Influence of Selected Salts and Sugars on the Rheological Behavior of Quince Seed Mucilage

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ABSTRACT

Properties of solvent/cosolute in a food system obviously can influence the rheological properties of hydrocolloids. In this work, the impact of various concentrations of some sugars (sucrose and glucose at 10, 20, and 30\% w/w concentration) and salts (CaCl\textsubscript{2} and NaCl, 50, 100, and 150 mM) on the rheological properties of Quince Seed Mucilage (QSM) were investigated. QSM produced high viscosity dispersion with yield stress, which was affected by concentrations and types of salt and sugar. The salts altered the electrostatic interactions between the QSM chains and led to the viscosity reduction. Increasing the salt concentration, decreased the yield stress ($\tau_0$) and consistency coefficient ($k$) values, but led to increase in the flow behavior index ($n$) value. Sucrose and glucose increased the apparent viscosity of QSM dispersions. High sugar concentrations resulted in higher viscosity. Assessment of the time-dependent flow behavior of QSM dispersions proved that the structural kinetic model had the best data description. All the samples showed thixotropic behavior. The Atomic Force Microscope (AFM) results exhibited a proper understanding of the chain interactions of QSM and changes in the flow behavior. The results of this research showed that CaCl\textsubscript{2} and sucrose had more pronounced effect on the rheological properties of QSM.

Keywords: Hydrocolloid, Quince mucilage, Rheology, Structural kinetic model.

INTRODUCTION

Plant seed mucilage can be applied in the food products due to its interesting characteristics (texturizing, emulsifying, and thickening) and dietary properties. The physicochemical and functional characteristics of mucilage are a function of chemical composition, molecular configuration, and extraction and processing circumstances (Williams and Phillips, 2000).

Quince (Cydonia oblonga Miller, Rosaceae family) is a fruit with high nutritional and therapeutic properties. This fruit has some functional characteristics such as anticarcinogenic, antimicrobial, antioxidant, and anti-allergic activities, which are relevant to the existence of phenolic compounds (Wojdylo \textit{et al.}, 2013; Legua \textit{et al.}, 2013; Sharma \textit{et al.}, 2011).

Quince seed also has a high content of mucilage (11.58\%) and is known as biocompatible and biodegradable mucilage (Jouki \textit{et al.}, 2014; Elboutachfaiti \textit{et al.}, 2017). Moreover, its low production cost, ready availability, easy extraction and high viscosity make Quince Seed Mucilage (QSM) attractive. QSM could be highly valuable for the development of stimuli-responsive intelligent/smart formulations for the targeted and sustained release of drug delivery systems on commercial scale because of its biocompatible nature, high swelling index, pH, salt responsiveness, and on-off switching properties (Hussain \textit{et al.}, 2019).

Average molecular weight of QSM is recorded as 9.61×10\textsuperscript{6} g mol\textsuperscript{-1}, which is greater than commercially available gums such as guar gum (1.45×10\textsuperscript{6}), gellan gum (1.64×10\textsuperscript{6}) and locust bean gum (1.6×10\textsuperscript{6}) (Rezagholi et al., 2014).
It can be applied in the medical, food industry, cosmetic, and pharmaceutical industries as a stabilizer (Soukoulis et al., 2009). Recently, the emulsifying properties of quince seed mucilage have been extensively studied and confirmed for a pH range of 6-8 (Ritzoulis et al., 2014). Jouki et al., (2014) also reported that QSM consisted of 2.71% protein and its emulsion stability was 94.89%.

Rezagholi et al. (2018) have reported that β-1,4-D-xylan with the fraction of glucuronic acid residues is the main water-soluble polysaccharide of QSM. A mixture of aldobionic acids, arabinose, and a cellulose segment is found in QSM structure. According to Abbastabar et al. (2015), QSM exhibits shear-thinning behavior and has considerable gelling capacity. They found that the high hydrodynamic volume of QSM (due to high critical concentration of 0.077 g 100 mL⁻¹ and intrinsic viscosity of 1530 mL g⁻¹), result in improving its gel production in aqueous solution. Furthermore, it is proposed that QSM has stiff conformation based on its salt tolerance value (Rezagholi et al., 2018).

