

Network Formation by Pilot Plant and Laboratory-Extracted Barley β -Glucan and Its Rheological Properties in Aqueous Solutions

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ABSTRACT

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Barley and oat β -glucans of low viscosity form reversible gels when prepared in sufficiently high concentrations. Solutions of three barley β -glucan gums differing in molecular weight and thus in viscosity were prepared at 1.0, 2.5, or 5.0% (w/w) concentration levels. Medium- and high-viscosity gums were prepared in a pilot plant (PP) and laboratory (LAB), respectively. Low-viscosity (LV) gum was extracted in the laboratory at pH 7, which allowed for native enzymatic activity and decreased molecular weight. Network formation was monitored overnight through changes in storage (G') and loss (G'') moduli. The strength of the

formed network was determined from oscillatory rheological measurements by increasing the strain from 2 to 100%. Findings demonstrate that gelation of β -glucan is molecular weight dependent and practically an instantaneous process for low-viscosity gum solutions at concentrations of $\leq 5\%$ gum (or $\leq 4\%$ β -glucan), levels lower than previously anticipated. The purity of β -glucan also seems to affect gelation rate. Better understanding of the β -glucan gelation behavior is important for its functionality in both food product applications and physiological mechanisms of its health benefits.

Health benefits of cereal β -glucans, such as cholesterol reduction and regulation of blood glucose levels, have been related to its viscosity (Wood et al 1994, 2000). To exploit β -glucan's health benefits, it should be incorporated into food products as an ingredient, thickener, or stabilizer etc. However, to develop wholesome and shelf-stable products, in-depth knowledge of β -glucan's physicochemical properties is essential. Gelation is one such functional property, and better understanding of gelation dynamics is needed.

Gelling ability means the formation of a three-dimensional network that sets to form a solid-like product trapping the water within the network. Storage modulus (G') and loss modulus (G'') were the parameters used by Doublier and Wood (1995) to demonstrate the gel-like behavior of partially hydrolyzed oat gum. Gelation of low viscosity (LV) barley β -glucan (BBG) was confirmed by Burkus and Temelli (1999) and Morgan and Ofman (1998). They both demonstrated that LV β -glucan forms gels at concentrations $\geq 5\%$ when left overnight at room temperature.

The existence of a network in a hydrocolloid solution results in a fracture point. However, determination of the fracture point, if it exists, is very difficult when a hydrocolloid is present at low concentrations because it requires the measurement of a very low true shear stress. Excessive increase in gum concentration may not help in fracture point determination because it enhances the formation of a true gel and shortens the setting time (Burkus and Temelli 1999). The formation of a network by 2% (w/w) wheat gum solution composed of β -glucan and pentosans (83.5% purity, containing 77% pentosans, 22.9% β -glucan) was reported by Cui et al (1999) when they measured G' and G'' development over time. It has been observed in our laboratory (data not published) that LV β -glucan solutions and emulsions formed a gel after long holding periods, even at concentrations $\leq 1\%$, with gel particulates settling out of aqueous solution. This observation indicates that a network is formed first, but the time dependence of gelation in such solutions is not known. Bohm and Kulicke (1999a,b) reported dynamics of β -glucan gelation in very concentrated solutions containing 6–10% β -glucan gum. In such a highly concentrated solution, hydration of β -glucan is incomplete due to low water-to-gum ratio (Burkus and Temelli 1999).

More recently, Skendi et al (2003) and Lazaridou et al (2003) tested gelation dynamics of very concentrated oat β -glucan solutions (8–10%) and found that the rate of gelation is inversely proportional to molecular weight. Because the lowest molecular weight oat gum (35,000 MW) had the lowest proportion of cellulose-like segments, Lazaridou et al (2003) stated that "molecular size rather than the fine structure is the most important determinant of gelling behavior for oat β -glucan". In these studies, Skendi et al (2003) achieved $\geq 85\%$ purity of oat gum, while Lazaridou et al (2003), after additional purification, achieved $>93\%$ oat gum purity.

Similar conclusions were reached by Vaikousi et al (2004), who tested barley β -glucan gums of $>89\%$ purity in 8% aqueous solutions. Gum with 210,000 MW needed >25 hr for G' to be equal to G'' , indicating network formation, while gum with 250,000 MW needed almost 50 hr to set a network at 25°C. When concentration of BBG was decreased to 6% by Irakli et al (2004), network setting time of very pure BBG gums ($\geq 93\%$) increased from >60 hr to ≈ 130 hr, depending on MW. However, Irakli et al (2004) performed simple aqueous extraction at 47°C, which is favorable for the activity of native β -glucanases or β -glucanases present on the surface of the grains due to contamination or possible mold growth. The differences in MW of BBG gums obtained from different cultivars were attributed to cultivar differences by Irakli et al (2004); however, the impact of differences in the level of β -glucanase activity and experimental variability in extraction procedures on MW should not be overlooked.

