Gel structure protects cereal β-glucan from radical induced degradation in aqueous systems

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ABSTRACT

The beneficial health effects of β-glucan are closely related to its rheological properties in the intestine, and therefore factors such as food composition and processing that may affect viscosity are of great interest in developing foods rich in β-glucan. We report a protective effect of gel structure on radical mediated degradation of β-glucan.

INTRODUCTION

β-glucan is a cell wall polysaccharide and a cereal dietary fibre composed of mixed linked glucose units. Once ingested at sufficient amounts (3 g/d) β-glucan helps in decreasing the total and LDL-cholesterol levels in the blood. It may also attenuate glucose absorption and insulin production after meals, and affect the feeling of satiety after meal. These health benefits are generally thought to be related to the rheological properties of β-glucan in the intestine. Further, once used as a structuring agent in foods, β-glucan molecules should stay in the desired size and shape in storage. Therefore, the physicochemical stability of β-glucan during processing and storing is fundamentally important in foods that are rich in β-glucan.

Cereal β-glucan is known to degrade in food processing (heating, baking) and subsequent storage1,2. The degradation is most often thought to be a result of enzymatic or acid hydrolysis. However, we have recently shown that β-glucan may be degraded also by radical oxygen species (ROS), namely hydroxyl radical, in systems where acid and enzymatic hydrolyses are prevented[3]. In this mechanism transition metals such as copper or iron react with hydrogen peroxide forming hydroxyl radicals in Fenton-type reaction (Eq. 1). Reducing agents such as ascorbic acid (AH_2 or in the reduced state AH) may keep the metal in the active reduced state (Eq. 2a), and are also capable of reducing dissolved oxygen and thus form hydrogen peroxide (Eq. 2b). This cycle of reactions is known to be responsible for polymer degradation, especially in aqueous systems [4].

$$Cu^{+}/Fe^{2+} + H_2O_2 \rightarrow OH^{\bullet} + OH^{-} + Cu^{2+}/Fe^{3+} \quad (1)$$

$$AH_2 + 2\ Cu^{2+}/Fe^{3+} \rightarrow AH + 2\ H^{+} + 2\ Cu^{+}/Fe^{2+} \quad (2a)$$

$$AH_2 + O_2 \rightarrow AH + H_2O_2 \quad (2b)$$

Degradation of oat β-glucan, as indicated by a reduced average molecular weight in a juice was demonstrated by Åman et al.[2]. They also showed that in a more solid matrix, such as a fruit/berry containing oat bran porridge, no significant degradation of β-glucan was observed. It was concluded that degradation in a juice was caused by acid hydrolysis. However, a very low pH with simultaneous heating is needed for acid

hydrolysis to cleave glycosidic bonds[5], and hence the degradation of β-glucan in juice may have been a result of ascorbic acid induced radical attack.

The aim of this study was to study the stability of β-glucan to see whether a gel matrix (the porridge compared to the beverage) could be a protective mechanism in radical induced degradation of β -glucan

MATERIALS AND METHODS

Extraction of β-glucan

β-glucan was extracted from oat bran concentrate (14 % β-glucan, 9 g) with water (150 ml) at 37 °C. The extract was centrifuged (10 min, 10000 rpm), soluble proteins were denatured by heating the extract in a boiling water bath, and centrifugation was repeated. The content (w/w) of β-glucan in the extract was 0.2 %.

Preparation of starch gels

Solid starch (waxy maize amylopectin, Amioca Powder, Garcill) was mixed to the extract at 0, 1, 2.5 and 4 % concentrations and the starch was gelatinized under mixing using a Rapid Visco Analyzer instrument to heat the mixture to 95 °C for 10 min. Ascorbic acid (2 mM) was added to the mixture after cooling, and the samples were stored overnight at +6 °C.

