Gelation of Barley ß-Glucan Concentrate

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ABSTRACT

The gel behavior of barley ß-glucan (BBG) gum extracted in our laboratory was compared to low- and high-viscosity commercial BBG gum and cornstarch using compression between parallel plates. Effects of ß-glucan concentration and hydration temperature on gel behavior were examined. BBG gum gelled at ≥5% concentration and gel strength increased (p<0.05), but not proportionally, with concentration. Hydration temperature did not influence gel strength. Commercial ß-glucan had higher (p<0.05) gel strength than our BBG gum at 5% concentration. Cornstarch produced ~78% softer gel than BBG gum at 6% concentration. BBG may have potential as a gelling agent.

Key Words: barley, ß-glucan, gel, gelation, stress-strain

INTRODUCTION

ß-Glucan has been reported to have beneficial health properties such as cholesterol lowering (Newman et al., 1992; Kahlou et al., 1993; Pick, 1994), blood glucose regulation (Wood, 1993; Pick, 1994; Gosain, 1996), immunostimulation and antitumor activity (Eastwood, 1987). The richest natural sources of ß-glucan are barley and oats. Barley contains a higher level of ß-glucan (usually 4–7%), with some waxy types reaching as high as 15% (LaBella, 1998). Therefore, waxy barley may be an important commercial source of ß-glucan. Information on its functional properties such as thickening, stabilizing and gelation characteristics may lead to developing new food applications of ß-glucan. However, possible thermodynamic incompatibility of ß-glucan with other food components such as proteins and starch at certain concentration levels (Burkus, 1996) requires further investigation. Dawkins and Nnanna (1995) compared oat ß-glucan with xanthan, locust bean, guar and arabic gums and suggested oat ß-glucan as a thickener and stabilizer in food products and biomedical applications. Temelli (1997) reported such functional properties of barley ß-glucan gum. Doublier and Wood (1995) reported gel-like behavior of partially hydrolyzed oat ß-glucan, but did not investigate its gelling ability.

Gelation is the association or cross-linking of long polymer chains to form a 3-dimensional continuous network, which traps and immobilizes liquid to form a structure resistant to flow under pressure (Glicksman, 1982). Some hydrocolloids which have such ability are agar, carrageenan, alginate, fucellularan, gelatin, pectin and starch. All except starch, are charged molecules and usually need special conditions to form a gel such as presence of sugars, specific ions (i.e. Ca<sup>++</sup>) for gelation of alginate) and/or specific pH.

Differences in the degree of branching of amylose and amylopectin molecules impart different properties to starch gels. Amylopectin does not form a gel within the concentration range of 1–10%, as amyllose does (Glicksman, 1969). Amylose and ß-glucan are both linear chains of glucose. In amylose, the linkages between glucose units are α-(1→4) resulting in a tendency to take α-helix conforma-

tion (Whistler and Daniel, 1985). Amylose chains can align among themselves through hydrogen bonding and create a gel (Glicksman, 1969). This alignment is a characteristic of cellulose where it creates insoluble crystalline regions due to hydrophobic attractions of (1→4)-ß regions (Whistler and Daniel, 1985). The (1→4)-(1→3)-ß-linkages in ß-glucan create short (1→4) cellulosic regions interrupted with (1→3) kinks (Buliga et al., 1986). These give the molecule an irregular shape reducing its tendency to pack into stable, regular molecular aggregates (MacGregor and Fincher, 1993). Such cellulosic (1→4) regions are insoluble (MacGregor and Fincher, 1993) and attractions among such regions may result in formation of knots of a gel network. Therefore, we hypothesized that ß-glucan may set into a gel structure similar to amylose. However, no information has been published on the gelation of (1→3)(1→4)-ß-D-glucan.

The gelation behavior of starches has been reported extensively (Christianson et al., 1985; Bagley et al., 1985; Christianson et al., 1986) and the compression between parallel plates has been used to determine the stress-strain behavior of starch gels. This testing methodology, which was also used for other polysaccharide gels, may be appropriate for potential testing of ß-glucan gels.