Lazaridou et al (2004) compared the gelation kinetics of 8% β -glucan solutions from barley, oat, wheat, and lichens with $\approx 100,000$ or 200,000 MW. While barley gum of 200,000 MW formed a network after 21.2 hr, network formation for samples of 100,000 MW required 10.7 hr. Oat gum solutions needed much longer times of 41.8–167.4 hr for 110,000 and 200,000 MW, respectively. Wheat β -glucan (200,000 MW) had equal G' and G'' values in ≈ 3.3 hr, while shorter β -glucan from lichens (100,000 MW) formed a network instantly with $G' > G''$ at the beginning of measurements. Faster gelation rate was attributed to higher ratio of cellotriose (DP3) to cellotetraose (DP4) when the regions of structural regularity with few consecutive cellotriose units could serve as association points or junction zones for network formation. Wheat and lichenan β -glucans also had lower purity of 82.9 and 76.5%, respectively.

A similar pattern in the strength of 6% gels was demonstrated by Tosh et al (2004a) when a very good correlation ($R^2 = 0.974$) was found between gel G' and molar percentage of DP3. Again, oat gel, after aging for seven days at 5°C, had the lowest G' and the lowest DP3-to-DP4 ratio, while lichenan had the highest. Tosh

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et al (2004b) could not confirm plateau values for G' after seven days of aging at 5°C.

A review of the literature as summarized above indicated that the dynamics of gelation in less concentrated β -glucan solutions (1–5%) or gelation behavior of BBG obtained in a pilot plant (PP) setting have not been reported. Therefore, the objectives of this study were to study network formation in 1–5% BBG solutions using BBG extracted in a PP or a laboratory through monitoring changes in G' and G'' over time and to test the existence of fracture point in such BBG solutions as well as the strength of produced gels.

MATERIALS AND METHODS

Materials

Barley β -glucan gums were extracted from Bly Blend waxy barley (a mixture of two experimental cultivars [SB89528 and SB89497]) under alkali conditions at PP and laboratory (LAB), as previously described by Burkus and Temelli (2004) with details provided by Burkus (2001). The composition of gums is shown in Table I. β -Glucan content of PP and LAB gums (83.3 and 78.0% db, respectively) was determined according to McCleary and Glennie-Holmes (1985). These two gums also contained 1.2% and 0.5% starch (db) determined according to Holm et al (1986), 1.5 and 3.6% protein determined using a FP-428 nitrogen determinator (Leco Corp., St. Joseph, MI), and 1.7 and 4.1% pentosans determined according to Hashimoto et al (1987), respectively, while both contained 4.1% ash. Additional LV BBG (71.5%, w/w, β -glucan, db) was extracted from Condor barley (a regular starch type) as described by Burkus and Temelli (1999). Its starch and protein contents were 11.7 and 6.5%, db, respectively. Lipids were not detected in any of the gum samples by the Goldfish procedure due to the extensive washing with 99.9% ethanol before drying. All three gum samples were prepared by aqueous/alkali extraction followed by separation of insolubles by centrifugation, acid precipitation and centrifugation of proteins, and precipitation of β -glucan by adding an equal volume of ethanol. Thermostable α -amylase was used for further purification of PP and LAB gum extracts but not of LV gum because LV gum obtained using such a protocol in a previous study (Burkus and Temelli 1999) demonstrated quick gelling properties at high concentrations.

Molecular weight of PP and LAB gums was determined as 198,000 and 595,000 MW (Burkus and Temelli 2003), while intrinsic viscosity of PP and LAB gums was determined from Mark-Howink relationship as 338 and 1,125 mL/g, respectively. During these measurements, a concentration range of 0.025–0.200% was used for the determination of reduced and intrinsic viscosities. Even though similar alkali extraction procedures were used for the production of both PP and LAB gums, high shear involved in industrial centrifuges lowered viscosity of PP gum. A similar degradation of viscosity during large-scale production was also described by Wood et al (1989). Condor gum had an estimated MW of 60,000 \pm 5,000, based on viscosity measurements, which would result in the intrinsic viscosity of only 88 mL/g using the same

extrapolation from Burkus and Temelli (2003). Condor gum was extracted in the laboratory using water at pH 7 and 55°C and further processed (starch and protein separation) without stabilization by heat treatment. Under such conditions, the β -glucanase enzymes (native or due to surface contamination) are active, resulting in a lower MW β -glucan product. Later, stability of Condor gum solutions was achieved by heat treatment.

