

RHEOLOGICAL PROPERTIES OF MIXTURES OF SPRUCE GALACTOGLUCOMANNANS AND KONJAC GLUCOMANNAN OR SOME OTHER POLYSACCHARIDES

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Spruce galactoglucomannan is a wood-derived polysaccharide with a modest molar mass that has recently been made available in kg-scale for research and development of value-added products. To promote the application of spruce galactoglucomannans in, for example, food products, it is vital to understand also the rheological behaviour of the mixtures of galactoglucomannans with other polysaccharides. Rheological measurements were applied to study the rheological properties of mixtures of spruce galactoglucomannans and high-molar-mass konjac glucomannan, xanthan, guar gum, locust bean gum, and carrageenan. Shear rate-dependence of viscosity and applicability of the Cox-Merz relationship of mixtures of spruce galactoglucomannans with the other polysaccharides were studied. Spray-dried and ethanol-precipitated galactoglucomannans were also prepared for comparison. The effects of polysaccharide mixture ratio, temperature, ionic strength, and deacetylation are discussed. Mixtures of spray-dried galactoglucomannans and konjac glucomannan showed lower elastic properties than those of ethanol precipitated galactoglucomannans and konjac glucomannan. The viscoelastic spectra of mixtures of both galactoglucomannans and deacetylated galactoglucomannans with konjac glucomannan showed temperature dependency throughout the cooling process. Ionic strength had an effect on the rheological properties of mixtures of galactoglucomannans with konjac glucomannan. Deacetylation of galactoglucomannans did not affect the viscoelastic spectra significantly.

Keywords: Spruce galactoglucomannans; Rheological properties; Konjac glucomannan; Polysaccharides; Mixture ratio; Temperature dependence; Ionic strength; Deacetylation

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INTRODUCTION

The water-soluble *O*-acetyl galactoglucomannans (GGM), biodegradable natural polymers from a renewable source, are the main hemicellulose type in most industrially important softwood species, with a content portion of 10-20% of the wood material (Sjöström 1993; Willför et al. 2003b; Willför et al. 2005). The most common commercial polysaccharides are konjac glucomannan, xanthan, guar gum, locust bean gum, and carrageenan. Konjac glucomannan (KGM) is a copolymer of β -D-mannopyranosyl and β -D-gucopyranosyl in the approximate ratio 1.6-2:1 (Nishinari et al. 1992; Crescenzi et al. 2002). The water solubility of KGM is controlled by the *O*-acetyl groups on C-2, which constitutes a 2-6% variation from the original KGM (Dea and Morrison 1975). KGM has been used as a gel or thickener in food for a long time (Williams et al. 2000; Kokie and

Suzuki 2001). Xanthan is an exopolysaccharide from *Xanthomonas campestris* (Sworn 2000), with a trisaccharidic branch on every other glucopyranosyl unit of the cellulosic backbone (Jansson et al. 1975; Melton et al. 1976). Xanthan water solutions have a high viscosity, high pseudoplasticity, significant yield stress, and strong stability (Whitcomb and Macosko 1978). Guar gum is a galactomannan with a linear backbone of (1 → 4)-β-D-mannopyranosyl units, to which single α-D-galactopyranosyl is attached at C-6 (Stephen 1983). Guar gum has been used as a food ingredient for thickening, gelling, and stabilizing properties (Juneja et al. 2001). Locust bean gum (LBG), a galactomannan obtained from the seeds of the carob tree (*Ceratonia siliqua*), has a linear (1 → 4)-β-D-mannopyranosyl chain with varying amounts of single α-D-galactopyranosyl substituents linked by (1 → 6) glycosidic bonds (Wielinga 2000). Carrageenan, mainly available from *Eucheuma cottonii* and *E. spinosum*, is a high viscosity polysaccharide with a backbone consisting of galactopyranosyl and 3,6-anhydrogalactopyranosyl units, both sulfated and non-sulfated, which are randomly linked by α-(1 → 3) and β-(1 → 4) glycosidic linkages (Imeson 2000).

Binary mixtures of polysaccharides have been thoroughly studied for the purpose of gaining a fundamental understanding, and also to discover industrial applications, especially in food systems (Harding et al. 1995). Intermolecular association may or may not occur in solutions with two polysaccharides. Association occurs to form a gel, for example, in mixtures of glucomannan and xanthan (Mannion et al. 1992; Goycoolea et al. 1995; Schorsch et al. 1997; Paradossi et al. 2002; Kim et al. 2006). However, little is known about mixtures of spruce GGM and other polysaccharides.

In our group, we have recently shown that GGM can be readily recovered from pulping process waters in mills producing mechanical pulp from Norway spruce (Willför et al. 2003a; Xu et al. 2007), which may supply sufficient amounts of polymeric GGM for more extensive research and potential applications in industrial fields. Consequently, spruce GGM is now available in kg-scale for fundamental research, and development of high-value products. In two earlier papers we reported on the physico-chemical properties of GGM in water solutions (Xu et al. 2007; 2008). To broaden the application of GGM and its derivatives in food areas, it is necessary to know the solution properties, especially rheological behaviour, of mixtures of GGM and other polysaccharides.

The aim of the present work was to understand the rheological properties of mixtures of GGM and other polysaccharides, mainly konjac glucomannan, which has a similar chemical structure. Rheological measurements were conducted. GGM was mixed with KGM to investigate the mixture's rheological properties, and the effects of concentration, deacetylation, drying methods producing GGM, ionic strength, and temperature. Mixtures of GGM and xanthan, guar gum, LBG, and carrageenan were also briefly studied.

