

Processing and formulation effects on rheological behavior of barley β -glucan aqueous dispersions

H. Vaikousi, C.G. Biliaderis *

^a Department of Food Science and Technology, School of Agriculture, Aristotle University, GR-540 06, Thessaloniki, Greece

Received 19 January 2004; accepted 8 April 2004

Abstract

A freeze–thaw cycling process applied to barley β -glucan aqueous dispersions resulted in network structure development, which remained intact after thawing in both acidic and neutral conditions. The effects of freeze–thaw cycling were milder in the presence of sucrose where β -glucans were less prone to cryogel formation, giving weaker cryostructures. The effect of three operating factors (β -glucan content, sucrose content and salt content) and their interactions on viscosity at shear rates of 10, 50 and 125 s⁻¹ was studied using response surface methodology. Significant positive linear effects were identified for all the factors on the first two models, while salt was not significant for the response at 125 s⁻¹. The β -glucan also exhibited significant negative quadratic effects for all three responses. Significant negative interactions were observed between β -glucan and sucrose, and β -glucan and salt for the viscosity at 10 and 50 s⁻¹, while for the viscosity at 125 s⁻¹, only the interaction between β -glucan and sucrose was significant. Response surface methodology and a second order regression model were used for the study of three factors (pH, temperature and time) influencing the viscosity of β -glucan dispersions of a low and a high molecular weight sample, following acid hydrolysis. Significant linear effects on viscosity of the low and high molecular weight samples were obtained for all the factors. A significant positive interaction effect was observed between pH and time for the viscosity of the lower molecular weight sample, while time exhibited a significant negative quadratic effect for the response of the high molecular weight sample. Acid hydrolysis had a stronger impact on viscosity reduction of the high molecular weight sample.

© 2004 Elsevier Ltd. All rights reserved.

Keywords: (1 → 3)(1 → 4)- β -D-glucan; Gelation; Freeze–thaw; Cryogels; Rheology; Flow behavior; Response surface methodology; Mathematical modeling; Acid hydrolysis

1. Introduction

The (1 → 3)(1 → 4)- β -D-glucans are cell wall polysaccharides of cereal endosperm and aleurone cells. Generally, they are linear polysaccharides containing a single type of monosaccharide, i.e., β -D-glucose. Most β -D-glucans contain approximately 30% (1 → 3)- and 70% (1 → 4)-linkages that are organized mainly into blocks of two or three consecutive (1 → 4) residues sep-

arated by (1 → 3)-linked residues. The β -(1 → 3)-linked cellobiosyl unit is the major building block (58–72%), followed by the β -(1 → 3)-linked cellotriosyl unit (tetrasaccharide). The (1 → 4) linkages occurring in groups greater than three are also present, but at an extremely lower frequency (Cui, 2001). Despite the similarity in structural features of β -glucans from different origins, as studied by ¹³C NMR, significant variations are revealed in their molecular weight and oligosaccharide composition obtained by enzyme hydrolysis with lichenase (Cui, 2001; Cui, Wood, Blackwell, & Nikiforuk, 2000; Wood, Weisz, & Blackwell, 1991). Thus, the M_w values reported in the literature for cereal β -glucans vary

* Corresponding author. Tel.: +30 2310 998785/471467; fax: +30 2310 471257.

E-mail address: biliader@agro.auth.gr (C.G. Biliaderis).

widely within the range of 0.065–3, 0.009–5.4, and 0.25– 0.7×10^6 for oat, barley and wheat, respectively (Beer, Wood, & Weisz, 1997; Böhm & Kulicke, 1999; Cui, 2001; Cui & Wood, 2000; Cui et al., 2000; Gomez, Navarro, Manzanares, Horta, & Carbonell, 1997; Grimm, Krüger, & Burchard, 1995; Lazaridou, Biliaderis, & Izydorczyk, 2003; Saulnier, Gévaudan, & Tribault, 1994; Varum & Smidsrod, 1988; Wood et al., 1991).

In the USA, the Food and Drug Administration (FDA) has accepted that oat β -glucan is a functional bio-active ingredient, allowing a health claim for an association between consumption of oatmeal, rolled oats and oat bran, and reduced risk of coronary heart disease (Cui & Wood, 2000). In clinical studies, β -glucans were shown to reduce serum cholesterol levels and attenuate postprandial blood glucose and insulin responses in a viscosity related fashion (Kahlon, Chow, Knuckles, & Chiu, 1993; Klopfenstein, 1988). Moreover, β -glucans can find use in the food industry as natural hydrocolloids due to their gelling capacity and ability to increase the viscosity of aqueous solutions (Izydorczyk & Biliaderis, 2000). It has been claimed that they may modify texture and appearance of gravies, salad dressings and ice creams (Wood, 1986), or act as fat mimetics in calorie reduced foods (Inglett, 1990).

Aqueous solutions of cereal β -glucans can form network structures under certain conditions. Most of the studies examined the mechanism and kinetics of β -glucan gelation at temperatures above 0 °C, as a function of the molecular size, fine structure, polysaccharide concentration and gel curing temperature (Böhm & Kulicke, 1999; Cui & Wood, 2000; Cui et al., 2000; Lazaridou et al., 2003; Vaikousi, Biliaderis, & Izydorczyk, 2004). However, there are very few studies on the gelling ability of cereal β -glucans at sub zero temperatures. The first gelatinous or fibrous precipitate of barley β -glucans was produced by Morgan and Ofman (1998) via a freeze–thaw cycling process. In another study, Lazaridou and Biliaderis (2004) tried to reveal structure and molecular size effects on β -glucan gelation phenomena during a repeated freezing–thawing process at low initial polysaccharide concentrations. Their findings included macroscopic morphological observations of the gelled materials, as well as yield, thermal, and mechanical properties of the formed cryostructures, as influenced by initial solution concentration, number of freeze–thaw cycles and β -glucan structural features.

Despite the limited knowledge for cryogelation phenomena in cereal β -glucans, the physical changes occurring during freezing, frozen storage and subsequent thawing procedures are a well known phenomenon for aqueous solutions of many synthetic and natural polymers such as polyvinyl alcohol (PVA), xanthan, locust bean gum, amylopectin, amylose and maltodextrins (Damshkaln, Simenel, & Lozinsky, 1999; Dea et al., 1977; Giannouli & Morris, 2003; Lozinsky, Damshkaln,

Brown, & Norton, 2000a, Lozinsky, Damshkaln, Brown, & Norton, 2000b, 2000c, 2002; Tanaka, Hatakeyama, & Hatakeyama, 1998). Many researchers have emphasized the improved functionality of the cryogels produced by these systems compared with the gels developed with non-cryogenic treatments, making them applicable in the medicinal, biotechnology and food industries (Lozinsky & Plieva, 1998; Patmore, Goff, & Fernandes, 2003; Wan, Campbell, Zhang, Hui, & Boughner, 2002).

As the demand for ready to eat items rises, a variety of frozen food products are continually introduced in markets. However, freezing is not a guarantee of an indefinite shelf life for food products; it is only a process to reduce or limit temporarily the rate of different phenomena (physical, chemical and enzymatic reactions) occurring in the unfrozen phase of a frozen product. Furthermore, frozen storage of food and temperature fluctuations during storage have been associated with loss of integrity on thawing and damage to food texture through the disruption of food structure, due to ice recrystallization. The observed changes in the viscoelastic properties of foods that have undergone freezing or freeze–thaw treatments are of practical interest for their acceptance and consumption, and may be controlled by modifications in the composition of food products. Changes in the composition can lead to changes in the distribution and size of ice crystals formed with direct impact on product quality. Polymer hydrocolloids are frequently used as additives to control the texture and stability of frozen foods (Goff, Caldwell, Stanley, & Maurice, 1993; Levine & Slade, 1988; Lo & Ramsden, 2000), while differences have been reported in their stabilizing action related to the specific structure and molecular mass of each polysaccharide. In the case of foods, various ionic substances, as long as such solutes are components of liquid media, influence the flow behavior of thawed products.

