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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 4.6×10^3, 3.2×10^3, and 2.7×10^3 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.

1. Introduction

Galactomannans consist of a main chain of (1,4)-β-D-mannose as units and a side group of (1,6)-α-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: ~2 for g-gum, ~3 for t-gum, and ~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 5.4×10^1 to 2.1×10^2 kg m^{-3} (ca. 5–20 wt%), and in the calculation of c, the density of BmimCl was assumed to be 1.08×10^3 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 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 (ω) dependence curves of the storage modulus (G') and the loss modulus (G'') were measured in the range of ω from 0.01 to 100 s^{-1}. The amplitude of the oscillatory strain (γ) 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 5.4×10^1 and 2.1×10^2 kg m^{-3}. At both concentrations, the ω 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 (η_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 η_0 of the solvent to G'' was ignored. At low ωa_T the flow region can be seen clearly on the G' and G'' curves. In the middle ωa_T region in the figure the rubbery plateau exists on both G' curves. The rubbery plateau originates from the entanglement coupling between polymer 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.

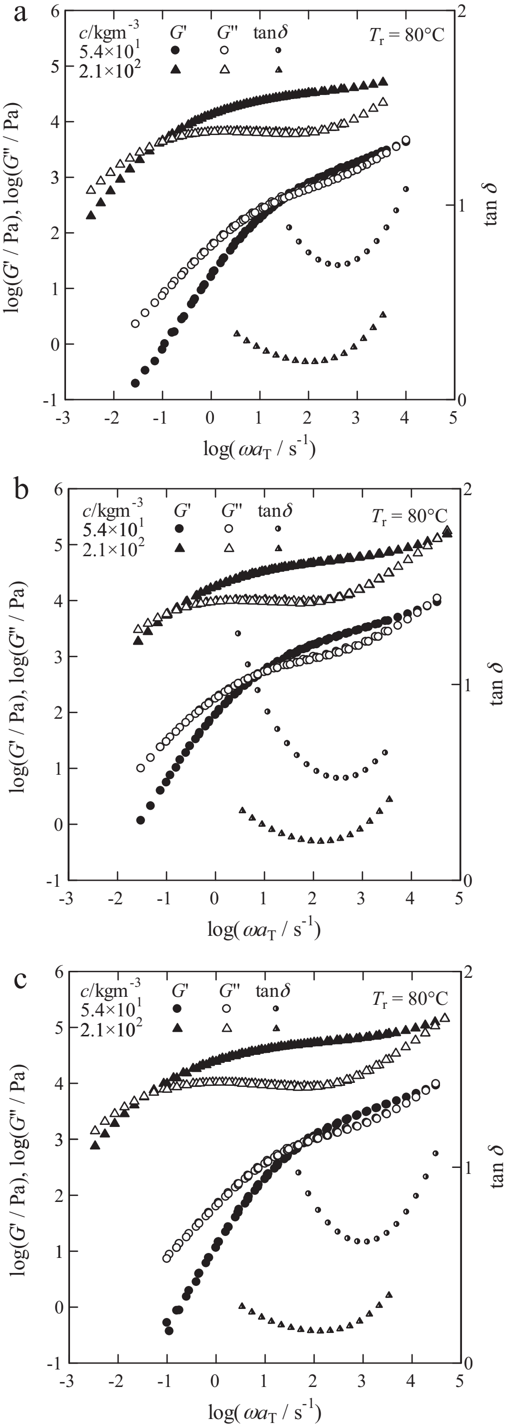

Fig. 1. Master curves of ω dependence of G' and G'' for 5.4×10^1 and 2.1×10^2 kg m^3 solutions of (a) g-gum, (b) t-gum, and (c) lb-gum. T_r = 80 °C. The $\tan\delta$ curve is also included.