EXPERIMENTAL

Materials

At a Finnish mill producing thermomechanical spruce pulp, GGM from the process water was concentrated using different filtration and ultrafiltration techniques.

The resulting concentrate 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 daltons. Deacetylated GGM (GGMDeAc) was prepared by treating GGMSpDr with NaOH and performing dialysis. The degree of acetylation, calculated on the molar amount of GGM, was approximately 15% (Xu et al. 2007). The average molar mass of GGMSpDR and GGMEtOH was approximately 39 kDa and 46 kDa, respectively, using size-exclusion chromatogram and multi-angle laser light scattering detection.

Konjac glucomannan was purchased from C. E. Roeper GmbH, Hamburg, Germany. Xanthan gum from *xanthomonas campestris*, guar gum, locust bean gum, and carrageenan with a molar mass higher than 100 kDa were purchased from Sigma-Aldrich Chemie.

Preparation of Solutions and Mixtures

Polysaccharide solutions were prepared by adding a known weight of the dried sample to distilled water at room temperature. The temperature was then raised to 80°C for two hours, under continuous stirring. Finally, the solution was stirred overnight at room temperature. Mixtures were prepared by mixing two solutions in a certain ratio and stirring for at least two hours to make them homogeneous.

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 the 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 25.0°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.

RESULTS AND DISCUSSION

The oscillatory measurements were performed at a small amplitude oscillatory shear, in which the polymeric structure was not significantly disturbed from its equilibrium state. The rheological properties of GGM mixtures with KGM and other polysaccharides were studied. The effects of drying methods to produce GGM, temperature, salt addition, and deacetylation of GGM on the rheological properties are discussed. Oscillatory measurements provide the characteristics of random-coil polysaccharides. The spectra of storage modulus, G' , and loss modulus, G'' , were of the expected entanglement solution form.

GGM and KGM Mixtures

Figure 1a shows the shear rate-dependence on viscosity of GGMSpDr, KGM, and their mixtures with different mixing ratios at a total concentration of 0.5 wt%. GGM and KGM solutions, as well as solutions of their mixtures showed shear-thinning. GGM solutions exhibited a near-Newtonian, but still slightly shear-thinning behaviour, where a reduction of viscosity occurred. With an increase in the ratio of KGM in the mixtures, shear-thinning became more dramatic. The disruption of entanglements and formation of new ones always occurs when an imposed deformation is applied. However, when more entanglements are disrupted and more time is required to form new ones, shear-thinning occurs (Graessley 1974; Morris et al. 1981). And thus, the extent of entanglement is less, and viscosity is reduced.

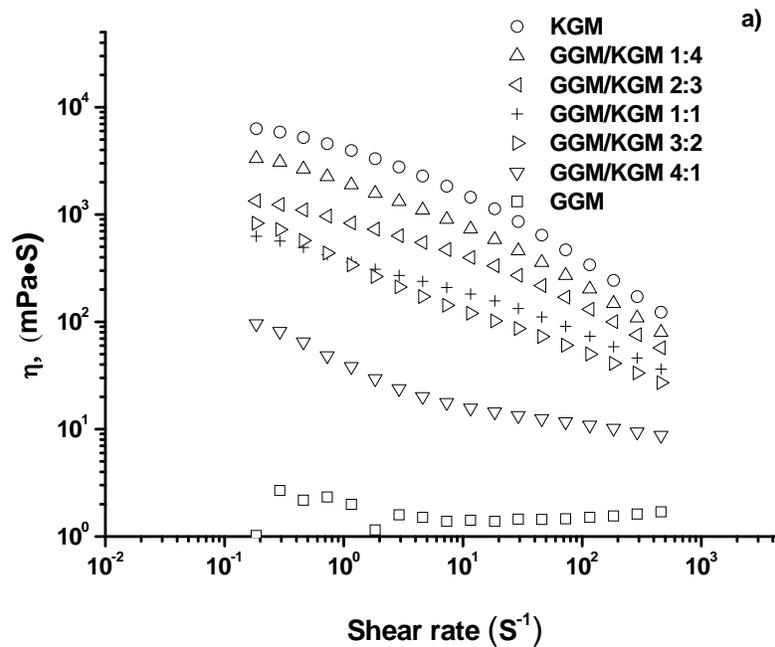


Fig. 1. (a) Shear rate dependence of viscosity η for GGM, KGM, and their mixtures (open symbols)

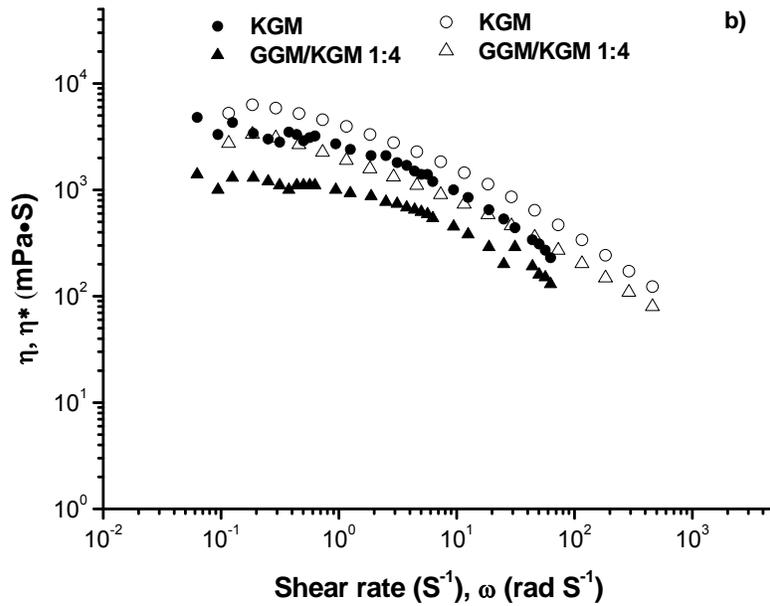


Fig. 1. (b) Re-plotting of shear rate dependence of viscosity η (open symbols) and the frequency of dynamic viscosity for KGM and one mixture solutions (closed symbols)

