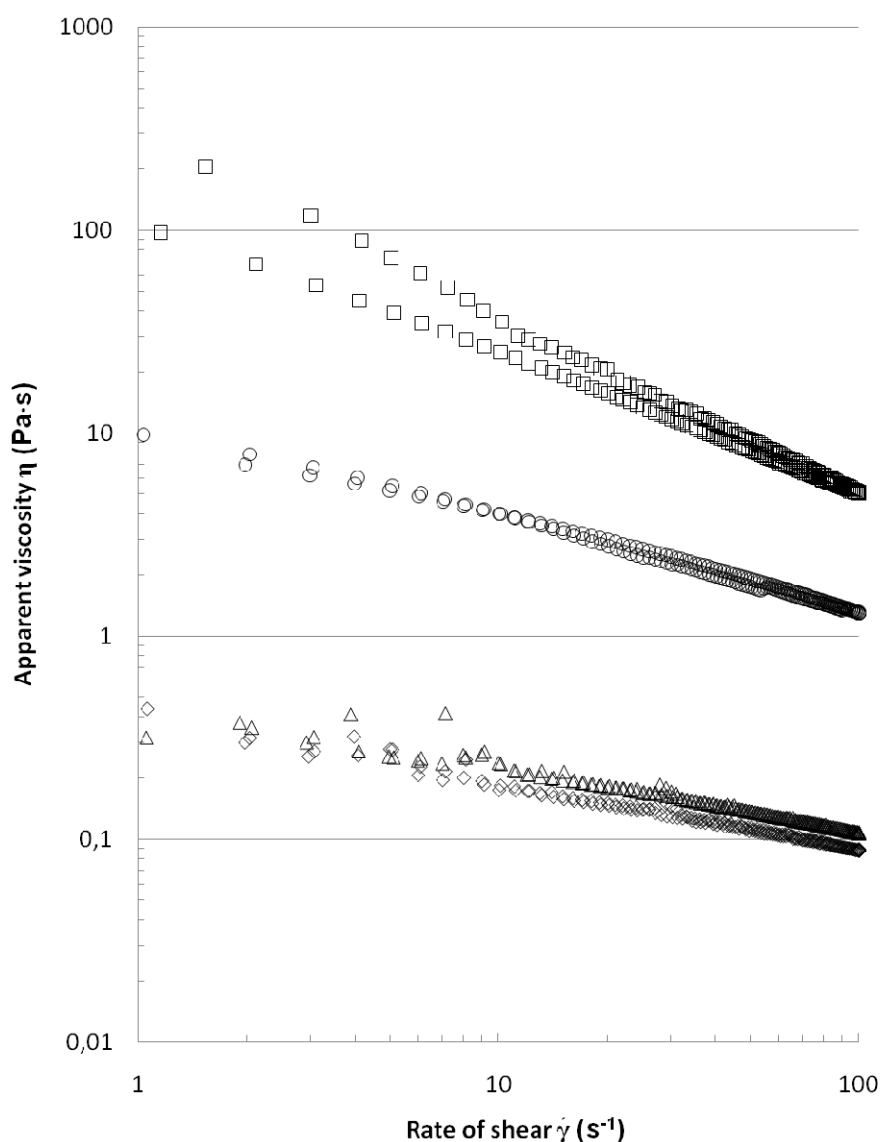


Figure 1. Apparent viscosity curves at 25°C of rye arabinoxylan preparations (5%, w/v) not modified (LP AX ○), hydrolyzed (LP HYD △), cross-linked (LP CR □) and hydrolyzed and cross-linked (LP HCR ◇).