In the present study, the effect of a freeze–thaw cycling process on the rheological behavior of β -glucan dispersions in acidic and neutral environments and in the presence of solutes such as sucrose was examined. Moreover, in food manufacturing the viscosity of liquid foods largely contributes to the sensory properties and usability of the final products, and therefore information on interactions between different food ingredients during processing is of great importance. In this context, the viscosity dependence of the continuous phase of a mayonnaise type dispersion, where β -glucans would act as stabilizer, on different polysaccharide, sucrose and salt content combinations was examined, using response surface methodology. Finally, the effect of acid hydrolysis on the flow behavior of aqueous β -glucan dispersions that are subjected to heat treatment, was modeled; the pH, temperature and time effects on solution rheology of two β -glucan samples differing in molecular

weight were evaluated using response surface methodology.

2. Materials and methods

2.1. Materials

Three water-soluble barley β -D-glucan samples (BGL110, BGL140 and BGL250) differing in molecular weight were used in this study. The above preparations were derived from a mixture of two Greek barley cultivars and further purified according to the protocol described by Vaikousi et al. (2004). In that study, the molecular size of the samples was estimated with high performance size exclusion chromatography (HPSEC) combined with a refractive index detector (RI), and found to be 110, 140 and 250×10^3 Da, for BGL110, BGL140 and BGL250, respectively. In addition, BGL110, BGL140, and BGL250 preparations were characterized for their high β -glucan content (89.3%, 91.8% and 95% d.b.) and low protein levels (1.40%, 0.61% and 1.23% d.b.).

Sucrose, Sodium Chloride (salt), Glacial acetic acid and phosphoric acid were provided either from Sigma–Aldrich Co. (Gillingham, Dorset) or from Merck (Darmstadt, Germany). Double distilled water was used for preparation of the solutions.

2.2. Preparation of samples

The behavior of β -glucan solutions at sub-zero temperatures and the formation of network structures (cryogels or cryostructures) caused by a freeze–thaw cycling process was the first objective of this study. Dispersions of BGL110 were prepared by dissolution of β -glucan (4% w/w) in double distilled water under mild stirring at 85 °C until complete solubilization of the material. The solutions were cooled at room temperature and water was added in order to give the desired concentration as water losses occurred due to evaporation. The pH of the dispersions was either neutral (pH 7.0) or was adjusted to pH 2.0 with 2 N H_3PO_4 after the cooling process and before the addition of water. The effect of added solutes, such as sucrose (30% w/w) in β -glucan aqueous dispersions was, also, investigated under both acidic (pH 2.0) and neutral (pH 7.0) conditions. The β -glucan dispersions, immediately after their preparation, were poured into cylindrical plastic molds (each one contained 6 ml of the prepared solution), closed with their plastic lids and put in a freezer at -30 °C, where they were stored for 2 days. Following storage, the samples were thawed at room temperature for 2 h and subsequently were frozen again for another 2 day period. The above process of holding samples at -30 °C for 2 days and then at room temperature for 2

h is defined as one freeze–thaw cycle. Samples were subjected up to 10 repeated freeze–thaw cycles while measurements were performed in triplicate after 1, 2, 6 and 10 cycles. At the freezing temperature of -30 °C samples containing 30% w/w sucrose were also able to freeze.

Dispersions of different compositions (Section 2.4) containing β -glucan (BDL140), sucrose and salt (sodium chloride) were prepared in order to study the flow behavior of the continuous phase of a mayonnaise type product, in which β -glucans could be used as a stabilizer of the oil in water dispersion. Appropriate portions of BGL140 were dissolved as described above, cooled and then certain amounts of sucrose and salt were incorporated into them, at room temperature. All preparations contained a fixed vinegar concentration (acetic acid, 2% v/w) as the basic constituent of the aqueous phase of such product type. Viscosity measurements were made immediately after the preparation of samples to avoid aggregation phenomena that would lead to misleading conclusions.

Finally, the effect of three operating factors, pH, temperature and time (Section 2.4), on the extent of acid hydrolysis of two barley β -glucan samples of different molecular weight was examined. Dispersions of BGL140 and BGL250 at a concentration of 4% w/v were dissolved at 85 °C until complete solubilization and cooled at room temperature. The pH was adjusted with 2 N H_3PO_4 according to the levels induced by the experimental design used, and then poured into hermetically sealed glass vials. Samples were heated in water baths at a specified temperature for different time intervals. Exerting the glass vials from the water baths followed by rapid cooling to 20 °C immediately stopped acid hydrolysis of the samples. Flow behavior of the acid hydrolyzed samples was examined immediately as described below.

2.3. Rheological measurements

The flow behavior and viscoelastic properties of barley β -glucan dispersions were studied by a rotational Physica MCR 300 rheometer (Physica Masstechnik GmbH, Stuttgart, Germany) using either a parallel plate geometry (25 mm diameter and 1 mm gap) or a double gap cylindrical geometry, depending on the nature of the material tested, gel or liquid, respectively; temperature was regulated by a Paar Physica circulating bath and a controlled peltier system (TEZ 150P/MCR) with an accuracy of ± 0.1 °C. The data of the rheological measurements were analyzed with the supporting software US200 V2.21. Two types of rheological measurements were performed: (a) flow behavior was obtained by measuring steady shear viscosity (η) over a range of shear rates, between 0.1 and 1200 s^{-1} at 20 ± 0.1 °C; (b) oscillatory measurements of G' (storage modulus), G'' (loss modulus) were performed with a strain of

0.1% and a range of frequencies (0.1–100 Hz) at 20 ± 0.1 °C. In the case of dispersions that were subjected to the freeze–thaw cycling process, the viscoelastic properties and flow behavior of fresh solutions (after their preparation and before putting them in the freezer) were examined using the double gap cylindrical geometry. As the freeze–thaw cycling process was repeated, there was an obvious morphological differentiation in the thawed samples. Insoluble precipitates that progressively converted to more compact cryogels, with increasing freeze–thaw cycles, were analyzed by using the parallel plate geometry. Separating the gelled material of the liquid phase by filtration, the samples were placed onto the lower plate of the rheometer, and dynamic measurements were performed at 20 °C. On the other hand, steady shear viscosity measurements of the thawed β -glucan dispersions or liquid-like cryostructures (different replicate of the same batch preparation) were obtained using the double gap cylindrical geometry fixture.

2.4. Experimental design and statistical analysis

For multivariate analysis of the flow behavior of barley β -glucan aqueous dispersions two experimental designs were used. The first design examined the viscosity as influenced by different levels of β -glucan, sucrose and salt. Each of these three independent variables was tested at three levels (–1, 0, 1) and 20 experiments were conducted according to the face central composite statistical design ($\alpha = 1$) used, Table 1. The actual, high and low levels of the factors used in the experimental design were chosen according to some formulation protocols used by the food industry in the development of mayonnaise type of products (Tressler & Woodroof, 1976). A full term second order polynomial response surface model was fitted to each of the response variables, namely log of viscosity ($\text{Log } \eta$), at three different shear rates, 10, 50 and 125 s^{-1} in order to evaluate the flow behavior of the material in a variety of shear rate conditions. The shear rates between 0.1 and 10 s^{-1} approximate a normal Brookfield viscometer reading, values of $10\text{--}100 \text{ s}^{-1}$ approximate tumbling or pouring, a value of 50 s^{-1} approximates the shear rate encountered in the mouth during chewing and the range of $100\text{--}1000 \text{ s}^{-1}$ is encountered for most of home mixers (Krumel & Sarkar, 1975). The second order response function for the three quantitative factors is given by the equation

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3,$$

where X_1 , X_2 , X_3 , are the levels of the independent variables in their coded values as shown in Table 1, while β_0 , β_1 , \dots , β_{23} represent the estimated regression coefficients, with β_0 having the role of a scaling constant;

Table 1

Experimental design and levels of factors in actual and coded values for the study of three constituents affecting the viscosity of the aqueous phase of a mayonnaise type dispersion.