The pH, concentration, molecular weight, temperature, and counter-ions are the important variables that affect the rheological behavior of hydrocolloids (Kar and Arsalan, 1999). The most abundant low-molecular ingredients that are generally used as food additives are NaCl and CaCl₂. For the investigation of functional and rheological attributes of hydrocolloid, we should determine the impact of the concentration and type of salt on the functional characteristics of hydrocolloid (Koocheki et al., 2009). The arrangement of polysaccharide chains and their physicochemical properties are related to the electrostatic forces (Lin and Lai, 2009).

Sucrose and glucose are the most prevalent sugars that are applied in the food products. Glucose is extensively applied in the food industry, especially in syrups, due to the higher water activity, lower kinematic viscosity and molecular weight compared to the sucrose (Imeson, 2010). The sucrose modifies the texture and flavor of the product, extends the freshness, and plays an important role in moisture retention (Torres et al., 2013).

The influence of salt and sugar types on the flow behavior of hydrocolloids is reported by other researchers. According to Farahmandfar and Naji-Tabasi (2020), alteration of electrostatic interactions between chains of basil seed gum led to the viscosity reduction in the presence of CaCl₂, NaCl, and KCl. They investigated the time-dependent rheological properties of BSG. The time-independent properties of semi-dilute seed gum solution were affected by the different sugars and salts (Yousefi et al., 2016). Steady-shear flow behavior of semi-dilute guar gum was investigated by Chenlo et al. (2011) and a synergic impact on the apparent viscosity due to the addition of sugar was reported. This effect was correlated with sugar concentration. Zhang et al. (2007) also reported that the addition of salts (CaCl₂ and KCl) decreased the initial viscosity of semi-dilute solutions of hydroxypropyl guar gum, which caused the lowering of thixotropic properties.

Hydration and molecular hydrodynamic volume of soluble polysaccharides depend on the type of interactions (attraction or repulsion) among chain fragments. The configuration of chains in the polysaccharide structure determines the molecular volume. Inclusion of additives such as sugars and salts influence the electrostatic repulsion among chains and chains interactions (Van Aken, 2006).

Additives such as sugars and slats can alter the viscosity of hydrocolloids, which changes depend on the type and concentration of the additives. Despite great potential of additive impact on the rheological characteristics of mucilage in complex systems such as food, no comprehensive research has been reported about QSM. The objective of this work was to study the influence of different concentrations of NaCl, CaCl₂, sucrose and glucose on the rheological characteristics (shear-rate dependency and time-dependency) of QSM and to investigate the molecular structure and interactions of QSM chains with salts and sugars by using AFM.
MATERIALS AND METHODS

The quince seeds were purchased from a local market in Mashhad, Iran. Different salts (sodium chloride and calcium chloride) and sugars (sucrose and glucose) were purchased from Merck Co., Germany.

Quince Seed Mucilage Extraction

Quince seeds were cleaned manually to remove all the foreign matters. The quince seed mucilage was extracted according to the optimized conditions reported by Farahmand et al. (2016). Briefly, the optimized conditions were: Water/Seed ratio of 32.5:1, temperature of 47°C and time of 45 minutes. An electrical mixer (1,000 rpm) was used to mix the seed-water slurry. After the extraction, seeds were separated and recovering by mixing with three volumes of 96% ethanol. The precipitates were collected and dried overnight at 50°C, then, it was milled and sieved through a mesh 18 sifter. Then, the mucilage powders were packed and kept in the dry and cold conditions.

Preparation of QSM Dispersion

The QSM dispersions (0.25% w/w) were prepared in de-ionized water with different concentrations of salts (NaCl and CaCl$_2$) (50, 100, and 150 mM) and sugars (glucose and sucrose) (10, 20, and 30% w/w). In order to complete hydration, the dispersions were mixed using a roller mixer for 24 hours at 25°C.

