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Rheological properties of water-soluble spruce *O*-acetyl galactoglucomannans

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ABSTRACT

The thermal and rheological properties of spray-dried, ethanol-precipitated, purified, and deacetylated spruce galactoglucomannans (GGM) were investigated by rheological measurements and differential scanning calorimetry. The shear rate dependence of viscosity and the effects of the drying method, temperature, ionic strength, and deacetylation on rheological properties were studied. GGM solutions exhibited a shear thinning behaviour. GGM solutions did not obey the Cox–Merz rule. The storage modulus of GGM solutions increased with an increase in concentration; gradually until a concentration of 5%, but rapidly at higher concentrations. Ethanol-precipitated GGM solutions showed a more elastic behaviour than spray-dried GGM solutions. Deacetylation caused an increase in apparent viscosity and more significantly in storage modulus. The storage modulus increased slightly with a decrease in temperature. A small amount addition of NaCl slightly changed the oscillatory behaviour. The effects of above factors were discussed in terms of molecular interactions. The rheological measurements of GGM solutions provide the basis of functionalities of GGM solutions.

1. Introduction

Polysaccharides derived from various natural sources, i.e. plant (Crescenzi et al., 2002; Murphy, 2000), animal (Ledward, 1990; Taghizadeh & Davari, 2006), and bacterial sources (Bradshaw, Nisbet, Kerr, & Sutherland, 1983; Carbonero et al., 2005), as well as from seaweeds (Armisen, 1991; Fan & Chen, 1988; Imeson, 2000), are nowadays of great interest. This interest is generated by the features of these natural sources, such as being able to produce biodegradable and biocompatible new products and as value-added materials (Hannuksela & Holmbom, 2003; Kokie & Suzuki, 2001; Martinichen-Herrero, Carbonero, Sassaki, Gorin, & Iacomini, 2005; Pang, Chen, Park, Cha, & Kennedy, 2007; Tanaka, Nakatsuka, & Suzuki, 1977; Vuksan et al., 2001; Wu & Shen, 2001; Zhang, 2004). Knowledge of solution properties is needed to understand the polysaccharides' behaviour in different applications. The main factors affecting the solution properties of polysaccharides are the molecular structures of the polysaccharides themselves, for example, the content of side galactose units and degree of substitution, molar mass, and temperature, pH, and ionic strength circumstances (Takigami, 2000; Wielinga, 2000).

The water-soluble *O*-acetyl galactoglucomannans, biodegradable natural polymers from a renewable source, are the main hemicellulose type in most softwood species, and they account for 10–20% of the wood material (Sjöström, 1993; Willför et al., 2003; Willför, Sundberg, Hemming, & Holmbom, 2005). The GGM consists of a main chain of randomly distributed (1 → 4)-linked β-D-mannospyranosyl and (1 → 4)-linked β-D-glucopyranosyl units. (1 → 6)-linked α-galactopyranosyl and β-galactopyranosyl units occur as single-unit side chains attached to both the mannose and glucose units in the main chain (Hannuksela & du Penhoat, 2004; Willför et al., 2003). The hydroxyl groups at C-2 and C-3 in the mannose units are partly substituted by *O*-acetyl groups. GGM can be recovered from process waters in mechanical pulp mills using spruce, where 5–10% of the cell wall GGM are dissolved (Willför et al., 2003). Recent pilot-scale trials have shown that even certain waste waters can be used for recovering GGM (Xu, Willför, Sundberg, Pettersson, & Holmbom, 2007). Some potential applications of GGM have been recently studied (Hannuksela, Tenkanen, & Holmbom, 2002; Sundberg & Holmbom, 1997; Sundberg, Thornton, Petterson, Holmbom, & Ekman, 1994). GGM-based hydrogels and films have also been investigated (Hartman, Albertsson, & Sjöberg, 2006; Mikkonen et al., 2006; Söderqvist-Lindblad, Albertsson, Ranucci, Laus, & Giani, 2005).

Spruce GGM is now available in large amounts, and thus it is important to study its physicochemical properties to provide basic information for its applications. In a previous study, the GGM showed good solubility and stability in aqueous solution (Xu et al., 2007). The viscosity of GGM was much lower than that of other mannans, which can be explained by a lower molar mass. In the present study, the thermal and rheological properties of

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GGM solutions were further investigated. The influence of the means of drying, temperature dependence, and ionic strength, as well as *O*-acetyl substitution was studied.

