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The effect of autoclaving on the dispersibility and stability of three neutral polysaccharides in dilute aqueous solutions

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Abstract

The dispersibility of three neutral polysaccharides, oat β-glucan, detarium xyloglucan and dextran in a dilute water–cadoxen mixture was studied by viscosity measurement. It was found that intrinsic viscosity measurement, with water–cadoxen mixtures as solvents, is a useful tool to distinguish polymer degradation from disruption of supramolecular aggregates. This approach, in conjunction with size exclusion chromatography, was used to study the effects of heat and pressure treatment on the dispersibility and stability of three polysaccharides in aqueous solutions. Autoclaving treatment at 121°C for 15 min may reduce the degree of aggregation. Following autoclaving in aqueous solution, the Huggins constants decreased from 0.66 to 0.42 for oat β-glucan and from 0.63 to 0.56 for detarium xyloglucan. It remains the same for dextran, indicating good solubility of this polymer in water. The current treatment did not cause evident changes in molecular weight and structures to detarium xyloglucan and dextran. However, degradation occurred with oat β-glucan. The Burchard–Stockmayer–Fixman approach was applied to estimate the unperturbed dimension of oat β-glucan and detarium xyloglucan on samples after autoclaving. The characteristic ratio C_∞ was found to be 7.3 for detarium xyloglucan and 4.7 for oat β-glucan, corresponding to the Kratky–Porod persistence lengths of 2.0 and 1.2 nm, respectively.

Keywords: Molecular aggregation; Autoclaving; Stability; Dispersibility; Polysaccharides

1. Introduction

The supramolecular aggregation of water-soluble polysaccharides in aqueous solution is a critical barrier to the accurate characterization of the molecular properties of these polymers using light scattering techniques. In batch measurement the aggregation can be minimized to some extent by choosing different solvents. However, this approach may not be possible for on-line light scattering measurements following size exclusion chromatography because of possible incompatibility of the solvent with the column medium. Using heat and pressure treatment in water to fully disperse polymer molecules is a possible solution. This method has been successfully applied to starch (Aberle, Burchard, Vorwerg & Radosta, 1994) and xyloglucan (Wang, Ellis, Ross-Murphy & Burchard, 1997). The prerequisite for this method is that the polymer does not undergo depolymerisation through covalent bond scission during the heat and pressure treatment.

Although viscosity loss is often used to monitor depolymerisation of polysaccharides, it is difficult to distinguish whether any small changes in viscosity resulted from the disruption of aggregates or from covalent bond cleavage in the polymer chains. In a previous study (Wang, Wood, Cui & Ross-Murphy, 2000), the dispersibility of several polysaccharides in water was different from those in water–cadoxen mixtures. Addition of cadoxen to solutions of polysaccharides in water up to a certain concentration may effectively reduce the aggregation of polysaccharides. This can be detected by the dependence of the specific viscosity (η_{sp}) on concentration according to the Huggins equation:

$$\eta_{sp}/c = [\eta] + k[\eta]^2 c, \quad (1)$$

where $[\eta]$ is intrinsic viscosity, c polymer concentration and k the Huggins constant, a characteristic of the given solvent–polymer pair. Thus, the different dispersibility of polysaccharide in water and in water–cadoxen mixtures might be used as an indicator for distinguishing polymer degradation from disruption of aggregates. In the current paper, this method was applied to study the stability of selected polysaccharides after heat and pressure treatment.

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Since many water-soluble polysaccharides, when used in food and pharmaceutical applications to provide such functionality as thickening, stabilizing and water binding, are often sterilized by autoclaving, the stability of these polymers during autoclaving is critical to their functionality. Therefore, a standard autoclaving treatment (121°C, 15 min) for food sterilizing was used to investigate the effect of heat and pressure treatment on the stability and dispersibility of three polysaccharides: oat β-glucan, detarium gum, and dextran.

2. Materials and methods

2.1. Materials

The β-glucan was extracted and purified as described previously (Wood, Weisz & Blackwell, 1991). The β-glucan content was determined according to the McCleary method (McCleary & Glennie-Holmes, 1985) and it was found to be 88% on a dry weight basis. The ratio of β-(1→4) to β-(1→3) linked glucopyranosyl residues is approximately 7:3 (Parrish, Perlin & Reese, 1960). Detarium gum was prepared and analyzed in the same way as in a previous paper (Wang, Ellis, Ross-Murphy & Reid, 1996). The monosaccharide ratio of the polymer was glucose:xylose:galactose = 1.00:0.72:0.37 (Wang et al., 1996), which raises the effective residue molecular weight from 162 to an average of 317. Dextran T500 was purchased from Pharmacia Fine Chemicals AB, Sweden, without further purification. According to the manufacture, it is of high purity and the weight-average molecular weight is between 450,000 and 550,000. Pharmacia dextran samples with $M_w > \sim 10^5$ are known to be significantly branched, and the branching increases with M_w.