Rheological Experiments

The rheological tests were performed using a rotational viscometer (Model RVDV-II, Brookfield, Inc. USA). In order to equilibrate the temperature of the dispersions at 25°C, a jacket with a water circulating system (Model ULA-40Y, Brookfield, Inc. USA) was used. The steady shear data of QSM were measured by spindle 18 at 25°C (±0.1°C). All the tests were carried out twice and the data was reported as an average of each test value.

Time-Independence

The steady shear rheological behavior was assessed in the shear rate range of 10-220 s$^{-1}$. Fitting the data of shear stress ($\tau$)-shear rate ($\dot{\gamma}$) was conducted with the Herschel-Bulkley model (Equation 1):

$$\tau = k \gamma^n + \tau_0$$

Where, $\tau$ is the shear stress (Pa), $\dot{\gamma}$ is known as the shear rate (s$^{-1}$), $k$ is the consistency coefficient (Pa.s$^n$), $\tau_0$ is the yield stress, and $n$ is the flow behavior index (dimensionless).

Time-Dependence

Investigation of the time-dependent characteristics was performed at a constant shear rate (50 s$^{-1}$) as a simulated oral shear rate and the shear stress ($\tau$) was reported as a function of shearing time (t) until shear stress achieved a constant value. Fitting the obtained data was carried out with the structural kinetic model (Equation 2):

$$\left( \frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} \right)^{1-n} = (n-1)kt + 1$$

Where, $\eta_0$ is the initial apparent viscosity at t= 0 (structured state), and $\eta_\infty$ is the steady-state apparent viscosity at $t_\infty$ (non-structured state). $n$ and $k$ are the order of the structure breakdown and the breakdown rate constant, respectively.

AFM Measurement

AFM images (ARA-AFM, Iran) were obtained in tapping mode at a constant temperature (25°C). The AFM sample was prepared by drying the QSM dispersions (0.25% w/w) in presence of CaCl$_2$ (150 mM).
Table 1. The rheological parameters of Herschel–Bulkley models obtained for quince seed mucilage dispersion (0.25% w/w) at different salts and sugars concentrations.  

<table>
<thead>
<tr>
<th>Salt concentration (mM)</th>
<th>Herschel–Bulkley model</th>
<th>R²</th>
<th>RMSE</th>
<th>SSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>k (Pa s^n)</td>
<td>n</td>
<td>τ₀ (Pa)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.19±0.01^aA</td>
<td>0.59±0.10^aA</td>
<td>0.14±0.07^aD</td>
<td>0.99</td>
</tr>
<tr>
<td>NaCl 50</td>
<td>0.11±0.02^b</td>
<td>0.60±0.20^c</td>
<td>0.12±0.15^b</td>
<td>0.99</td>
</tr>
<tr>
<td>100</td>
<td>0.08±0.01^c</td>
<td>0.63±0.10^d</td>
<td>0.11±0.19^c</td>
<td>0.99</td>
</tr>
<tr>
<td>150</td>
<td>0.07±0.05^d</td>
<td>0.65±0.30^c</td>
<td>0.11±0.04^c</td>
<td>0.99</td>
</tr>
<tr>
<td>CaCl₂ 50</td>
<td>0.08±0.02^c</td>
<td>0.65±0.12^c</td>
<td>0.12±0.09^b</td>
<td>0.99</td>
</tr>
<tr>
<td>100</td>
<td>0.07±0.03^d</td>
<td>0.67±0.16^b</td>
<td>0.11±0.16^c</td>
<td>0.99</td>
</tr>
<tr>
<td>150</td>
<td>0.05±0.05^f</td>
<td>0.69±0.20^a</td>
<td>0.10±0.08^d</td>
<td>0.99</td>
</tr>
<tr>
<td>Sugar concentration (%w/w)</td>
<td>Herschel–Bulkley model</td>
<td>R²</td>
<td>RMSE</td>
<td>SSE</td>
</tr>
<tr>
<td>Glucose 10</td>
<td>k (Pa s^n)</td>
<td>n</td>
<td>τ₀ (Pa)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.18±0.01^e</td>
<td>0.59±0.25^A</td>
<td>0.13±0.03^D</td>
<td>0.98</td>
</tr>
<tr>
<td>20</td>
<td>0.2±0.01^D</td>
<td>0.59±0.3^A</td>
<td>0.21±0.24^C</td>
<td>0.99</td>
</tr>
<tr>
<td>30</td>
<td>0.43±0.00^C</td>
<td>0.55±0.18^C</td>
<td>0.3±0.06^B</td>
<td>0.99</td>
</tr>
<tr>
<td>Sucrose 10</td>
<td>k (Pa s^n)</td>
<td>n</td>
<td>τ₀ (Pa)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.24±0.01^D</td>
<td>0.57±0.39^B</td>
<td>0.14±0.07^D</td>
<td>0.99</td>
</tr>
<tr>
<td>20</td>
<td>0.47±0.01^D</td>
<td>0.55±0.42^C</td>
<td>0.22±0.21^C</td>
<td>0.99</td>
</tr>
<tr>
<td>30</td>
<td>0.62±0.01^D</td>
<td>0.53±0.47^D</td>
<td>0.38±0.18^A</td>
<td>0.99</td>
</tr>
</tbody>
</table>