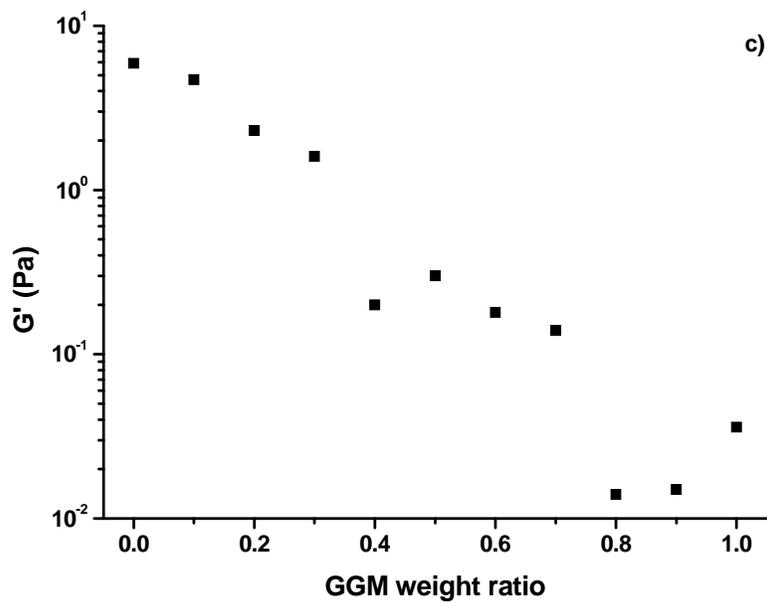


Fig. 1. (c) Storage modulus G' for GGM/KGM mixtures (total polysaccharide concentration 0.5 wt%) as a function of polysaccharide weight ratio at 1 Hz at 25°C

The applicability of the Cox-Merz relationship was investigated by plotting complex dynamic viscosity η^* (ω) (Fig. 1b). The Cox-Merz rule states that dynamic viscosity η^* (ω) is almost identical to the shear viscosity η as a function of shear rate (Cox and Merz 1958). Dynamic viscosity η^* of only two solutions, KGM and a mixture with a GGM/KGM ratio of 1:4, are shown in the Figure 1b for clear observation. Both single and binary solutions showed deviations of η^* from η . The dynamic viscosity η^* of KGM and mixtures solutions was lower than shear viscosity η . The deviation is probably due to different types of molecular rearrangements occurring in the two flow patterns over the applied shear rate or frequency range (Richardson and Ross-Murphy 1987a, 1987b), which can be attributed to more-specific molecular associations of longer timescale or hyperentanglements than non-specific physical entanglements (Morris et al. 1981; Robinson et al. 1982).

Figure 1c shows the storage modulus of GGM/KGM mixtures with respect to the polysaccharide ratio. The storage modulus was reduced significantly when the GGM ratio increased in the mixtures. This indicates that no synergistic interaction occurred in the applied conditions (Mannion et al. 1992, Paradossi et al. 2002). Spruce GGM has a very low viscosity compared to KGM (Xu et al. 2007). GGM molecules, which are much smaller than KGM molecules, may interact with the KGM molecules and hinder the intermolecular association between the KGM molecules, which thus leads to a lower storage modulus.

Figure 2 shows the viscoelastic properties of KGM and a mixture of GGMSpDr and KGM in 1:1 a ratio, respectively, at a total concentration of 0.5 wt % at 25°C. The storage and loss moduli of the mixture were much lower than those of KGM alone. However, both solutions showed the characteristics of a concentrated polymer solution, which was not found in the solution of GGM alone, although the storage modulus of the mixture was closer to that of GGM (Xu et al. 2008). In the rheological measurements on the mixture, G' was lower than G'' at lower frequencies, showing the viscous behaviour of the solution, while G' went above G'' when the frequency reached 7 Hz. However, G' of the KGM solution went above G'' when the frequency reached 2 Hz. GGM solution with a concentration of 0.5 wt% shows a completely viscous behaviour (Xu et al. 2008).

Difference between GGMSpDr and GGMEtOH

Figure 3 shows a comparison of the frequency dependent G' of mixtures of GGMSpDr and GGMEtOH with KGM in 1:1 ratio at a total polysaccharide concentration of 0.5 wt%. The G' of GGMSpDr was lower than that of GGMEtOH throughout the frequency range from 0.01 Hz to 10 Hz. The stronger elastic properties of the GGMEtOH/KGM mixture can be ascribed to higher elastic properties of GGMEtOH compared to those of GGMSpDr.