Dynamic rheology

Oscillatory measurements were obtained from the different extract+starch -systems right after cooling. Frequency sweeps were determined with a rheometer (ThermoHaake RheoStress 600, Thermo Electron GmbH, Dreieich, Germany) over a frequency rate 0.05-50 using cone and plate geometry (60/1°). The amplitude was determined by amplitude sweep (1Hz)of the extract to be 0.02 Pa.

Viscosity measurements

The AH_2-treated and control samples stored overnight were treated with Termamyl (Megazyme) to hydrolyse starch. Viscosities of the remaining β-glucan were analysed using the rheometer. Flow curves were obtained over a shear rate range of 0.3-300-0.3 s^{-1} using cone and plate geometry (60/1°). The ratio η(AH_2-treated)/ η(control without AH_2) was taken to indicate OH-radical induced degradation of β-glucan.

RESULTS AND DISCUSSION

Viscoelastic behaviour of starch systems

The sample containing 4 % starch showed weak gel-like behaviour. The other samples containing less starch were viscoelastic solutions, with crossover points (G'=G'') moving towards y-axis with increasing starch content (9, 4.5 and 3 rad/s in β-glucan extract with 0 %, 1 % and 2.5 % of starch respectively) (Fig. 1). Also the values of both modulus increased with increasing starch content and the slope of G'' shifted from 1 toward 2 approaching to G' at low frequencies. All this indicated flow restriction and thus higher tendency for gel-like behaviour with increasing starch concentration.

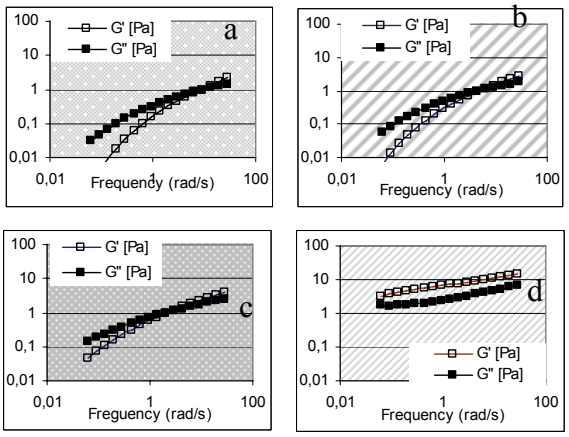
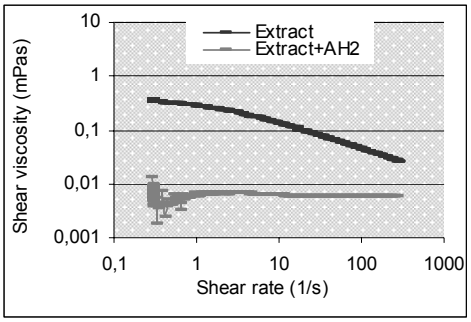


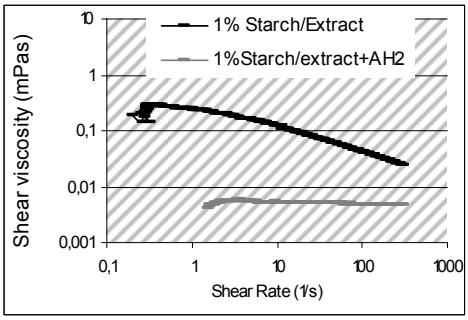
Figure 1. The frequency sweeps of a) extract b) extract+1% starch c) extract+2.5% starch d) extract+4% starch right after cooling (+6 °C)