Note: (a-f) and (A-E): Different letters show significant differences (P< 0.05) (small letters for salts and capital letters for sugars), ns: Not significant.

and sucrose (30% w/w) on a mica surface at room temperature.

RESULTS AND DISCUSSION

Statistical Analysis

Rheological parameters were analyzed with MATLAB (2016a). The data were statistically analyzed by the Analysis Of Variance (ANOVA) based on a completely randomized design. Then, the Duncan Multiple Range Test was used to determine the difference between means (P< 0.05). All the experiments were done at least in triplicate.

Time-Independent Rheological Properties of QSM

The best description of the steady-shear flow behavior of QSM dispersions in the presence of salts and sugars was acquired by the Herschel-Bulkley model. For this model, the ranges of R² and RMSE were 0.99 and 0.012-0.281, respectively. The rheological properties of QSM dispersions are presented in Table 1.
According to the results, increasing the shear rates (10-220 s⁻¹) led to the viscosity reduction, which signified the shear-thinning behavior of the QSM dispersions. As shown in Figure 1, a drastic reduction occurred with increasing the shear rates from 10 to 40 s⁻¹. This decrement trend has been observed at higher shear rates (40-220 S⁻¹), but the viscosity reduction was not pronounced. Intertwining the chains of the polysaccharide can produce a network, making a unique viscosity in solution. When the shear is applied, this network can be disrupted easily, which can explain the shear-thinning behavior of QSM (Morris et al., 1981; Yanbei et al., 2015).

**Influence of Salts**

Shear-dependent rheological characteristics of the QSM dispersions at various concentrations of the salts are presented in Table 1 and Figure 1. The aqueous mucilage dispersions also showed the pseudoplastic properties in the presence of salts (n values were lower than 1 for all the samples).

Adding salts (50, 100 and 150 mM) reduced the apparent viscosity noticeably, and CaCl₂ compared to NaCl decreased the viscosity of the QSM dispersion to a greater extent. The amounts of viscosity reduction compared to the control sample at shear rate of 100 s⁻¹ were 3.51 and 12.19% for NaCl and CaCl₂ at 50 mM, respectively (Figure 1).

As shown in Table 1, the flow behavior index (n) increased significantly in the presence of salts (P> 0.05). According to the Tukey test (ANOVA), the impact of type and concentration of salt and also their interactions on k, τ₀ and n values were significant (P< 0.05). The higher concentration of salts had more influence on the flow behavior index. Farahmandfar and Naji-Tabasi (2020) also reported a similar trend for n value in the presence of salt addition. The consistency coefficient value (k) decreased from 0.193 to 0.056 Pa sⁿ in the presence of cations compared to the control (P<0.05). Increasing the salt concentration had a negative impact on the amount of τ₀ value, which decreased from 0.14 to 0.11 Pa at 150 mM NaCl and from 0.14 to 0.10 Pa at 150 mM CaCl₂ (P< 0.05) (Table 1). According to Yousefi et al. (2016), the effect of KCl and MgCl₂ on the sage seed gum (SSG) dispersions was similar to our results. They reported that

![Figure 1. Impact of the various concentrations (50, 100 and 150 mM) of NaCl and CaCl₂ on the apparent viscosity of QSM dispersions.](image-url)
Sisko (R^2= 0.995-0.999) and Herschel-Bulkley (R^2= 0.994-0.999) models showed suitable results to describe the steady-shear behavior of SSG. According to their study, salts decreased the yield stress and consistency coefficient of SSG.