Solution Preparation

β -Glucan solutions were prepared in the desired concentration (w/w) in duplicate according to Burkus and Temelli (1998). LAB gum was prepared in 0.25, 0.50, and 1.0% concentrations, while PP and Condor gums were prepared in 1.0, 2.5, and 5.0% concentrations. Distilled water was from the local supply. Both PP and LAB gums did not exhibit thixotropy at 1% concentration (Burkus and Temelli 2004), which was in agreement with Autio et al (1987) and Wikstrom et al (1994).

Rheological Measurements

Viscosity was determined by consecutive fixed speed tests using a rheometer (PAAR Physica UDS 200, Glenn Allen, VA) equipped with a Peltier heating system and controlled by US200 v. 2.00 programming. The instrument was calibrated with S3 standard oil (3.408 mPa·sec at 25°C, Cannon Instrument, State College, PA) for LV measurements and the Brookfield Viscosity Standard Fluid 500 standard oil (482 mPa·sec at 25°C, Brookfield Engineering Laboratories, Middleboro, MA) for high viscosity (HV) measurements. Tests were performed at the desired temperature ($\pm 0.03^\circ\text{C}$) using the DG 27 cup and bob geometry with double gap. Sample size was not measured by volume but by weight. The clean DG 27 cup was placed on the balance, tared, and 7.01 \pm

TABLE I
Composition of Laboratory (LAB), Pilot Plant (PP),
and Low Viscosity (LV) Condor Gums (% w/w, db)

	LAB	PP	LV Condor
Protein	3.6	1.5	6.5
Lipid	0	0	0
Ash	4.1	4.1	7.7
Carbohydrates	92.3	94.4	85.8
Starch	1.2	0.5	11.7
β -Glucan	78.0	83.3	71.5
Pentosans	4.1	1.7	nd ^a

^a Not determined.

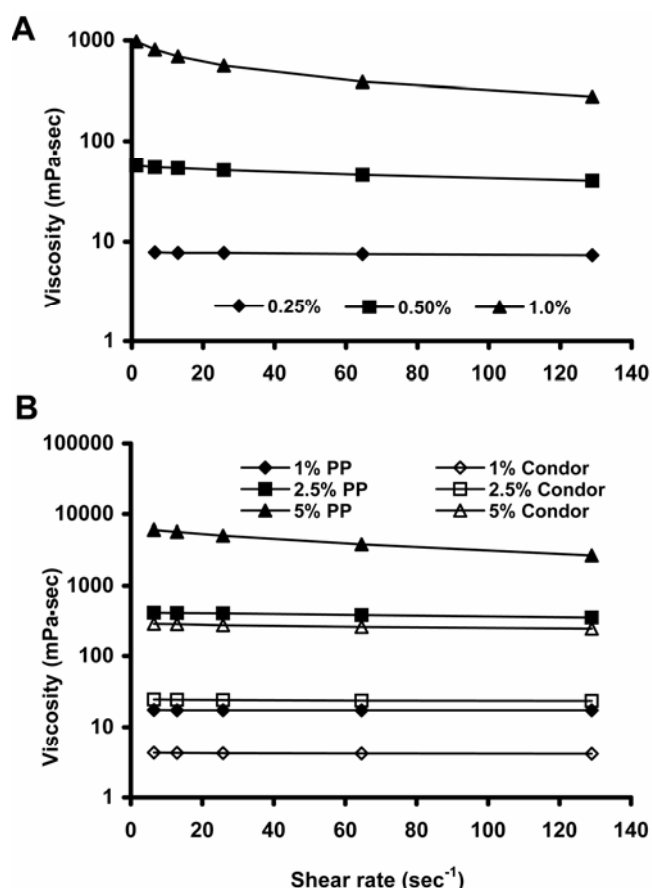


Fig. 1. Concentration dependence of viscosity vs. shear rate for (A) laboratory (LAB) gum and (B) Condor (open symbols) and pilot plant (PP) gum solutions (solid symbols).

0.005 g of sample was weighed directly into the cup. Shear rate data are reported as rpm or sec^{-1} after multiplication by conversion factor 1.29 based on manufacturer's specifications. Pseudoplastic behavior was described by the power law model as $SS = c SR^n$ where SS is shear stress (N/m^2), SR is shear rate (sec^{-1}), c is consistency coefficient, and n is flow behavior index.