The objectives of this study were to find out whether barley ß-glucan forms gels and to determine the minimal concentration and conditions required. With successful gelation, additional specific objectives were to determine: (a) the effects of ß-glucan concentration on gel behavior, (b) the effect of hydration temperature of ß-glucan solution on gelation, and (c) any differences in gel behavior of laboratory extracted barley ß-glucan (BBG) gum with that of pure commercial BBG gum and cornstarch.

MATERIALS & METHODS

Materials

ß-Glucan concentrates were extracted from non-waxy Condor and waxy barley (mix of SB89528 and SB89497) cultivars according to Wood et al. (1978). Extraction pH was maintained at pH 6.7, 7 or 8 at 55°C for 0.5h. This procedure resulted in low viscosity (LV, <20 mPa·s for 1% w/v solution) and medium viscosity (MV, 20–100 mPa·s) gums. High viscosity gums (HV, >100 mPa·s) were produced by refluxing whole barley flour in 70% ethanol for 2h with or without additional purification with Terramyn 120LN (thermostable α-amylase from Bacillus licheniformis, E.C. 3.2.1.1., Novo Nordisk BioChem North America, Inc., Franklin, NC) as described by Burkus and Temelli (1998). Pure (>99% purity) barley ß-glucan gums of LV (5.9 mPa·s) and HV (114 mPa·s) type (1% w/v solution in Ostwald C-type Viscometer at 30°C) and molecular weights of 137,000 and 327,000 daltons, respectively, were purchased from Megazyme International Ireland Ltd. (Bray Business Park, Bray, County Wicklow, Ireland). Paraffin mineral oil was purchased from Fisher Scientific Co. (Fair Lawn, NJ). Commercial cornstarch was obtained in a local grocery store.

Methods

ß-Glucan and amylose content determination. ß-Glucan content of the extracted barley gums was determined according to McCleary and Glennie-Holmes (1985) using Megazyme (Ireland) enzyme assay kit. Amylose content of cornstarch was determined according to Chrastil (1987).
Viscosity measurements. Viscosity measurements were performed using a Haake Rotoviscometer (model RV-3, Gruber Haake, Berlin, Germany) equipped with MK 500 measuring head and NV viscosity sensor system (8 mL cup) with tempering vessel to maintain constant temperature (25±0.2°C). BBG gum solutions (1%, w/w) were prepared as follows: Gum was dispersed in distilled water, boiled for 5 min on a hot plate stirrer, and held at ~77°C for 1 h while stirring for complete hydration. Then, the solution was cooled to room temperature for 1 h while stirring and concentration was adjusted with distilled water. Apparent viscosity was measured as 32 rpm.

Gel preparation. Preliminary tests were carried out to determine whether BBG gums would form gels. BBG gum was dispersed in distilled water in concentrations of 3, 4, and 5% (w/w, as is basis) and then hydrated as described for viscosity measurements. Beakers containing BBG solutions were covered with Parafilm® (American Can Co., Greenwich, CT) and stored overnight at ~4°C or 22°C. The onset of gelation was observed by tilting the beakers slowly and checking for flow. The lack of flow after tilting the beakers 90° was considered to be a sign of gel setting.

For compression testing, solutions were prepared in the same manner as for preliminary testing in concentrations of 5, 5.5 and 6% (w/w, as is), poured into cylindrical plastic molds (20 mm × 40.38 mm i.d.) and held at 22°C for 24 h. Top and bottom plates of the molds were made of Acrylite® FF (San Diego Plastics, Inc., San Diego, CA) and the molds were lubricated with mineral oil. Additionally, the effect of hydration temperature was studied by heating Diepko instead of boiling.