2.2. Preparation of sample solutions

Polysaccharide solutions were prepared by dissolving the sample at 80°C for 1 h and then leaving overnight (~19 h) at room temperature under constant stirring. Typical concentrations used for autoclaving treatment were 0.14% (w/v) for β-glucan and detarium xyloglucan and 1.2% for dextran. These concentrations were selected because they were found to be the appropriate concentrations for the high-performance size-exclusion chromatograph (HPSEC) analysis and intrinsic viscosity measurements by capillary viscometer. The solution was syringed through a 0.45 μm filter to remove large particles before any further treatments, i.e. adding cadoxen or applying autoclaving.

Cadoxen is a solvent well known to workers in the cellulose industries, and despite its toxicity and aggressive nature it is still widely used (see for example Ross-Murphy, 1985). It was prepared as follows. A 29% aqueous solution of ethylenediamine was saturated with cadmium oxide (CdO) in an ice-water bath under vigorous stirring and kept overnight. The solution was then filtered through a sand filter and refrigerated until use. The polysaccharide solutions in different volume fractions of cadoxen were made by mixing the filtered aqueous solutions with the required volume of cadoxen and stirring for at least 1 h before any measurements were made.

2.3. Autoclaving

Autoclaving treatment was performed at 121°C for 15 min. The whole treatment cycle (heating–stabilizing–cooling) took ~50 min. The treated sample solution was cooled to room temperature in a cold-water bath and immediately injected into the HPSEC column.

2.4. High-performance size-exclusion chromatography

The high-performance size-exclusion chromatographic system used was a Shimadzu SCL-10Avp unit (Shimadzu Scientific Instruments Inc., Columbia, Maryland 21046, USA). The column set consisted of two columns in series: a Shodex Ohpak KB-806M (Showa Denko K.K., Tokyo, Japan), and a Ultrahydrogel linear (Waters, Milford, CT, USA). The columns were maintained at 40°C. The mobile phase was 0.1 M $NaNO_3$ with 0.03% (w/w) NaN_3 and the flow rate was 0.6 ml/min. The Viscotec triple detector (Viscotek, Houston, TX) was used for the molecular weight determination, which includes a refractive index detector, a viscometer (Model 250), and a right angle laser light scattering detector. Pullulan standards (P-82, JM Science Inc., NY) were used for calibration of the detectors (but not the columns). Molecular parameters were calculated by the software TriSEC3.0 (Viscotek, Houston, TX). A value of 0.144 ml/g as a refractive index increment was used (Vårum, Smidsrod & Brant, 1992). As stated above, the light scattering detector measures only at a scattering angle of 90°, and for most dilute systems this would tend to underestimate the molecular weight of each fraction (assuming the virial term is small, which it must be for such dilute systems) because of the positive slope of the zero angle extrapolation of the angular (Debye) plot. A correction is made in the TriSEC software for this effect and has been described in detail previously (Beer, Wood & Weisz, 1999). This correction depends upon the value of the radius of gyration. A recent interlaboratory study showed that the molecular weight of a series of β-glucan samples (MW 0.1–0.5 million) obtained from the HPSEC coupled with the triple detector agreed well with data from the multi-angle light scattering detector (Christensen et al., 2000).

2.5. Intrinsic viscosity measurement

The intrinsic viscosity was determined according to the Huggins equation (Eq. (1)) using a dilution capillary viscometer. The capillary viscometer was immersed in a glycerin–water bath to maintain the temperature at 25.0 ± 0.1°C. The measurement was carried out in a fume

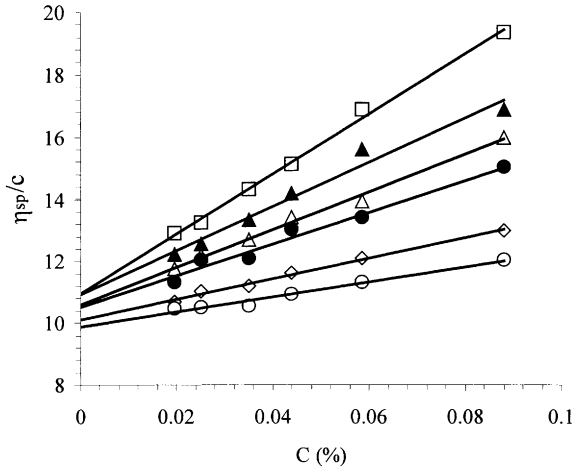

Fig. 1. Huggins plots of oat β-glucan solutions in water and water–cadoxen mixtures with different volume fractions of cadoxen (V_{cad}). (□) 0.00, (▲) 0.05, (△) 0.1, (●) 0.2, (◇) 0.4, and (○) 0.5.

