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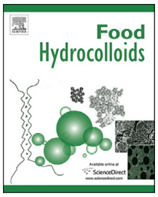

Concentration and shear rate dependence of solution viscosity for arabinoxylans from different sources☆

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ABSTRACT

Arabinoxylans are cell wall polysaccharides abundant in plants. Alkaline extraction is commonly used to isolate arabinoxylans from cell wall rich materials, such as cereal brans, crop residues etc. While arabinoxylans from certain sources such as wheat endosperm, corn bran and rye bran have been widely studied, there is a lack of studies focusing on the rheological and molecular properties of arabinoxylans from a wide variety of different sources. In this study, we report the concentration and shear rate dependence of solution viscosity of alkali extractable arabinoxylans from seven different sources. All the polymers are found to show Newtonian flow behavior, particularly at low concentrations, which is considered unusual in high molecular weight polysaccharides. The concentration dependence data shows the presence of a single critical concentration, suggestive of random coil conformation, while the rate of viscosity change in the two regimes suggests a more rigid conformation. This seemingly contradictory behavior is explained on the basis of a semi-flexible conformation of arabinoxylans in solution, which has been reported previously. The critical concentration of the arabinoxylans showed a strong correlation with their molecular weight, thus suggesting that fine structural differences do not significantly affect this aspect of rheological behavior. This is the first comparative study of alkali soluble arabinoxylans from different sources, and suggests that this class of polymers has significant similarities in spite of heterogeneity of fine structure.

1. Introduction

Arabinoxylans are cell wall polysaccharides consisting of a backbone of β (1,4) linked D-xylopyranose residues, with branches consisting of mainly L-arabinofuranose, and smaller quantities of D-galactose, D-glucose, D-xylose and D-glucuronic acid (Izydorczyk & Biliaderis, 1995). They also contain small but significant amounts of protein, lipids and phenolic acids such as ferulic acid and *p*-coumaric acid (Yadav, Moreau, & Hicks, 2007; Yadav, Nunez, & Hicks, 2011). They have been isolated from various tissues of cereal grains, and are most abundant in the thick cell walls of the outer layers of kernels. Although the most commonly studied arabinoxylans are isolated from cereal endosperm and brans, they are also found in other plant sources such as rye grass, bamboo shoots, switchgrass and miscanthus (Izydorczyk & Biliaderis, 1995). Most, though not all, of the arabinoxylans in cell walls are not water-extractable, owing mainly to extensive crosslinking of the polymers within the cell wall via diferulate ester bridges (Geissmann & Neukom, 1973). These water-unextractable arabinoxylans can be solubilized in the presence of alkali, such as sodium hydroxide, barium hydroxide or calcium hydroxide (Bergmans, Beldman, Gruppen, & Voragen, 1996; Maes & Delcour, 2001; Yadav, Parris, Johnston, & Hicks, 2008). Alkali-extractable arabinoxylans are high molecular weight, water soluble polymers with interesting functional and nutritional properties.

While arabinoxylans from cereal tissues such as wheat endosperm, corn bran, rye bran and sorghum bran have been widely studied, particularly in terms of their structural properties, there are relatively few studies focusing on the rheological properties of arabinoxylans from different sources, and the relationships between rheological and molecular characteristics. Additionally, most studies have focused on arabinoxylans from one or two sources

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(and therefore having a limited range of structures), thus resulting in a lack of data for comparing rheological properties of arabinoxylans with a wide variety of molecular properties.

Rheological properties of all polymers are governed by their molecular characteristics, such as monomer units, molecular weight, degree and pattern of branching, conformation, hydrodynamic volume and intrinsic viscosity. Synthetic polymers, which can be prepared with well-defined molecular characteristics, have been widely studied in terms of the relationship between their structure and rheological properties. Natural polymers, such as polysaccharides, also exhibit similar relationships, in spite of their inherent heterogeneity. Strong relationships between concentration and viscosity of various polysaccharides have been established (Morris, Cutler, Ross-Murphy, & Price, 1981).

In general, viscosity of polymer solutions increases with increasing concentration. However, the rate of increase is not constant, and various researchers have found two or three regimes, depending on polymer conformation, in which the increase in viscosity with concentration follows linear trends with different slopes (Izydorczyk & Biliaderis, 1992; Morris et al., 1981). Polymers with random coil conformation in solution exhibit two distinct regimes (dilute and concentrated). The concentration(s) at which the viscosity regime changes is known as the critical concentration (c^*). Below the critical concentration, polymer molecules behave as individual ‘particles’ in solution, while above c^*, interaction, interpenetration and entanglement of the molecules is said to occur. Thus, above c^*, the viscosity of the solution increases much more rapidly with concentration than below c^*. Polymers which have rigid, rod-like conformation in solution exhibit an intermediate ‘semi-dilute’ regime in which the rate of viscosity increase with concentration is greater than that for dilute solutions and less than that of concentrated solutions (Izydorczyk & Biliaderis, 1992; Skendi, Biliaderis, Lazaridou, & Izydorczyk, 2003).