Compression testing of gels. Compression tests were performed using an Instron Universal Testing Instrument (model 4201, Instron Corp., Canton, MA) with a 5 kg load cell at cross head speed 5 mm/min and load and displacement were measured until break occurred. Platens were covered with Saran Wrap® and lubricated with mineral oil. Data were collected and processed with Instron Series IX software. The raw data, load (kg) and displacement (mm), were used to calculate stress and strain at failure, respectively. Apparent stress (σ, Pa) is expressed by

\[ \sigma = F/\pi R_0^2 \]  

(1)

where \( F \) is the force (or load) applied to the gels with a cross-sectional area \( \pi R_0^2 \). Conversion of apparent stress to “true stress” takes into account the change in the geometry of a gel during compression according to

\[ \sigma_{TR} = (F/\pi R_0^2) - (h/h_0) \]  

(2)

where \( h \) is the height of a sample at failure and \( h_0 \) is the initial height (20 mm) (Christianson et al., 1985). Strain (ε, mm/mm) is calculated as

\[ \varepsilon = \Delta h/h_0 \]  

(3)

where \( \Delta h \) is the change in the height of a sample during compression (displacement). Similar to stress, strain can be converted to “true strain” as

\[ \varepsilon_{TR} = \ln(h/h) \]  

(4)

where \( h \) is the height of a sample at failure (Peleg, 1977). A factor that contributed to variations in the strain data was the difficulty in manual positioning the upper platen to exactly the same point for every sample.

Statistical analysis of data

Gels of each gum at each concentration were prepared and tested in duplicate. Analysis of variance of results was performed using General Linear Model procedure of SAS Statistical Software, Version 6.12 (SAS Institute, Inc., 1989). Multiple comparisons of the means were carried out by least significant difference (LSD) test. Significance of differences was defined at \( p \leq 0.05 \).

RESULTS & DISCUSSION

Preliminary gelation tests

Different concentrations of gums of low-, medium- and high-viscosity were tested to determine if they would form gels after holding the BBG gum solutions at 4°C or 22°C. High-viscosity gums did not gel at 3 or 4% (w/w) after 24 h at 4°C or 22°C. It was impossible to achieve 5% level of HV gum due to poor hydration and mixing in a very viscous solution and formation of a thin layer on top. Condor barley gum (LV) extracted at pH 7 did not gel at 4% concentration. However, gelation occurred at 5% level after 3 days at 4°C. When waxy barley gums extracted at pH 7 (LV) and pH 8 (MV) were tested at 5% levels, 5 days at 4°C were required for gelation.

Doublier and Wood (1995) reported that hydrolyzed oat gums exhibited gel-like behavior and speculated that high viscosity of oat gums could prevent gelation. Therefore, the higher viscosity of barley gums held at 4°C may have had a delaying effect on gelation onset. When 5% solutions of Condor barley gum extracted at pH 7 and waxy gums extracted at pH 6, 7 (LV) or pH 8 (MV) were allowed to set at 22°C instead of 4°C, the setting time was substantially shortened to as low as 24 h for LV gums. β-Glucan content and viscosity of these gums were compared (Table 1). Condor gum extracted at pH 7 was chosen for further testing.

Based on preliminary tests, we concluded that: (a) 5% concentration of BBG was necessary for proper gelation, (b) gum should have a low viscosity <15 mPa·s to set a gel within 24 h, (c) gum must have a high β-glucan content, >70% (dry matter basis), and (d) gel setting should be carried out at 22°C.

Effect of β-glucan concentration and hydration temperature on gel behavior

Compression tests were performed on 5, 5.5 and 6% (w/w, as is basis) gels of Condor gum extracted at pH 7 and load vs displacement plots were compared (Fig. 1). Note that only a 10% shift in concentration from 5 to 5.5% produced a 2.5 times stronger gel (1.84 vs 4.67 kPa). A further increase in concentration to 6% resulted in an additional increase in gel strength of only 36% to 6.33 kPa. An increase in gel strength with gum concentration was expected since similar behavior had been reported for curdlan, carrageenan, agar-agar and konjac (Nakao et al., 1991). The reported increase in gel strength had been in agreement with Damodaran (1989) who found that the strength of soy protein gels was proportional to the square of protein concentration. However, such proportionality was not exhibited by BBG gels.