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 °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

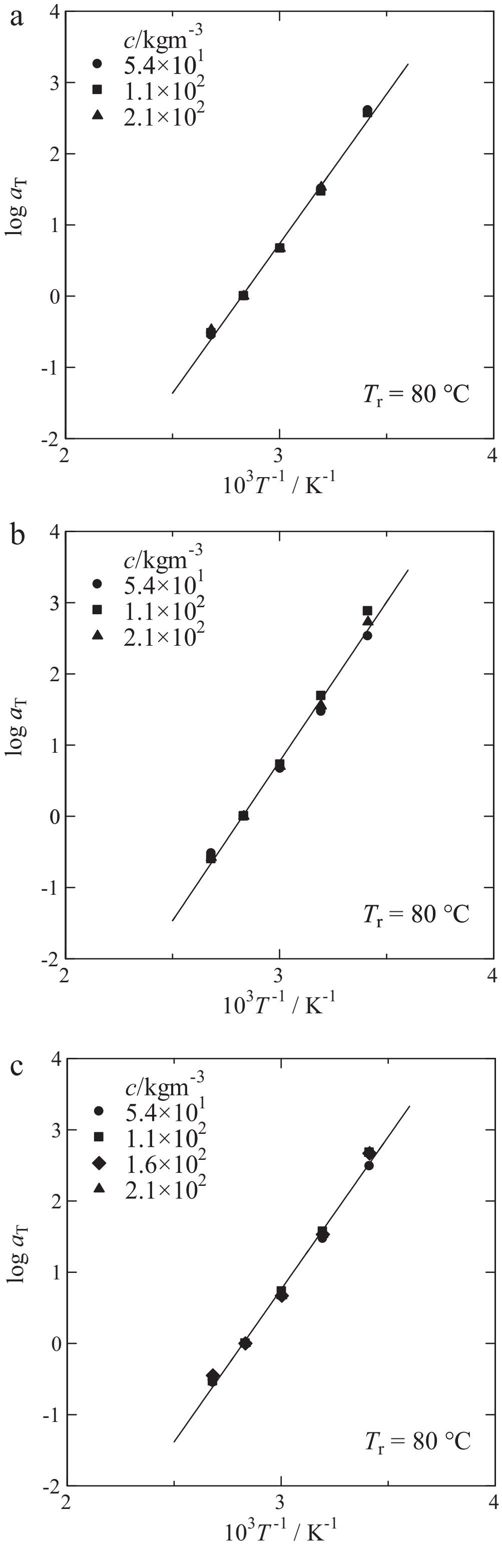

Fig. 2. Shift factor for: (a) g-gum, (b) t-gum, and (c) lb-gum solutions of c from 5.4×10^1 to 2.1×10^2 kg m^{-3} plotted against the reciprocal of T. In each figure, all data points fall on a single line.

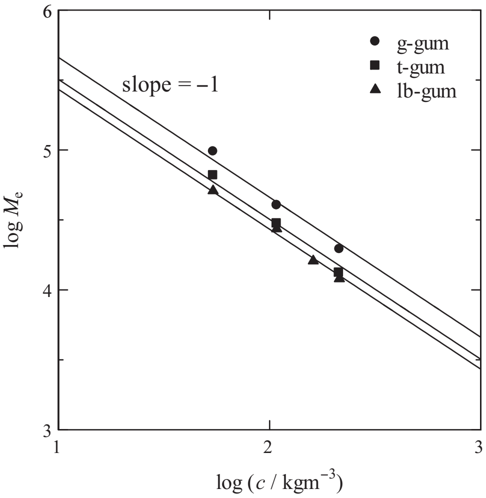

Fig. 3. Double-logarithmic plot of M_e against c for galactomannans in solution. Each line is the best fit with a slope of 1. $M_{e,melt}$ for galactomannans are determined as M_e at $c = 10^3$ kg m^{-3}.

data points fall on a single line. These are common to the three figures ((a)–(c)). The above indicates that the T-dependence curve of a_T can be represented by an Arrhenius-type equation and that even below the melting point of BmimCl, a_T has the same T dependence as above the melting point. Similar behavior has been observed for other polysaccharides in BmimCl (Horinaka et al., 2011a; Horinaka, Yasuda, & Takigawa, 2012).

From the analogy with the rubber elasticity, M_e for a polymer at a concentration c can be calculated by

$$M_e = \frac{10^3 cRT}{G_N^0} \tag{1}$$

Here, G_N^0 is the plateau modulus in the rubbery region and R is the gas constant. (Doi & Edwards, 1986; Ferry, 1980; Onogi, Masuda, & Kitagawa, 1970) As stated previously, the actual G' curves in this study were tilted, so that we defined here G_N^0 as the G' value at ωa_T where the tan δ versus ω curve stays at a minimum. This leads to the results that the 5.4×10^1 and 2.1×10^2 kg m^{-3} solutions of g-gum respectively have G_N^0 of 1.6×10^3 and 3.2×10^4 Pa (Fig. 1(a)), finally giving M_e of 9.8×10^4 and 2.0×10^4, respectively. The values of M_e for the solutions of other galactomannans were obtained in a similar way.