Storage and loss modulus (G' and G'' , respectively) were recorded in overnight tests of at least 18 hr duration. The UDS 200 rheometer was in amplitude sweep and controlled shear displacement (CSD) mode with a constant strain of 3–5% and frequency (ω) of 0.5–1 Hz. Data points were recorded every 5–10 min. All samples were prepared and tested in duplicate. PP and Condor gums were tested at 1, 2.5, and 5% (w/w) concentration, whereas LAB gum was tested at 1% concentration. To prevent evaporation and formation of a skin-like layer on the surface of the samples during overnight tests, 0.5 mL of S3 standard oil was layered onto the samples in the DG27 cup. Samples were placed in the cup and the bob was brought into measurement position. It was slowly rotated manually to wet the walls of the cup and bob uniformly. Then the bob was pulled out 5–6 mm and approximately one half of the oil was dosed onto the sample inside the concentric cylinder of the bob. The bob was placed back into measurement position, the remainder of the oil was put into the outside gap, and the test was started.

The fracture point of the formed network was tested before and after G' and G'' determination using the same amplitude sweep and CSD testing mode with strain increasing from 2 to 100% during automatic flow curve measurement at a frequency of 1 Hz, with 30–50 points being recorded. There is no time setting for this kind of test. Fracture point of Condor and PP gum solutions at 2.5 and 5% concentration was measured in duplicate, before and after overnight testing for G' and G'' , respectively.

RESULTS AND DISCUSSION

Effect of Shear on Viscosity

The viscosity of LAB gum (0.25–1.0%, w/w), PP, and LV Condor gum solutions (1.0–5.0%, w/w) as a function of shear rate at 20°C is shown in Fig. 1. As expected, viscosity increased with concentration. Viscosity of HV LAB solution increased from 7.9 mPa·sec at 0.25% to 976 mPa·sec at 1% at 1 rpm (1.29 sec^{-1}). Thus, a fourfold increase in concentration (0.25–1.0%) resulted in two orders of magnitude increase in viscosity. When the concentration of LV Condor gum solution was increased from 1 to 5%, viscosity increased from 4.3 to 284 mPa·sec at 5 rpm (6.45 sec^{-1}), while the viscosity of the more viscous PP gum increased from 18 to 6,080 mPa·sec in the same concentration range and at the same shear rate. Viscosity of a fresh 5% LV Condor solution at 5 rpm (6.45 sec^{-1}) increased from 284 to 330 mPa·sec (17% increase) in 14 min after 3 consecutive measurements. That was an early indication of technically instantaneous beginning of network formation.

Power law parameters for the three gums tested at different concentrations are presented in Table II. LAB gum exhibited Newtonian-like behavior at 0.25% concentration with flow behavior index of 0.98, while at higher concentrations (0.5–1.0%) its behavior was pseudoplastic. Similarly, PP and LV Condor gum solutions behaved like Newtonian fluids at the lowest tested concentration (1%), whereas at 5.0% concentration both gum solutions were pseudoplastic. At 2.5% concentration, fresh LV Condor solution was Newtonian-like with the flow behavior index of 0.984, whereas PP gum solution was pseudoplastic.

Rheological behavior of β -glucan solutions is also dependent on the molecular weight of β -glucan. Large differences in MW of barley cultivars such as those described by Irakli et al (2004) may be attributed to other factors. Because Irakli et al (2004) used aqueous extraction for the recovery of β -glucan, differences in MW should be primarily ascribed to differences in enzymatic activity, native or acquired. One should also keep in mind that neither ethanol reflux of flour nor high pH alone (i.e., pH 10, 55°C) does completely inactivate β -glucanase activity as demonstrated by Burkus and Temelli (1998). On the other hand, MW of β -glucan can be substantially lower after a wet preharvest or harvest season due to partial sprouting (β -glucan degradation) or heavy infestation with molds. At this stage, differences in MW and viscosity between different species such as those described by Skendi et al (2003) between *Avena sativa* and *A. bysantina* can not be precluded.

Network Formation

Storage modulus (G') and loss modulus (G'') measurements over time confirmed the β -glucan network formation for LV gums within a 24-hr timeframe but at much lower concentrations than those determined previously by Burkus and Temelli (1999), Bohm and Kulicke (1999a,b), Vaikousi et al (2004), Irakli et al (2004), Lazaridou et al (2004), and Tosh et al (2004a). The time corresponding to the intersection of G' and G'' curves was taken as the time necessary for network formation. The quick gelling LV Condor gum at 5% concentration (3.36% β -glucan concentration, Table I) needed ≈ 1.5 hr to form a network (Fig. 2), but when the concentration of gum was decreased to 2.5% (1.68% β -glucan, Table I), time to gel increased to ≈ 13.5 hr (Fig. 3). In a repeated test, gelation time for the 2.5% sample was ≈ 18 hr. The first sample was used in some other tests before overnight testing of G' and G'' , while the second sample underwent testing immediately after hydration and cooling. It seems that the history of a sample plays a significant role in network formation and underlines the importance of consistent treatment of samples and exact timing of each step. At the end of 18 hr of testing the 2.5% solution, G' was still increasing, while G'' reached a plateau, which implies continued gel strengthening. This was similar to Tosh et al (2004b), who found that G' in β -glucan solutions had not reached a plateau even after seven days at 5°C. At the 1% level, Condor