Factors	Name (% w/w)	Levels		
		–1	0	1
X_1	β -glucan content	1	3.5	6
X_2	Sucrose content	10	25	40
X_3	Salt content	3	7.5	12
Run	Factors			
	β -glucan content (% w/w)	Sucrose content (% w/w)	Salt content (% w/w)	
1	1	10	3	
2	1	10	12	
3	1	25	7.5	
4	1	40	3	
5	1	40	12	
6	3.5	25	3	
7	3.5	10	7.5	
8	3.5	25	12	
9	3.5	40	7.5	
10	3.5	25	7.5	
11	6	10	3	
12	6	10	12	
13	6	25	7.5	
14	6	40	3	
15	6	40	12	
16	3.5	25	7.5	
17	3.5	25	7.5	
18	3.5	25	7.5	
19	3.5	25	7.5	
20	3.5	25	7.5	

β_1 , β_2 , β_3 represent the linear effects, β_{11} , β_{22} , β_{33} the quadratic effects and β_{12} , β_{13} , β_{23} the interaction effects. The statistical analysis of the data was performed using coded units with the aid of the MINITAB Statistical Software, Release 13.1.

With the second experimental design used in this study it was attempted to evaluate the effect of acid hydrolysis on the viscosity of two β -glucan samples (BGL140 and BGL250). Three experimental factors related to acid hydrolysis were examined (pH of β -glucan dispersions, temperature and time of heating) each one at five levels. Table 2 represents the range of pH, temperature and time values used to monitor the response variables, namely viscosity, η , of BGL140 and BGL250 at 37 and 1 s^{-1} , respectively, shear rate regions where the viscosity of the tested acid hydrolyzed samples exhibited Newtonian behavior as well as the 20 experiments that were performed according to the central composite statistical design ($\alpha = 1.682$) used. The high and low levels of the three independent variables were chosen according to experimental trials (not shown here) which revealed that the viscosity drop during acid hydrolysis was negligible at pH values higher than 4.5, at temperatures lower than 70 °C and when samples were heated for time intervals shorter than 15 min. In

Table 2
Experimental design and levels of factors in actual and coded values for the study of the viscosity of β -glucan dispersions following acid hydrolysis

Factors	Name	Levels				
		-1.682	-1	0	+1	+1.682
X_1	pH	2.66	3	3.5	4	4.34
X_2	Temperature ($^{\circ}$ C)	69.9	75	82.5	90	95.1
X_3	Time (min)	3.68	18	39	60	74.3
Run	Factors					
	pH	Temperature ($^{\circ}$ C)	Time (min)			
1	2.66	82.5	39			
2	3	75	18			
3	3	75	60			
4	3	90	18			
5	3	90	60			
6	3.5	69.9	39			
7	3.5	82.5	3.68			
8	3.5	82.5	74.3			
9	3.5	82.5	39			
10	3.5	82.5	39			
11	3.5	82.5	39			
12	3.5	82.5	39			
13	3.5	82.5	39			
14	3.5	82.5	39			
15	3.5	95.1	39			
16	4	75	18			
17	4	75	60			
18	4	90	18			
19	4	90	60			
20	4.34	82.5	39			

addition, the pH range used in this study was typical of the pH usually met in acidic food products like fruit and tomato juices, while temperature and time ranges reflected well the conditions under which the pasteurization process of such products occurs in most of the food industries. Response surfaces were developed using the same quadratic model as before. Analysis of variance was used to detect significant effects at $p \leq 0.05$.

3. Results and discussion

3.1. Cryogelation of barley β -glucans

Aqueous β -glucan solutions with or without added sucrose, at neutral or acidic environments underwent physical changes as a result of freezing, frozen storage, subsequent thawing, and repeated freeze–thaw cycling processes. The above cryogenic treatment caused the formation of the so-called β -glucan cryogels. The cryostructures formed differed in their morphological characteristics and the time period in which they were formed; these depended on the pH, the composition of the initial solution, and the number of freeze–thaw cycles. With increasing number of freeze–thaw cycles, preparations of BGL110 containing only the polysaccharide

(4% w/w) at both pH conditions tested, were gradually transformed from concentrated viscous solutions (before freezing and after the first freeze–thaw cycle) through cryoprecipitate matters with small insoluble particles, which were suspended in the bulk liquid, into finally compact cryogels with a transparent upper liquid layer. Preparations of BGL110, where sucrose was added (30% w/w), exhibited similar changes of the structured matter, but with a definitely smaller transformation rate as cryogelation occurred only after six or 10 repeated freeze–thaw cycles for samples with pH 2.0 and 7.0, respectively. In addition, these cryoprecipitates were characterized as less strong and weaker cryogels, compared to the structures formed by solutions that did not contain sucrose. The cryostructuring property of cereal β -glucans has recently been reported by Lazaridou and Biladeris (2004), in a study where both structural and molecular size effects were tested. Previous studies of polysaccharide cryogelation have dealt with locust bean galactomannan (Dea et al., 1977; Lozinsky et al., 2000a; Tanaka et al., 1998), amylose and amylopectin (Lozinsky et al., 2000b, Lozinsky, Damshkaln, Brown, & Norton, 2000c), xanthan (Giannouli & Morris, 2003) and maltodextrins (Lozinsky, Damshkaln, Brown, & Norton, 2002). According to Lazaridou and Biladeris (2004) cereal β -glucan cryogels are physically crosslinked gels whose three-dimensional structure is stabilized mainly by multiple inter- and intra-chain hydrogen bonds in the junction zones of the polymeric network. In the case of cryostructuring processes at sub zero temperatures, the pure solvent is crystallized, while the solutes are concentrated in unfrozen regions of the system's bulk, or in the so called "unfrozen liquid microphase". The cryotropic gelation events proceed here because of the cryoconcentration phenomena; the polymer–polymer interactions are strengthened as compared with the initial liquid solution, thus favoring intermolecular H-bonding and the formation of junction zones. Cryoconcentration phenomena seem to govern the cryogelation of other polymer systems by shifting the critical gelling concentration towards lower values compared with the concentration values that those polysaccharides need for network formation at temperatures above zero. This has been previously reported for locust bean gum (Lozinsky et al., 2000a; Tanaka et al., 1998), maltodextrins (Lozinsky et al., 2002), amylose and amylopectin (Lozinsky et al., 2000b, 2000c), suggesting that freezing simply accelerated a process that would occur much more slowly in unfrozen solutions. However, cryogelation of xanthan that has been studied by Giannouli and Morris (2003) seemed to involve a different process that does not occur in unfrozen solutions of the same polymer concentration, even on a much longer time scale.

