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# What Are the Characteristics of Arabinoxylan Gels?

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## Abstract

Arabinoxylan gels are commonly characterized to determine the feasibility of utilizing them in numerous applications such as drug delivery systems. The general characteristics of numerous types of arabinoxylan gels as well as their susceptibility to degradation are discussed in this manuscript. There are two main types of arabinoxylan: water-extractable and alkali-extractable. The physicochemical characteristics of the arabinoxylan determine its extractability and gelling characteristics. Gels can be created from numerous types of arabinoxylan including wheat (*Triticum aestivum* L.) and maize (*Zea mays* L.). These gels can also be developed with the addition of protein and/or $\beta$-glucan, which results in modified mechanical properties of the gels. To create a sound gel, arabinoxylan must be cross-linked, which is often done through ferulic acid. When this takes place, the gel developed is thermo-irreversible, unsusceptible to pH and electrolyte interactions, and does not undergo syneresis during storage. Despite these strengths, arabinoxylan gels can be broken down by the enzymes produced by *Bifidobacterium*, which is present in the human large intestine. After further development and research on these gels, they could be utilized for many purposes.

## Keywords

Arabinoxylan, Gel, Rheology, Water Extractable, Alkali Extractable, Wheat, Maize, Polysaccharide

## 1. Introduction

Arabinoxylan (AX) is a structural non-starch polysaccharide located in the cell walls of cereal crops [1] [2] [3]. This type of non-starch polysaccharide is considered dietary fiber and can impart many health benefits when regularly consumed [1] [4] [5]. The exact AX content depends upon the type of cereal and the

location of AX in the grain. For example, in wheat the AX content increases going from the endosperm out to the bran, however the cell walls of all portions of the kernel are about 70% AX [6] [7] [8]. Arabinoxylan is one type of pentosan composed of arabinose and xylose [8] [9] [10]. Arabinoxylan has a $\beta$-1,4-D-xylopyranosyl backbone with $\alpha$-L-arabinofuranosyl substituents that are O-2 and/or O-3 linked and can form cross-linkages with ferulic acid, as shown in **Figure 1**. The O-2 linkages are not very common in wheat but predominate in other cereals [11]. The substitution level of wheat AX is about 21% monosubstituted, 13% disubstituted, and 66% unsubstituted [12]. The amount of substitution on the xylose backbone of maize AX is less than wheat AX [13]. The level of substitution plays a vital role in the formation of AX gels [14].

Arabinoxylan can have several substituents, including ferulic acid, that impact its solubility and rheology [1] [2] [15]. Ferulic acid is most often esterified to O-5 arabinose that is linked via an O-3 linkage to the xylose backbone [2] [16]. In addition, ferulic acid is localized in the bran of cereal grains [17]. Arabinoxylan can also have 3-methoxy and 4-hidrocinnamic acid substituents [13]. The result of this is that there are many different molecular structures for AX that have different rheological properties. In addition, AX is either soluble or insoluble in water, which impacts its extractability [1] [5] [8]. The arabinose to xylose ratio (A:X) can vary depending upon cereal type and processing methods [1] [8]. As the A:X decreases, the AX becomes less water soluble because hydrogen bonding stabilizes the molecular structure [1]. Also, as ferulic acid content

