Gum tragacanth dispersions: Particle size and rheological properties affected by high-shear homogenization

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1. Introduction

Polysaccharide gums have wide functional properties including thickening, emulsifying, gelling, stabilization, and controlling the crystal growth of ice and sugar [1,2]. Their behavior helps modifying different properties of products in food, pharmaceutical, and cosmetic industries [3,4].

Plant hydrocolloids are high molecular weight biopolymers which are often polysaccharides composed of more than one type of monosaccharide unit [5–7]. Arabic, karaya, ghatti and tragacanth gums are the most commonly used exudate gums [8–10]. Increasing interest in plant gums from a scientific, technological and economic standpoint, calls for further studies about them [11].

Gum tragacanth (GT) is a plant gum exuded from the stems and branches of various species of Astragalus with a branched heterogeneous anionic structure, containing carboxylic acid groups [12]. The linear backbone is composed of 1, 4 linked α-d-galacturonic acid units and the branches consist of arabinose, xylose, glucose, fucose, galactose, and rhamnose units [13]. There are various species of GT which have different physicochemical and rheological properties. All species of GT are made up of two different fractions; tragacanth which is the water soluble part and bassorin which is water swellable [14]. The two parts are probably in a physical mixture since they separate easily [13]. It is reported that the ratio of the two fractions is different among various species [15,16].

It has been reported that physical treatments such as mixing, homogenizing, ultrasonication and gamma irradiation could affect the characteristics of hydrocolloid dispersions [17]. Meanwhile different homogenization devices such as high speed blenders, rotor–stator systems, high pressure valve homogenizers, microfluidizers, ultrasonic and membrane homogenizers are widely used to produce food emulsions [18]. The disruptive forces in the most widely used homogenization techniques depend on the flow conditions (laminar, turbulent, or cavitation) and therefore on the type of homogenizer used [19,20]. These forces are able to cause degradation of polysaccharide molecules [21].

It was reported that homogenization techniques could influence the molecular and functional properties of polysaccharides. Kivelä et al. [22] studied the effect of colloid mill, high pressure homogenization and microfluidization on the properties of oat β-glucan solution and reported a clear and irreversible fall in viscosity and a loss in shear thinning.

By investigating the effect of dynamic high pressure homogenization on some polysaccharides, Villay et al. [23] found that the sensitivity of polysaccharides depends strongly on their structure.
so that globular branched structures were nearly unaffected, while linear stiff polymers underwent depolymerization.

The homogenization effects on the properties of several other polysaccharides such as xanthan [21,24], methylcellulose [25], modified starches [26], chitosan [27], inulin [28], pectin [17,29], and flaxseed gum [2] have also been investigated.

The most widely used mechanical homogenization techniques include rotor/stator homogenization and high pressure homogenization [19,20]. In rotor/stator homogenizers the forces are mainly generated by the collision of accelerated fluid with the device wall and by rapid rotation of the rotor in the gap of the rotor and stator, causing shear stress [18].

The aim of the present study was to investigate the effect of high-shear homogenization via a rotor/stator system on the particle size and rheological properties of three different species of GT dispersions in order to gain better insight into the behavior of this gum through identical processing in the industry.

2. Materials and methods

2.1. Materials

Three species of Iranian GT exuded by Astragalus gossypinus (ribbon type), A. compactus and A. rahensis (flakes) were collected. The raw gum was ground, and then sieved for obtaining powders with a size between 100 and 500 μm. Some physicochemical properties of these gums are presented in Table 1 [13].

2.2. Preparation of GT dispersions

0.5% (w/w) GT dispersions were prepared by adding 0.5 g of gum powder to 99.5 g of distilled water that had been heated up to 35 °C. Sodium azide (0.02% w/w) was added to prevent microbial growth. Dispersions were then stirred for 2 h at 700 rpm and stored at 4 °C overnight to ensure the complete hydration. The resulted dispersions were homogenized for 0, 5, 10, 15 and 20 min at 13,500 rpm by Ultraturax (IKA-T25, Germany). Dispersions were ice-coated in order to prevent temperature fluctuations. Each sample was prepared in triplicate.