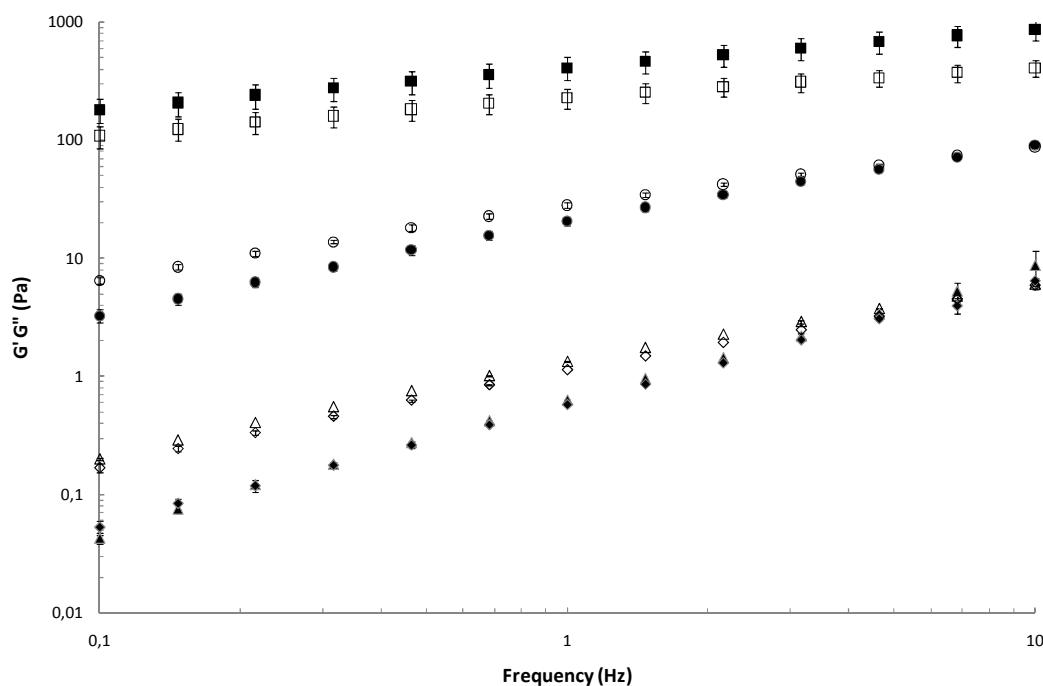


Figure 2. Mechanical moduli of pentosan preparations: Native: LP AX (G' ●, G'' ○) and Modified by hydrolysis: LP HYD (G' ▲, G'' △); Cross-linking: LP CR (G' ■, G'' □), Hydrolysis followed by cross-linking: LP HCR (G' ◆, G'' ◇). Data obtained at 25°C and 5% strain.

(shear-thinning) behavior. This could be seen from the constant decrease of their apparent viscosity with shear rate ($\dot{\gamma}$) (Figure 1) and the value of flow behavior index $n < 1$ (Table 3), which was the lowest in the case of LP CR.

Cross-linked arabinoxylans revealed highest apparent viscosity and lowest flow behavior index (Figure 1, Table 3). This is another proof that the cross-linking was efficient, because such molecules have the

most complex structure, the highest molecular mass and behavior of their solutions deviated from Newtonian fluids (Girhammar and Nair, 1995).

Hydrolyzed, and hydrolyzed/cross-linked preparations revealed lower apparent viscosity and higher “ n ” than unmodified and cross-linked (Figure 1, Table 3). The effect of hydrolysis seems obvious, as it corresponds to a decrease of chain length. It should be, however, noticed that LP HCR

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LP HYD ^c	0.49 ± 0.04 ^a	0.669 ± 0.013 ^c	2.364 ± 0.018 ^d
LP HCR ^d	0.38 ± 0.02 ^a	0.676 ± 0.006 ^c	1.963 ± 0.021 ^c
LP CR ^e	228.30 ± 40.73 ^c	0.149 ± 0.000 ^a	0.534 ± 0.032 ^a

^a Laboratory preparation of arabinoxylans; ^b Laboratory preparation, hydrolyzed; ^c Laboratory preparation, modified by hydrolysis and following cross-linking; ^d Laboratory preparation, cross-linked. Means in the same line followed by the same letter are not significantly different ($P < 0.05$).



preparation was not very different from LP HYD sample in its rheological behavior, although the first one exhibited slightly higher molecular mass.