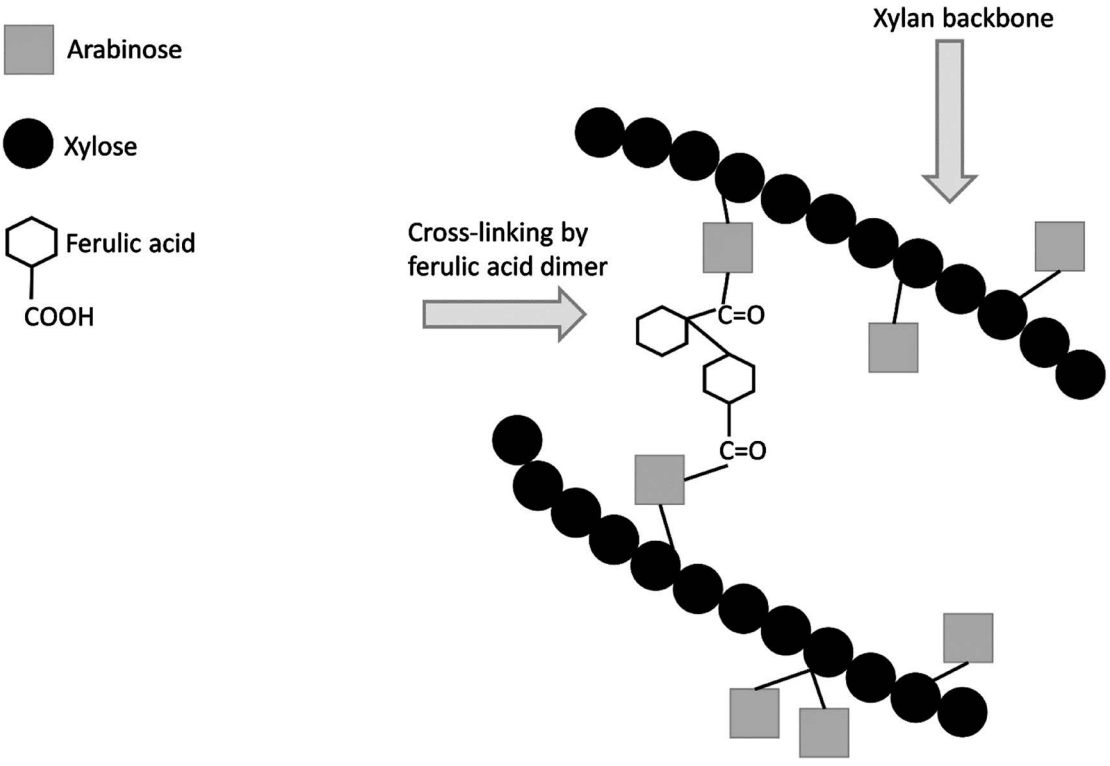



**Figure 1.** Arabinoxylan cross-linking via a ferulic acid dimer such as in an arabinoxylan gel reproduced based on Kiszonas *et al.* [12].

in AX increases, the AX becomes less water soluble [1] [6]. However, all these solubility trends also depend on pH [1] [18].

Gels are one type of semisolid material that remains intact when no force is applied as they are highly viscous [19]. These materials are held together by cross-linkages, which impart strength to the gels via covalent bonding. When AX is used as the basis for gels, cross-linkages must be created under oxidative conditions catalyzed by enzymes such as hydrogen peroxide and peroxidase or laccase [3] [15]. These cross-linkages are most commonly formed between ferulic acid and adjacent AX polymers [20] [21]. After formation of these gels, numerous mechanical properties can be assessed to characterize the strengths and weaknesses of the gels. The storage modulus of a gel is how stiff the gel is, which represents the amount of energy stored in the gel [22]. Conversely, the loss modulus is a measure of the ability of the gel to lose energy. The final modulus often calculated for AX gels is the elastic modulus [23]. This modulus provides a quantification of the deformation characteristics of a gel. Gel hardness is also used as a measure of resistance to deformation.

## 2. Cereal Arabinoxylan and Health

Arabinoxylan is known to have many health benefits including limitation or prevention of the following: type two diabetes, cancers of the digestive system, and cardiovascular disease [1] [4]. One reason for these health benefits is that AX is dietary fiber, which means that it resists digestion in the human small intestine and is fermented by the microbiota in the large intestine [1] [5] [24]. Due to these things, AX is considered a prebiotic that aids in the production and growth of beneficial bacteria in the intestines [4] [25]. This prebiotic behavior of AX can help prevent inflammatory bowel disease, Type I diabetes, and rheumatoid arthritis [4]. These benefits of consuming AX are outlined in **Figure 2**.

### 2.1. Cereal Arabinoxylan and Baking

Arabinoxylan also plays an important role in many properties of foods including textural characteristics, shelf life, water binding capacity, and the stability of foams [1] [6] [26]. In addition, water extractable wheat AX acts as a cryostabalizing agent by preventing the growth of ice crystals when doughs are refrigerated or frozen [5] [11]. When in bread dough, AX increases the viscosity of the dough and increases the interactions between proteins and starch during mixing [5] [27]. When AX cross-links with ferulic acid during mixing, the development of the gluten matrix is hindered [28]. In addition, water migration from the gluten network to the AX polymers occurs, resulting in poor baking quality [28]. The result of these things is an increase in the size of the gas cells formed during fermentation due to their increased stability. High molecular weight water extractable AX improves the loaf volume and texture when bread is baked [5]. In addition, AX extends the shelf life of baked goods by preventing starch crystallization, which leads to staling [6].