hood because cadoxen is a toxic solvent. The polysaccharide concentration of filtered (0.45 μm) sample solution was measured by HPSEC with an on-line refractometer (part of the triple detector). The sample recovery of the HPSEC system was supposed to be 100%, although the actual recovery was usually between 90 and 100%. This may cause a slight underestimation of the concentration, and thus overestimation of the intrinsic viscosity. However, the primary purpose of this study was not to determine the absolute value of the intrinsic viscosity, but to follow the changes of the intrinsic viscosity in the same solution after autoclaving, or after adding cadoxen.

3. Results and discussion

3.1. Dispersibility of polysaccharides in water and water–cadoxen mixtures

In order to study the dispersibility of polysaccharides in dilute solutions, the specific viscosity (η_{sp}) of the solution was monitored and the data was analyzed using Huggins equation. The intercept of the plot η_{sp}/c against c gives the intrinsic viscosity, and the slope (dividing by $[\eta]^2$) yields the Huggins constant k, which is a measure of the solvent power (Sakai, 1968). Fig. 1 shows the effect on Huggins plots of adding different amounts of cadoxen to water solutions of oat β-glucan. The Huggins constants were found to decrease rapidly from 0.81 ± 0.05 to 0.32 ± 0.04 when the volume fraction of cadoxen (V_{cad}) increased from 0.0 to ~0.4, then consistently decreased at a much lower rate (Table 1). The other two polysaccharides behaved in a samilar manner, i.e. the Huggins constants of water solutions were significantly larger than those of water–cadoxen solutions (Table 1). This indicates that cadoxen is a better solvent for these polysaccharides. The quality of the solvent was improved by the addition of cadoxen to water solution and, according to our understanding of the excluded volume effect, the association between polysaccharide molecules was reduced. The changes in intrinsic viscosity on addition of cadoxen were different among the three polymers (Table 1). The intrinsic viscosity of xyloglucan decreased from 9.3 ± 0.5 dl/g in water to 5.0 ± 0.2 dl/g in 0.65 (V_{cad}) water–cadoxen mixture, while that for oat β-glucan decreased only slightly from 11.0 ± 0.5 in water to 9.9 ± 0.2 in 0.65 (V_{cad}) water–cadoxen mixture. In contrast, the intrinsic viscosity of dextran increased from 0.51 ± 0.03 in water to 0.91 ± 0.03 in 0.5 (V_{cad}) water–cadoxen mixture.

In summary, the addition of cadoxen to an aqueous solution of a polysaccharide improved the dispersibility of the polymers. It seems that a transition from large aggregates to unimers (or smaller aggregates) occurred at a solvent composition of about $0.0 < V_{cad} < 0.4$. Thus a 0.5 (V_{cad}) water–cadoxen mixture could effectively reduce the aggregation of the polysaccharides studied. This provides a convenient approach to distinguish polymer degradation from the dissociation of aggregates. The hypothesis is that if a treatment, such as autoclaving in water, only causes the dissociation of aggregates, the intrinsic viscosity and the Huggins constant in 0.5 (V_{cad}) water–cadoxen solution should not be changed significantly before and after the treatment. However, if the treatment caused polymer degradation, the intrinsic viscosity, but not the Huggins constants,

Table 1
Summary of Huggins constants (k) and intrinsic viscosity $[\eta]$ in water–cadoxen mixtures with different volume fractions of cadoxen (V_{cad}). Values are means of duplicates. The standard errors for $[\eta]$ were less than 0.2 and they were less than 0.05 for k (n.d., not determined)

Sample	k or $[\eta]$ (dl/g)	V_{cad}						
		0.0	0.10	0.20	0.30	0.40	0.50	0.65
Detarium xyloglucan	k	0.63	0.54	0.51	0.48	0.43	0.42	0.40
	$[\eta]$	9.3	7.0	6.0	5.5	5.3	5.1	5.0
Oat β-glucan	k	0.81	0.54	0.46	n.d.	0.32	n.d.	0.25
	$[\eta]$	11.0	10.6	10.5	n.d.	10.1	n.d.	9.9
Dextran	k	0.62	0.40	n.d.	0.36	0.30	0.24	0.22
	$[\eta]$	0.51	0.57	n.d.	0.69	0.76	0.91	n.d.