2. Materials and methods

2.1. Materials

At a Finnish mill producing thermomechanical spruce pulp, GGM from the process water was concentrated using filtration and ultrafiltration techniques. The concentrate obtained was either spray-dried (GGMSpDr) or precipitated in ethanol and then dried in a vacuum oven at 40 °C (GGMEtOH). Purified GGM (GGMPuDi) was prepared by redissolving GGMSpDr and performing dialysis using a membrane with 12–14,000 Da. Deacetylated GGM (GGMDeAc) was prepared by treating GGMSpDr solution with adding 1 M NaOH to pH 11 at 60 °C for 2 h and performing dialysis as previously indicated.

The chemical characteristics of the GGM samples are shown in Table 1. The degree of acetylation, calculated on the molar amount of GGM (assuming a ratio of Man:Glc:Gal of 4:1:0.5), was approximately 15%, for both GGMSpDr and GGMEtOH. The average molar mass of GGMSpDr and GGMEtOH was approximately 39 and 46 kDa, respectively, determined by size exclusion chromatogram and multi-angle laser-light-scattering.

2.2. Preparation of mannans solutions

The GGM solutions were prepared at different concentrations, by adding a known weight of the dried sample to distilled water at room temperature. The temperature was then raised to 80 °C and this temperature was kept constant for 2 h, under continuous stirring with a magnetic stirrer. Finally, the solution was stirred overnight at room temperature.

2.3. Rheological measurements

Rheological measurements were conducted with a Bohlin VOR rheometer system using ordinary concentric cylinder geometry (C25 cup and bob geometry). A thin layer of paraffin oil was applied on top of the sample to avoid evaporation. The rheometer was equipped with a temperature regulator in the sample chamber within 0.1 °C of the set value. All rheological experiments were conducted at 25 °C. Both steady and oscillatory tests were conducted on freshly made samples. The values of the strain amplitude were checked to ensure that all oscillatory shear experiments were performed within the linear viscoelastic regime, where the dynamic storage modulus (G') and loss modulus (G'') are independent of the strain amplitude. All measurements were repeated twice.

Table 1
The characteristics of the two differently dried GGMs

	GGMSpDr	GGMEtOH
Sugar composition, mol %		
Mannose	53	58
Glucose	23	18
Galactose	13	13
Galacturonic acid	4.3	4.1
Other	<7	<7
GGM mol %[a]	73	80
Degree of acetylation (DA), %[b]	16	14
Average molar mass, kDa	39	46

[a] Assuming a ratio of Man:Glc:Gal of 4:1:0.5.

[b] Calculated on the assumed molar amount of GGM.

2.4. Differential scanning calorimetry (DSC)

Thermal analysis was conducted with a TA Instrument Q1000 MDSC utilizing the Modulated Differential Scanning Calorimetry (MDSC) mode. Approximately 20 mg of sample dispersion was put into a hermetic aluminium crucible which was sealed by an encapsulating press forming a fused hermetic seal. The samples were heated from 25 to 120 °C at 2 °C/min heating rate, with an applied modulation of the heating rate of ±1.27 °C amplitude during a 60 s period. An empty crucible was used as a reference. Indium was used to calibrate the instrument. Analysis of data was made using TA Universal Analysis software. The measurement was repeated twice.

3. Results and discussion

3.1. Rheological properties

The oscillatory measurements were now performed at a small amplitude oscillatory shear, in which the polymeric structure was not significantly disturbed from its equilibrium state. The rheological properties of GGMSpDr, GGMEtOH, GGMPuDi, and GGMDeAc were studied. The effects of drying methods, temperature, salt addition and deacetylation on the rheological properties are discussed. Oscillatory measurements provide the characteristics of random-coil polysaccharides (Brummer, Cui, & Wang, 2003; Mitchell, 1979). The spectra of storage modulus, G', and loss modulus, G'', were of the expected entanglement solution form.