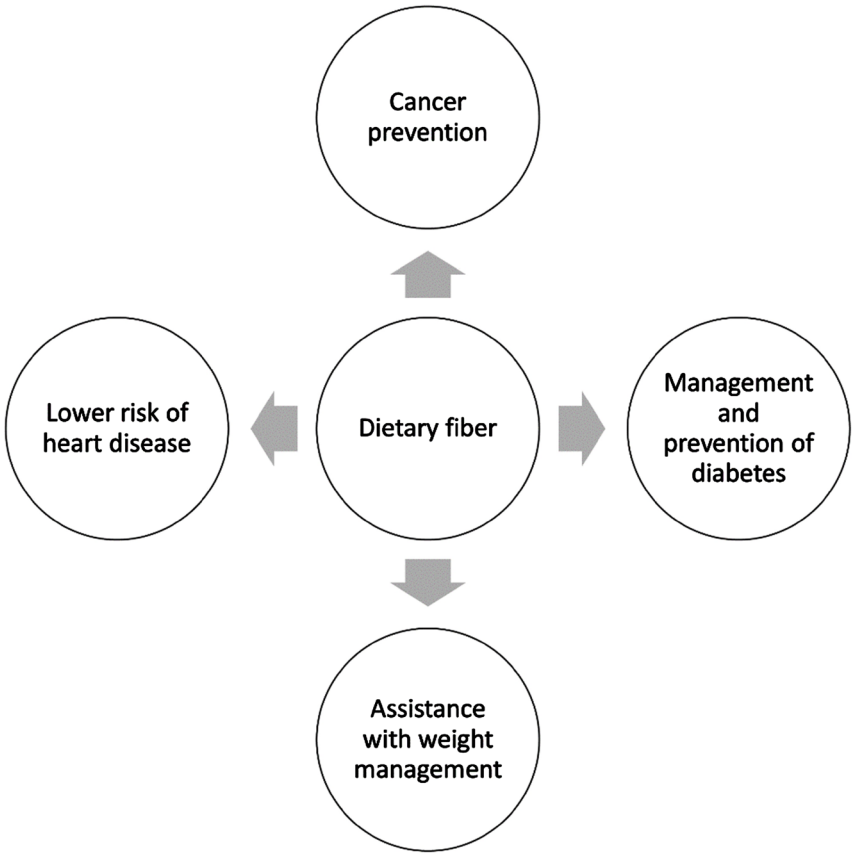



**Figure 2.** Health benefits of consuming dietary fiber such as arabinoxylan.

## 2.2. Rheology of Arabinoxylan Gels

For a proper gel to form from polysaccharides such as AX, they must cross-link via covalent bonding [6] [13] [20]. In AX, this takes place via a dimerization reaction that forms dehydrodimers (5-5', 8-O-4', 8-5', and 8-8') and/or isomers that are dehydrotrimers (8-O-4/8-O-4, 8-8'/8-O-4) [13]. These covalent bonds are interactions between AX chains or AX and another chemical species such as ferulic acid or protein that provide the AX gels with their physical and chemical properties [6] [20]. These interactions occur under oxidative coupled cross-linking, which can be catalyzed by laccase or a hydrogen peroxide/peroxidase system [2] [20]. Gels made from AX have a neutral taste and little to no odor, are stable under heat, not susceptible to pH changes or electrolytes, have a high water binding capacity, and do not exhibit syneresis during storage [13].

Small deformation oscillatory rheometry with small amplitude oscillatory shear provides the gelation profile of gels made from AX [2] [3]. The rheological properties of AX gels differ depending upon the solvent used, AX extraction conditions temperature of testing, frequency utilized, strain rate employed, AX concentration of the gel, AX mesh size, and the pH of the gel during testing [15] [29]. These factors can be manipulated to obtain gels with favorable characteristics. This results in the ability to produce a wide variety of AX gels for numerous applications.

Intrinsic viscosity, the viscosity of AX based mainly on molecular weight, is positively correlated to gel strength [11] [14] [30]. The intrinsic viscosity is a measure of the hydrodynamic radius of AX molecules determined using a viscometer, and the molecular weight of the AX can be extrapolated from this information using the Mark-Houwink relationship [15] [30]. Arabinoxylan has a random coil conformation in solution, which can be flexible [6] [31]. In addition, the initial formation of cross-linkages can result in less movement of the AX, which restricts the amount of further cross-linking that can occur [1] [30]. However, these cross-linkages result in an increased water binding ability [6].

## 2.3. Rheology of Water Extractable Wheat Arabinoxylan Gels

Water extractable wheat AX can be used to create gels that have a variety of properties depending upon the type of water extractable wheat AX and the other species present in the gel [11] [30]. This material forms cross-linkages when exposed to hydrogen peroxide and peroxidase [2]. These enzymes facilitate the cross-linking of ferulic acid with two AX polymers through an oxidation reaction that generates free radicals [2] [18] [28]. Izydorczyk *et al.* researched the properties of water extractable AX gels that had a mesh size of 0.4 to 0.5 mm, used water as a solvent at 25 °C with 10% strain, and 1 Hz frequency (pH not provided) [30]. The viscosities of these gels made with 0.10% (w $v^{-1}$) water extractable wheat AX ranged from 2.82 to 4.20 Pa s. In addition, these cross-linked water extractable wheat AX could hold up to 100 g water for every 1 g water extractable wheat AX, which has also been confirmed by another research group [18] [30]. Furthermore, this type of gel was able to stabilize protein foams when heated [6] [26] [30].