The drastic change of all barley β -glucan preparations from liquid to gel was clearly shown by dynamic and steady shear rheological measurements. The mechanical

spectra of the thawed β -glucan dispersions, with or without added sucrose, under acidic and neutral conditions, with increasing freeze–thaw cycles (0–10), are illustrated in Fig. 1. The frequency dependence of storage modulus, G' , and loss modulus, G'' , of the four different dispersions immediately after their preparation and before putting them in the freezer (0 cycles), revealed the viscous or liquid-like character of the system. Fresh β -glucan dispersions behaved as random coil polysaccharides at the concentrated regime, that is G'' was greater than G' and both moduli increased with increasing frequency over the frequency-range tested. However, the expected G' – G'' crossover showing the solid-like behavior at high frequencies was not seen and this presumably occurs beyond 100 Hz, as happens to all sample preparations with low polysaccharide concentrations or low molecular weight. The spectra of the two dynamic parameters remained typical of concentrated polymer solution even after the first freeze–thaw cycle for the samples that contained only the polysaccharide (at pH 2.0 and 7.0), whereas after the second freezing–thawing cycle there was a gradual transition from solution to a gel system (Fig. 1(a) and (c)); i.e. the G' was higher than G'' and both moduli showed very little frequency dependence (particularly at low frequencies), which means that the visco-

elastic properties are dominated by the established network structure. Also, the elastic character (G') and viscous response (G'') increased with increasing number of freeze–thaw cycles and became almost constant after the sixth cycle. At the end of the frozen storage and the freezing–thawing treatment (10 cycles), G' was about one order of magnitude higher than the G'' tending towards the same equilibrium value for both pH environments, and indicating that the formation of strong cryostructures was independent of the initial pH of the β -glucan samples. The increase of G' with increasing number of freezing–thawing cycles and subsequently the strengthening of the resultant cryogels has also been reported for other cryostructures of cereal β -glucans (Lazaridou & Biliaderis, 2004), locust bean gum (Tanaka et al., 1998), xanthan (Giannouli & Morris, 2003), and galactomannans in ice cream model systems (Patmore et al., 2003). This behavior has been attributed to additional cross-linking of polymer chains as a result of repeated freeze–thawing cycles. The same freezing–thawing process was carried out for the aqueous dispersions of 4% w/w β -glucan containing sucrose as co-solute at a level of 30% w/w in order to examine the effect of polyol on cryogelation of the polysaccharide. Frequency sweeps of storage and loss moduli were measured at pH

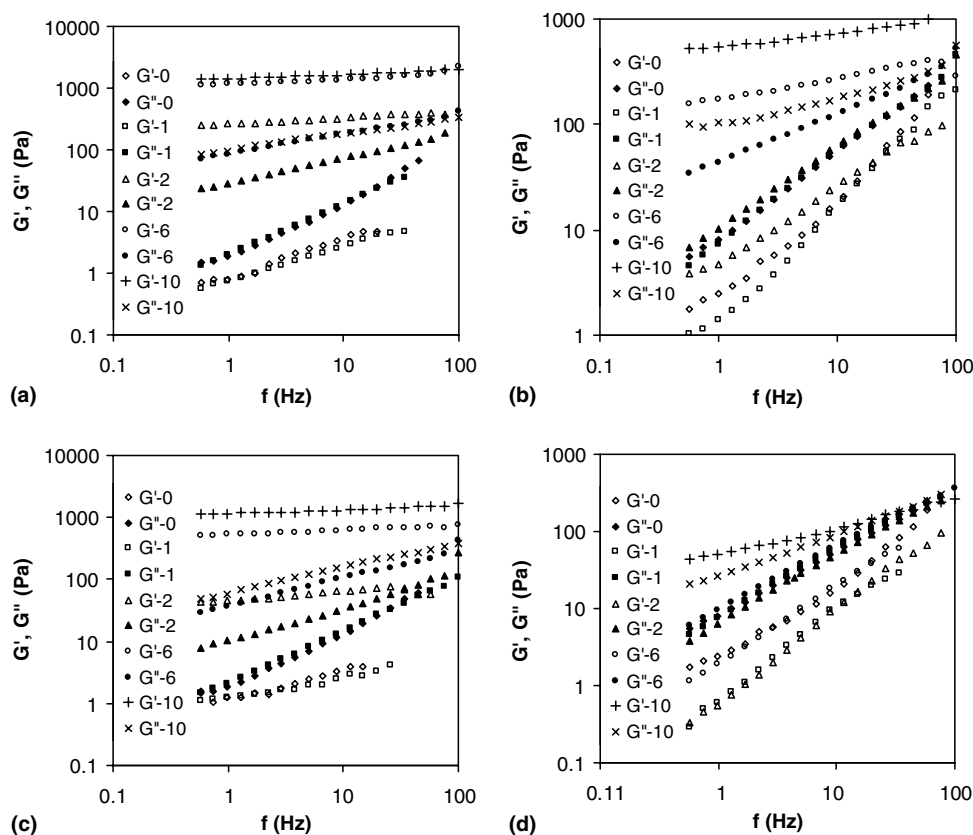


Fig. 1. Mechanical spectra of β -glucan dispersions (BGL110, 4% w/w) at 20 °C, after 0–10 freeze–thaw cycles; 4% w/w β -glucan, pH 2.0: (a) 4% w/w β -glucan and 30% w/w sucrose, pH 2.0; (b) 4% w/w β -glucan, pH 7.0; (c) 4% w/w β -glucan and 30% w/w sucrose, pH 7.0; (d) freezing at -30 °C for 48 h, thawing at room temperature for 2 h.

2.0 and 7.0, as shown in Fig. 1(b) and (d). Only small changes were observed in G' , G'' -frequency curves before and after the first two and six cycles of freezing–thawing treatment for acidic and neutral dispersions, respectively. The viscous response was greater than the elastic parameter at all frequencies tested, while there was a higher dependence on frequency for both dynamic moduli compared with the preparations where no sucrose was added. With increasing number of freezing–thawing cycles, the two responses slightly increased whereas the domination of the elastic character of the system and the subsequent cryogel formation occurred after six and 10 repeated freeze–thaw cycles for the dispersions with pH 2.0 and 7.0, respectively. In addition, the difference between G' and G'' at the end of the freezing–thawing treatment was much smaller and both moduli reached lower final values especially for the preparations at neutral conditions (Fig. 1(d)), suggesting that sucrose tended to nullify the effect of freeze–thaw cycling on the extent of cryogelation or that the network structure was weakened by the addition of sucrose. The presence of sucrose in β -glucan aqueous dispersions probably caused a depression in the freezing point of the system with a consequent decrease in the extent of ice crystallization. The resultant increase in the volume of the unfrozen liquid microphase regions of the system's bulk phase, due to the additional presence of sugar, caused a decrease in the concentration of the polymer macromolecules in these unfrozen inclusions, thus weakening the effective polymer–polymer interactions. Alternatively, in the presence of sucrose the molecular mobility of the aqueous phase at sub-zero temperatures ($-30\text{ }^{\circ}\text{C}$) is lower compared to the system where only the hydrocolloid is present; i.e. the T_g' is elevated by the sugar (Levine & Slade, 1988) and thereby chain mobility of the polysaccharide is further reduced. However, the repeated freezing–thawing process finally seems to result in a polymer chain conformation that promotes intermolecular associations and formation of junction zones giving a three dimensional weak gel cryostructure. The effect of sucrose addition on strength of β -glucan cryogels are in close agreement with the findings of Giannouli and Morris (2003) who reported that the incorporation of sucrose at concentrations above 10 wt% caused large reductions in both dynamic moduli (G, G'') of xanthan cryogels. In contrast, cryogels of locust bean gum increased in strength when sucrose or other sugars were added up to a concentration of 50 wt%, with reductions in moduli occurring only at higher concentrations. Moreover, it has been shown that incorporation of sucrose at high concentrations promotes gelation phenomena of locust bean gum without the need to go through the freeze–thaw process (Dea et al., 1977; Richardson & Norton, 1998).