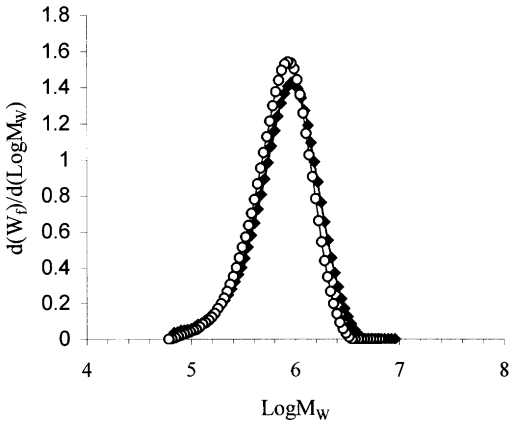

Fig. 2. Molecular weight distribution obtained from HPSEC of detarium xyloglucan before (◆) and after (○) autoclaving obtained from HPSEC.

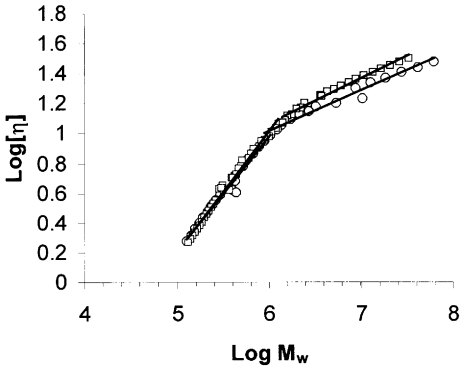

Fig. 4. Mark-Houwink plots of detarium gum in water solution showing that the molecular structure remains virtually unchanged after autoclaving. (□) before autoclaving, and (○) after autoclaving.

in 0.5 (V_{cad}) water–cadoxen mixture will be significantly lower for the treated sample than for the non-treated sample. This approach was tested and applied to the following autoclaving study.

3.2. Effects of autoclaving

3.2.1. Detarium xyloglucan

Fig. 2 shows a normalized molecular weight distribution for a detarium gum solution before and after autoclaving, obtained from HPSEC analysis. The distribution curve was shifted slightly towards the low molecular weight end by autoclaving but the shape remained unchanged. The lower end of the distribution curve did not shift to the left, indicating that the heat and pressure treatment reduced the apparent particle size in the solution but did not produce a significant amount of small molecular species. The HPSEC trace did not distinguish whether the changes in apparent particle size were caused by a reduction in chain length or by the disruption of aggregates. This was evaluated by comparing the intrinsic viscosity of the samples, before and after the autoclaving treatment, in water–cadoxen mixtures. Huggins plots of detarium xyloglucan in water and in 0.5 (V_{cad})

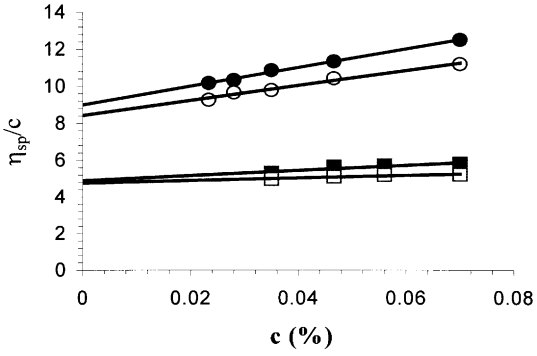

Fig. 3. Huggins plots of detarium xyloglucan solutions before and after autoclaving. (●) before autoclaving in H_2O; (○) after autoclaving in H_2O; (■) before autoclaving in 0.5 V_{cad} cadoxen; and □ after autoclaving in 0.5 V_{cad} cadoxen.

water–cadoxen mixture, before and after autoclaving (Fig. 3), showed that the intrinsic viscosity of detarium xyloglucan in water solution decreased slightly from 9.0 ± 0.3 to 8.4 ± 0.2 dl/g after autoclaving, indicating some reduction in particle size. The slope of the Huggins plot also decreased significantly from 52 to 40, corresponding to a change in the Huggins constant from 0.63 ± 0.05 to 0.56 ± 0.03. This indicates that the association between polymer molecules was reduced by the heat and pressure treatment. However, since the intrinsic viscosities in 0.5 (V_{cad}) cadoxen before and after autoclaving were almost identical (4.9 ± 0.2 and 4.8 ± 0.2 dl/g), the decrease in intrinsic viscosity in water solution after autoclaving is most likely caused by the disruption of aggregates, rather than the degradation of polymer chains.