These characteristics all play important roles in the food systems that involve water extractable wheat AX [18] [30]. Depending upon the food system, water extractable wheat AX can be modified to have properties that are desirable. Water extractable wheat AX increases the viscosity of food systems more than arabinogalactan and gums [11]. Water extractable wheat AX is a pseudo plastic material because it exhibits Newtonian behavior at concentrations less than 1% (w $v^{-1}$) (as shear rate increases) and shear thinning behavior at concentrations 1% (w $v^{-1}$) or greater (as shear rate increases) [11] [30].

Water extractable wheat AX has the ability to hold large amounts of water without dissolving, which gives it the unique ability to form hydrogels (gels that absorb many times their weight in water) [32] [33]. Due to this, water extractable wheat AX gels can be used for many delivery systems in the food, medical, cosmetic, and agronomy industries [33]. Gels made with AX become more rigid and have an increased storage modulus as the water extractable AX content increases [30]. This allows for manipulation of materials characteristics through gel AX content modification.

## 2.4. Rheology of Alkali Extractable Wheat Arabinoxylan Gels

In addition to water extractable wheat AX, there is also alkali extractable wheat

AX [15] [29]. This type of AX is most commonly extracted using dilute sodium hydroxide [34]. Extraction with dilute sodium hydroxide breaks ester bonds, breaks the hydrogen bonds between the cellulose and AX, and causes uronic acids to become negative resulting in repulsion and increased AX extractability. This type of AX is linked to ferulic acid in a similar fashion (at the O-5 location) as in water extractable wheat AX, but there is typically more ferulic acid present in alkaline extractable wheat AX [15].

According to the research published by Berlanga-Reyes *et al.* [15], the length of extraction time correlates to the fine structure and rheology of alkaline extractable wheat AX. As the alkaline treatment time during extraction was increased from 30 to 120 minutes, the A:X decreased, the amount of ferulic acid present decreased, the molecular weight decreased, and the intrinsic viscosity decreased, as shown in **Figure 3**. In addition, as the extraction time increases, the hardness of the gels decreased, and the swelling ratio of the gels increased. This is most likely due to a decrease in the molecular size resulting in a lower water absorption, which is observed in almost all polymers [15] [35].

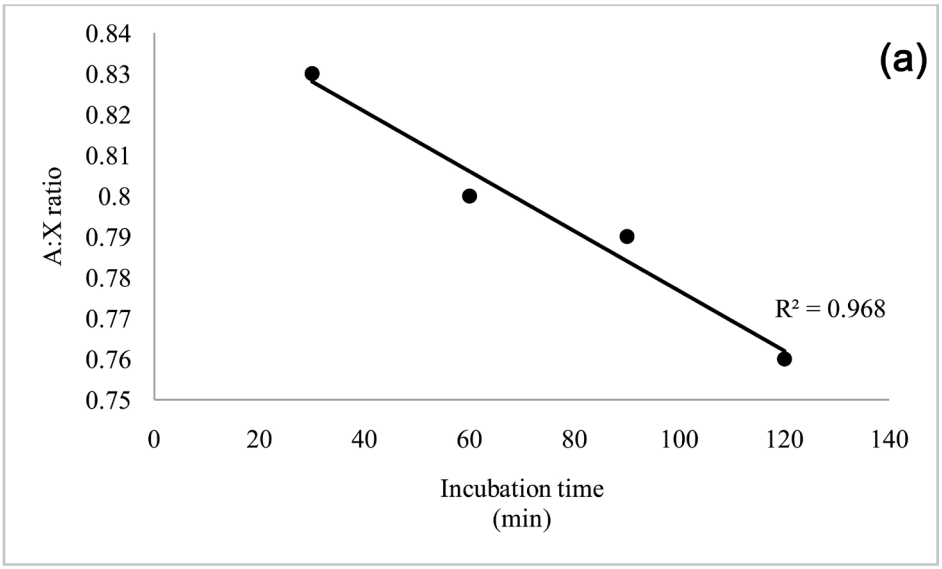
## 2.5. Rheology of Water Extractable Wheat Arabinoxylan Gels with Copper Ions and $\beta$-Glucan