Rheological properties characterized by Ostwald-de Weale Equation parameters (n and K) of LP un-modified preparation were between those observed for cross-linked and hydrolyzed samples.

The results of mechanical spectra measurements of LP preparations (at 5% strain) are presented in Table 3 and Figure 2.

All LP preparations, except for LP CR, displayed mainly viscous character, because $G'' > G'$ and $\tan \delta > 1$ (Table 3). LP CR, which contained cross-linked polymers, was weakly elastic ($G' > G''$, $\tan \delta < 1$) and had stable moduli G' and G'' in the whole frequency range (Figure 2, Table 3).

Another stage of the study was to check the effect of arabinoxylans addition on water absorption of rye flour. To balance the amount of added arabinoxylans, the preparations isolated by laboratory method were added in the amount of 1 and 2% on flour basis. It could be observed that pure flour samples differed in their water absorption. Higher water binding capacity was found for flour type 1,150, in comparison to type 720, because of higher concentration of native arabinoxylans and other fractions of dietary fiber. The observed increase of water absorption, after the

addition of arabinoxylan preparation was, however, higher in the case of type 720 rye flour.

The addition of arabinoxylans to rye flours resulted in an increase of water needed to reach the final consistency of 150 FU (Table 4) and the change was proportional to the addition level. Such effect on wheat dough was earlier described by many authors (Michniewicz *et al.*, 1991; Denli and Ercan, 2001, Cleemput *et al.*, 1993; Biliaderis *et al.*, 1995; Vanhamel *et al.*, 1993).

Among the applied samples, LP CR proved to be the most effective in increasing water absorption. The difference between unmodified and LP HCR preparations was generally low, while hydrolyzed samples were significantly less effective from all the preparations mentioned above.

PCA analysis allows to visually represent properties which are mostly affected by the changes in dough composition caused by e.g. the addition of different arabinoxylan preparation. The results that were taken into account in the study were collected for both flour types (720 and 1,150) so as to limit the influence of their composition, and for two addition levels of 1 and 2%. Besides the molecular mass of arabinoxylans, their structural properties such as substitution ratio and dispersity were also taken into account. It should be kept in mind, however, that the analyzed values describe only

Table 4. Water addition to flours with different share of arabinoxylan preparations in resulting dough with consistency of 150 FU.

Type of arabinoxylans added	Arabinoxylans preparation level (%)	Water addition to CF1150 (ml)	Water addition to CF720 (ml)
Control	0	52.5 ± 0.4 ^a	39.3 ± 0.1 ^a
LP AX ^a	1	53.8 ± 0.1 ^{def}	42.4 ± 0.4 ^b
LP AX	2	56.5 ± 0.0 ^h	46.7 ± 0.2 ^e
LP HYD ^b	1	53.3 ± 0.4 ^{bcd}	43.3 ± 0.4 ^c
LP HYD	2	55.3 ± 0.4 ^g	46.1 ± 0.1 ^e
LP HCR ^c	1	54.3 ± 0.4 ^f	44.8 ± 0.4 ^d
LP HCR	2	56.1 ± 0.2 ^h	47.6 ± 0.1 ^f
LP CR ^d	1	55.3 ± 0.1 ^g	46.5 ± 0.2 ^e
LP CR	2	58.3 ± 0.4 ⁱ	49.6 ± 0.3 ^g

^a Laboratory preparation of arabinoxylans; ^b Laboratory preparation, hydrolyzed; ^c Laboratory preparation, modified by hydrolysis and following cross-linking; ^d Laboratory preparation, cross-linked. Means in the same line followed by the same letter are not significantly different ($P < 0.05$).

molecules added in the preparation and not those naturally present in both flour types.

The first two dimensions explained 98.41% of the variation (eigenvalues: 9.02 and 1.80, respectively). The first factor is mostly dependent on water absorption, rheological parameters (n , K and $\tan \delta$), and molecular mass (contribution of these variables in the sum is 90%). The second factor is dependent on the dispersity (\mathcal{D}) and SR ratio (contribution of these variables in the sum is 62%).