TABLE II
Power Law Constants for Fresh Laboratory (LAB), Pilot Plant (PP), and Condor Gums at 20°C in Shear Rate Range of 6.46–129 sec^{-1} (5–100 rpm)

Gum	Concentration (% , w/w)	β -Glucan (% , w/w)	Consistency Coefficient	Flow Behavior Index	R^2
LAB	0.25	0.18	8.16	0.980	1
	0.50	0.36	72.1 ^a	0.885 ^b	0.9977
	1.0	0.71	1,690 ^c	0.641 ^d	0.9945
PP	1.0	0.79	17.7	0.996	1
	2.5	1.97	455.2	0.9501	0.9995
	5.0	3.93	11,027	0.7286	0.9893
Condor	1.0	0.67	4.38	0.9886	1
	2.5	1.68	25.57	0.9842	1
	5.0	3.36	320.6	0.9437	0.9999

^a 62.1 in the 1.29–129 sec^{-1} range (1–100 rpm).

^b 0.926 in the 1.29–129 sec^{-1} range (1–100 rpm).

^c 1229.1 in the 1.29–129 sec^{-1} range (1–100 rpm).

^d 0.726 in the 1.29–129 sec^{-1} range (1–100 rpm).

gum exhibited a strong gelling tendency, with both G' and G'' increasing substantially overnight, whereas the more viscous PP gum had flat values throughout the test at 1% concentration.

PP gum at 5% concentration (3.93% β -glucan, Table I) behaved similarly to LV Condor gum, forming a network in ≈ 6.2 hr (Fig. 4). This is slower than the gelation time for 5% LV Condor gum (≈ 1.5 hr), which confirms the observations of Burkus and Temelli (1999), Bohm and Kulicke (1999a), Vaikousi et al (2004), and Lazaridou et al (2004) that lower MW and lower viscosity of barley β -glucan enhance gelation. PP gum is more viscous than Condor gum (18.6 vs. 4.3 mPa·sec for a 1% solution, Fig. 1) and higher viscosity inhibits gelation. That was even more apparent for 2.5% PP gum, which did not form a network within 24 hr, whereas the less viscous Condor gum exhibited network formation at 13.5 hr at the same concentration (Fig. 3). For the 2.5% PP gum, G' increased from 0.06 to 0.11 Pa, while G'' stayed almost constant at ≈ 2.6 Pa over 24 hr. Less dense packing of the hydrocolloid in the 2.5% solution combined with higher viscosity extends gelling time and probably days, if not weeks, could be needed for G' to surpass G'' . The effect of further dilution was noticeable for 1% PP gum. Although some association was evident from the increase in G' at 2.5% concentration, at 1% there was no substantial change in G' throughout the overnight test.

High viscosity LAB gum at 1% concentration did not form a network, showing no changes in G' and G'' within 24 hr. Overnight testing at 3% strain and 0.5 Hz resulted in fairly straight lines for $G' \approx 2 \times 10^{-7}$ Pa and $G'' \approx 1.92$ Pa. LAB gum was not tested at higher concentrations because PP gum at 2.5% already had extended gelling time >24 hr and LAB gum (HV type) would probably require substantially longer time for gel formation. Increasing the concentration would also increase viscosity and, as discussed above, high viscosity is detrimental for gel setting. A sterilized sample of 1% LAB gum solution left sitting in a refrigerator for more than six months had no apparent change in consistency; however, after 1.5 years, a weak amorphous gel-like structure was apparent.

This work demonstrated that the rate of BBG gelation increases with concentration and decreases with MW as described earlier by Morgan and Ofman (1998), Vaikousi et al (2004), Irakli et al (2004), and Lazaridou et al (2004). Compared with gums in other studies, PP gum was industrially produced in a PP setting and had lower purity. Comparison of setting times to those reported previously indicates that the impurities seem to increase the rate of gelation. PP solution with 5% of gum (3.93% of β -glucan) and MW $\approx 200,000$ set a network in 6.2 hr. BBG gum of similar MW reported by Lazaridou et al (2004) set a network in 21.3 hr despite the concentration level of 8% (w/v). Less pure LV Condor gum with only 3.36% of β -glucan in 5% gum solution set a network