2.3. Particle size analysis

The particle size distributions of dispersions were determined at room temperature with a laser diffraction particle size analyzer (Cilas 1090, Orleans, France) equipped with a 5 mW He/Ne (635 nm) laser beam. Dispersions were diluted with deionized water (1:100) to avoid multiple scattering effects. Size measurements are reported as the volume weighted mean diameter (D_{4,3}) and diameter on surface (D_{2,1}):

\[ D_{4,3} = \frac{\sum n_i d_i^3}{\sum n_i d_i} \]
\[ D_{2,1} = \frac{\sum n_i d_i^2}{\sum n_i d_i} \]  

where \( n_i \) is the number of particles of class \( i \), and \( d_i \) is the diameter of class \( i \).

Also, the distribution width of droplet size, in term of polydispersity index (span) was determined from the following equation [30]:

\[ \text{Span} = \frac{d_{0.9} - d_{0.1}}{d_{0.5}} \]

where \( d_{0.1}, d_{0.5} \) and \( d_{0.9} \) are diameters at 10%, 50%, and 90% cumulative volume, respectively.

2.4. Rheological properties

Steady shear viscosity, strain and frequency sweep oscillatory shear tests were performed with a Physica MCR 301 rheometer (Anton Paar GmbH, Graz, Austria) equipped with a concentric cylinder measurement system (CC27) with internal diameter of 28.970 mm, cylinder diameter of 26.665 mm, cylinder length of 40.005 mm and radius ratio of 1.0846 (according to ISO 3219). The temperature was adjusted to 25 °C with a peltier system equipped with fluid circulator with an accuracy of 10⁻² °C. Rheological data were collected using Rheoplus software version 3.21 (Anton-Paar, Austria). A shear rate ramp increased logarithmically from 0.1 to 300 s⁻¹ (with 4 points per decade) and the total time required to run flow curves was about 6 min. A power-law model was used to describe the rheological properties of dispersions. Logarithmic plots of shear stress versus shear rate were used to calculate the consistency coefficient and flow behavior index:

\[ \sigma = \gamma^n \]

where \( \sigma \) is the shear stress (Pa), \( m \) is the consistency coefficient (Pa s^n), \( \gamma \) is shear rate (s⁻¹) and \( n \) is the flow behavior index (dimensionless).

Strain sweep tests were performed at strain of 0.05–300% and fixed frequency of 1 Hz to determine the linear region of viscoelasticity. Frequency sweep tests were carried out at frequency of 0.01–15 Hz and constant strain of 1% (according to the strain-sweep data) to evaluate the dynamic rheological properties.

2.5. Statistical analysis

All treatments were performed in triplicate and analysis of variance (ANOVA) was performed. Significant differences between means were identified (\( p \) values < 0.05) using SAS software (SAS Release 9.1, SAS Institute Inc., Cary, NC, USA).

3. Results and discussion

3.1. Particle size characteristics

The light scattering techniques may be used as an alternative method to observe the degradation of polysaccharides as the decrease of average molecular weight is accompanied with a reduction in particle size [17]. Fig. 1 illustrates the particle size distributions of GT dispersions before and after the treatment determined using static light scattering. Our dispersions consist of
bassorin and tragacanthin particles. The hydrodynamic diameter of tragacanthin is about 0.12 μm vs. the Sauter diameter of more than 200 μm for bassorin. In previous study by Mohammadiar et al. [14] the number average diameter of tragacanthin was measured by DLS and the results were compared with laser diffraction technique. The results obtained by laser diffraction technique were in good conformance with DLS.

All dispersions presented a wide distribution with different sizes depending on species, before the processing. So GT is a polydisperse system due to the presence of tragacanthin and bassorin. López-Franco et al. [11] reported that the insoluble part is less branched and produces natural aggregates and the larger the ratio of insoluble components, the larger the resulting aggregates will be. On the contrary, the soluble component is highly branched and does not normally produce aggregates. In fact, the variation in particle size distribution of different species of gum dispersions may be attributed to differences in the swelling power of the gum particles which seems to be related to the ratio of soluble to insoluble part. As expected, A. gossypinus possessed the largest particles since it has the highest insoluble ratio (Table 1) and so the largest aggregates. Accordingly, A. rahensis which contains the highest soluble fraction (Table 1), showed the smallest particle size.