Results of PCA (Figure 3) show that high

water absorption of rye flours type 720 and type 1,150 after the addition of the same amount of arabinoxylans (1 or 2 %) was mainly related to high molecular mass and structural properties of soluble arabinoxylans, such as substitution ratio (SR, positive correlation) and, to a lesser extent, to low dispersity (\mathcal{D}).

Rheological properties (characterized by K , n and $\tan \delta$) of arabinoxylans solutions were related to the structural properties of arabinoxylans. Therefore, it could be concluded that the knowledge of rheology of

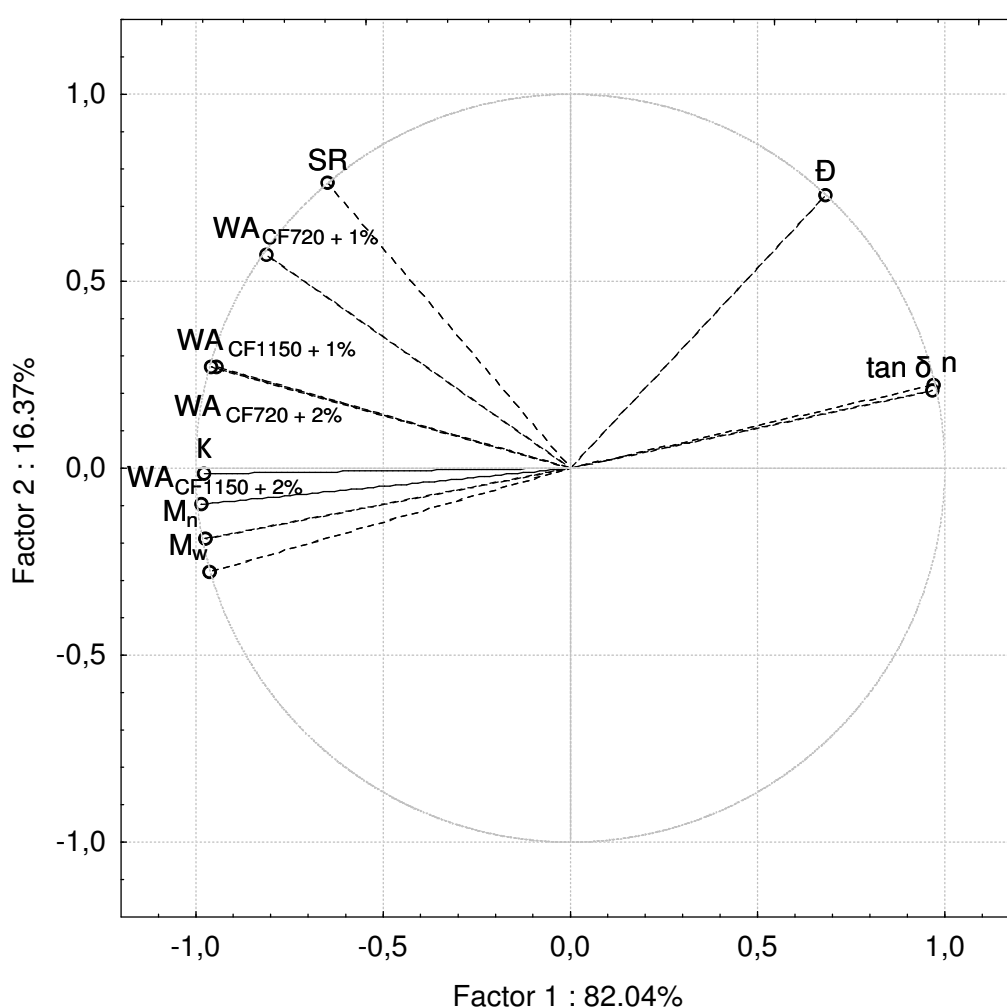


Figure 3. Principal component analysis (PCA) with distribution of analyzed parameters. $WA_{CF720+1\%}$, $WA_{CF720+2\%}$: Water addition to commercial flour type 720 with 1 and 2% share of arabinoxylan preparation, respectively; $WA_{CF1150+1\%}$, $WA_{CF1150+2\%}$: Water addition to commercial flour type 1150 with 1 and 2% share of arabinoxylan preparation, respectively; SR: Substitution Ratio; M_w and M_n : Weight and Number average molecular mass; \mathcal{D} : Dispersity; K : Flow consistency index; n : Flow behavior index, $\tan \delta$: Phase tangent.



arabinoxylan system allows prediction of their effect on water binding of the dough.