The transition of β -glucan dispersions from solution to a gel state was further confirmed by steady shear rhe-

ological measurements. The effect of the freeze–thaw cycling process on the apparent viscosity of the β -glucan preparations was recorded as a function of increasing shear rate (Fig. 2). The freshly prepared samples of BGL110, measured immediately after their preparation (0 cycles), revealed typical pseudoplastic flow behavior. That is, the viscosity exhibited a Newtonian-like plateau at the low shear rate region followed by a reduction (shear thinning behavior) at high shear rates, which was more pronounced for the more concentrated dispersions that contained sucrose. However, as the storage time at subzero temperatures and the repeated freezing–thawing cycles increased, the flow curves exhibited strong shear thinning behavior at low shear rates, indicating the presence of some kind of three-dimensional network structures at rest. The latter flow curve profiles are similar to the patterns given by ordered polymers such as xanthan and gellan gum aqueous solutions that show weak-gel behavior. Xanthan exists in solution in a rigid, ordered chain conformation and exhibits a shear thinning-behavior with no evidence of Newtonian plateau at low shear rates, i.e. typical pseudogel-like behavior (Morris, 1984), while in the case of gellan gum it has been found that at low temperatures and in the presence of salts such as CaCl_2 or KCl , weak gels are formed showing shear thinning behavior and no Newtonian region at low shear rates (Miyoshi & Nishinari, 1999). Barley β -glucan samples of low molecular weight also exhibited unusual shear thinning behavior at low shear rates when stored at room temperature, due to their high tendency for molecular aggregation (Vaikousi et al., 2004). The above departure from the typical pseudoplastic flow behavior of β -glucan preparations occurred after the second freeze–thaw cycle for the dispersions containing only the polysaccharide, and the shear thinning behavior was more intense with increasing number of freeze–thaw cycles (Fig. 1(a) and (c)). In contrast, there was a significant delay of the shear thinning behavior at low shear rates for the samples where sucrose was added and finally this was observed after six and 10 repeated cycles for the acidic and neutral dispersions, respectively. These observations were in accord with the results obtained from the mechanical spectra. Closer inspection of Fig. 2 also reveals that viscosity reached higher values and the slopes of viscosity plots were considerably steeper for the samples containing only β -glucan. On the other hand, when sucrose is present as co-solute the viscosity breakdown due to shearing is less for the respective cryostructures.

3.2. Effect of the presence of sucrose and salt on apparent viscosity of the aqueous phase of a mayonnaise type dispersion containing barley β -glucans

The effect of three operating variables (i.e. β -glucan, sucrose and salt content) each at three levels and their

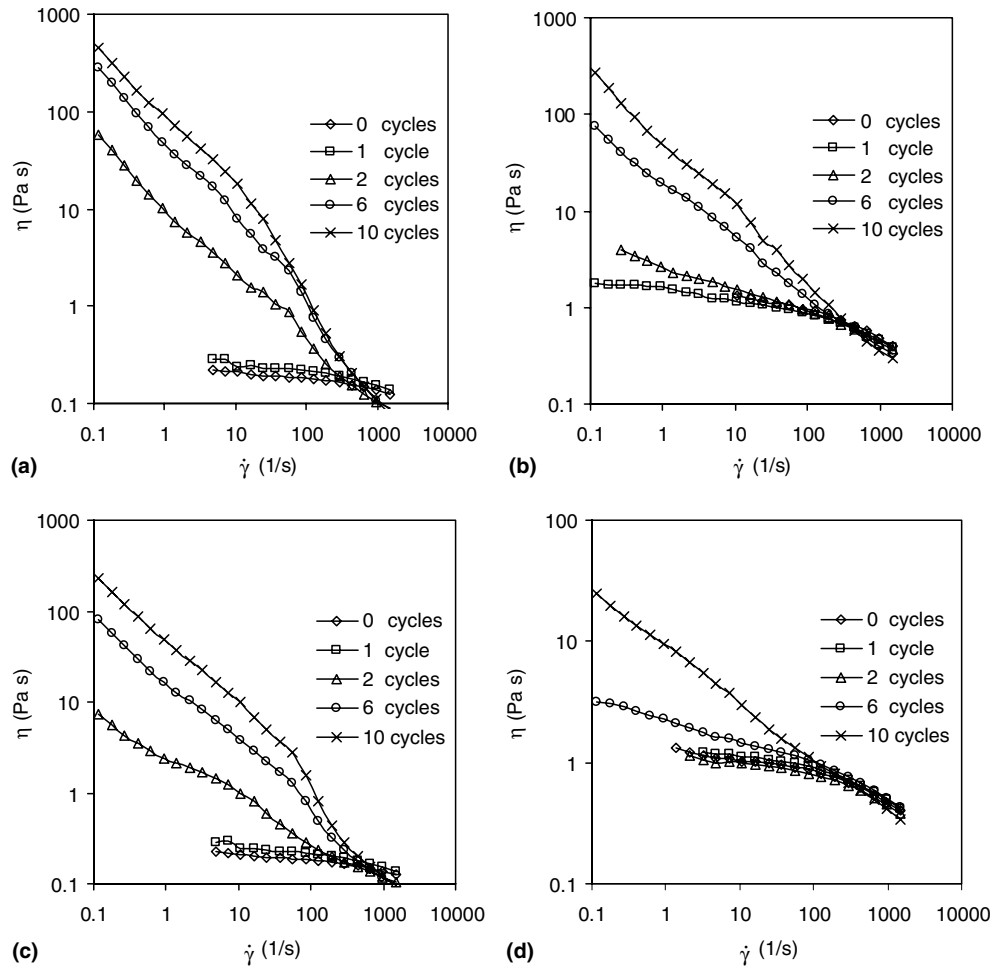


Fig. 2. Effect of freeze–thaw cycling process (0–10 repeated cycles) on apparent viscosity of thawed β -glucan dispersions (BGL110, 4% w/w) at 20 °C; 4% w/w β -glucan, pH 2.0: (a) 4% w/w β -glucan and 30% w/w sucrose, pH 2.0; (b) 4% w/w β -glucan, pH 7.0; (c) 4% w/w β -glucan and 30% w/w sucrose, pH 7.0; (d) Freezing was at -30 °C for 48 h and thawing at room temperature for 2 h.

interactions on flow behavior ($\log \eta$ at 10, 50 and 125 s^{-1}) has been examined. For each of the response variables an analysis of variance was produced which tested the value of the applied model and determined if a more complex model could have a better fit. Table 3 summarizes the estimated regression coefficients of the quadratic polynomial models for the three response variables, along with the corresponding R^2 and F values. If the F test for the model is significant at the 5% level (i.e. $p < 0.05$), there is evidence that the model has some power to explain the variation in the responses. In addition, if the F test for lack of fit is significant then there is evidence that a more complex model would give a better fit. As shown in Table 3, the R^2 values ranged from 0.997 to 0.993, suggesting that the generated models adequately explained the variation of the responses. Moreover, the F test for the regression was significant at a level of 5% ($p < 0.05$), while the lack of fit was not significant at

the 5% level in all responses. These results show that the models that have been chosen can satisfactorily explain the effects of the three factors on the Log of viscosity at three different shear rates. Significant positive linear effects were identified for all the three factors examined on the first two models, with that of β -glucan being the most pronounced. Salt was not a significant factor in affecting the viscosity at 125 s^{-1} ; i.e. the response variable depended mostly on the β -glucan content and subsequently on sucrose, as the linear effects of these factors were significant in the third polynomial equation. The β -glucan concentration as independent variable exhibited also significant negative quadratic effects for all three responses. Finally, significant quadratic negative interactions were noted between β -glucan and sucrose and β -glucan and salt for the log of viscosity at 10 and 50 s^{-1} , while for the viscosity at higher shear rates (125 s^{-1}), only the negative interaction between β -glucan and sucrose was found to be significant. It

Table 3
Regression coefficients of the second-order polynomial models for the response variables (analysis has been performed using coded units)