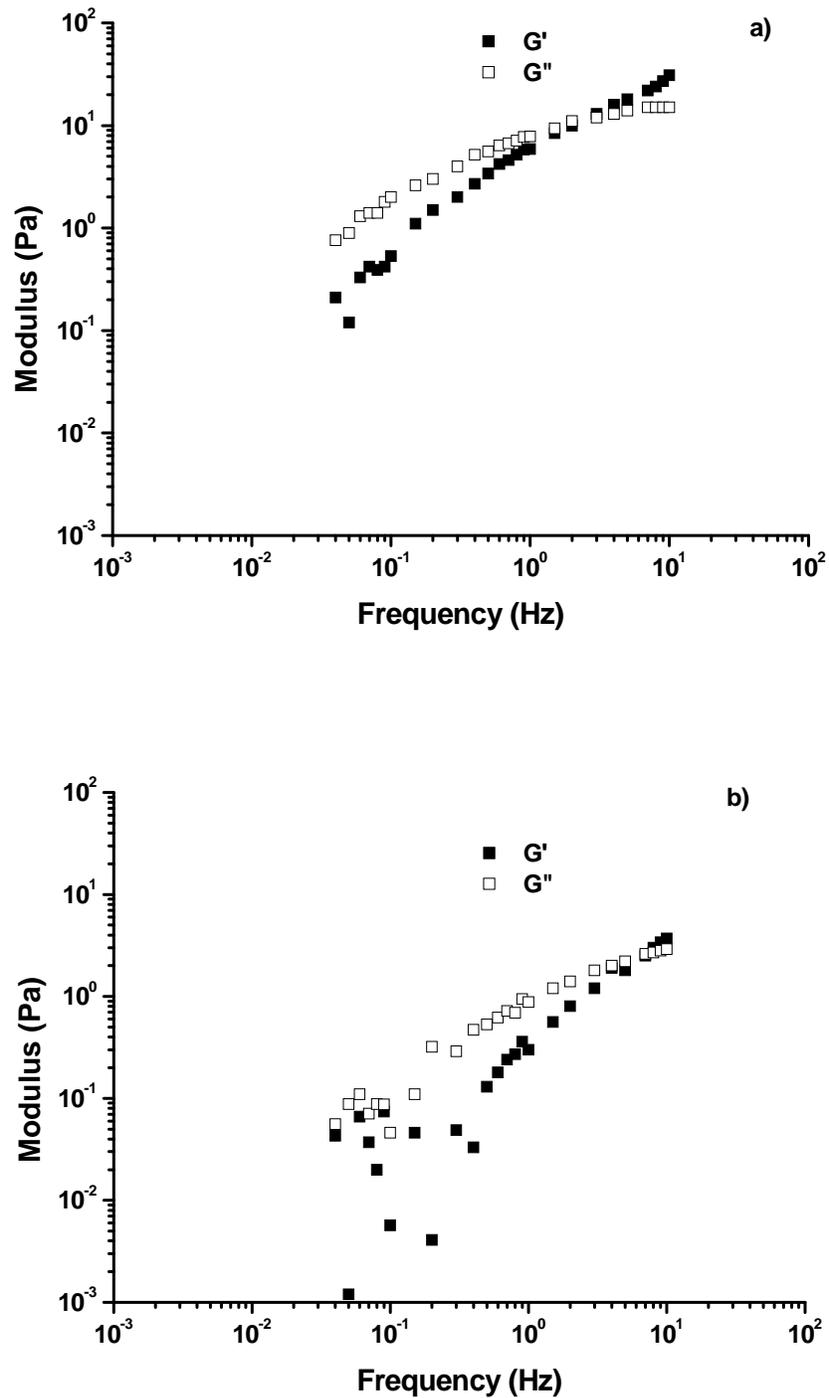


Fig. 2. Frequency dependent modulus of (a) KGM and (b) Mixture of GGM and KGM (total polysaccharide concentration 0.5 wt%) with a ratio of 1:1

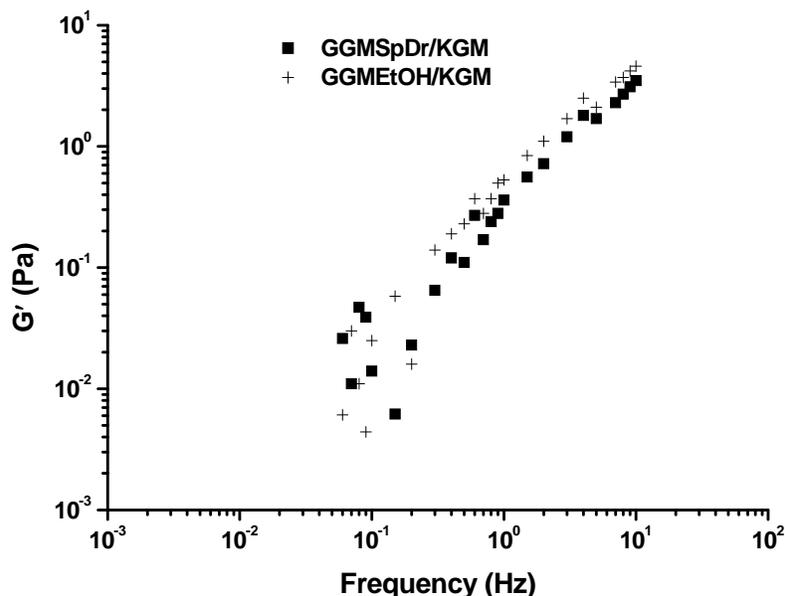


Fig. 3. Frequency dependent G' modulus of mixtures of GGMSpDr/KGM (square) and GGMEtOH/KGM (plus) (total polysaccharide concentration 0.5 wt%)

GGMSpDr and GGMEtOH have the same structural features, except that the molar mass was slightly lower for GGMSpDr. During the preparation of the two mannans, a higher treatment temperature was applied for spray-drying, compared to ethanol precipitation. Therefore, it can be hypothesized that spray-drying led to a more severe dehydration and formation of more inter- and intra-molecular hydrogen bonds, which then are less accessible to water. Hence, GGMSpDr has a smaller hydrodynamic volume in water than GGMEtOH. In other words, GGMEtOH has more free coils available for entanglements between GGM themselves and GGM with KGM. This contributed to a more elastic behaviour for the mixture of GGMEtOH and KGM.