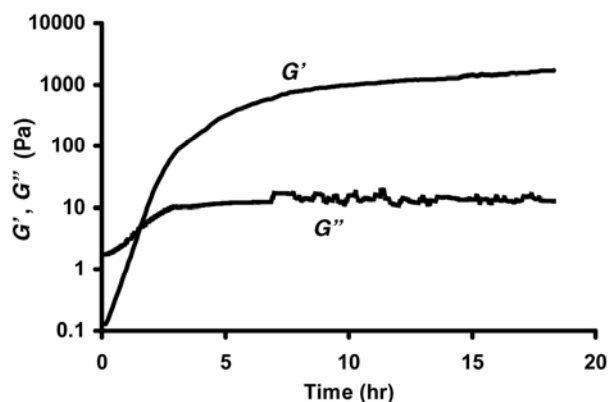


Fig. 2. Storage modulus (G') and loss modulus (G'') development over time for a 5% (w/w) solution of Condor gum determined at 5% strain and 1 Hz frequency. G' exceeds G'' at ≈ 1.5 hr.

even faster in only 1.5 hr. This gum also contained some amylose or dextrans because α -amylase was not used for purification during extraction. Analysis results indicate the presence of 11.7% starchy material. Extraction was performed at 55°C to minimize starch gelatinization, but such a treatment is sufficient to liberate some amylose or for native enzymes to form dextrans. Starch was removed by centrifugation of the low viscosity supernatant and the final precipitation of β -glucan gum was performed at 50% ethanol concentration, leaving starchy material co-precipitated with β -glucan gum.

Gelation pattern of high purity BBG gums ($>90\%$) may not be applicable to commercial food products because the production of such gums on a large scale would be prohibitively expensive. Indeed, Temelli et al (2004) utilized the same industrially produced PP gum in the development of a β -glucan-enriched orange-flavored beverage, while Morin et al (2002) used the PP gum in reduced-fat breakfast sausage. Additionally, impurities such as pentosans are also dietary fiber components and their presence may be beneficial. The presence of impurities may affect the stability of β -glucan solution when incorporated into real food systems, but the same will be true for high-purity β -glucan gums because real food systems are multicomponent and possible interactions or incompatibilities between β -glucan and other food components are not sufficiently known. The presence of impurities in the β -glucan gums may also contribute to gel network formation as discussed later.

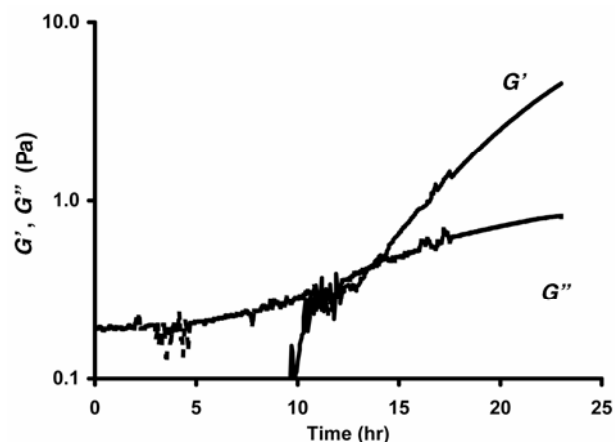


Fig. 3. Storage modulus (G') and loss modulus (G'') development over time for a 2.5% (w/w) solution of Condor gum determined at 5% strain and 1 Hz frequency. G' exceeds G'' at ≈ 13.5 hr.

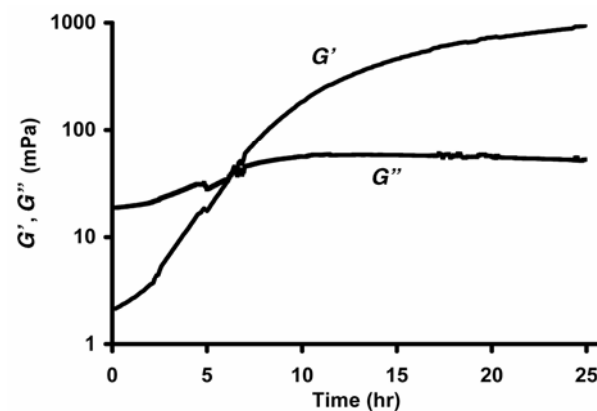


Fig. 4. Storage modulus (G') and loss modulus (G'') development over time for 5% (w/w) pilot plant (PP) gum solution determined at 3% strain and 0.5 Hz frequency. G' exceeds G'' at ≈ 6.2 hr.