It is known that water present in the neighborhood of arabinoxylan is bound through hydrogen bonds to saccharide residues and forms characteristic solvation shells that are arranged into consecutive layers (Cui, 2005; Biliaderis and Izydorczyk, 2007; Glasser *et al.*, 2012). Relation of the water absorption of arabinoxylans to their structure is based on the hydrodynamic volume of arabinoxylans, which increases with the number of large molecules with small dispersity and high degree of xylan substitution with arabinose. Such molecules in water solution adopt an extended, wormlike, and rather stiff conformation (Biliaderis *et al.*, 2005) with hydrodynamic volume increasing with molecular mass. On the basis of observations in PCA relations, model of possible structures formed by arabinoxylans surrounded by water shells in aqueous media was proposed (Figure 4).

The unmodified arabinoxylans, especially those present in LP preparation and highly substituted with arabinose (Figure 4-a),

bound much water due to the formation of multiple hydrogen bonds as well as immobilization of water molecules in cavities between junction zones, i.e. regions where polysaccharide chains are connected through hydrogen bonds (Cui, 2005; Biliaderis and Izydorczyk, 2007).

The highest water binding, however, was observed for cross-linked arabinoxylans, which formed long, branched, and highly-substituted-by-arabinose hydrated chains (Figure 4-b) (Biliaderis and Izydorczyk, 2007). The presence of ferulic acid cross-links, apart from the above mentioned junction zones, resulted in an increase of apparent viscosity and water binding in comparison to unmodified pentosans (Biliaderis and Izydorczyk, 2007), although such molecules were visibly less soluble. The presence of oxidative ferulic acid cross-links made gels more elastic and increased the strength and permanence of water-holding capacity, but at the same time reduced penetration of the gel interior by other macromolecules present in the dough, such as starch and protein.

