



# Rheological properties of concentrated solutions of galactomannans in an ionic liquid

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## ABSTRACT

The rheological behavior of galactomannans in concentrated solutions was examined by using dynamic viscoelasticity measurements. Concentrated solutions of three galactomannans, guar gum, tara gum, and locust bean gum were prepared with an ionic liquid 1-butyl-3-methylimidazolium chloride as the solvent. Each galactomannan solution showed angular frequency dependence curves of the storage modulus and the loss modulus which were characteristic of a solution of entangled polymer chains. The molecular weight between entanglements ( $M_e$ ) was obtained from the plateau modulus and the concentration dependence of  $M_e$  showed  $M_e$  in the molten state ( $M_{e,melt}$ ) to be  $4.6 \times 10^3$ ,  $3.2 \times 10^3$ , and  $2.7 \times 10^3$  for guar gum, tara gum, and locust bean gum, respectively. It was found that the material constant  $M_{e,melt}$  depends on the mannose/galactose ratio of the galactomannans. The number of monosaccharide units between entanglements in the molten state for the galactomannans varied within the range found for other polysaccharides such as cellulose and agarose in ionic liquids, suggesting that all the galactomannans take a random-coil conformation in ionic liquid solutions.

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## 1. Introduction

Galactomannans consist of a main chain of (1,4)- $\beta$ -D-mannose as units and a side group of (1,6)- $\alpha$ -linked D-galactose. Among them guar gum (g-gum), tara gum (t-gum) and locust bean gum (lb-gum) are specifically well-known. They differ in the mannose/galactose ( $m/g$ ) ratio:  $\sim 2$  for g-gum,  $\sim 3$  for t-gum, and  $\sim 4$  for lb-gum (Sittikijyothin, Torres, & Goncalves, 2005; Wientjes, Duit, Jongschaap, & Mellema, 2000; Wu, Cui, Eskin, & Goff, 2009; Wu, Li, Cui, Eskin, & Goff, 2012). The three galactomannans have been widely used in the food industry as ingredients to enhance viscosities in processing (Cerqueira et al., 2011), but the degree of enhancement depends on the species, or more precisely the  $m/g$  ratio. Similarly, how the  $m/g$  ratio is important to consider the viscoelastic properties of the solutions has been reported by many research groups (Sittikijyothin et al., 2005; Wu et al., 2009, 2012). The  $m/g$  ratio is really one of the important factors determining the solution properties of the galactomannans, but the origin on the molecular basis is still controversial (Morris, Cutler, Ross-Murphy, & Rees, 1981; Richardson & Ross-Murphy, 1987; Robinson, Ross-Murphy, & Morris, 1982; Wu et al., 2009). The galactose units are not randomly distributed along the main chain made of mannose for galactomannans, which generates a blockiness: galactose-poor blocks (g-poor blocks, i.e., mannose-rich blocks) and galactose-rich

(g-rich) blocks on a chain. Of course, the blockiness is not clear, but the mannose blocks easily form molecular association through hydrogen bonds, while such attractive interaction is small for the g-rich blocks (Sanderson, 1990; Urlacher & Dalbe, 1994). This intermolecular association, enhanced with increasing the  $m/g$  ratio, may explain the difference in solution properties of the galactomannans.

The viscoelastic properties of the concentrated solutions of galactomannans are controlled firstly by the number density of entanglements on a polymer chain, as is the case of other homogeneous polymer liquids (Doi & Edwards, 1986; Ferry, 1980), and the number density is a material constant reflecting the molecular parameters of the polymer chains such as the stiffness of the polymer chain. The molecular weight between entanglements ( $M_e$ ) is often used to describe the spacing between entanglements and  $M_e$  in the molten state ( $M_{e,melt}$ ) becomes a material constant. It is interesting to know if the chain stiffness and accordingly the spacing between entanglements change with the  $m/g$  ratio (McCleary, Amado, Waibel, & Neukom, 1981). However, we have no information of the values of  $M_{e,melt}$  for the galactomannans at present. This is partly due to the difficulty in preparing concentrated solutions, solutions of overlapping polymers, of the galactomannans with conventional solvents. The aim of this study is to estimate  $M_{e,melt}$  for the galactomannans. It should be noted that the rheological behavior reflecting  $M_{e,melt}$  (or  $M_e$ ) appears in much shorter time region than the intermolecular associations described above. Dynamic viscoelasticity is examined for concentrated solutions by using an ionic liquid as a good solvent. Ionic liquids are known