3.1.1. Shear rate dependence of viscosity

Fig. 1 shows the effect of shear rate on viscosity of GGMSpDr and GGMEtOH at different concentrations. Similar to other random-coil polysaccharides (Brummer et al., 2003), the viscosity of GGMSpDr and GGMEtOH solutions was shear rate-dependent at high concentrations, while Newtonian flow behaviour was observed at low concentrations. The increase in viscosity of 0.5% GGMSpDr and 0.5% and 5% GGMEtOH solutions at low shear rates is probably not a shear thickening behaviour, but so-called 'zero error' which is often due to mechanical or electrical offsets in the zero reading (Barnes, 2002). Shear thinning is the expected behaviour for GGM solutions at concentrations higher than 0.5%, above which GGM solutions were suggested to be semi-dilute and concentrated (Xu et al., 2007). Both GGM solutions at 0.5% exhibited a near Newtonian, but slight shear thinning behaviour. Shear thinning is more dramatic at higher concentrations. As stated by Morris, Cutler, Ross-Murphy, Rees, and Price (1981) and Graessley (1974), the mechanism of reduction in viscosity is entirely different for dilute and concentrated solutions. The reduction for dilute solutions is ascribed to alignment of transiently elongated coils in the direction of flow, which might be applied to interpret the behaviour for GGMSpDr and GGMSpDr solutions at concentrations lower than 0.5%. But for concentrated solutions, an imposed deformation is applied to disrupt the entanglements while the new entanglements form at the same time to replace the disrupted ones. The greater rate of disruption of entanglements than formation of new entanglements causes a reduction in viscosity, when shear thinning occurs. For a more concentrated solution, more entanglements are disrupted and more time is required to form new ones. Therefore, the rate of disruption of entanglements increases faster than that of formation of new entanglements with increasing in concentration.

Applicability of the Cox–Merz relationship was also investigated by plotting complex dynamic viscosity η^* against frequency (Fig. 1). The Cox–Merz rule states that η^* as a function of frequency is almost identical to η as a function of shear rate (Cox & Merz,

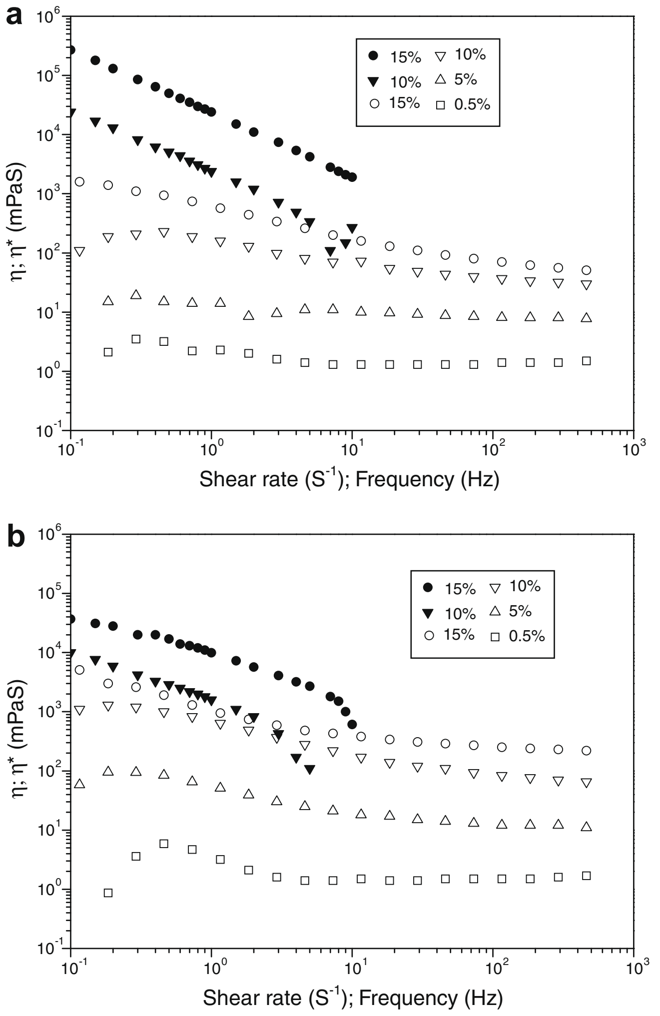

Fig. 1. (a) Shear rate dependence of viscosity *η* for GGMSpDr at concentration concentrations of 0.5 (□), 5 (Δ), 10 (∇), and 15% (○). The frequency of dynamic viscosity *η** is also shown for the 10 (▼) and 15% (●) solutions. (b) Shear rate dependence of viscosity *η* for GGMSpDr at concentration concentrations of 0.5 (□), 5 (Δ), 10 (∇), and 15% (○). The frequency of dynamic viscosity is also shown for the 10 (▼) and 15% (●) solutions.