The particle size analysis of dispersions revealed that the treatment made the size distributions sharper and by increasing the time of processing, the particle size gradually shifted to smaller regions so that an infinitesimal peak appeared at smaller sizes (≈10 μm) which grew with time of homogenization. A. compactus and A. rahensis dispersions showed more pronounceable alterations following the treatment compared with A. gossypinus. In the case of A. gossypinus and A. rahensis, the particle size distributions were identical for 15 and 20 min treatment indicating no significant changes after 15 min.

Table 2 demonstrates the evolution of particle size parameters after high-shear homogenization for three species. It should be noted that, in comparison to $D_{3,2}$, $D_{2,1}$ is more sensitive to the number of particles and this parameter was used in order to have the signal of smaller particles. All parameters including $D_{0.1}$, $D_{0.5}$, $D_{0.9}$, $D_{4,3}$ and $D_{2,1}$ reduced with processing time for all three species. It is noticeable that there were no significant differences between 15 and 20 min treatment for all species. Therefore, it was revealed that the applied treatment caused particle size reduction of dispersions. A reduction in the molecular weight of xanthan [21], methylcellulose [25], inulin [28], pectin [17, 29], and flaxseed gum [2], have been also reported after high-pressure homogenization and microfluidization processes. The volume weighted mean diameter ($D_{3,2}$) showed a reduction of 1.84, 2.28 and 1.86 times for A. gossypinus, A. compactus and A. rahensis, respectively. Nevertheless, the span values showed different trends for various species. This index decreased in the case of A. gossypinus and increased for A. compactus and A. rahensis after 15 min homogenization. The high values of polydispersity indexes (1.39 to 1.89) indicate a chemical and structural heterogeneity within samples which is completely usual for biopolymers. The reason of size reduction after the treatment may be the degradation due to the chain scissoring or the dissociation of aggregates. Additional investigation is needed to clarify the exact reason.

3.2. Flow properties

Steady-shear rheological behavior of three species was determined before and after 15 min homogenization. All samples showed shear-thinning behavior before the treatment (Fig. 2). Apparent viscosities for these species within the investigated range of shear rates, before the treatment, followed the order of A. compactus > A. gossypinus > A. rahensis (Fig. 2).

The viscosity increased after 15 min homogenization and the behavior became more shear-thinning (Fig. 2). The viscosity increase was more pronounced in the case of A. gossypinus, so that the apparent viscosity of this species became even more than A. compactus after the treatment.

Power-law parameters for dispersions before and after 15 min homogenization are presented in Table 3. The model was well fitted to the flow curves ($R^2 > 0.96$). While n values reduced nearly 1.5 times for all species after homogenization, m values increased 47, 3.9 and 5 times for A. gossypinus, A. compactus and A. rahensis, respectively. The increase in consistency coefficients shows the augmentation of intermolecular interactions. This behavior was in marked contrast to what have been reported about other
polysaccharides. Floury et al. [25] studied degradation of methylcellulose during high-pressure homogenization and noted that the dispersion had weaker thickening characteristics after this treatment. Kivelä et al. [22] reported that homogenization caused a significant fall in viscosity, a loss in shear thinning behavior and size reduction of β-glucan solution. They doubted whether the size reduction was due to chain scissoring, dissociation of aggregates or both of them. A reduction of thickening and stabilizing properties was also reported for other polysaccharides such as xanthan, alginic, κ-carrageenan, pectin and flaxseed gum [22,21,29,31].

This difference between GT and other hydrocolloids is probably because of the fact that GT consists of two various fractions with a different behavior in aggregate formation. It was reported that changing the rheological behavior of biopolymer solutions must be related to the modifications of interchain interactions and the molecular orientation and deformation [21]. It is also reported that if the biopolymer becomes smaller in size or less swollen in shape, the viscosity generally decreases [22]. In spite of particle size reduction in GT species, the viscosity increased after the homogenization process. Thus, it is implausible that the decrease of particle size after the treatment was due to the chain scissoring and molecular weight reduction. It seems that only large aggregates are influenced and are dissociated to the smaller ones. In fact the homogenization process provided the molecules with more opportunity to contact each other by breaking the large aggregates and unfolding their structures. Since the fluid phase is generally entrapped in these aggregates, the reduction of aggregates size led to more particle interactions and the formation of a network which held water and solubilized components in its structure and caused the augmentation of viscosity. A. gossypinus which possessed the highest insoluble fraction showed the maximum increase in viscosity after the treatment.