Effect of Temperature

The rheological measurements were conducted by controlling the temperature from 80°C to 5°C. Figure 4 shows the temperature dependence of G' and G'' during the cooling process for a GGM/KGM mixture in 1:1 ratio with a total polysaccharide concentration of 0.5 wt% at 1 Hz. Like GGM and KGM on their own, G' and G'' of the mixture increased by cooling. G' was below G'' throughout the cooling process from 80°C to 5°C, showing the solution to be a viscous system. The difference between G' and G'' was smaller when the temperature was lower. Some other polysaccharides may form a gel by decreasing the temperature, which increased the G' rapidly at low temperatures and went above G'' (Nishinari 2000).

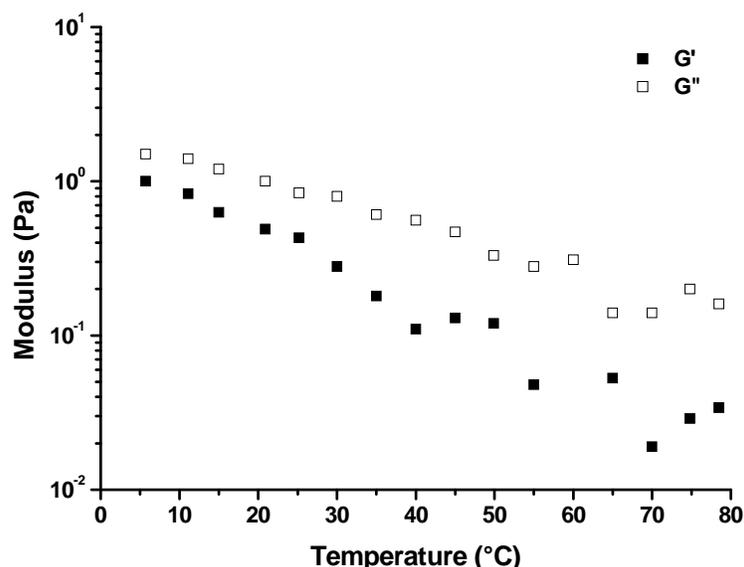


Fig. 4. Temperature dependence of the moduli of a mixture of GGMPuDi and KGM (total polysaccharide concentration 0.5 wt%). Data measured at a frequency of 1 Hz

Figure 5 shows the temperature dependence of G' and G'' during the cooling process for GGMDAc/KGM mixture in 1:1 ratio with a total polysaccharide concentration of 0.5 wt% at 1 Hz. G' remaining below G'' throughout the cooling process from 80°C to 5°C. Both the moduli increased throughout the cooling process. This was also the case for the GGM/KGM mixture. However, both moduli of the GGMDAc/KGM mixture were higher than those of the GGM/KGM mixture. This may be ascribed to higher moduli of deacetylated GGM than of GGM alone. For the GGMDAc/KGM mixture, G' and G'' were very close and even crossing when temperature was higher than 60°C, showing that deacetylation increased the elastic behaviour of the mixture. As discussed in the previous study, more specific intermolecular associations might occur after the *O*-acetyl groups were removed (Xu et al. 2008).

Effect of Ionic Strength

Figure 6 shows the storage modulus G' for mixtures of GGMPuDi/KGM with and without NaCl. The storage modulus did not change at low frequencies but decreased dramatically at higher frequencies with the addition of 0.05 M NaCl. Further addition of NaCl to 0.5 M NaCl did not affect the mixture further. Figure 7 shows the frequency dependent G' of GGMPuDi, KGM, and a mixture of GGMPuDi and KGM at a 1:1 ratio with a total polysaccharide concentration of 0.5 wt% in 0.05 M NaCl. Both GGMPuDi and the mixture with the addition of salt showed a viscous character. KGM with the addition of salt showed an elastic character with storage modulus G' above loss modulus G'' throughout the frequency. Compared to the moduli of mixture with addition of NaCl, the moduli of mixture without addition of NaCl showed a more dramatic elastic character (Fig. 2), in which the storage modulus G' was below G'' , but crossed at 7 Hz and then went above.

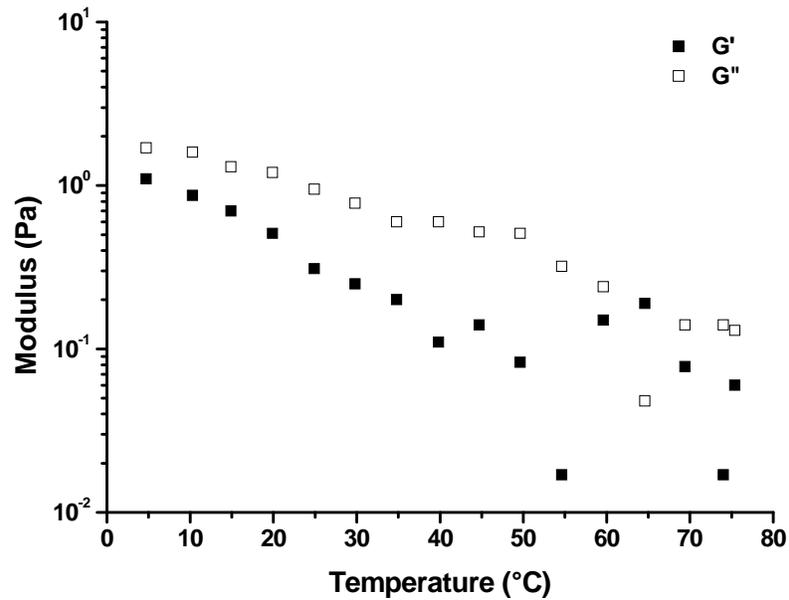


Fig. 5. Effect of temperature on the moduli of Deacetylated GGM and KGM (total polysaccharide concentration 0.5 wt%). Data measured at a frequency of 1 Hz