The combination of intrinsic viscosity measurements with the HPSEC profiles showed that detarium xyloglucan in water solution did not degrade after autoclaving at 120°C for 15 min, but the aggregation was reduced. Fig. 4 is the Mark–Houwink plots of detarium gum in water solution corresponding to the data in Fig. 2. The two plots (i.e. before and after autoclaving) were superimposed when the MW $< \sim 10^6$, indicating the molecular structure remains virtually unchanged after autoclaving, which confirms earlier findings (Wang et al., 1997). The difference when MW $> 10^6$ is also considered minimal. It is interesting to notice that there is clearly a downward curvature at MW $> \sim 10^6$. The Mark–Houwink exponents for samples after autoclaving were 0.81 when MW $< \sim 10^6$ and 0.3 at MW $> \sim 10^6$. The former figure agrees well with the value (0.8) expected for an excluded volume linear chain in a good solvent. The latter value (0.3) implies a more compact structure of the high molecular weight fractions. This observation is again consistent with the finding in the previous paper (Wang et al., 1997), in which a low degree of long chain branching structure was assigned to this polysaccharide, and a finding recently confirmed by scattering measurements on chemical derived samples in non-aqueous solution (K. Kajiwara and M. Dentini, personal communication). The low Mark–Houwink exponent at high molecular weight end suggests

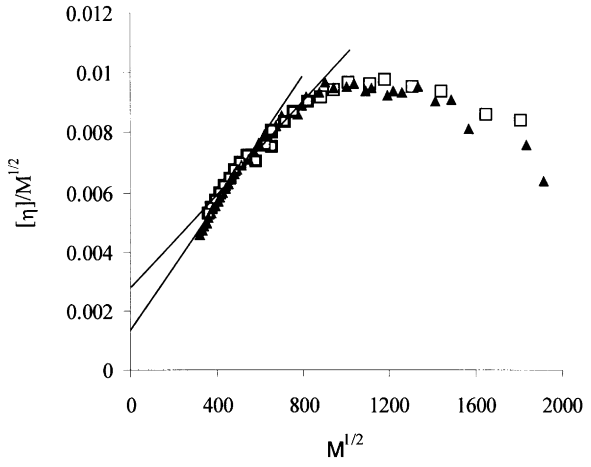

Fig. 5. BSF plots of detarium gum in water solution before (□) and after (▲) autoclaving.

that the high molecular weight species have a higher segment density within the coil, likely a consequence of molecular branching. It is also possible that these fractions still contained some molecular aggregates.

The same data were plotted in a form of $[\eta]M^{-1/2}$ versus $M^{1/2}$ (the well-known Burchard–Stockmayer–Fixman or BSF plot, Fig. 5) in order to estimate the unperturbed dimensions of the polymer, which is based on the following relationships (Morris & Ross-Murphy, 1981; Stockmayer, 1963):

$$[\eta]M^{-1/2} = K_\theta + 0.036\Phi BM^{1/2} \quad (2)$$

$$[\eta] = \Phi l^3 (C_\infty/m)^{3/2} \quad M^{1/2} = K_\theta M^{1/2} \quad (3)$$

where l is the length of one chain segment and M is the molecular weight of this segment. Φ is the Flory–Fox parameter, $\approx 2.6 \times 10^{26}\ \mathrm{kg}^{-1}$ for random coils. C_∞ is the characteristic ratio, a measure of the restriction of chain flexibility. From Eq. (2), the intercept of the plot $[\eta]M^{-1/2}$ versus $M^{1/2}$ yields K_θ, the value of $[\eta]M^{-1/2}$ in Θ-conditions. This is the simplest extrapolation for estimating unperturbed coil dimensions from perturbed dimensions. The BSF plots

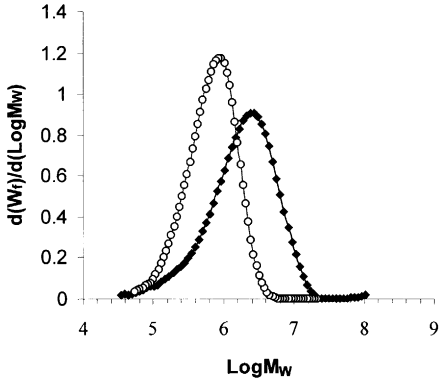

Fig. 6. Molecular weight distribution of oat β-glucan solutions before (◆) and after (○) autoclaving obtained from HPSEC.

