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Kyoto University
Rheological properties of concentrated solutions of galactomannans in an ionic liquid

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Key Words: galactomannan; molecular weight between entanglements; guar gum; tara gum; locust bean gum; ionic liquid
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.
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, Bourbon, Pinheiro, Martins, Souza, Teixeira, & Vicente, 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, Torres, & Goncalves, 2005; Wu, Cui, Eskin, & Goff, 2009; Wu, Li, Cui, Eskin, & Goff, 2012). The m/g ratio is really one of 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, Cui, Eskin, & Goff, 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 (Ferry, 1980; Doi, & Edwards, 1986), 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 to dissolve several polysaccharides which are insoluble to conventional organic solvents. For each of 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 $2.1 \times 10^2$ kgm$^{-3}$ (ca. 5 to 20 wt %), and in the calculation of $c$, the density of BmimCl was assumed to be $1.08 \times 10^3$ kgm$^{-3}$, as reported previously (Horinaka, Yasuda, Takigawa, 2011a; Horinaka, Yasuda, Takigawa, 2011b). The densities for the galactomannans
were commonly assumed to be $10^3$ kgm$^{-3}$, since the values for the purely amorphous polymers are not available (Horinaka, Yasuda, Takigawa, 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 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, Honda, Takigawa, 2009; Horinaka, Yasuda, Takigawa, 2011a)

3. Results and Discussion

Figure 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 $c = 5.4 \times 10^1$ and $2.1 \times 10^2$ kgm$^{-3}$. 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 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.

Figures 1 (b) and (c) show 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.

Figures 2 shows log $a_T (T_r = 80 \degree C)$ 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 data points fall on a single line. These are common to the three figures ((a) to (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, Yasuda, Takigawa, 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

\[
M_e = \frac{10^3 cRT}{G_N^0}
\]  

(1)

Here, \( G_N^0 \) is the plateau modulus in the rubbery region and \( R \) is the gas constant. (Ferry, 1980; Doi, & Edwards, 1986; 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 \( \omega a_T \) where the \( \tan\delta \) versus \( \omega \) curve stays at a minimum. This leads to the results that the \( 5.4 \times 10^1 \) and \( 2.1 \times 10^2 \) kgm\(^{-3}\) solutions of g-gum respectively have \( G_N^0 \) of \( 1.6 \times 10^3 \) and \( 3.2 \times 10^4 \) Pa (Figure 1(a)), finally giving \( M_e \) of \( 9.8 \times 10^4 \) and \( 2.0 \times 10^4 \), respectively. The values of \( M_e \) for the solutions of other galactomannans were obtained in a similar way.

Figure 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 \( c^{\frac{1}{2}} \) 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 Figure 3 (or, more precisely, the value of \( M_e \) at \( c = 10^3 \text{ kg m}^{-3} \)), by assuming the density of all galactomannans to be \( 1.0 \times 10^3 \text{ kg m}^{-3} \). The obtained values of \( M_{e,melt} \) are \( 4.6 \times 10^3 \), \( 3.2 \times 10^3 \), and \( 2.7 \times 10^3 \) 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 (\( N_{\text{unit}} \)) from \( M_{e,melt} \) and \( M_{\text{unit}} \), with \( M_{\text{unit}} \) being the molecular weight of a repeating unit for the galactomannans. Here, \( M_{\text{unit}} \) 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 \( N_{\text{unit}} \) as the number of mannose units along the main chain, not counting a galactose side group, i.e., \( N_{\text{unit}} = (\text{the number of mannose units in a unit}) \times (M_{e,melt} / M_{\text{unit}}) \). Table 1 lists \( N_{\text{unit}} \) for the galactomannans together with \( M_{e,melt} \) and \( M_{\text{unit}} \). The values of \( N_{\text{unit}} \) lie in almost the same range (13 to 19). If we see them more precisely, however, we may have a tendency that \( N_{\text{unit}} \) 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, Yasuda, & Takigawa, 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, Ross-Murphy, & Morris, 1982).

4. Conclusions

Dynamic viscoelasticity of concentrated solutions of g-gum, t-gum, and lb-gum in BmimCl was examined to estimate $M_{\text{e,melt}}$ of the galactomannans. The values of $M_{\text{e,melt}}$ are $4.6 \times 10^3$, $3.2 \times 10^3$, and $2.7 \times 10^3$ for g-gum, t-gum, and lb-gum, respectively; namely, $M_{\text{e,melt}}$ for the galactomannans is dependent on the m/g ratio. As a whole, however, $N_{\text{unit}}$ 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.
References


Figure Captions

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

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

Figure 3 Double-logarithmic plot of $M_e$ against $c$ for galactomannans in solution. Each line is the best fit with a slope of $\Delta1$. $M_{e,melt}$ for galactomannans are determined as $M_e$ at $c = 10^3$ kgm$^{-3}$. 
Fig. 1(a)
Fig. 1(b)
Fig. 1(c)
Fig. 2(a)

$T_r = 80 \, ^\circ C$

- $c/\text{kgm}^{-3}$
- $5.4 \times 10^1$
- $1.1 \times 10^2$
- $2.1 \times 10^2$

$\log a_T$

$10^3 T^{-1} / \text{K}^{-1}$
Fig. 2(b)
Fig. 2(c)
slope = -1

\[ \log M_e = \log (c / \text{kgm}^{-3}) \]

Fig. 3
Table 1. Material constants for galactomannans

<table>
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<tr>
<th>sample</th>
<th>$M_{\text{unit}}$</th>
<th>$M_{\text{e,melt}}$</th>
<th>$N_{\text{unit}}^*$</th>
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<tr>
<td>g-gum</td>
<td>486</td>
<td>$4.6 \times 10^3$</td>
<td>19</td>
</tr>
<tr>
<td>t-gum</td>
<td>648</td>
<td>$3.2 \times 10^3$</td>
<td>15</td>
</tr>
<tr>
<td>lb-gum</td>
<td>810</td>
<td>$2.7 \times 10^3$</td>
<td>13</td>
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* excluding a galactose side group