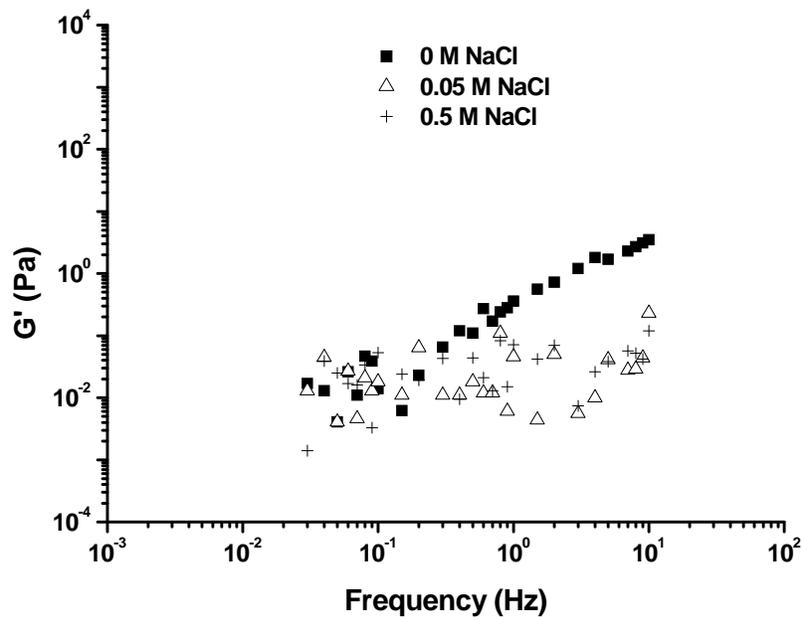


Fig. 6. Effect of added salt on the elastic modulus G' of mixture of GGMPuDi and KGM in water (closed square) (total polysaccharide concentration 0.5 wt%), in 0.05 M NaCl (down open triangle) and in 0.5 M NaCl (plus)

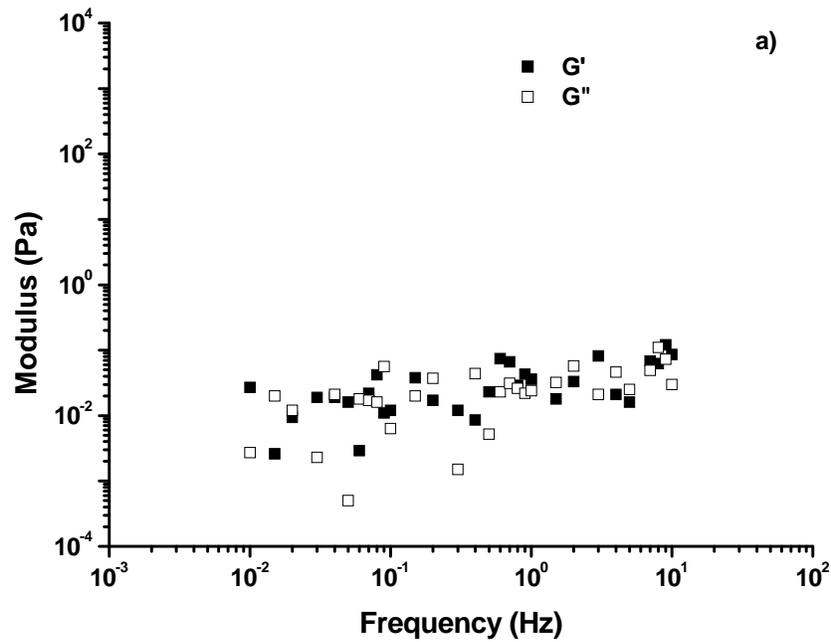


Fig. 7 (a). Modulus of GGMPuDi in 0.05 M NaCl (total polysaccharide concentration 0.5 wt%)

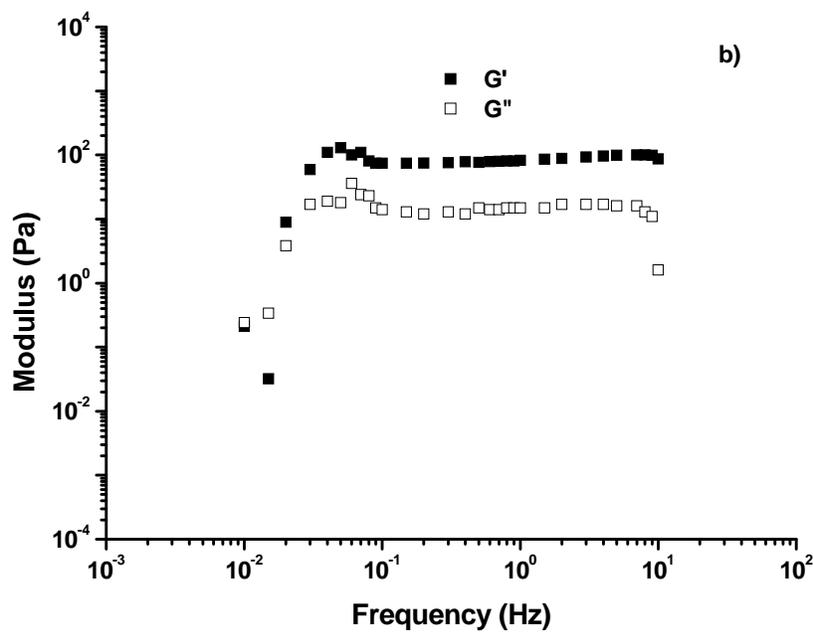


Fig. 7 (b). Modulus of KGM in 0.05 M NaCl (total polysaccharide concentration 0.5 wt%)