1958). The dynamic viscosity η^* of only two concentrations, 10% and 15%, is shown for clear observation in the figure. Both solutions showed deviations, in which η^* was higher than η, especially at low values of shear rate or frequency. This indicates that different types of molecular rearrangements were occurring in the two flow patterns over the applied shear rate or frequency range (Richardson & Ross-Murphy, 1987a, 1987b). It can be attributed to more-specific molecular associations of longer timescale or hyperentanglements than non-specific physical entanglements (Morris et al., 1981; Robinson, Ross-Murphy, & Morris, 1982).

3.1.2. Effect of drying methods

Different drying methods can affect the properties of the final product. GGMSpDr and GGMEtOH were now compared. The GGMEtOH had a higher viscosity than GGMSpDr at a settled concentration (Fig. 2). Shear thinning behaviour was also slightly more dramatic for GGMEtOH solution at the same concentration. As shown in Fig. 2a, the frequency-dependent moduli of GGMSpDr at different concentrations were presented. At a concentration of 5%, *G*′ was lower than *G*″ at low frequencies, but went above *G*″ when the frequency reached 10 Hz. At a concentration of 10%, *G*′ crossed G″ at 0.04 Hz. The GGMSpDr solution at 15% showed a strong elastic property where *G*′ was above *G*″ throughout the applied frequency. As shown in Fig. 2b, GGMEtOH obtained similar viscoelastic properties. The GGMEtOH solution showed viscous properties at a concentration lower than 5%. At 5%, GGMEtOH showed a typical behaviour of a concentrated polymer solution, in which *G*′ and *G*″ crossed at a frequency of around 0.5 Hz. In general, the elastic contribution is greater when the cross-over frequency value is lower. The GGMEtOH solutions at 10% and 15% showed more elastic properties than GGMSpDr solutions, since the *G*′ value at each concentration was much higher than the *G*″ value throughout the applied frequency.

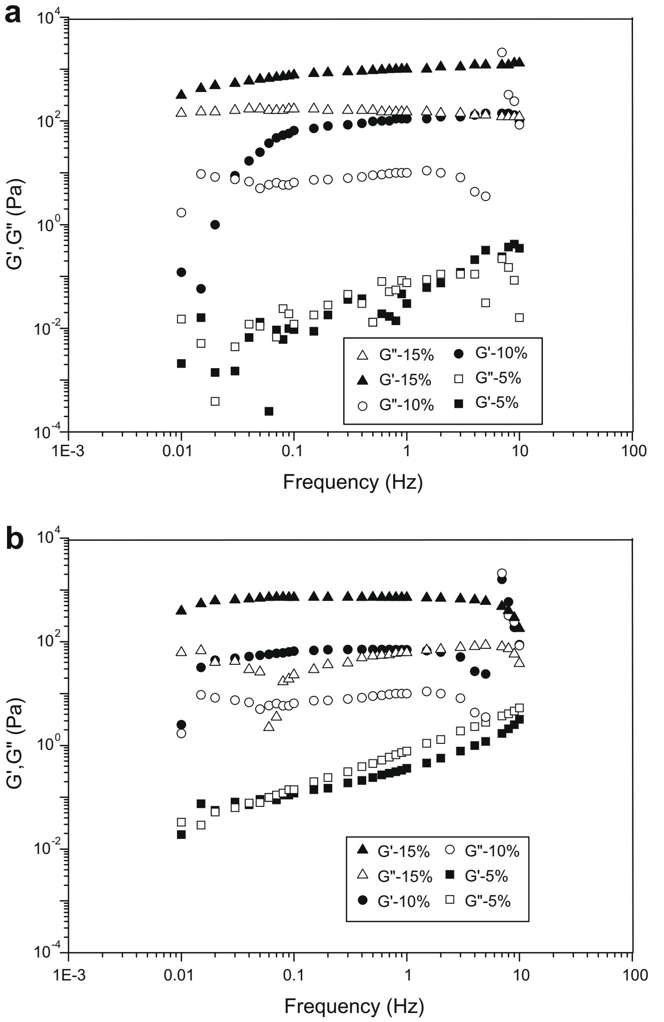

Fig. 2. Frequency-dependent and concentration-dependent modulus of GGMSpDr (a), and GGMEtOH (b). Measurements were made at 25 °C.