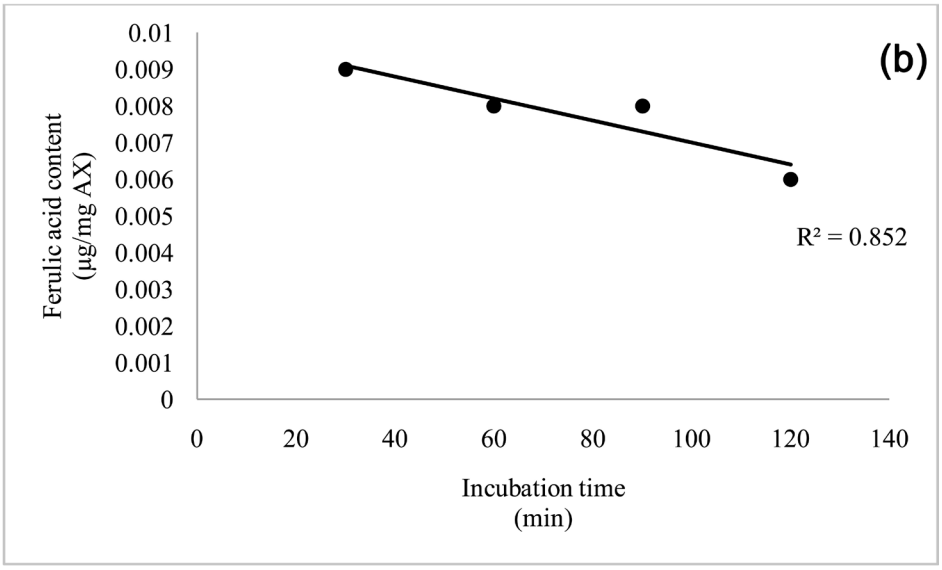
In addition to molecular weight, ferulic acid content, and level of cross-linking, the presence of $Cu^{2+}$ and barley $\beta$-glucan can impact the rheology of water extractable wheat AX gels [2] [36]. Copper ions facilitate the oxidation of water extractable wheat AX [2] [37]. This causes the formation of cross-linkages in AX gels in the same way peroxidase/hydrogen peroxide systems and laccase (as laccase contains copper ions) [37]. In research by Skendi and Biliaderis [2] on AX gels made with $Cu^{2+}$, it was determined that as the concentration of $Cu^{2+}$ increased, the complex viscosity of the gels also increased, as shown in **Figure 4**. These gels had an increase in storage modulus and loss modulus followed by a plateau, which indicates the formation of cross-linkages [2] [29] [38]. These gels were also thermo-irreversible and had an optimal gelation temperature of 15°C [2]. Lastly, it was determined that water extractable wheat AX gels could not form at $Cu^{2+}$ concentrations less than 0.31 mM.

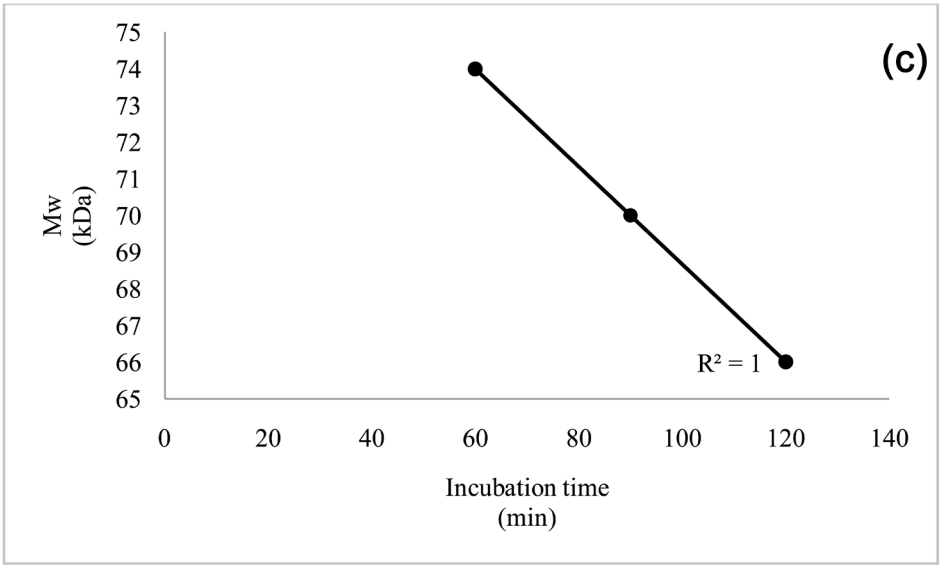
Skendi and Biliaderis also researched the effects of $\beta$-glucan concentration on AX gels [2]. As the $\beta$-glucan concentration in the gels in this research of was decreased, the gelling ability of the water extractable wheat AX/$\beta$-glucan gel decreased. However, it has also been determined that $\beta$-glucan competes with AX for water in gels, and as the $\beta$-glucan content in AX gels increases, the gelling ability of the material decreases [39]. In addition, as the water extractable wheat AX to $\beta$-glucan ratio decreased from 2:0 to 0:5, the storage modulus of the gels increased [2]. This indicates that $\beta$-glucan formed stronger gels than water extractable wheat AX.