Factors	Log of viscosity at 10 s ⁻¹ (Pa s)	Log of viscosity at 50 s ⁻¹ (Pa s)	Log of viscosity at 125 s ⁻¹ (Pa s)
Constant	0.563 ^{***}	0.406 ^{***}	0.278 ^{***}
β-Glucan	1.22 ^{***}	1.056 ^{***}	0.993 ^{***}
Sucrose	0.421 ^{***}	0.357 ^{***}	0.329 ^{***}
Salt	0.103 ^{**}	0.088 ^{***}	0.063 (NS)
(β-Glucan) ²	-0.511 ^{***}	-0.538 ^{***}	-0.543 ^{***}
(Sucrose) ²	0.039 (NS)	0.041 (NS)	0.043 (NS)
(Salt) ²	0.014 (NS)	0.029 (NS)	0.028 (NS)
β-Glucan × sucrose	-0.080 [*]	-0.128 ^{***}	-0.131 ^{***}
β-Glucan × salt	-0.069 [*]	-0.075 [*]	-0.060 (NS)
Sucrose × salt	0.027 (NS)	0.034 (NS)	0.038 (NS)
R ²	0.997	0.996	0.993
F	352	312	149
Probability of F	P ≤ 0.0001	P ≤ 0.0001	P ≤ 0.0001
Lack of fit	2.79	1.46	3.24
Probability of lack of fit	0.143	0.345	0.111

* P ≤ 0.05.

** P ≤ 0.01.

*** P ≤ 0.001.

would be noticed here that the regression coefficient values decreased as Log of viscosity was measured at higher shear rates, which means that the response values for viscosity were lower at higher shear rates due to the shear thinning behavior of the solutions.

Fig. 3 gives representative surface plots for Log of viscosity at 50 s⁻¹ and its dependence on β-glucan and sucrose content or β-glucan and salt content with the third factor held constant at its middle level. The surface plots describing the variation of the other two responses (not given here) had more or less the same shape. At low levels of sucrose content an increase in β-glucan concentration resulted in a significant increase in viscosity values; instead at high sucrose levels the observed enhancement of viscosity was smaller (Fig. 3(a)). The positive linear effect of sucrose on Log of viscosity was

prominent at low levels of β-glucan content. At high levels of the latter factor, the Log of viscosity reached a plateau, which is reflected in the negative quadratic effect of β-glucan. The negative interaction effect between β-glucan and sucrose can be easily explained as follows: an increase in sucrose concentration at low β-glucan levels increased the response variable, whereas at high β-glucan content Log of viscosity was marginally increased or maintained constant, especially in the case where both factors were combined at their high levels, presumably due to insufficient or incomplete hydration of the polysaccharide in these highly concentrated dispersions. Indeed, many studies have revealed that the combination of polysaccharides with sugars results in a reduction of viscosity values beyond a certain concentration of the incorporated co-solutes (Carlson & Ziegenfuss, 1965; D'Appolonia, 1972; Richardson & Norton, 1998; Richardson, Willmer, & Foster, 1998; Sudhakar, Singhal, & Kulkarni, 1995). In most of these works concerning starch or locust bean gum it was shown that the addition of sucrose up to a concentration of 30% in the aqueous polysaccharide dispersion increases the viscosity of the mixture, whereas sucrose incorporation beyond this level lead to decreased viscosity. The behavior of starch–gum combinations in the presence of sucrose (up to 30%) was explained by Sudhakar et al. (1995) with respect to the two types of interactions occurring in such a ternary system as previously identified by Elfak, Pass, Phillips, and Morley (1977): (1) polymer–polymer interactions; (2) polymer–solvent interactions. These authors reported that in a starch–guar gum system and in the absence of sucrose both interactions take place, giving rise to increased viscosity with increasing gum content. However, in the presence of sugar, polymer–polymer interactions are favored as compared to polymer–solvent interactions due to the preferential solvation of the co-solute. As sugar concentration increase, the polymer–polymer interactions also increase, giving rise to higher cold paste viscosity. In contrast, for starch–xanthan gum systems the apparent viscosity of the starch paste containing

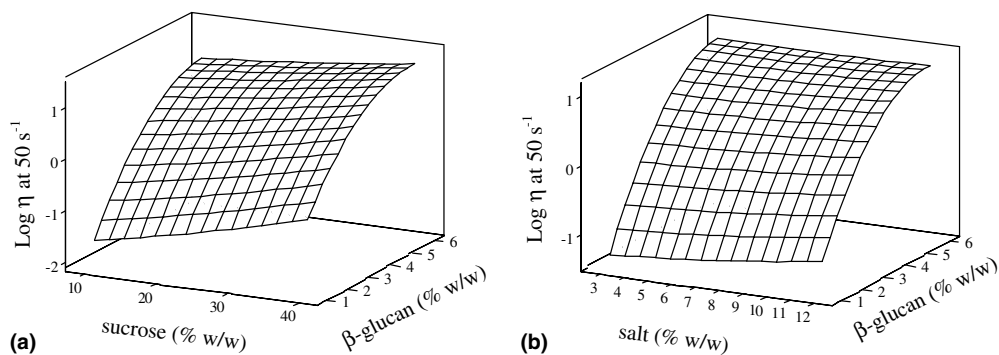


Fig. 3. Response surface pots for log of viscosity at 50 s⁻¹ of BGL140 sample vs. β-glucan and sucrose contents at 7.5 % w/w salt: (a) vs. β-glucan and salt contents at 25% w/w sucrose (b).

0.1% and 0.25% xanthan gum decreased with an increase in sugar concentration from 10% to 30%; this response was attributed to incomplete hydration of starch–xanthan combinations at high sucrose levels. In another study where the intrinsic viscosities of guar, native and purified LBG were recorded as a function of sucrose concentration (0–40%), the 20% w/w sucrose, was claimed to be the best solvent for these polysaccharides (Richardson et al., 1998). It was suggested that at that level the intrinsic viscosity took the maximum value as a result of a balance of competition for water and sucrose/biopolymer mutual compatibility, whereas at 40% w/w sucrose the intrinsic viscosity decreased due to competition for water resulting in a tendency for polymer chain collapse.

Fig. 3b displays the effect of different β -glucan and salt combinations on log of viscosity at 50 s^{-1} with the sucrose held constant at the middle level. At low levels of β -glucan content, increasing salt concentration augmented the response values (higher viscosities were noted), while such a positive effect was not noticed at high levels of the former factor, where the polysaccharide becomes the major determinant of viscosity.

3.3. Effect of acid hydrolysis on apparent viscosity of two barley β -glucan samples differing in molecular weight

The effect of the different acid hydrolysis conditions (in coded level of variables) on the apparent viscosity (η) of BGL140 and BGL250 at 37 and 1 s^{-1} , respectively, are revealed by the coefficients of the sec-

ond order polynomials (Table 4) along with the corresponding R^2 and F values. The analysis of variance showed that the effects of acid hydrolysis on the response variables (apparent viscosity of BGL140 and BGL250) could be effectively modeled (probability of $F < 0.001$). Quite high R^2 values (0.955 and 0.94 for the two models, respectively), as well as insignificant lack of fit ($p > 0.05$) were noted, indicating that the two models adequately described the flow behavior of these systems. For the β -glucan sample of low molecular weight (BGL140) acid hydrolysis showed significant linear effects for all three independent variables, along with a significant positive interaction between pH and time. Comparing the absolute values of regression coefficients for the model describing the variation in apparent viscosity of BGL 140, one could conclude that acid hydrolysis is highly dependent on pH, followed by the effects of time, temperature and pH–time interaction. The same treatment applied to the highest molecular weight sample led to similar conclusions. The viscosity of BGL250 dispersions mainly depended on the linear effects of the three factors examined. The major difference between the two models developed, was that a significant negative quadratic effect of hydrolysis time appeared to affect the variation in apparent viscosity of the BGL250. In addition, no interaction effects among the examined factors were observed. Time of heating was identified as the most important factor (higher absolute value of the regression coefficient) governing the viscosity variations during acid hydrolysis of this high molecular weight sample. Subsequently, there followed, with decreasing order of significance, temperature and pH linear effects, and finally the quadratic negative effect of time. To aid visualization of apparent viscosity dependence of β -glucan dispersions on the three operating factors during acid hydrolysis, three dimensional plots for flow behavior of BGL250 sample are given in Fig. 4. The positive linear effect of pH was obvious from the small viscosity changes observed with pH for short times of hydrolysis (Fig. 4(a)) or for low temperatures (Fig. 4(b)). Larger were the viscosity drops with rising temperature (negative linear effect), a fact that is confirmed by the steeper slopes of the surface contours on the axis describing temperature variation. The curvilinear effect of time suggests that viscosity values, beginning from a maximum at short times, ended up in much lower levels (both at high and low pH conditions) when the temperature was held constant at a middle level ($82.5 \text{ }^\circ\text{C}$).