There is no notable difference for the purity of GGMSpDr and GGMEtOH (Table 1). A higher temperature was applied for spray-drying compared to ethanol-precipitation, which probably led to a more severe dehydration. Consequently, one hypothesis is that the severe dehydration forced hydroxyl groups to form intramolecular hydrogen bonds, which are not accessible to water any more. Therefore, the GGMSpDr molecules had smaller hydrodynamic volume than GGMEtOH ones, which is supported by lower light-scattering index for the fore dilute solutions after filtration removing most the supermolecular particles (data not published). As shown in Table 1, the slightly lower molar mass of GGMSpDr is also probably due to the higher temperature for spray-drying. For dilute solutions, polymeric intrinsic viscosity increases with its molar mass, according to the Mark–Houwink relationship. For concentrated solutions, polymers interacting by physical entanglements and also more-specific hyperentanglements between polymers contribute to the solution viscosity as well (Morris et al., 1981; Newlin, Lovell, Saunders, & Ferry, 1962). A higher molar mass and perhaps more accessible hydroxyl groups of GGMEtOH allow more polymer interacting opportunities in GGMEtOH solutions, which, consequently, exhibit a more obvious elastic behaviour. The rate of disruption of entanglements is also more greater than that of formation of new entanglements in GGMEtOH solutions compared to GGMSpDr ones.

3.1.3. Effect of temperature

The oscillatory rheology of polysaccharide solutions is fairly temperature-dependent (Lee & Brant, 2002). The temperature-dependent moduli of the 5% GGMSpDr solution at the frequency of 1 Hz are shown in Fig. 3a. Both G' and G'' increased slightly with decreasing temperature. G' was below G'' throughout the temperature range, showing a viscous behaviour. In general, the viscosity of a polymer solution decreases with increasing temperature. However, in some cases where 'heat set' gels are formed, the viscosity increases rapidly when temperature reaches a certain value (Nishinari, 2000). GGMSpDr solutions at concentrations lower than 15% did not form a gel. In order to investigate the effect of deacetylation, the temperature-dependent moduli of GGMDeAc are shown in Fig. 3b. The storage modulus G' also increased slightly with decreasing temperature. The storage modulus G' was above the G'' throughout the temperature range. The deacetylated GGM showed an elastic behaviour throughout the temperature range at 1 Hz. It is worthful to mention that a dramatic decrease in viscous modulus was observed when the temperature was decreased to 45 °C and lower. This might be ascribed to specific intermolecular associations, which occur after the *O*-acetyl groups were removed and dominate when the temperature was lower than 40 °C.

3.1.4. Effect of ionic strength

GGM is basically a neutral polysaccharide, with a solution pH of around 5. However, there are small amounts of galacturonic acid units associated with the polymer, which can affect the properties. Viscosity as a function of shear rate for 5% GGM solutions with a NaCl concentration of 0.05 and 0.5 M showed the same and deviated from that for 5% GGM solution. Fig. 4 shows the frequency-dependent moduli of 5% GGMSpDr solutions without the addition of NaCl and with the addition of 0.05 M NaCl. The scattered data are probably due to that the measurements are too close to the resolution of the rheometer. Both solutions showed a typical characteristic of concentrated polymer solutions, where G' and G'' increased with frequency and crossed at around 2 Hz, while G' went above G'' after 2 Hz. G' of the solution clearly increased after addition of 0.05 M NaCl.

Glucomannans from other resources, for example konjac plants, were found not to be affected by salt concentration (Takigami,