yielded a good linear region from the low molecular weight fractions, and curved downward when the molecular weights were above 10^6. Yamamoto, Fujii, Tanaka and Yamakawa (1971) also observed this curvature for polystyrene with high molecular weights ($>10^6$). The BSF method assumes that, at low molecular weights, all flexible linear polymers behave as Gaussian or random flight chains, where $[\eta]$ is proportional to $M^{0.5}$. At higher molecular weights and for good solvents the excluded volume terms contribute and $[\eta]$ becomes proportional to $M^{0.6}$. From the initial linear part, the K_θ value was found to be 2.7×10^{-4} and $1.4 \times 10^{-4}\ \mathrm{m^3\,kg^{-1}}$, for samples before and after autoclaving, respectively. On the basis that each molecule is single-stranded and each β-(1 → 4)-linked anhydro glucopyranosyl residue (including the side substitutes) in the back bone is taken as one segment of the chain, using the residue length $l = 0.54$ nm (Morris & Ross-Murphy, 1981) and average molecular weight of residue $M = 317$, the characteristic ratio was calculated according to Eq. (3) as 11.2 and 7.5 for samples before and after autoclaving, respectively. Since C_∞ is simply the ratio of the Kuhn or statistical segment length l_K to the residue length l for linear polymers (Burchard, 1994), this gives the Kuhn length as 6.1 and 4.1 nm, respectively. Other measures of chain "stiffness" are defined, including the Kratky–Porod (KP) and Yamakawa–Fujii (YF) persistence lengths (which are not quite the same for semi-flexible macromolecules). For such systems, the KP length, q, is well approximated as $l_K/2$, giving values of 3.1 and 2.0 nm for the before and after autoclaving systems. A further detailed analysis is limited by the previously mentioned evidence for long chain branching. Although characteristic ratios can be defined for branched systems, it is more usual to make the comparison with the overall dimensions of corresponding linear chains, as suggested by Zimm and Stockmayer (Burchard, 1994).

The decrease in C_∞ after heat and pressure treatment again indicates dissociation of the molecular aggregates, and is expected to improve the description of the molecular characteristics. The C_∞ value after autoclaving (7.5) is slightly lower than those reported for other linear polysaccharides bearing a diequatorial, β-(1 → 4)-linked backbone, such as carboxymethylcellulose (14.2) (Brown & Henley, 1964) and guar galactomannan (12.6) (Robinson, Ross-Murphy & Morris, 1982). This would not be expected if the xyloglucan were essentially an unbranched polymer, because the heavy glycosyl substitution of the glucan chain tends to restrict the degree of free rotation of the coil more, leading to an increase in C_∞. In addition, this value is much lower than the C_∞ value of 110, reported for tamarind xyloglucan (Gidley et al., 1991). However, in retrospect (W. Burchard, personal communication), it is evident that much of the physico-chemical data obtained for tamarind (Gidley et al., 1991) reflected a highly associated system. Certainly the value of the characteristic ratio here is much larger than would be expected on the basis of

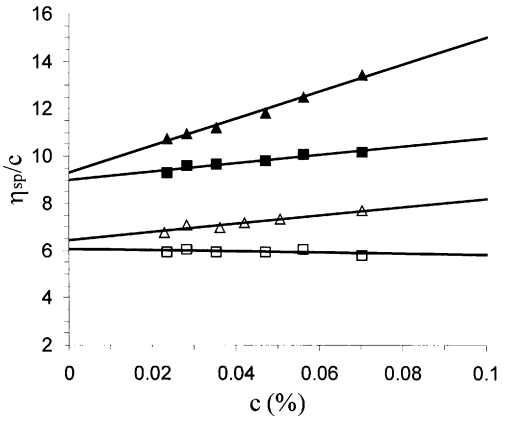

Fig. 7. Huggins plots of oat β-glucan solutions before and after autoclaving. (▲) before autoclaving in H_2O; (△) after autoclaving in H_2O; (■) before autoclaving in 0.5 (V_{cad}) cadoxen; and (□) after autoclaving in 0.5 (V_{cad}) cadoxen.