Fig. 3 shows double-logarithmic plots of M_e against c for the three galactomannans. For each galactomannan, a straight line with a slope of −1 is drawn with the best fit method. This is based on the assumption that a relation for polymers $M_e \propto c^{-1}$ is also applied to the galactomannans (Doi & Edwards, 1986; Masuda, Toda, Aoto, & Onogi, 1972; Nemoto, Ogawa, Odani, & Kurata, 1972). It is seen that data points for each galactomannan are fitted well by the line of slope −1, indicating that the c^{-1} dependence of M_e also holds well for the galactomannan solutions examined in this study. Comparing the values of M_e at a given c, we have the order g-gum > t-gum > lb-gum although the difference between t-gum and lb-gum is rather small. The quantity, $M_{e,melt}$ for the galactomannans can be determined as a value of the intercept on the right-hand ordinate in Fig. 3 (or, more precisely, the value of M_e at $c = 10^3$ kg m^{-3}), by assuming the density of all galactomannans to be 1.0×10^3 kg m^{-3}. The obtained values of $M_{e,melt}$ are 4.6×10^3, 3.2×10^3, and 2.7×10^3 for g-gum, t-gum and lb-gum, respectively; namely, $M_{e,melt}$ becomes smaller with increasing the m/g ratio. Since $M_{e,melt}$ is a material constant, it is interesting to calculate the number of monosaccharide units between entanglements in the molten state (N_{unit}) from $M_{e,melt}$ and M_{unit}, with M_{unit} being the molecular weight of a repeating unit for the galactomannans. Here, M_{unit} was calculated based on the assumption that the m/g ratios are the typical values, i.e., 2 for g-gum, 3 for t-gum, and 4 for lb-gum, and that a galactose side group was included in a unit. We define N_{unit} as the number of mannose units along the main chain, not

Table 1
Material constants for galactomannans.

Sample	M_{unit}	$M_{e,melt}$	N_{unit} [a]
g-Gum	486	4.6×10^3	19
t-Gum	648	3.2×10^3	15
lb-Gum	810	2.7×10^3	13

[a] Excluding a galactose side group.

counting a galactose side group, i.e., N_{unit} = (the number of mannose units in a unit) × ($M_{e,melt}/M_{unit}$). Table 1 lists N_{unit} for the galactomannans together with $M_{e,melt}$ and M_{unit}. The values of N_{unit} lie in almost the same range (13–19). If we see them more precisely, however, we may have a tendency that N_{unit} decreases with increasing the m/g ratio. The values for the galactomannans can also be compared with those for other polysaccharides estimated in our previous studies. We have 19 for cellulose, 15 for agarose and 14 for gellan, which are almost the same and are typical for polysaccharides with the random-coil conformation in the ionic liquid (Horinaka et al., 2011a). The values for the galactomannans are really close to those of the other polysaccharides with the random coil conformation, suggesting that the galactomannans in the ionic liquid here take the random coil conformation. This is, at least for g-gum, consistent with the previous prediction made from the intrinsic viscosity measurement that a g-gum molecule behaves as a random coil in water (Robinson et al., 1982).

4. Conclusions

Dynamic viscoelasticity of concentrated solutions of g-gum, t-gum, and lb-gum in BmimCl was examined to estimate $M_{e,melt}$ of the galactomannans. The values of $M_{e,melt}$ are 4.6×10^3, 3.2×10^3, and 2.7×10^3 for g-gum, t-gum, and lb-gum, respectively; namely, $M_{e,melt}$ for the galactomannans is dependent on the m/g ratio. As a whole, however, N_{unit} for the three galactomannans are rather close to each other being in the same range as for other polysaccharides such as cellulose and agarose. This suggests that the galactomannans take the random coil conformation in ionic liquid. It seems that a galactose side group causes no conformational changes of galactomannans, for example, to a helix.

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