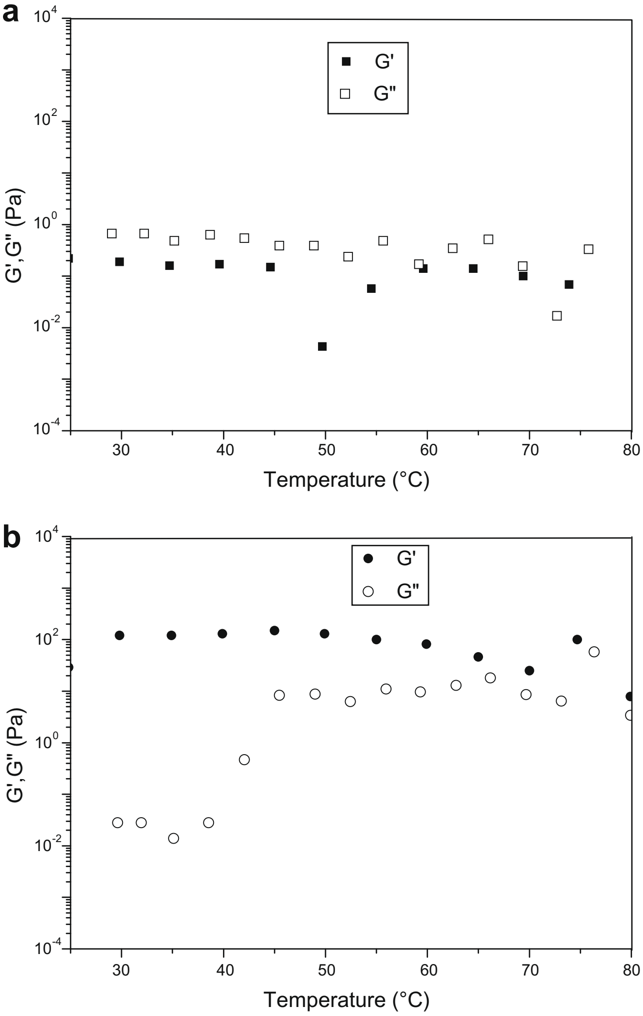

Fig. 3. Effect of temperature on moduli of GGMSpDr (a) and GGMDeAc (b) at a concentration of 5%. Data measured at a frequency of 1 Hz.

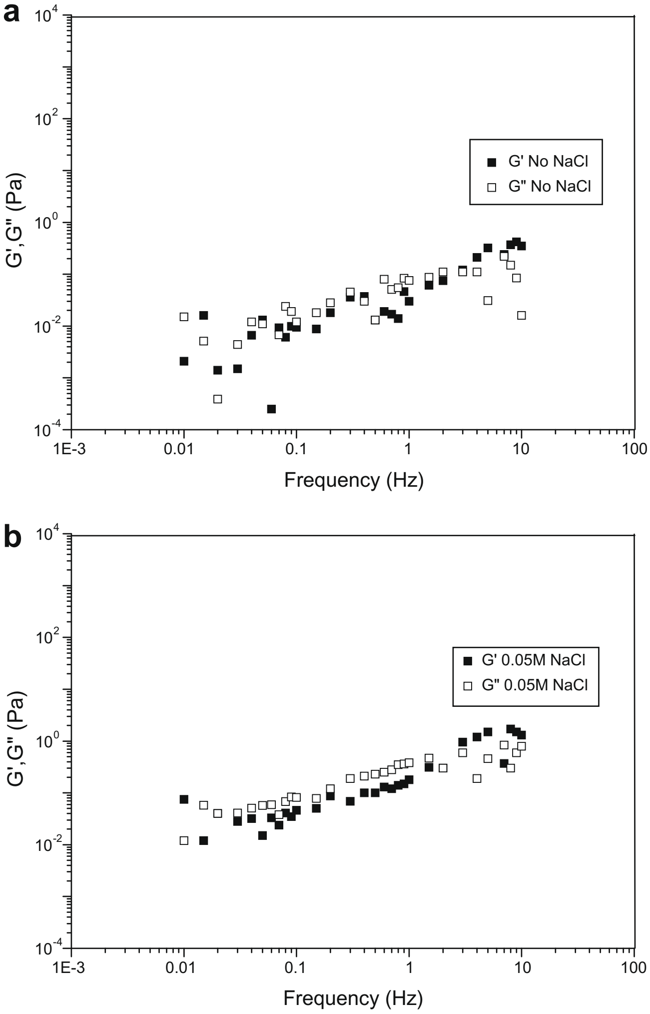

Fig. 4. The moduli of GGMSpDr at a concentration of 5% without salt addition (a) and with addition of 0.05 M NaCl (b). Measurements were made at 25 °C.

2000). A study with xanthan showed that the rheological properties of the xanthan solutions were greatly influenced by the presence of electrolytes and the storage moduli showed a tendency to increase with the order of water → monovalent cations → divalent cations (Annable, Williams, & Nishinari, 1994). This mechanism is ascribed to an order to disorder conformational transition (Milas & Rinaudo, 1979). The rheological properties of GGM solution were also influenced by the presence of salt. However, the mechanism could be different since GGM is an amorphous polysaccharide. The galacturonic acid, present as impurities in the GGM, causes a repelling force between polymeric coils and thereby hinders the coils from forming physical entanglements and also more-specific molecular associations. With addition of salts, new entanglements formed in both specific and non-specific ways. Therefore, the elastic property of GGM solution was enhanced by addition of salt. However, the further concentrated salt concentration, 0.5 M, did not show more dramatic effect.