Generally, comparing the two models for the acid hydrolysis, the most pronounced effects were observed for the high molecular weight β -glucan sample. The initial high apparent viscosity of BGL250 dispersions, compared with those of BGL140, finally reached at lower values at the end of acid hydrolysis treatment. Moreover, different were the dominant factors affecting

Table 4

Regression coefficients of the second order regression polynomial model representing the viscosity of β -glucan samples BGL140 and BGL250 following acid hydrolysis (analysis has been performed using coded units)

Factors	Viscosity (η) for BGL140 at 37 s^{-1}	Viscosity (η) for BGL250 at 1 s^{-1}
Constant	0.637***	10.3***
pH	0.037***	0.628**
Temperature	-0.02***	-1.002***
Time	-0.030***	-1.539***
(pH) ²	-0.002 (NS)	0.034 (NS)
(Temperature) ²	-0.006 (NS)	-0.182 (NS)
(Time) ²	0.004 (NS)	-0.427*
pH \times Temperature	-0.008 (NS)	0.225 (NS)
pH \times Time	0.013*	0.310 (NS)
Temperature \times Time	-0.005 (NS)	0.052 (NS)
R^2	0.945	0.94
F	19.1	17.5
Probability of F	$P \leq 0.0001$	$P \leq 0.0001$
Lack of fit	3.21	3.00
Probability of lack of fit	0.113	0.126

* $P \leq 0.05$.

** $P \leq 0.01$.

*** $P \leq 0.001$.

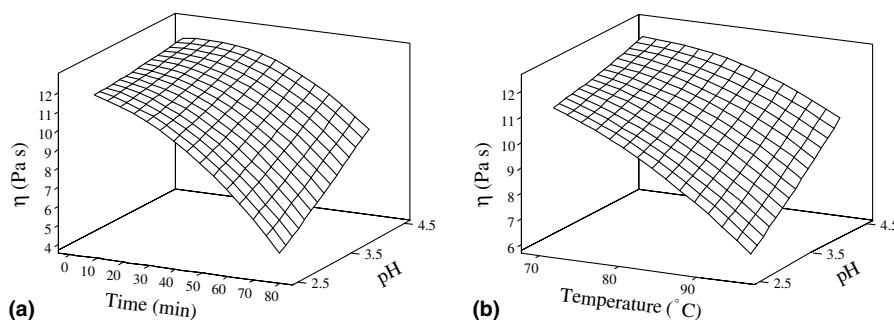


Fig. 4. Response surface plots for apparent viscosity (η) of BGL250 sample (4% w/w, initial β -glucan concentration) after acid hydrolysis at 1 s^{-1} as a function of different pH and time levels at $82.5 \text{ }^\circ\text{C}$: (a) as a function of different pH and temperature levels at a constant hydrolysis time of 39 min (b).

viscosity changes in the two models; i.e. pH and time for BGL140 and BGL250, respectively. Consequently, the influence of acid hydrolysis during thermal processing of acidic food products containing β -glucans on the rheology of the system would depend on the molecular size of the polysaccharide.

4. Conclusions

Barley β -glucan aqueous dispersions underwent morphological changes during freezing and repeated freezing–thawing processing, resulting in the formation of three dimensional network structures under either acidic or neutral conditions. The developed cryostructures were of similar strength irrespective of the initial pH of the dispersion. The same cryogelation process was also evaluated in the presence of sucrose. There was a significant delay in the transition of β -glucan solution to a gel state, due to sucrose incorporation, especially for the preparations with neutral pH, and the resultant cryogels were weaker. The viscosity, at three different shear rates, of aqueous β -glucan dispersions containing different combinations of sucrose and salt concentrations was satisfactorily described by a second order regression model, using response surface methodology. The observations put forward in this study are important for understanding the flow behavior of such multi-component systems, but further research is needed for the detection of potential interactions in the presence of fatty substances, trying to mimic the conditions of a real food dispersion. Response surface methodology was also used for the expression of viscosity variations occurring during thermal processing of acidic media containing β -glucans of two different molecular weights. The viscosity reductions, as a consequence of acid hydrolysis were dependent on pH, temperature and time, factors that were well fitted in second order polynomial equations. Acid hydrolysis was more pronounced for the high molecular weight sample, indicating potential differences in the flow behavior of liquid products containing β -glu-

cans of different molecular size, during thermal processing of acidic products.

Acknowledgements

This work has been carried out with the financial support from the Commission of the European Communities, project QLKI-CT-2000-00535 “Design of Foods with Improved Functionality and Superior Health Effects Using Cereal β -glucans”. It does not necessarily reflect its views and in no way anticipates the Commission’s future policy in this area.

References

- Beer, M. U., Wood, P. J., & Weisz, J. (1997). Molecular weight distribution and (1 \rightarrow 3)(1 \rightarrow 4)- β -D-glucan content of consecutive extracts of various oat and barley cultivars. *Cereal Chemistry*, *74*, 476–480.
- Böhm, N., & Kulicke, W. M. (1999). Rheological studies of barley (1 \rightarrow 3)(1 \rightarrow 4)- β -D-glucan in concentrated solution: mechanistic and kinetic investigation of the gel formation. *Carbohydrate Research*, *315*, 302–311.
- Carlson, W. A., & Ziegenfuss, E. M. (1965). The effect of sugar on guar gum as a thickening agent. *Food Technology*, *19*(6), 954–958.
- Cui, S. W. (2001). *Polysaccharides gums from agricultural products: Processing, structure and functionality*. Lancaster, USA: Technomic Publishing Company Inc.
- Cui, W., & Wood, P. J. (2000). Relationships between structural features, molecular weight and rheological properties of cereal β -D-glucan. In K. Nishinari (Ed.), *Hydrocolloids – Part 1* (pp. 159–168). Amsterdam: Elsevier Science B.V.
- Cui, W., Wood, P. J., Blackwell, B., & Nikiforuk, J. (2000). Physicochemical properties and structural characterization by two-dimensional NMR spectroscopy of wheat β -D-glucan – Comparison with other cereal β -D-glucans. *Carbohydrate Polymers*, *41*, 249–258.
- Damshkaln, L. G., Simenel, I. A., & Lozinsky, V. I. (1999). Study of the cryostructure of polymer systems. XV. Freeze–thaw induced formation of cryoprecipitates matter from low-concentrated aqueous solutions of poly(vinyl alcohol). *Journal of Applied Polymer Science*, *74*, 1978–1986.
- D’Appolonia, B. L. (1972). Effect of bread ingredients on starch-gelatinization. Properties as measured by the Amylograph. *Cereal Chemistry*, *49*, 532–543.