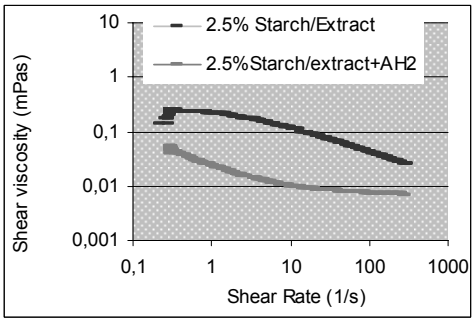
Viscosity of β-glucan

The flow curves of β-glucan showed shear thinning behaviour for all the control samples (without ascorbic acid) after starch hydrolysis without any significant differences between them (Fig. 2). The

ascorbic acid treatment degraded β-glucan in all systems, but the degradation was less in the systems containing 2.5% and 4% starch than in systems with 0% and 1% starch. In samples with 0 and 1% starch treated with AH_2, the viscosity behaviour was Newtonian which indicates the reaching of critical concentration due to depolymerisation of β-glucan.. The flow properties of sample containing 4% starch remained after AH_2-treatment and only the level of shear viscosity decreased. The effect of increased maltose content from hydrolysed starch on viscosity was not taken into account.







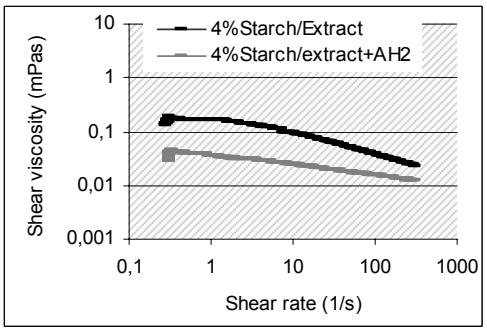


Figure 2. Flow curves of samples; extract, 1% starch+extract, 2.5% starch+extract, 4% starch+extract (black curves) after storage (1 day) and starch hydrolysis compared to ascorbic acid treated sample (grey curves).

The decrease of apparent viscosity at 10 s^{-1} (slow pouring) is shown in Fig. 3. The ratio of $\eta_{10s\text{-}1}(AH_2\text{-treated})/\eta_{10s\text{-}1}$ (control) was figured out as a proportion of the β-glucan, which was remained in storage of AH_2-treated samples. The addition of 1% starch to the extract appeared did not to protect the β-glucan in extract of ascorbic acid induced degradation (5% of η remained). The addition of 2% starch could protect about 10% and after addition of 4%, 25% of the viscosity of β-glucan was left. In other words, the more starch was added, the less β-glucan was degraded.

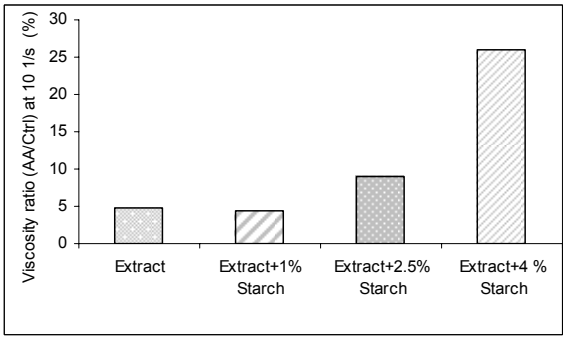


Figure 3. The ratio of apparent viscosities (at 10 s^{-1}) of control and ascorbic acid treated samples after storage (1 day) in different starch contents:

When the results of the remaining viscosity (Fig. 3) are related to the oscillatory tests (Fig. 1), a correlation can be

observed. The addition of 1% starch did not protect the β -gucan from AH_2-induced degradation and had neither a significant affect on the gelation properties when compared to the exctract. The addition of 2 % starch decreased the flow in the system and similarly the AH_2-induced β-glucan degradation was decreased. Only the 4 % starch containing sample showed solid elastic properties and also the degradation of β-glucan was slowed down significantly only in this system.

A correlation between the flow restriction and the retarded degradation of β-glucan was found. It appears that a gel-like structure in cereal-based fruit/berry snack products (shots) may be a factor protecting β-glucan from the ROS-induced degradation.

ABBREVIATIONS

AH_2, ascorbic acid; $AH^{\cdot}$ reduced ascorbic acid; ROS, radical oxygen species

ACKNOWLEDGMENTS

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