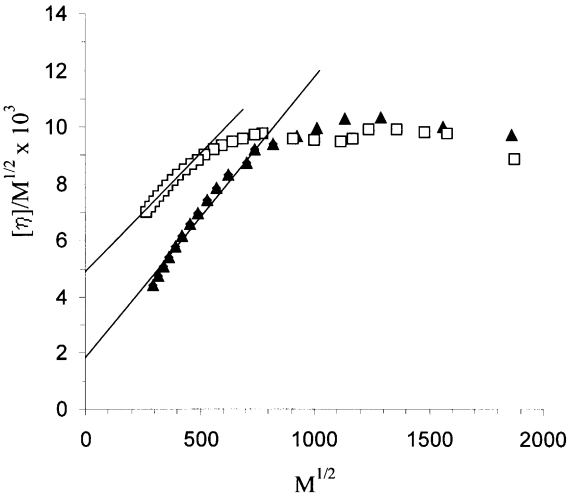

Fig. 9. BSF plots of oat β-glucan water solution before (□) and after (▲) autoclaving.

the chain backbone. Comparison of detarium with tamarind xyloglucan is planned.

3.2.2. Oat β-glucan

The HPSEC molecular weight distribution curves of oat β-glucan in water solution showed shifts to the low molecular weight end after autoclaving (Fig. 6). Also, the intrinsic viscosities of autoclaved samples in both water and 0.5 (V_{cad}) water–cadoxen mixture are much smaller than those of non-autoclaved samples (Fig. 7). Both results from HPSEC and intrinsic viscosity measurement indicated clearly that autoclaving resulted in polymer degradation. The same effect was seen with guar gum (Kök, Hill & Mitchell, 1999), but in this case reflected oxidative processes that could be reduced by addition of anti-oxidants, or heating under nitrogen. Studies of this nature with oat β-glucan are planned.

Following autoclaving, the slope of the Huggins plot for β-glucan in water decreased by a greater extent than observed for detarium gum, from 56 to 17, corresponding to a change in the Huggins constant from 0.68 ± 0.05 to 0.42 ± 0.03[1]. This is consistent with the observation that oat β-glucan is more difficult than detarium xyloglucan to dissolve in water and has a greater tendency to form aggregates in water solution.

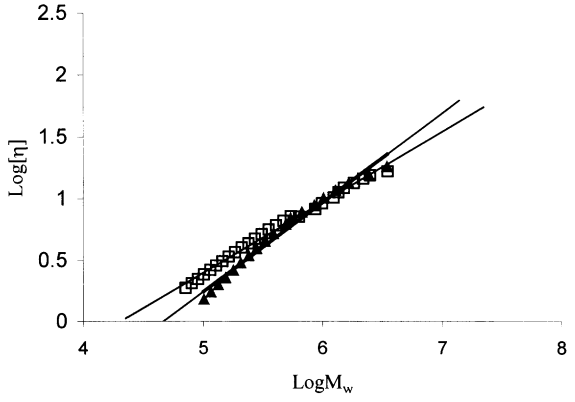

Fig. 8. Mark–Houwink plots of oat β-glucan in water solution showing that the increase of Mark–Houwink parameter α after autoclaving. (□) before autoclaving and (▲) after autoclaving.

The Mark–Houwink plots of oat β-glucan in water solution obtained from HPSEC before and after autoclaving (Fig. 8), showed that the exponent (α) increased from 0.57 to 0.73 after autoclaving. This may be ascribed to the break up of aggregates, because the more compact structure usual for aggregates leads to a lower value of α, just as for highly branched polymers such as the high molecular weight dextrans. The same data were also analyzed by the BSF extrapolation (Fig. 9). The values of K_θ were found to be 4.9×10^{-4} and $1.9 \times 10^{-4}\ m^3\ kg^{-1}$ for samples before and after autoclaving, respectively. Since oat β-glucan is a copolymer consisting of β-(1 → 3)- and β-(1 → 4)-linked glucosyl residues, an average residue length (l) has to be used to estimate the C_∞. This is defined as $l^2 = P_3 l_3^2 + P_4 l_4^2$ (Buliga & Brant, 1986), where P_3 and P_4 are the mole fraction of β-(1 → 3) and β-(1 → 4) residues, and l_3, l_4 are the corresponding residue lengths, respectively. Using $l_3 = 0.48$ nm, $l_4 = 0.54$ nm (Morris & Ross-Murphy, 1981) and $M = 162$, the calculated values for C_∞ were 9.2 and 4.7, respectively. Using our previous discussion, these correspond to the Kratky–Porod persistence lengths of 2.3 and 1.2 nm, respectively. The values were lower than those obtained for detarium xyloglucan, probably because of the interruption of the β-(1 → 3)-linkages, which will reduce the persistence of orientation of the cellulosic backbone. Calculations from molecular modeling (Buliga & Brant, 1986) agreed with experimentally determined values of C_∞ of 18 for barley β-glucan although, historically, calculated values of characteristic ratio for polysaccharides have

[1] β-glucan sample used here was different from the sample used in Section 3.1.