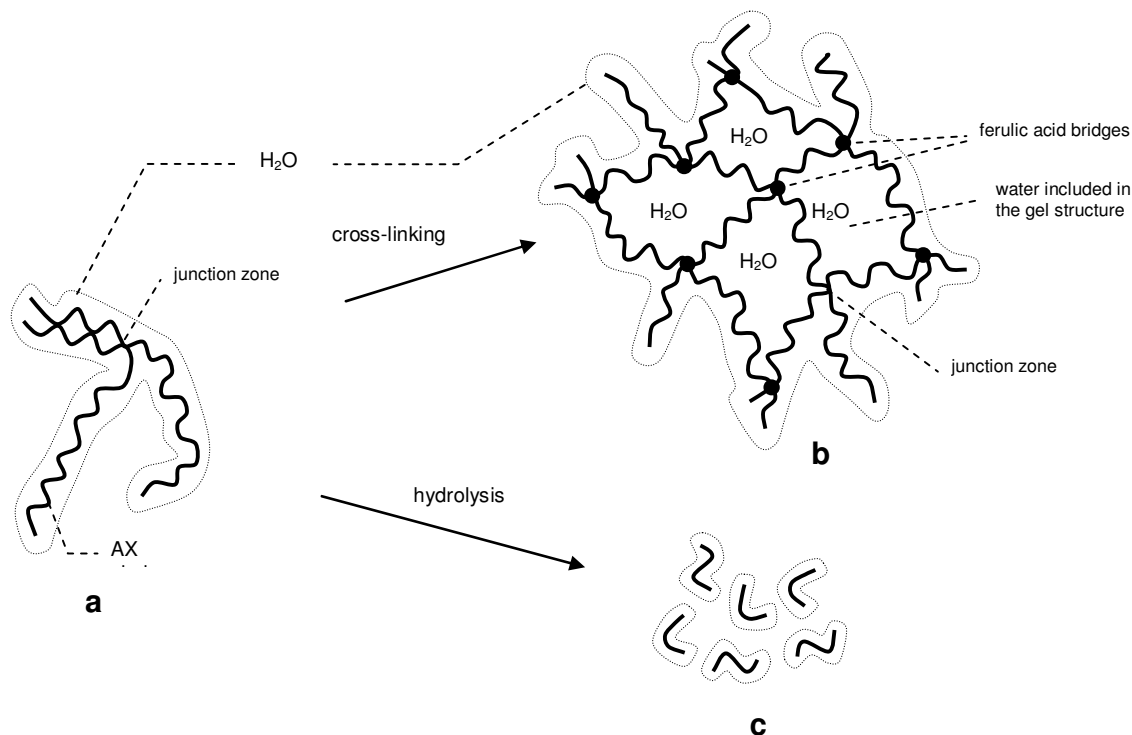


Figure 4. Model of possible structures formed by arabinoxylans (AX) molecules surrounded by water shells in aqueous media: (a) Not modified; (b) Cross-linked, (c) Hydrolysed arabinoxylan chains.

The lowest water binding was observed for hydrolyzed arabinoxylans, with smallest chains (lowest molar mass and apparent viscosity) and varying length i.e. high dispersity (Figure 4-c), which were the most mobile and formed unstable junction zones, so their effects on water binding of the dough were least significant.

CONCLUSIONS

Cross-linking and hydrolysis of arabinoxylans had opposite effect on isolated arabinoxylans. When the two modifications were combined, the effect of hydrolysis was stronger.

Water absorption of the two types of rye flours with the same amount of arabinoxylan preparations was mainly related to modification of their structure.

The addition of all preparations to rye flour resulted in an increase of water absorption, but the effect was much stronger in the case of cross-linked arabinoxylan (LP CR) samples.

The rheological parameters, which depend on arabinoxylan structure, allow prediction of the effect of arabinoxylan preparation on water binding of rye flour.

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ظرفیت جذب آب در آرد چاودار با افزودن فرآورده های ارابینوکسیلان اصلی و تغییر یافته

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چکیده

با وجود نقش بسیار مفید ارابینوکسیلان های (arabinoxylans) محلول در آب، اطلاعات در باره اثر افزودن آن روی خواص خمیر چاودار موجود نیست. هدف این پژوهش بررسی اثر خواص و روش تغییر این مواد روی ظرفیت جذب آب (آب پذیری) آرد چاودار و ارایه پیشنهاداتی در باره عمل اجزای مختلف ارابینوکسیلان ها بود. به این منظور، سه روش تغییر برای جدا سازی ارابینوکسیلان ها به کار رفت: هیدرولیز آنزیمی، پیوند تقاطعی (cross-linking) و ترکیبی از هر دو. فرآورده هایی که به صورت افزودنی استفاده شدند از نظر ویژگی های مولکولی ارابینوکسیلان ها و تغییرات شکلی آن ها در حرکت (rheological behavior) تفاوت داشتند. افزودن همه فرآورده ها به مقدار ۱٪ و ۲٪ به آرد چاودار نوع ۷۲۰ و ۱۱۵۰ جذب آب را در آن ها زیاد کرد. این افزایش جذب آب آردهای مزبور در شرایط افزودن مقدار برابر از فرآورده های ارابینوکسیلان ها عمدتاً مربوط می شد به ویژگی های ساختمانی ارابینوکسیلان ها مانند جرم مولکولی و نسبت جایگزینی. بر پایه نتایج این بررسی، ویژگی های ساختمانی مزبور مسول رفتار حرکتی نمونه ها بودند که پیش بینی جذب نهایی آب در آرد چاودار را ممکن می سازند.