3.1.5. Effect of deacetylation

Deacetylated GGM was prepared by treating GGM solution at pH 11 with addition of 1 M NaOH for two hours at 60 °C. Deacetylation caused an increase in the apparent viscosity of GGM, as shown in Fig. 5. Fig. 6 shows the frequency-dependent moduli of a GGMDeAc solution. G' is above G'' throughout the applied frequency. The G' was significantly higher than G'', indicating that the deacetylated GGM solution obtained elastic properties with increasing frequency, as also shown in Fig. 3. GGM's solution properties are affected by the *O*-acetyl substituents at C-2 and C-3 in the mannose units (Timell, 1965). The removal of acetyl groups decreases the solubility of GGM, leading to formation of aggregates, as shown in a previous study (Xu et al., 2007). In addition, the difference in oscillatory data is markedly more dramatic compared to the difference in viscosity. This can probably be attributed to the disruption of structure under steady shear conditions.

It is generally accepted that acetyl groups increase the solubility of an aqueous solution of glucomannans (Crescenzi et al., 2002). Konjac glucomannan itself cannot form gels below a concentration of 7% (Fujiwara, Hirota, Nakazato, Muzutani, & Mitsuoka, 1991). The deacetylation generated by the addition of alkali is a crucial step which leads glucomannan to gelation (Maekaji, 1974, 1978). The gelation behaviour of glucomannan dispersions shows strong dependence on the amount of acetyl groups (Gao & Nishinari 2004a, 2004b). An acetylated glucomannan needs a longer gelation time than that of a non-acetylated one (Huang, Rheo, Shinsaku, Tokuzo, & Katsuyoshi 2002). The acetyl groups also hinder the interaction with other molecules, especially when mixing with a different polysaccharide. If the acetyl groups are removed from polymeric chains, the entanglements become more severe. For example, it has been reported that the removal of acetyl groups from acetan promotes its synergistic interaction with guar gum or konjac glucomannan (Ojinnaka, Brownsey, Morris, & Morris, 1998). In GGM solutions, entanglements increase in forms of both physical ones and specific intermolecular associations or hyperentanglements after the removal of acetyl groups. Here, one of the specific intermolecular associations is attributed to hydrogen bonds formed.

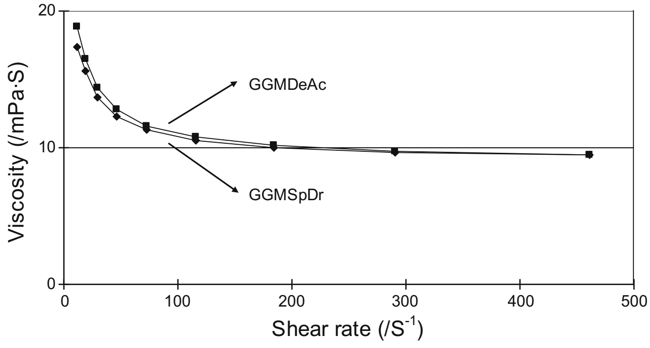

Fig. 5. Apparent viscosity of GGMSpDr and GGMDeAc at 5% concentration. Measurements were made at 25 °C.

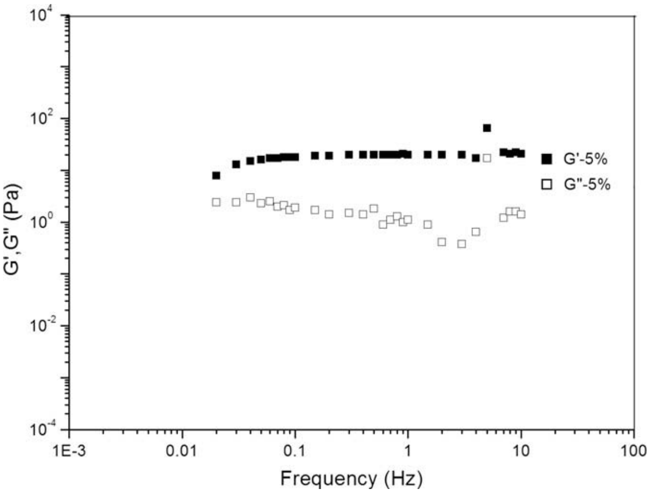

Fig. 6. The modulus of GGMDeAc at 5% concentration. Measurements were made at 25 °C.