## 2.6. Rheology of Gels Made from Wheat Arabinoxylan and Protein

The presence of proteins including insulin, ovalbumin, or bovine serum albumin,


(a)
A:X ratio
0.84
0.83
0.82
0.81
0.8
0.79
0.78
0.77
0.76
0.75
R² = 0.968
0
20
40
60
80
100
120
140
Incubation time
(min)


(b)
Ferulic acid content
(μg/mg AX)
0.01
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
R² = 0.852
0
20
40
60
80
100
120
140
Incubation time
(min)


(c)
Mw
(kDa)
75
74
73
72
71
70
69
68
67
66
65
R² = 1
0
20
40
60
80
100
120
140
Incubation time
(min)

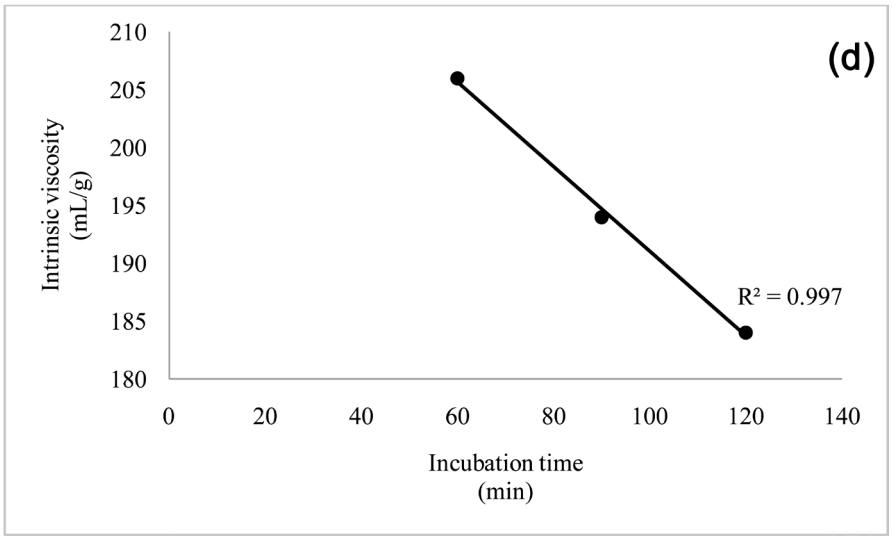



**Figure 3.** Rheological properties of alkali extractable wheat bran arabinoxylan gels based on extraction incubation time according to Berlanga-Reyes *et al.* [15]. (a) Changes in A:X ratio with incubation time; (b) Changes in ferulic acid content with incubation time; (c) Changes in molecular weight with incubation time (values not given prior to 60 minutes); (d) Changes in intrinsic viscosity with incubation time (values not given prior to 60 minutes).

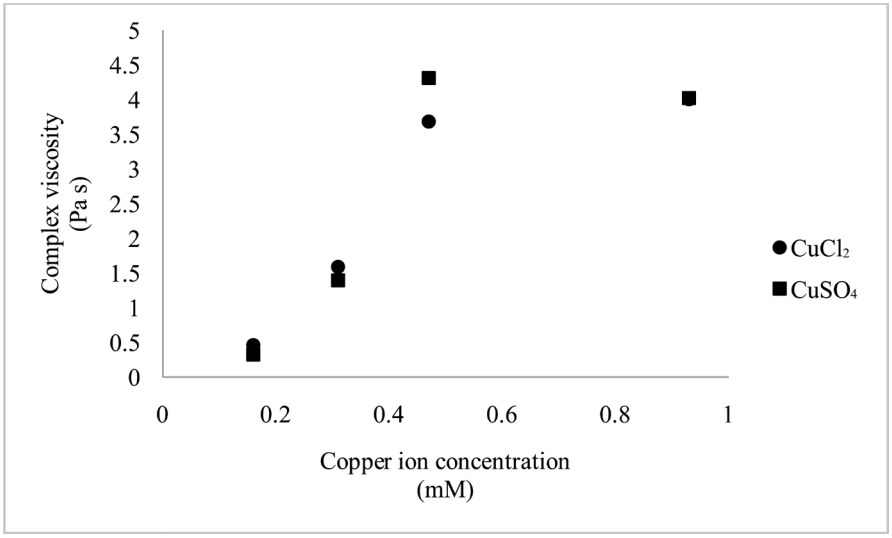



**Figure 4.** Impact of copper on the complex viscosity of arabinoxylan gels according to Skendi and Biliaderis [2].

in wheat bran AX gels affects the rheological properties of these gels [18] [40] [41]. Berlanga-Reyes *et al.* determined that the presence of proteins affects wheat bran AX gel elasticity and viscosity but does not interfere with the formation of covalent cross-linkages [15]. This type of gel has a less compact structure than a pure AX gel due to the high level of interaction of both AX and protein with water [42]. Proteins in these gels aggregated in clusters when the protein to wheat bran AX ratios were higher than 1:4 [18]. These clusters were not distributed in a homogeneous manner, which suggests that phase separation had taken place.

This phase separation was due to thermodynamic incompatibility between the proteins and AX in the gel [18] [43]. Aggregations such as these lower the mechanical strength of the gels by decreasing crystallinity of the AX polymers in a similar fashion to plasticization [44]. However, as mechanical strength decreases pliability typically increases.