In terms of shear rate dependence, most polysaccharides exhibit pseudoplastic or shear thinning flow behavior. In other words, the viscosity of polysaccharide solutions usually decreases as the shear rate increases. This phenomenon has been reported for wheat endosperm arabinoxylans, and the shear rate at onset of shear thinning was found to depend on molecular weight of the arabinoxylan (Izydorczyk & Biliaderis, 1992). However, some other researchers have observed Newtonian flow behavior, marked by constant viscosity, in solutions of high molecular weight arabinoxylans, particularly those extracted from corn bran (Rumpagaporn, Kaur, Campanella, Patterson, & Hamaker, 2012). Thus, it is unclear whether arabinoxylans with different molecular characteristics show varying shear rate dependence of flow behavior.

In this study, we focus on the effects of shear rate and concentration on flow behavior of arabinoxylans from different sources. Pure water was used as the solvent in order to study interactions between polymer molecules in their native state, with no external mitigation of electrostatic interactions using salt addition or pH adjustments. Since these polymers are of similar chemical nature, an attempt was made to establish a generalized relationship between their molecular characteristics and rheological behavior.

2. Materials and methods

Sorghum brans (Sumac milled, Burgundy milled and Black milled) were procured from Nu Life Market, Scott City, Kansas, USA. Corn bran and wheat bran were obtained from Z Trim Holdings, Inc. and switchgrass and corn stover from USDA-ARS laboratory at University Park, PA and a private farmer, Larry Shrawder respectively.

Table 1
Sugar composition of alkali extractable arabinoxylans from different sources (relative mole %).

Source of arabinoxylan	Ara	Xyl	Gal	Glc	Rha	GalA	GlcA	Total
Sumac sorghum bran	34.60	48.85	3.07	8.13	0.98	1.00	3.37	100
Burgundy sorghum bran	32.48	47.93	4.66	7.79	1.42	1.45	4.26	100
Black sorghum bran	34.39	49.83	3.25	4.29	0.98	3.06	4.20	100
Switchgrass	19.10	61.89	7.27	6.35	1.12	1.67	2.58	100
Corn stover	18.14	52.69	10.94	9.66	1.33	1.77	5.47	100
Wheat bran	31.10	46.03	5.27	14.00	0.55	0.83	2.21	100
Corn bran	27.46	48.52	12.08	4.28	0.43	1.02	6.21	100

2.1. Arabinoxylan extraction

Arabinoxylans from corn stover, wheat bran, switchgrass and three varieties of sorghum brans were isolated by an alkaline solution following our previously published method (Yadav, Cooke, Johnston, & Hicks, 2010). Food grade corn bran arabinoxylan was a kind gift from Z-Trim Holdings, Inc. (Mundelein, IL).

2.2. Monosaccharide composition analysis

The sugar composition of samples was determined by HPAEC-PAD using methanolysis combined with TFA hydrolysis as described previously (Yadav, Johnston, & Hicks, 2007).

2.3. Molecular weight determination

Molecular weight of arabinoxylans was determined by a high-performance size-exclusion chromatography (HPSEC) system, which comprised two PL Aquagel OH-60 and one OH-40 columns (Polymer Laboratories, Amherst, MA) (Yadav, Fishman, Chau, Johnston, & Hicks, 2007). Multi-angle laser light scattering (MALLS) and refractive index detectors (Wyatt Technology Corporation, Santa Barbara, CA) were used with the HPSEC system.

2.4. Rheological measurements

Viscosity of arabinoxylan solutions of varying concentrations was measured using an Anton Paar MCR 102 rotational rheometer with the concentric cylinder geometry. Measurements were made at 25 °C and shear rate was varied from 1 to 100 s^{-1}.

2.5. Determination of Power Law parameters and critical concentration

The values of Power Law parameters K and n were determined by fitting double log plots of viscosity versus concentration using Microsoft Excel®. The viscosity-concentration data was fitted with least squares regression to determine the best fit for two different regimes, using a Fortran-based code. The critical concentration for each sample was determined by calculating the point of intersection of the two best fit lines in the dilute and concentrated regimes.

Table 2
Molecular weight of alkali extractable arabinoxylans from different sources.

Source of arabinoxylan	Weight average molecular weight (M_w) ($\times 10^3$ da)
Sumac sorghum bran	363 ± 10
Burgundy sorghum bran	373 ± 3
Black sorghum bran	342 ± 7
Switchgrass	130 ± 5
Corn stover	367 ± 3
Wheat bran	437 ± 6
Corn bran	362 ± 3