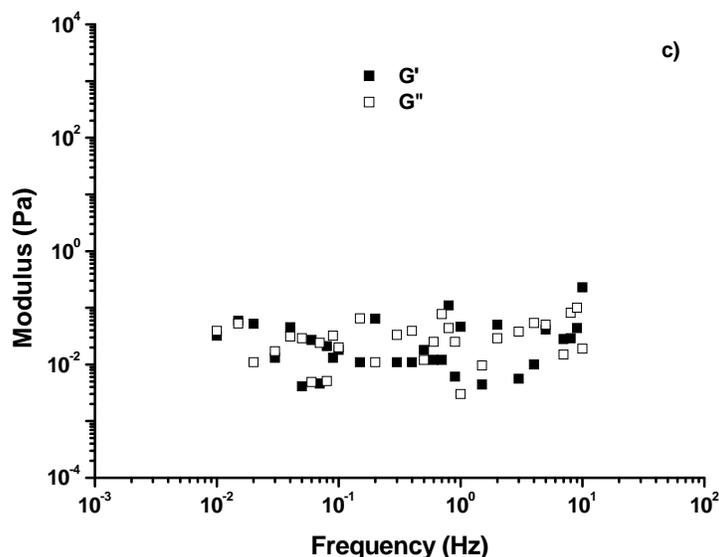


Fig. 7 (c). Modulus of a mixture of GGMPuDi and KGM in 0.05 M NaCl (total polysaccharide concentration 0.5 wt%)

It was stated that the viscoelastic properties of KGM were not affected by the addition of salt (Takigami 2000). The viscoelastic properties of GGM were slightly affected by the addition of salt (Xu et al. 2008). In the commercial preparations of polysaccharides, salts, especially Na^+ , K^+ , and Ca^{2+} ions, are significant constituents (Pettitt, 1982). The effect of ionic strength is generally investigated by adding NaCl, KCl, and CaCl_2 (Williams et al. 1993; Goycoolea et al. 1995; Miyoshi et al. 1996; Schorsch et al. 1997; Bresolin et al. 1998). Studies on xanthan and mixtures of xanthan and glucomannan with different salt forms showed that the salt addition may change the conformation of the polysaccharide molecules (Ross-Murphy et al. 1983; Goycoolea et al. 1995; Bresolin et al. 1998). However, the mechanism for mixtures of GGM and KGM should not be the same. Xanthan maintains a disorder to order conformational transition in the presence of electrolytes, but random coil GGM and KGM don't (Dea et al. 1977; Annable et al. 1994). The effect of salt on viscoelastic properties of mixtures of GGM and KGM might be ascribed to rearrangements of entanglements. With the presence of NaCl, the entanglements, both physical entanglements and specific entanglements between GGM and KGM are reorganized, resulting in that the specific entanglements are reduced. Therefore, the mixture with the addition of GGM showed a viscous character comparable to pure GGM. The decrease in storage modulus at high frequencies might be ascribed to a higher rate of disruption of entanglements than that of formation of new ones.

Effect of Deacetylation

Deacetylated GGM was blended with KGM to study the influence of deacetylation. Frequency-dependent modulus of mixtures of GGMDAc/KGM showed the same behaviour as mixtures of GGM/KGM, i.e. the typical characteristics of a

concentrated polymer (data not shown). The storage modulus G' of the mixture of GGMDAc/KGM was in between that of GGMDAc and KGM alone. The storage modulus G' of the mixture at 1 Hz was closer to that of GGMDAc than KGM. Figure 8 shows frequency-dependent storage modulus G' of mixtures of GGM and KGM before and after deacetylation. The two curves are surprisingly on the same course.

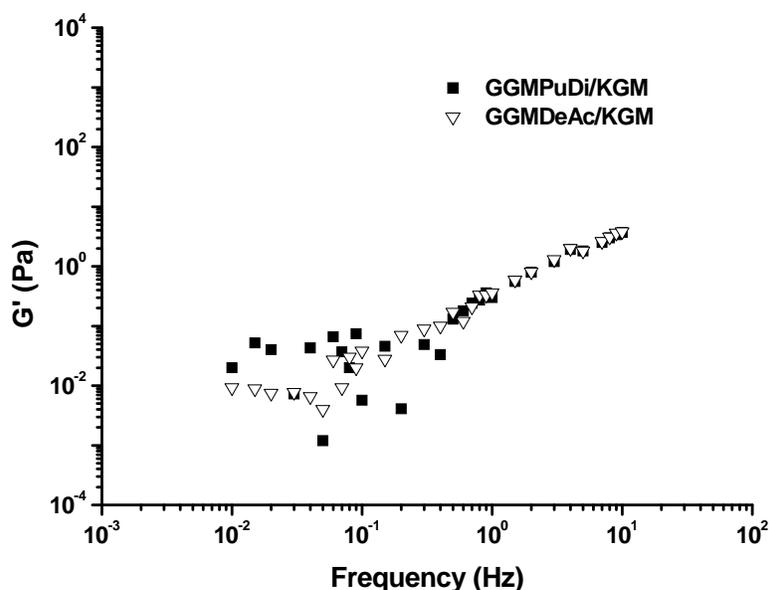


Fig. 8. Frequency dependent G' modulus of mixture of GGMPuDi and KGM (square) and mixture of GGMDAc and KGM (Triangle) (total polysaccharide concentration 0.5 wt%)