The true stress and strain at the break point were compared (Table 2) for gels of different Condor gum concentrations. The variation in load data was <4.6% for all samples except 5.5% gel, which had a relatively high variation of ±7.6% in the maximal load at breaking point. Higher (p≤0.05) stresses were required to break the gel with increasing gum concentration. As well, there was an increase (p≤0.05) in strain at break point with an increase in concentration from 5 to 5.5%. However, strains for 5.5 and 6% gels were similar (p>0.05).

Heating to 80°C instead of boiling the Condor gum solution produced only slightly (p>0.05) weaker gels (Table 2). The solution heated to 80°C was apparently more viscous and thus required a longer setting time. This delay in setting time could be the reason for the weakness of gels at 24 h.

Comparison of BBG to pure β-glucan and cornstarch gels

The gelation behavior of barley β-glucan concentrates prepared in our laboratory was compared to that of commercial LV and HV β-
Barley β-Glucan gelation...

**Table 1—Viscosity of 1% (w/w) solutions and β-glucan content of gels made of gums extracted from Condor and waxy barleys at different pH levels and commercial LV-pure β-glucan gum**

<table>
<thead>
<tr>
<th>Gum</th>
<th>Extraction pH</th>
<th>Gum conc (%)</th>
<th>β-Glucan in gum (°C)</th>
<th>β-Glucan in gel (mPa-s, 1% soln)</th>
<th>Apparent viscosity (mPa-s, 1% soln)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Condor</td>
<td>pH 7</td>
<td>5.0</td>
<td>67.2</td>
<td>3.4</td>
<td>4.9</td>
</tr>
<tr>
<td></td>
<td>pH 7</td>
<td>5.5</td>
<td>67.2</td>
<td>3.7</td>
<td>4.9</td>
</tr>
<tr>
<td></td>
<td>pH 7</td>
<td>6.0</td>
<td>67.2</td>
<td>4.0</td>
<td>4.9</td>
</tr>
<tr>
<td>Waxy</td>
<td>pH 6</td>
<td>5.0</td>
<td>55.4</td>
<td>2.8</td>
<td>6.4</td>
</tr>
<tr>
<td></td>
<td>pH 7</td>
<td>5.0</td>
<td>65.4</td>
<td>3.3</td>
<td>12.8</td>
</tr>
<tr>
<td></td>
<td>pH 8</td>
<td>5.0</td>
<td>72.0</td>
<td>3.6</td>
<td>37.5</td>
</tr>
<tr>
<td>LV-pure</td>
<td>—</td>
<td>5.0</td>
<td>90.0</td>
<td>4.5</td>
<td>10.8</td>
</tr>
</tbody>
</table>

**Table 2—True stress and strain at failure for gels made of Condor β-glucan gum extracted at pH 7, cornstarch and commercial low-viscosity (LV) pure β-glucan gum**

<table>
<thead>
<tr>
<th>Gum</th>
<th>Gum conc (%)</th>
<th>Hydration temp (°C)</th>
<th>True stress¹ (kPa)</th>
<th>True strain² (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Condor</td>
<td>5.0</td>
<td>98</td>
<td>1.84d</td>
<td>0.38e</td>
</tr>
<tr>
<td></td>
<td>5.5</td>
<td>98</td>
<td>4.67e</td>
<td>0.42f</td>
</tr>
<tr>
<td></td>
<td>6.0</td>
<td>98</td>
<td>6.33d</td>
<td>0.41d</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>80</td>
<td>1.70e</td>
<td>0.25f</td>
</tr>
<tr>
<td>LV-pure</td>
<td>5.0</td>
<td>98</td>
<td>3.44f</td>
<td>0.36g</td>
</tr>
<tr>
<td>Cornstarch</td>
<td>6.0</td>
<td>98</td>
<td>1.39d</td>
<td>0.73e</td>
</tr>
</tbody>
</table>

**REFERENCES**


**Fig. 1—Load-displacement plot for gels of different concentrations of Condor β-glucan extracted at pH 7, LV pure commercial barley gum and cornstarch prepared by heating to boiling.**

Gum extraction...
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