Water extractable wheat AX can be mixed with gluten to produce gels with different characteristics such as those in the research of Ma *et al.* [42]. In this research, it was demonstrated that the presence of water extractable wheat AX increased the viscoelasticity of the gluten, which resulted in a less compact microstructure of this protein. When gluten was mixed with water extractable wheat AX, cross-linkages were formed. Ma *et al.* speculated that the free sulfhydryl groups from the protein cross-linked with the water extractable wheat AX [42]. However, other research has shown that AX cross-links with protein through ferulic acid interacting with tyrosine [45] [46]. In addition, when gluten was mixed with water extractable wheat AX, glutenin demonstrated a greater change in conformation than gliadin [42]. These gels were more elastic than viscous, as indicated by a higher storage modulus than loss modulus.

### 2.7. Rheology of Maize Bran Arabinoxylan Gels

Maize bran AX forms gels in the presence of laccase given that ferulic acid is present to cross-link with the AX [3] [10] [47]. Maize bran AX has about 2.5 times more ferulic acid than wheat bran AX [48]. The level of ferulic acid substitution on the AX backbone can be modified by altering the alkalinity of the solvent used to extract the maize bran AX [10] [34]. As the alkalinity of the solvent increases, the level of ferulic acid substitution decreases.

For gels made with a 2% (w $v^{-1}$) solution of maize bran AX in water that utilize laccase as an oxidizing agent, the storage modulus is higher than the loss modulus [10]. This indicates that the gels formed are strong and in a semi-solid state. This relationship between storage modulus and loss modulus was also noted in maize bran AX gels formed using a hydrogen peroxide/peroxidase system for cross-linkage formation [49].

Kale *et al.* performed research on the rheological properties of maize bran AX gels, and the conditions utilized were as follows: 4% strain and frequency sweeps of 0.1 to 10 Hz [10]. In addition, the maize bran AX was extracted with sodium hydroxide that varied in concentration from 0.25 M to 0.5 M (all extractions were two hours in duration). It was demonstrated that as the sodium hydroxide concentration increased, the storage modulus decreased from about 500 Pa to about 10 Pa, and the ferulic acid content decreased from 1.2% to 0.3%. The alkaline solutions de-esterified the single ferulic acid residues and made the maize bran AX soluble [10] [34]. The result of this was that the maize bran AX was depleted of ferulic acid and could no longer form gels [10].

Carvajal-Millan *et al.* researched gels made with 1% to 2% (w $v^{-1}$) water extractable maize bran AX that utilized water as the solvent, were developed at a

pH of 5.5, and utilized laccase for catalysis of the cross-linkages between ferulic acid and AX [32]. This research demonstrated that as the maize bran AX concentration increased, the gel hardness and emulsion stability increased. This trend in gel hardness was also noted in research on alkali-extracted wheat bran AX gels [15], and similar trends were seen in emulsion stability in maize fiber gels [50].

## 2.8. Rheology of Maize Fiber and Maize Wastewater Arabinoxylan Gels

In maize fiber AX, the acid profile is dominated by ferulic acid, and the amount of branching on maize fiber AX is lower than for wheat AX [13] [51]. It was noted in research about the properties of maize fiber gels by Ayala-Soto *et al.* that the swelling capacity of maize fiber AX was 51 g water for every 1 g maize fiber AX, and this is inversely related to gel strength [13]. Also, as the ferulic acid concentration in the gels increased, so did the strength of the gels. This could be the result of increased formation of cross-linkages in the gels, which increased the mechanical strength of the gels as had been noted in multiple research findings [13] [52]. Another indication of the formation of cross-linkages in these gels was that as the time spent in the gelation process increased from 0 min to 120 min, the gel complex viscosity increased from 0.7 Pa s to 50.1 Pa s [13].

Paz-Samaniego *et al.* researched the development of gels developed from the AX extracted from maize wastewater after nixtamalization (cooking in an alkaline solution) [29]. When this was done, these gels had an initial increase in both the storage modulus and loss modulus before they plateau. This was indicative of the formation of cross-linkages forming between the ferulic acid and adjacent AX, which produced a three-dimensional gel network [29] [38]. When the cooking time during nixtamalization was decreased from 90 to 30 minutes, the ferulic acid content in the AX decreased [29]. The resulting gels exhibited minor elasticity in combination with a fragmented microstructure. The lower ferulic acid content retarded gel formation due to a decrease in the rate of cross-linking and caused in an increase in gelation time. An overview of these results is provided in **Table 1**.