In a single system of GGM solution, deacetylation causes a dramatic increase in elastic character (Xu et al. 2008), because the removal of acetyl groups allows more opportunities for polymer coils to interact with each other and form entanglements. In a single system of KGM solution, KGM forms a gel after deacetylation generated by the addition of alkali, which is a crucial step in leading glucomannan to gelation (Maekaji 1974). The gelation behaviour of the glucomannan dispersions shows strong dependence on the number of acetyl groups (Gao and Nishinari 2004a; 2004b; Huang et al. 2002). The acetyl groups hinder the molecules from getting close to each other and then from packing into the mannan lattice (Millane et al. 1992). In a study with an example of interaction between acetan and glucomannan (Ojinnaka et al. 1998), the removal of acetyl groups from acetan promoted its synergistic interaction with guar gum or konjac glucomannan because of the conformation transition from disorder to order (Ridout et al. 1998).

In a binary system of GGMDAc and KGM with a ratio of 1:1, entanglements including both physical ones and specific ones, formed between polymer coils. Because KGM has a much higher molar mass than GGM, the conformation of GGM molecules contributes less to the mixture than that of KGM. Consequently, among the entanglements, those between KGM themselves and KGM and GGM or GGMDAc are

in a majority and not significantly affected by the *O*-acetyl substitution of GGM. Therefore, deacetylation of GGM did not obviously affect the viscoelastic behaviour of mixtures of GGM with KGM.

Mixtures of GGM and other Polysaccharides

Figure 9 shows the storage modulus G' of 1:1 mixtures of GGM and xanthan, guar gum, locust bean gum, or carrageenan with a total polysaccharide concentration of 0.5 wt% as a function of GGM's weight ratio, at 25°C. Mixtures of GGM and guar gum, locust bean gum, and carrageenan showed a significant reduction in the storage modulus G' . The mixture of GGM with carrageenan decreased the most. This is different from binary mixtures without GGM (Mannion et al. 1992; Williams et al. 1993; Goycoolea et al. 1995; Nishinari et al. 1996; Schorsch et al. 1997; Ridout et al. 1998; Paradossi et al. 2002; Kim et al. 2006), in which the synergistic interaction dominated and caused significant enhancement of the storage modulus. The mixture of GGM and xanthan showed a different behaviour from other polysaccharides. It had a relatively high value of storage modulus G' , which indicates that synergistic interaction might exist in the mixture. The synergistic interaction of helix-forming polysaccharides, i.e. xanthan, and 1,4- β -D mannans has been extensively studied. It has been commonly agreed that there are junction zones formed in the mixtures that show synergistic interaction, although different molecular models of the interaction have been suggested and are still in debate (Mannion et al. 1992; Williams et al. 1993; Goycoolea et al. 1995; Nishinari et al. 1996; Ridout et al. 1998; Paradossi et al. 2002; Kim et al. 2006). Nevertheless, further study on the mechanism of synergistic interaction between xanthan and galactoglucomannans needs to be expanded in the future.

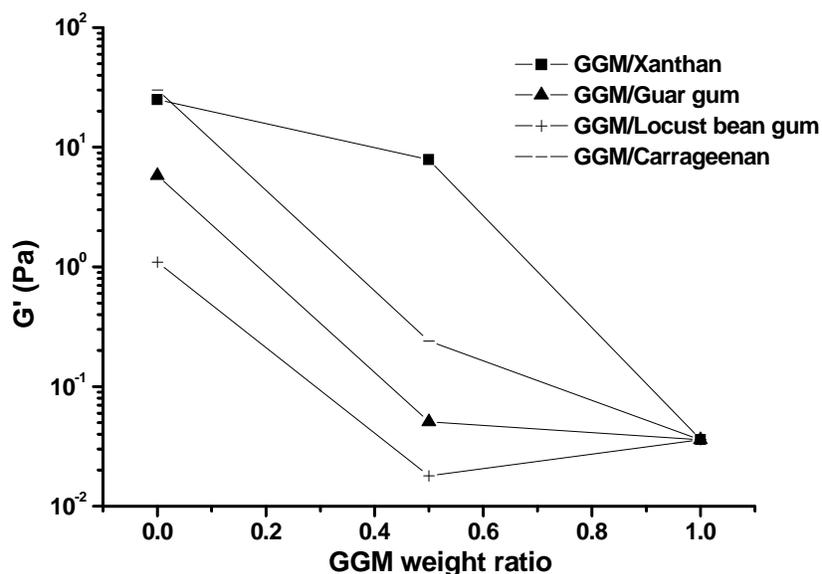


Fig. 9. Storage modulus G' of mixtures of GGMPuDi with xanthan (square), guar gum (triangle), locust bean gum (plus), and carrageenan (minus) (total polysaccharide concentration 0.5 wt%) as a function of polysaccharide weight ratio at 1 Hz at 25°C

CONCLUSIONS

1. No gel formation is found in mixtures of GGM with KGM, guar gum, locust bean gum, or carrageenan. Synergistic interaction may exist in the mixture of GGM and xanthan.
2. The mixture of spray-dried GGM and KGM shows a lower viscoelastic spectrum than that of ethanol-precipitated GGM with KGM.
3. The viscoelastic spectra of mixtures of both GGM and deacetylated GGM with KGM show temperature-dependency throughout the cooling process.
4. Ionic strength has an effect on the rheological properties of mixtures of GGM and KGM.
5. Deacetylation of GGM does not affect viscoelastic spectra significantly.

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