A gel network can be visualized as being very regular in appearance like a crystal structure or a 3-D fishing net. Nodes of the crystal structure must have at least four links to other nodes, similar to those in a diamond. Because such rigidity and regularity can not be expected of a β -glucan network, at least six bonds from each node should be protruding into space as in 3-D axes. To achieve this, at least three β -glucan chains should be joined in the form of micelles and all six endings should be free to interconnect with neighboring micelles. Again, such regularity can not be expected, which means that, on average, more than three β -glucan chains should be present in each micelle. It was already demonstrated by Grimm et al (1995) that micelles of short β -glucan molecules in beer can consist of ≥ 17 chains, while Varum et al (1992) reported that longer oat β -glucan formed micelles of four to five molecules. In addition, Burkus and Temelli (2003) noticed that pure barley β -glucan samples with MW of 31,000 and 32,000 did not exhibit further reduced viscosity when their concentration was increased from 0.75 to 1.0%, which could only be due to lateral aggregation of β -glucan chains.

If micelles were interconnected with nothing between them, that would create a very dense and rigid structure, which is not the case. Micelles are not the only form of β -glucan in solution and chains can be either associated into micelles or free-floating (Varum et al 1992). In this case, not only is it important to understand which mechanism, cellulose-like domains or DP3 consecutive regions, is dominant in the formation of micelles but also to demonstrate what molecular endings are made of. Tosh et al (2004b) reported that oat β -glucan hydrolyzed with cellulase formed more elastic gels with stronger junction zones than gels formed after hydrolysis with lichenase. These cellulose-like end-

ings can not be involved in micelle formation but can be quite involved in cross-linking of micelles and provide additional strength to a gel. This type of cross-linking has its limits if there are not enough free-floating molecules or the concentration is insufficient to connect all micelles into a continuous network. The consequence would be the formation of large flocks responsible for pseudoplasticity as was also speculated by Burkus (2001).

As well, Burkus and Temelli (2004) demonstrated that viscosity does not plateau with an increase in shear rate $>100 \text{ sec}^{-1}$. There was a substantial decrease in viscosity when shear rate reached $1,290 \text{ sec}^{-1}$ followed by a further viscosity decrease at $\approx 3,800 \text{ sec}^{-1}$. This would be the consequence of complete flock elongation and dissipation, and even the dissipation of micelles cannot be precluded. This change in structure was completely reversible because viscosity recovered to the original level after 4 min at 1.29 sec^{-1} (1 rpm). The existence of structures larger than flocks is not out of question. Indeed, Tosh et al (2004a) observed superstructures $10 \mu\text{m}$ in size after aging 6% β -glucan gels for seven days at 5°C . Similar aggregation was presented by Burkus (2001).

Fracture Point of Gels

Fracture point was tested for all gum solutions that showed at least some network formation (Figs. 5–7). In fresh solutions of BBG gum, there was no detectable fracture point with this kind of test, even in the case of a quick gelling gum like LV Condor at 5% concentration (Fig. 5). G' and G'' for fresh 2.5% Condor and 5% PP solutions did not preserve the clarity of figures (Figs. 6, 7) but exhibited a pattern similar to that of 5% Condor gum solution with constant G' and G'' . Upon standing overnight, the network is formed and G' exceeds G'' . After some time, G'' reaches a plateau, while G' continues to increase (Figs. 2–4). During an amplitude sweep, G' continues to increase until stress exceeds the strength of network structure, when G'' again exceeds G' (Figs. 5–7). Since these were fairly fresh gels ($\leq 24 \text{ hr}$), G' was still on the rise and the potential for syneresis that could lead to slip during testing can be precluded. In the case of slip, G'' would also lose its value due to the sudden loss of resistance and viscosity, which was not the case in this study.

Less concentrated 2.5% Condor gum had G' at the fracture point two orders of magnitude lower than that of 5% Condor gel (12.3 and 1,660 Pa, respectively). The strain at the breaking point of the 2.5% gel was 60.9%, while the 5% gel broke at 25.3% strain (Figs. 6 and 5, respectively). PP gum gel (5%) broke at 42.3% strain (Fig. 7), exhibiting higher elasticity than the 5% Condor gel, which could be a consequence of more flexible, longer polymeric chains. PP gum at 2.5% did not have a measurable fracture point after overnight aging despite some association registered through increased G' . PP gum with much higher MW had stronger and less brittle gels, which was in agreement with

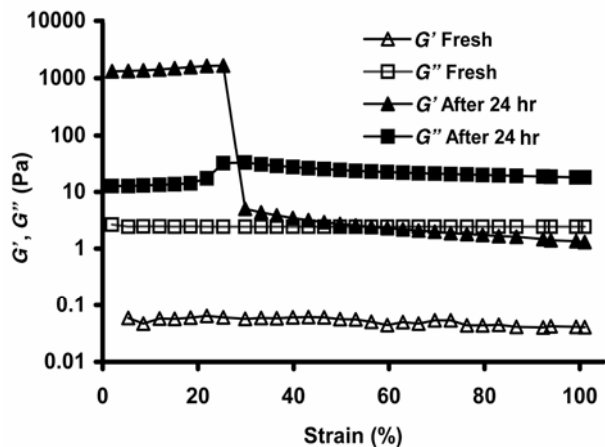


Fig. 5. Amplitude sweep at 2–100% strain and 1 Hz frequency for 5% (w/w) Condor gum before and after overnight test.