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to dissolve several polysaccharides which are insoluble to conventional organic solvents. For each of the galactomannans,  $M_e$  is determined as a function of the polymer concentration ( $c$ ), and then  $M_{e,melt}$  is estimated by extrapolation of the  $c$ -dependence curve of  $M_e$ .

## 2. Experimental

### 2.1. Materials

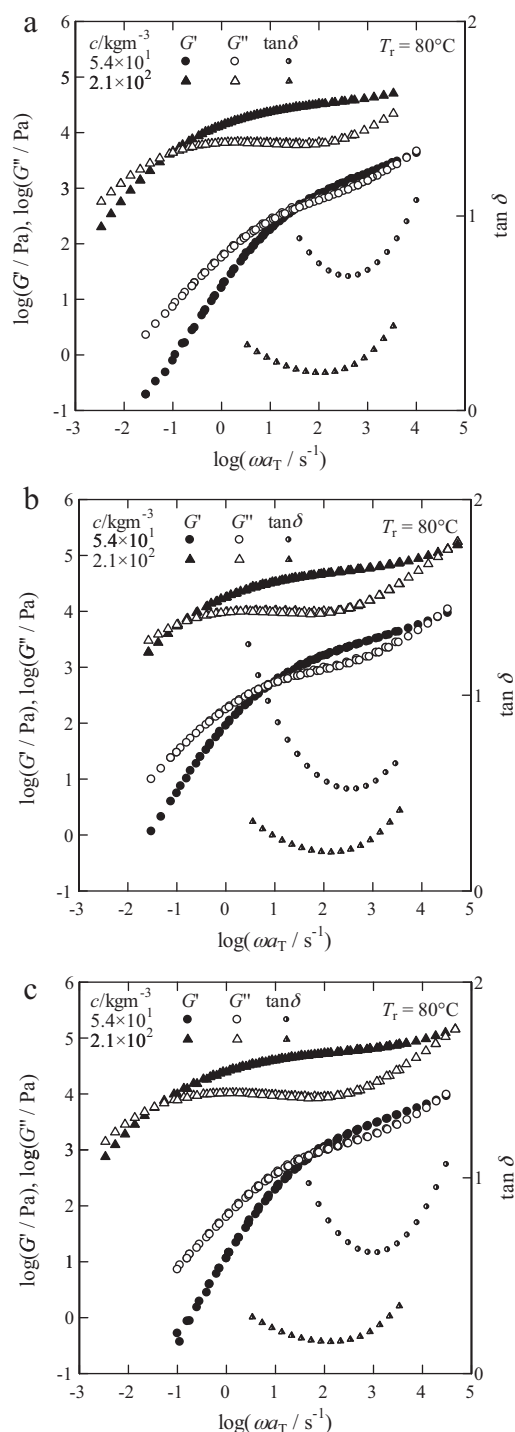
Galactomannan powders (g-gum, t-gum and lb-gum) were provided from MRC-Polysaccharide Co., Japan. All samples were used without further purification. A solvent 1-butyl-3-methylimidazolium chloride (BmimCl; Aldrich, USA) was used as received. According to the manufacturer's data sheet, the melting temperatures ( $T_m$ ) of BmimCl was reported to be 70 °C. The galactomannan solutions in BmimCl were prepared as follows: the powders were added into liquid BmimCl in a dry glass vessel, and then the mixture was quickly stirred with a stainless steel spatula on a hot plate at about 80 °C. After that the glass vessel was sealed and was left on the hot plate for complete melting. For every galactomannan  $c$  ranged from  $5.4 \times 10^1$  to  $2.1 \times 10^2 \text{ kg m}^{-3}$  (ca. 5–20 wt%), and in the calculation of  $c$ , the density of BmimCl was assumed to be  $1.08 \times 10^3 \text{ kg m}^{-3}$ , as reported previously (Horinaka, Yasuda, & Takigawa, 2011a; Horinaka, Yasuda, & Takigawa, 2011b). The densities for the galactomannans were commonly assumed to be  $10^3 \text{ kg m}^{-3}$ , since the values for the purely amorphous polymers are not available (Horinaka et al., 2011a). The viscoelasticity measurements were started just after finishing the sample preparation.