- Dea, I. C. M., Morris, E. R., Rees, D. A., Welsh, E. J., Barnes, H. A., & Price, J. (1977). Associations of like and unlike polysaccharides: mechanism and specificity in galactomannans, interacting bacterial polysaccharides, and related systems. *Carbohydrate Research*, 57, 249–272.
- Elfak, A. M., Pass, G., Phillips, G. O., & Morley, R. G. (1977). The viscosity of dilute solutions of guar gum and locust bean gum with and without added sugars. *Journal of Science and Food Agriculture*, 28, 895–899.
- Giannouli, P., & Morris, E. R. (2003). Cryogelation of xanthan. *Food Hydrocolloids*, 17(4), 495–501.
- Goff, H. D., Caldwell, K. B., Stanley, D. W., & Maurice, T. J. (1993). The influence of polysaccharides on the glass transition in frozen sucrose solutions and ice cream. *Journal of Dairy Science*, 76, 1268–1277.
- Gomez, C., Navarro, A., Manzanera, P., Horta, A., & Carbonell, J. V. (1997). Physical and structural-properties of barley (1 → 3), (1 → 4)- β -D-glucan. Part I. Determination of molecular weight and macromolecular radius by light scattering. *Carbohydrate Polymers*, 32, 7–15.
- Grimm, A., Krüger, E., & Burchard, W. (1995). Solution properties of β -D-(1,3)(1,4)-glucan isolated from beer. *Carbohydrate Polymers*, 27, 205–214.
- Inglett, G. E. (1990). USDA's oatrim replaces fat in many food products. *Food Technology*, 44(10), 100.
- Izydorczyk, M. S., & Biliaderis, C. G. (2000). Structural and functional aspects of cereal arabinoxylans and β -glucans. In G. Doxastakis & V. Kiosseoglou (Eds.), *Novel macromolecules in food systems* (pp. 361–384). Amsterdam: Elsevier Science B.V.
- Kahlon, T. S., Chow, F. I., Knuckles, B. E., & Chiu, M. M. (1993). Cholesterol-lowering effects in hamsters of β -glucan-enriched barley fraction, dehulled whole barley, rice bran, and oat bran and their combinations. *Cereal Chemistry*, 70, 435–440.
- Klopfenstein, C. F. (1988). The role of cereal beta glucans in nutrition and health. *Cereal Foods World*, 33(10), 865–869.
- Krumel, K. L., & Sarkar, N. (1975). Flow properties of gums useful to the food industry. *Food Technology*, 25(4), 36–44.
- Lazaridou, A., & Biliaderis, C. G. (2004). Cryogelation of cereal β -glucans: structure and molecular size effects. *Food Hydrocolloids*, 18, 933–947.
- Lazaridou, A., Biliaderis, C. G., & Izydorczyk, M. S. (2003). Molecular weight effects on rheological properties of oat β -glucans in solution and gels. *Food Hydrocolloids*, 17, 693–712.
- Levine, H., & Slade, L. (1988). Principles of cryostabilization technology from structure/property relationships of water-soluble food carbohydrates – a review. *Cryo-Letters*, 9, 21–63.
- Lo, C. T., & Ramsden, L. (2000). Effects of xanthan and galactomannan on the freeze-thaw properties of starch gels. *Nahrung*, 44(3), 211–214.
- Lozinsky, V. I., & Plieva, F. M. (1998). Poly(vinyl alcohol) cryogels employed as matrices for cell immobilization. 3. Overview of recent research and developments. *Enzyme and Microbial Technology*, 23, 227–242.
- Lozinsky, V. I., Damshkahn, L. G., Brown, R., & Norton, I. T. (2000a). Study of cryostructuring of polymer systems. XIX. On the nature of intermolecular links in the cryogels of locust bean gum. *Polymer International*, 49, 1434–1443.
- Lozinsky, V. I., Damshkahn, L. G., Brown, R., & Norton, I. T. (2000b). Study of cryostructuring of polymer systems. XVI. Freeze-thaw-induced effects in the low concentration systems amylopectin–water. *Journal of Applied Polymer Science*, 75, 1740–1748.
- Lozinsky, V. I., Damshkahn, L. G., Brown, R., & Norton, I. T. (2000c). Study of cryostructuring of polymer systems. XVIII. Freeze-thaw influence on water-solubilized artificial mixtures of amylopectin and amylose. *Journal of Applied Polymer Science*, 78, 371–381.
- Lozinsky, V. I., Damshkahn, L. G., Brown, R., & Norton, I. T. (2002). Study of cryostructuring of polymer systems. XXI. Cryotropic gel formation of the water–maltodextrin systems. *Journal of Applied Polymer Science*, 83, 1658–1667.
- Miyoshi, E., & Nishinari, K. (1999). Non-Newtonian flow behavior of gellan gum aqueous solutions. *Colloid and Polymer Science*, 277, 727–734.
- Morgan, K. R., & Ofman, D. J. (1998). Glucagel, a gelling β -glucan from barley. *Cereal Chemistry*, 75, 879–881.
- Morris, E. R. (1984). Applications of hydrocolloids. In G. O. Phillips, D. J. Wedlock, & P. A. Williams (Eds.), *Gums and Stabilizer for the Food Industry* (Vol. 2, pp. 57–78). Oxford, UK: Pergamon Press.
- Patmore, J. V., Goff, H. D., & Fernandes, S. (2003). Cryo-gelation of galactomannans in ice cream model systems. *Food Hydrocolloids*, 17, 161–169.
- Richardson, P. H., & Norton, I. T. (1998). Gelation behavior of concentrated locust bean gum solutions. *Macromolecules*, 31, 1575–1583.
- Richardson, P. H., Willmer, J., & Foster, T. J. (1998). Dilute solution properties of guar and locust bean gum in sucrose solutions. *Food Hydrocolloids*, 12, 339–348.
- Saulnier, L., Gévaudan, S., & Tribault, J. F. (1994). Extraction and partial characterization of β -glucan from the endosperm of two barley cultivars. *Journal of Cereal Science*, 19, 171–178.
- Sudhakar, V., Singhal, R. S., & Kulkarni, P. R. (1995). Effect of sucrose on starch hydrocolloid interactions. *Food Chemistry*, 52, 281–284.
- Tanaka, R., Hatakeyama, T., & Hatakeyama, H. (1998). Formation of locust bean gum hydrogel of freezing–thawing. *Polymer International*, 45, 118–126.
- Tressler, D. K., & Woodroof, J. G. (1976). Fruit, vegetable and nut products. *Food products Formulary* (Vol.3). Westport, Connecticut, USA: The AVI Publishing Co., Inc.
- Varum, K. M., & Smidsrod, O. (1988). Partial chemical and physical characterization of (1 → 3), (1 → 4)- β -glucans from oat (*Avena Sativa* L) aleurone. *Carbohydrate Polymers*, 9, 103–117.
- Vaikousi, H., Biliaderis, C. G., & Izydorczyk, M. S. (2004). Solution flow behavior and gelling properties of water-soluble barley β -glucans varying in molecular size. *Journal of Cereal Science*, 39, 119–137.
- Wan, W. K., Campbell, G., Zhang, Z. F., Hui, A. J., & Boughner, D. R. (2002). Optimizing the tensile properties of polyvinyl alcohol hydrogel for the construction of a bioprosthetic heart valve stent. *Journal of Biomedical Materials Research Part B: Applied Biomaterials*, 63, 854–861.
- Wood, P. J. (1986). Oat β -glucan: structure, location and properties. In F. H. Webster (Ed.), *Oats: chemistry and Technology* (pp. 121–152). St. Paul, MN: American Association of Cereal Chemists.
- Wood, P. J., Weisz, J., & Blackwell, B. A. (1991). Molecular characterization of cereal β -D-glucans. Structural analysis of oat β -D-glucan and rapid structural evaluation of β -D-glucans from different sources by high-performance liquid chromatography of oligosaccharides released by lichenase. *Cereal Chemistry*, 68, 31–39.