Our previous study on the effects of sonication on these species also showed that sonication caused an increase in apparent viscosity of A. gossypinus dispersions and a decrease in the viscosities of A. compactus and A. rahensis dispersions [32]. In addition, an increase

### Table 2

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Particle characteristics</th>
<th>A. gossypinus</th>
<th>A. compactus</th>
<th>A. rahensis</th>
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<td></td>
<td>d01</td>
<td>d05</td>
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* Values with different letters (a–e) in each column are significantly different (p < 0.05).

### Table 3

<table>
<thead>
<tr>
<th>Time (min)*</th>
<th>A. gossypinus</th>
<th>A. compactus</th>
<th>A. rahensis</th>
</tr>
</thead>
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<tr>
<td>m(Pa s^−1)</td>
<td>n</td>
<td>R²</td>
<td>SD</td>
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<tr>
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<td>0.7a</td>
<td>0.99</td>
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<td>4.29</td>
<td>0.41b</td>
<td>0.99</td>
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</table>

* Values with different letters (a–b) in each column are significantly different (p < 0.05).
in the viscosity of GT dispersions was reported at low doses of gamma irradiation, while at high doses the viscosity dropped significantly [33,34]. Low doses of γ-irradiation and short times of sonication (both processes cause free radical formation) cause the augmentation of viscosity while at high doses and/or longer times, the extreme breakage of the covalent bonds and monomer separating cause an increase in polydispersity and viscosity reduction. It seems that the critical dose of γ-irradiation and critical time of sonication are related to the soluble/insoluble ratio and are species dependent.

In our present experiment the treatment was not as severe as gamma irradiation, ultrasonication or high pressure homogenization, so it caused only mechanical breakage of aggregates. Hence by decreasing the particle size and also polydispersity, the apparent viscosity and consistency index increased.

3.3. Dynamic viscoelastic properties

3.3.1. Strain sweep test

Strain sweep test was performed to determine the strain limits of linear viscoelastic behavior in samples. Fig. 3 illustrates the strain sweep graphs for dispersions of three species before and after the treatment. It was found that the treatment caused an increase in dynamic moduli for all three species. The limiting values of strain ($\gamma_l$) were 2.9, 17.1 and 30.4% for A. gossypinus, A. compactus, and A. rahensis dispersions, respectively. Higher $\gamma_l$ represents samples with longer linear viscoelastic ranges, implying a higher stability of the viscoelastic material under the strain amplitude. Balaghi et al. [13] reported that the limiting values of strain are directly related to ratios of soluble to insoluble fractions. Results indicated that homogenization of A. gossypinus dispersions expanded the length of linear viscoelastic range (LVE) from 2.9% to 9.69% after 15 min. The two other species behaved differently, so that $\gamma_l$ decreased to 5.45 and 5.44% for A. compactus and A. rahensis dispersions, respectively. According to results, the structural strength ($G'_{LVE}$) rises after the

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**Fig. 3.** Variation of storage moduli ($G'$) with strain amplitude at 1 Hz for A. gossypinus (○), A. compactus (△) and A. rahensis (□) dispersions after 15 min treatment.

**Fig. 4.** Variation of elastic ($G'$) and viscous ($G''$) moduli with frequency for (a) A. gossypinus, (b) A. compactus and, (c) A. rahensis dispersions after 15 min treatment.
treatment for all species. According to strain sweep data, the strain of 1% was selected for frequency sweep test.

3.3.2. Frequency sweep

Fig. 4 demonstrates the frequency sweeps for dispersions at LVE range before and after the homogenization. It was observed that for untreated dispersion of A. gossypinus, increasing the frequency led to an increase in both moduli with a dominance of elastic behavior up the crossover point (Fig. 4a). The crossover point occurred at the frequency of 8.55 Hz, above which the viscous behavior prevailed. The alteration in behavior indicates a transition from weak-gel-like structure at low frequencies to fluid-like behavior at higher frequencies. This unusual pattern has been attributed to the fact that GT consists of two different fractions. It is reported that tragacanthin behaves like a Maxwellian liquid, while bassorin has a gel-like structure and the presence of these two fractions can undoubtedly affect the viscoelastic behavior of whole GT [34].