### 2.2. Measurements

The dynamic viscoelasticity measurements were carried out with an ARES rheometer (now TA Instruments, USA) under a nitrogen atmosphere with a cone-plate geometry. The diameter of the plates was 25 mm and the cone angle was 0.1 rad. The angular frequency ( $\omega$ ) dependence curves of the storage modulus ( $G'$ ) and the loss modulus ( $G''$ ) were measured in the range of  $\omega$  from 0.01 to  $100 \text{ s}^{-1}$ . The amplitude of the oscillatory strain ( $\gamma$ ) was settled to be 0.1 so that the linear viscoelasticity was realized. The measurement temperature ( $T$ ) ranged from 20 to 100 °C. The viscoelasticity measurements were successfully taken even at 20 °C, since the supercooled state of the BmimCl solutions was rather stable below  $T_m$  of 70 °C (Horinaka, Yasuda, & Takigawa, 2009; Horinaka et al., 2011a).

## 3. Results and discussion

Fig. 1(a) shows the master curves of  $G'$  and  $G''$  at the reference temperature ( $T_r$ ) of 80 °C for the solutions of g-gum at  $c =$  for  $5.4 \times 10^1$  and  $2.1 \times 10^2 \text{ kg m}^{-3}$ . At both concentrations, the  $\omega$  dependence curves at different temperatures were well superimposed to give the master curves only by a horizontal shift ( $a_T$ : the shift factor). This means that the time (or, angular frequency)–temperature superposition principle holds for these systems. The frequency-dependence of loss tangent ( $\tan \delta = G''/G'$ ) is also shown for the region in which the curves pass through a minimum. The zero-shear viscosity ( $\eta_0$ ) of the solvent, BmimCl, at  $T_r$  of 80 °C was much smaller than that of the solutions examined here, and therefore the contribution of  $\eta_0$  of the solvent to  $G''$  was ignored. At low  $\omega a_T$  the flow region can be seen clearly on the  $G'$  and  $G''$  curves. In the middle  $\omega a_T$  region in the figure the rubbery plateau exists in both  $G'$  curves. The rubbery plateau originates from the entanglement coupling between polymer



**Fig. 1.** Master curves of  $\omega$  dependence of  $G'$  and  $G''$  for  $5.4 \times 10^1$  and  $2.1 \times 10^2 \text{ kg m}^{-3}$  solutions of (a) g-gum, (b) t-gum, and (c) lb-gum.  $T_r = 80^\circ\text{C}$ . The  $\tan \delta$  curve is also included.

chains, indicating the existence of entanglements between g-gum chains. The tilted plateau suggests that the molecular weight distribution of the g-gum is broad.

Fig. 1(b) and (c) shows the master curves of  $G'$  and  $G''$  for the solutions of t-gum and lb-gum, respectively. Similar viscoelastic behavior to the g-gum solutions is observed for these galactomannans.

Fig. 2 shows  $\log a_T$  ( $T_r = 80^\circ\text{C}$ ) plotted against  $1/T$  from 20 to 100 °C for the solutions of g-gum, t-gum and lb-gum. The shift factor  $a_T$  at a given  $T$  is almost the same regardless of  $c$  and all

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