## 2.9. Degradation of Arabinoxylan Gels

In addition to the rheology of AX gels being important to their end use, their resistance to degradation is also vital. Degradation of AX gels must be carefully

**Table 1.** Overview of the rheological properties of maize wastewater gels created by Paz-Samaniego *et al.* [29].

| Cooking time (h) | Ferulic acid (μg/mg AX) | Storage modulus (Pa) | Loss modulus (Pa) | Gelation time (min) |
|---|---|---|---|---|
| 24 | 0.012 | 78 | 13 | 26 |
| 4 | 0.008 | 32 | 8 | 40 |

controlled when they are used for any purpose. One common purpose where this is especially applicable is when AX is used in drug delivery systems for oral medications [3]. The complexity of AX and its ability to for cross-linkages and agglomerations facilitates resistance to degradation [53]. As AX is a dietary fiber, it is not digested in the small intestine, but it is fermented by the microbiota in the large intestine [4] [16]. One type of microorganism present in the large intestine that ferments polysaccharides including AX are *Bifidobacteria* [54] [55]. The enzymes that *Bifidobacteria* use to break down AX gels include endo-xylanases, $\beta$-xylosidases, and $\alpha$-L-arabinofuranosidases are shown in **Figure 5** [3].

Degradation of AX gels is closely related to their structures [53]. As the AX and ferulic acid concentrations increase, cross-linking increases and the structure becomes more compact [3] [53]. This results in less degradation due to a reduction in the AX surface area available for action by the enzymes produced by *Bifidobacteria*. As AX gels are broken down, they develop many cavities in their microstructure where they have been enzymatically broken down [3]. Arabinoxylan gels can be completely broken down in 36 hours by *Bifidobacteria* regardless of AX concentration. When this takes place, the gels completely collapse and no longer hold gas. In addition, after the initial breakdown of the surface of an AX gel, it can be broken down enzymatically from the inside out.

## 3. Summary

The molecular weight, substitution pattern, and substituent identities vary greatly depending upon AX extraction method and AX source. All these factors play a role in the rheological properties of AX gels, so they must be fully characterized and understood. In general, as molecular weight of the AX polymer serving as the basis for the gel increases, so does the intrinsic viscosity of said gel. In addition, as the A:X and ferulic acid content increase, so does cross-linking, which results in an increase in gel strength. Arabinoxylan gels are pseudo plastic and show an increase in both storage and loss moduli during the formation of

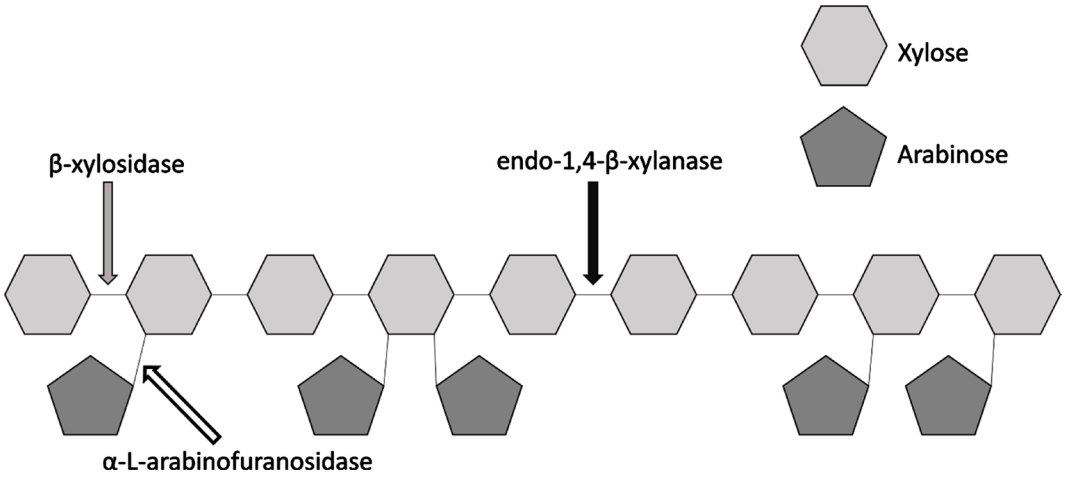



**Figure 5.** Action of three types of enzymes ($\beta$-xylosidase, $\alpha$-L-arabinofuranosidase, and endo-1,4-$\beta$-xylanase) on arabinoxylan according to Martinez-Lopez *et al.* [3].

cross-linkages, which result in a wide range of mechanical properties depending upon the gel formulation. Understanding the relationships between AX concentration and gelation time, swelling ratio, and gel strength allows for the development of gels with properties that could be tailored for specific purposes such as drug delivery. There are numerous chemical species that can be added to AX gels to modify their properties. However, some of these species including protein and $\beta$-glucan can cause phase separation in AX gels. This results in a decrease in mechanical strength but an increase in flexibility at those points. Ions such as $Cu^{2+}$ can be utilized to reduce the time required for gelling by increasing the rate of cross-linking in AX gels. All these structural characteristics are directly related to the ability of the gel to resist degradation and play an important role in the end use quality of AX gels. To further the use of AX gels, more research must be done on characterizing their chemical and mechanical characteristics. As there are numerous sources of AX, there are numerous opportunities to develop gels with a variety of mechanical properties. After further quantification and understanding of these gels, there will be many opportunities for their use.

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