As illustrated in Fig. 4b and c for untreated dispersions of A. compactus and A. rahensis, the increase in frequency caused the intensification of both \( G' \) and \( G'' \) with the dominance of viscous behavior over the entire range of frequency. This behavior is similar to that of unlinked polymers and represents a viscoelastic liquid. It seems that the presence of a high amount of soluble fraction is responsible for the liquid viscoelastic behavior of these two species. Also, at higher insoluble fraction content, the more pronounced elastic behavior was observed (tan \( \delta \) value decreased).

Homogenization caused an increase in both \( G' \) and \( G'' \), in all three species. Treating the A. gossypinus dispersion led to the prevalence of elastic behavior over the entire frequency range and the crossover point disappeared. Therefore, the behavior became more gel-like. In the case of A. compactus and A. rahensis dispersions, the treatment resulted in the domination of \( G' \) at low frequencies. As expected, the crossover frequency of A. compactus (9.71 Hz) was higher than that of A.rahensis dispersion (1.99 Hz), which indicates a larger elastic contribution [35].

It was observed that the extent of alteration in dynamic moduli due to the treatment was species dependent. For instance, at a constant frequency of 1.58 Hz, the value of \( G' \) increased 5.7, 21.3 and 37.6 times and \( G'' \) raised 10.5, 5.6 and 3.8 times after the treatment for A. gossypinus, A. compactus and A. rahensis, respectively. So, it seems that in species containing higher soluble fraction, the influence of treatment on the elastic module is more pronounced and the viscous module is less affected. This could be due to the entrapment of soluble fraction within aggregates.

The frequency dependence of \( G' \) and \( G'' \) for dispersions can be approximately described using the following equations [36]:

\[
G' = a \omega^x \tag{5}
\]

\[
G'' = b \omega^y \tag{6}
\]

where \( a \) and \( b \) represent the magnitude of \( G' \) and \( G'' \) at a frequency of 1 Hz, respectively, \( \omega \) is the angular frequency and \( x \) and \( y \) are frequency exponents which represent the slope of the relationship between modulus and frequency.

The power law parameters of \( G' \) and \( G'' \) for GT dispersions are presented in Table 4. The results indicate that A. gossypinus having the highest and \( a \) and \( b \) values and the least \( x \) and \( y \) values among the other species, possesses the strongest structure and the least frequency dependency of dynamic modulus. Moreover, according to the viscoelastic theory of Bohlin about weak gels \( (G' = A \times \omega^x)^Z \) in which \( Z \) is the coordination number) which assumes that in a flowing substance, flow depends on rheological units rather than on single molecular units [37], this species contains the highest number of flow units interacting with each other and the highest interaction strength between the rheological units.

In untreated dispersion of A. gossypinus, parameter \( a \) was higher than \( b \) indicating stronger elastic structure. The exponent \( x \) was less than \( y \) in this sample which shows that \( G' \) had less sensitivity to frequency variation. In the case of untreated A. compactus and A. rahensis dispersions parameter \( b \) was higher than \( a \) indicating that \( G'' \) predominates in the major part of the spectra and the behavior was liquid-like.

Homogenization caused an increase in \( a \) and \( b \) values, in all three species. There was no change in the behavior of A. gossypinus dispersion after the treatment but in the case of A. compactus and A. rahensis dispersions parameter \( a \) exceeded \( b \) which indicates that the gum dispersions became more elastic.

### Table 4
Power law parameters for dynamic moduli of dispersions before and after homogenization for 15 min.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>( G' )</th>
<th>( G'' )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( a )</td>
<td>( x )</td>
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<tr>
<td>A. gossypinus</td>
<td>0</td>
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<td>7.36(^b)</td>
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<tr>
<td></td>
<td>15</td>
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<td>A. rahensis</td>
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</tr>
<tr>
<td></td>
<td>15</td>
<td>0.238(^b)</td>
</tr>
</tbody>
</table>

\(^{a}\) Values with different letters (\(a\)–\(b\)) in each column are significantly different (\(p < 0.05\)).
should be carried out in order to gain more insight into the behavior of GT dispersions during the process.

Acknowledgments

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References