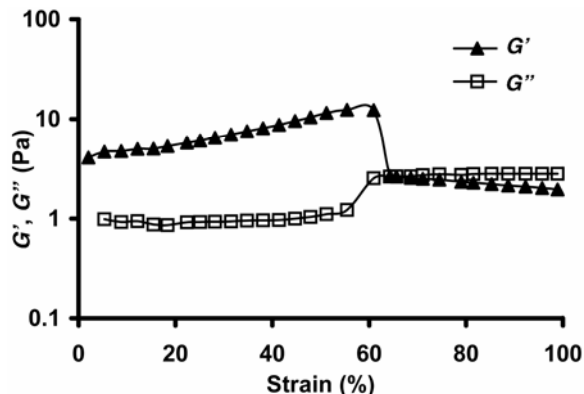


Fig. 6. Amplitude sweep at 2–100% strain and 1 Hz frequency for 2.5% (w/w) Condor gum after overnight test.

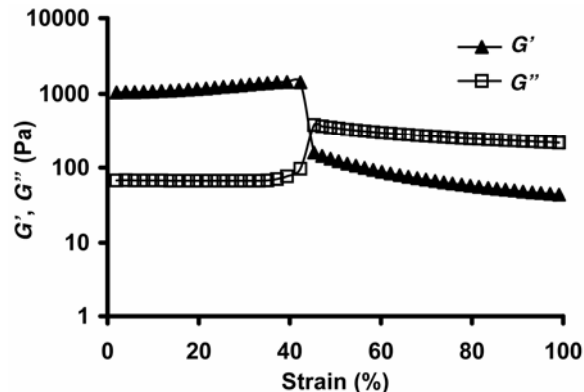


Fig. 7. Amplitude sweep at 2–100% strain and 1 Hz frequency for 5% (w/w) pilot plant (PP) gum after overnight test.

Lazaridou et al (2004), who observed the same trend for β -glucan gels of the same origin.

In a previous study, Burkus and Temelli (1999) tested the strength of β -glucan gels from different gums, including the same LV Condor gum used in this study, using compression testing between parallel plates of an Instron universal testing machine. They found that purified BBG gum had lower gel strength than Condor gum despite higher β -glucan content and attributed higher gel strength of Condor gum to the presence of impurities. This may be especially true for the Condor gum used in this study because it was extracted under different conditions and was not treated with thermostable α -amylase. Therefore, the presence of undigested starch/dextrin and pentosans may play a role in the formation of additional cross-linking between β -glucan micelles, most probably through hydrogen bonding.

CONCLUSIONS

High viscosity LAB gum at 1% concentration is highly pseudo-plastic but with a relatively high flow behavior index of ≈ 0.73 at 20°C, whereas low viscosity PP and Condor gums exhibited Newtonian behavior at 1% level.

Network formation in solutions of LV β -glucan is highly time- and concentration-dependent. The less viscous Condor gum at 5% concentration had already set a weak gel after 1.5 hr of testing when G' exceeded G'' . Decreasing the concentration by half extended the gelling time by at least ninefold. More viscous PP gum at the same 5% concentration needed at least 6.2 hr to gel, while at 2.5% concentration, PP gum did not form a continuous network overnight. Using the same ratio (ninefold) for the effect of concentration on time necessary for gel setting as for Condor gum, ≈ 2.5 days would be necessary for the gelling of 2.5% PP solution. The higher viscosity of PP gum should be an additional factor slowing down network formation. LAB gum at $\leq 1\%$ concentration showed no gelling tendency in 24 hr and was expected to stay as such over a period of a few months.

Yield point could not be detected in fresh β -glucan solutions with the testing mode applied, regardless of viscosity or concentration. But more concentrated solutions with a continuous network, in which G' exceeded G'' , exhibited a fracture point after overnight holding. Industrially produced β -glucan may behave differently and have different gelation dynamics compared with more pure laboratory samples. Impurities such as dextrans and pentosans may play a significant role in the behavior of β -glucan gels by forming additional cross-linking and increasing the gel strength as well as the rate of gelation.

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