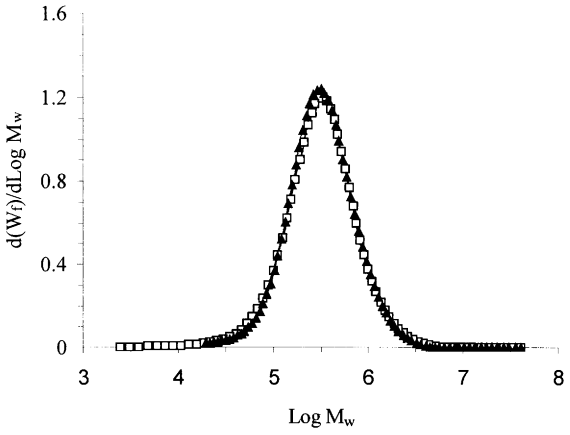

Fig. 10. HPSEC profiles of dextran water solutions before (□) and after (▲) autoclaving showing no difference in molecular weight distributions after the treatment.

often been considerably larger than those reported in experiments. Oat and barley β-glucan are predominantly composed of β-(1 → 3)-linked cellobiosyl and cellotriosyl units but barley β-glucan contains more of the former structural feature. A lower C_∞ for oat β-glucan would suggest a more flexible conformation or less aggregates. Certainly our observations suggest that the lower MW and greater regularity of structure of barley β-glucan promote chain association and gel formation (Cui & Wood, 2000). However, in the calculations of Buliga and Brant (1986), the present of longer sequences of consecutive β-(1 → 4)-linked glucopyranosyl units, in addition to the main structural units, played a significant role in determining the value of C_∞. The current calculation does not take this factor into count, which may underestimate the C_∞. Further study is needed in this respect.

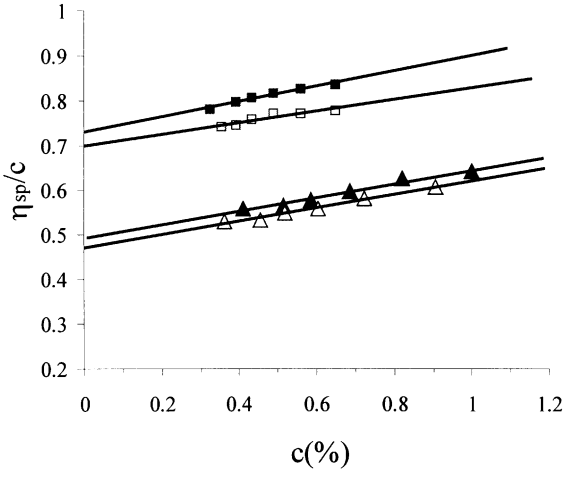

Fig. 11. Huggins plots of dextran water solutions before and after autoclaving. (▲) before autoclaving in H_2O; (△) after autoclaving in H_2O; (■) before autoclaving in 0.3 (V_{cad}) cadoxen; and (□) after autoclaving in 0.3 (V_{cad}) cadoxen.

3.2.3. Dextran

Fig. 10 shows the molecular weight distribution of dextran before and after autoclaving, and Fig. 11 is the corresponding Huggins plots in water and 0.3 (V_{cad}) water–cadoxen mixture. The intrinsic viscosities in water were 0.49 ± 0.02 and 0.47 ± 0.02 for samples before and after autoclaving, respectively; they were 0.70 ± 0.02 and 0.73 ± 0.02 in 0.3 (V_{cad}) water–cadoxen mixtures. Thus, autoclaving did not change $[\eta]$ significantly in either water or cadoxen. The Huggins constants were also similar before and after autoclaving: 0.62 ± 0.05 and 0.68 ± 0.04 in water and 0.32 ± 0.04 and 0.27 ± 0.04 in 0.3 (V_{cad}) water–cadoxen mixture, respectively. From these results, it is clear that the present autoclaving conditions did not cause degradation of dextran, which is consistent with the known excellent stability and solubility of dextrans in water.

4. Conclusions

The addition of cadoxen to neutral polysaccharide-water solutions may reduce the degree of aggregation. Intrinsic viscosity, with water–cadoxen mixtures as a solvent, is a measurement to distinguish polymer degradation from the disruption of aggregates. Autoclaving treatment at 121°C for 15 min reduced the degree of aggregation. For both detarium xyloglucan and dextran this did not induce changes in molecular weight and structure. However, molecular degradation did occur with oat β-glucan.

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