3.2. Thermal analysis

Spray-dried GGM was redissolved in water and purified by dialysis. The dispersion of GGMPuDi was prepared for MDSC measurements by adding 20 wt% water to the GGM. An endothermic peak on the heating curve appeared at around 50 °C (Fig. 7). The glass transitions of polysaccharides are very dependent on the thermal history of the material and also on their structural features. Plasticisers such as water and glycerol are known to induce this phenomenon in different starches and their derivatives using MDSC technology (Thiewes & Steeneken, 1997). It was known that all polysaccharides, for which glass transition behaviour is observed on a first heat, contain significant amounts of glycosidic linkages of the (1 → 6) type (Gidley, Cooke, & Ward-Smith, 1993). The galactomannan polysaccharides, locust bean gum, tara gum, and guar

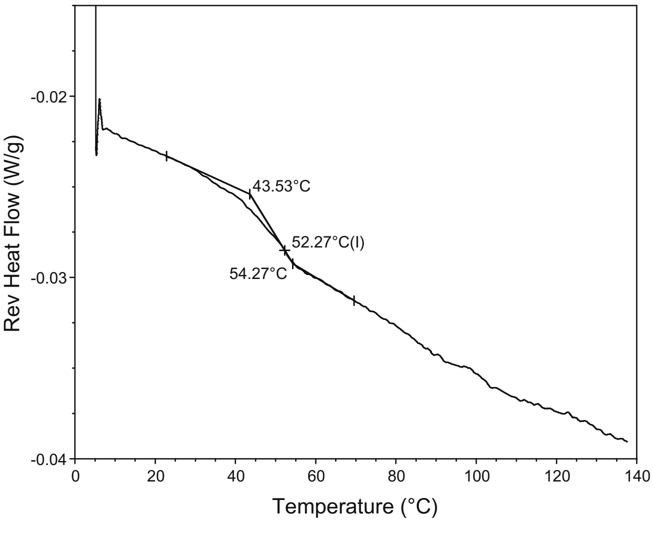

Fig. 7. Thermal analysis of GGMPuDi.

gum, consisting of (1 → 4)-linked β-D-mannose backbone and (1 → 6)-linked α-D-galactose side chains, with a ratio of 4:1, 3:1, and 2:1, respectively, were observed to show glass transition (Li & Chen, 2001; Naoi, Hatakeyama, & Hatakeyama, 2002). GGM also contains (1 → 6)-linked α- and β-D-galactose side chains, but in a much smaller content. The appearance of an endothermic step change of heat flow in GGM is probably attributed to the disordering of the structure or swelling of GGM macromolecules or their particles accompanying the disintegration of hydrogen bonds and described as the glass transition of the amorphous GGM.

4. Conclusions

The viscoelastic properties of spruce galactoglucomannans were studied. The main parameters, which influence the viscoelastic properties of galactoglucomannans, include drying methods, temperature, *O*-acetyl substitution, and ionic strength. Both solutions of spray-dried and ethanol-precipitated GGM showed a shear thinning behaviour. The solutions do not obey the Cox–Merz rule. The oscillatory moduli of spruce galactoglucomannans solutions increase with an increase in concentration. The storage modulus G' crosses and goes above loss modulus G'' at a certain frequency. The ethanol-precipitated galactoglucomannan solutions obtain a stronger elastic behaviour. The storage modulus G' is higher than loss modulus G'' throughout the frequency at concentrations higher than 5%. It is perhaps due to the slight higher molar mass and possible entanglements including both non-specific and specific ones of ethanol-precipitated GGM. Deacetylated GGM solution at 5% shows an elastic behaviour throughout the frequency from 0.01 to 100 Hz. probably because deacetylation causes specific intermolecular associations. The storage modulus of GGM solutions increases slightly with a decrease in temperature. For deacetylated GGM, an elastic behaviour was observed throughout controlling the temperature. And loss modulus is decreased dramatically when temperature is lowered to 45 °C. Addition of 0.05 M NaCl increases the storage modulus somewhat. The rheological measurements of GGM solutions provide the basis of functionalities of galactoglucomannan solutions and are especially useful in the case of additives in food emulsions and suspensions. The study may assist to build up molecular models and to explain structure–property relationships.

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