By adding a monovalent salt (NaCl), the values of k were higher than those that were obtained by adding the divalent salt (CaCl_2) to the QSM dispersion (Table 1). These alterations have an important role in viscosity reduction. The reduction of k value in a salty solution is related to the sulfate group and carboxylic acids in the polysaccharide chains (Alpizar-Reyes et al., 2018). The contraction of polysaccharide conformation induced by the salts led to viscosity reduction. A similar trend has been observed for chia mucilage (Velázquez-Gutiérrez et al., 2015), and Balangu seed gum (Razavi et al., 2016). The rheological characteristics of E. contortisiliquum gum by the addition of Na^+, Ca^{2+}, and Al^{3+} were evaluated by Oliveira et al. (2001). They reported that positive ions affinity of gum structure was a function of charge to ionic radius ratio of counter ions. The lower amounts of charge to ionic radius ratio resulted in the lower chain compression for hydrocolloid molecules in the solution. Therefore, gum solutions (at infinite dilution) containing sodium or aluminum ions caused the highest or least viscosity, respectively. The larger ions (Ca^{2+}) shield the electrostatic interaction among the QSM chains more strongly compared to the smaller cations (Na^+), as they have larger hydrated radius. (Harrison et al., 1999). Salehi et al. (2014) mentioned that the type of salt extremely affected the rheological characteristics of Balangu seed gum. These researchers found that the viscosity reduction by CaCl_2 was more obvious than NaCl.

Increasing the salts concentration caused the rapid reduction of viscosity. The reduction of viscosity was more predominate at high concentration of the salt (Figure 1 and Table 1). It seems that when the concentration of added salts was low, expanding the gum structure was obviously limited, which led to the viscosity reduction. Enhancing the salt concentration helps conformation change of hydrocolloid to a more compact coil. This is because of neutralization of the negatively charged residues of gum that were exposed to the cations. These processes reduced the hydrodynamic volume and electrostatic repulsion of hydrocolloid chains to a greater extent, which led to the more viscosity reduction.

It seemed that the QSM was anionic mucilage like a polyelectrolyte. Therefore, the addition of cations decreased the repulsion and then mucilage conformation collapsed. Our results confirmed that the QSM is a negatively charged polyelectrolyte in the solution. Drastic intermolecular electrostatic repulsion and more expanded molecule are responsible for inherent negative charge of the QSM. According to Ritzoulis et al. (2014), hydrocolloids extracted from the quince seed at four different pHs had negative charges and zeta potential of the hydrocolloid extracted at pH= 7 was about -55 mV. The existence of inorganic salt and positive ions with the opposite charge (via capability to form the salt bridges among acid groups) cover the electrostatic repulsion among charges along the structure of polyelectrolyte. Folding up the chain is a result of screening of the electrostatic interactions and assumed a smaller and more compact structure. As a result, the viscosity of the QSM dispersions decreased (Wyatt et al., 2011). According to Mazza and Biliaderis (1989), joining of the counter-ions with polymers structure could persuade NaCl to reduce the flaxseed mucilage viscosity; therefore, the electrostatic repulsion among charged groups of polymer chain was decreased.

According to Carrington et al. (1996), the molecular conformation of xanthan gum extremely changed due to the influence of salt addition on its rheological characteristics. The highest viscosity belongs to the control sample, whose structure was unfolded in the solution.
Alpizar-Reyes et al. (2018) declared that rheological characteristics of tamarind seed mucilage were influenced by the salts and their concentrations owing to the addition of cations, which decreases repulsion and allows molecular expansion, thereby promoting a significant reduction in viscosity. Lai et al. (2000) also reported that the impact of salt on the viscosity reduction of hsian-tao leaf gum was more obvious when using divalent positive ions. According to Razavi et al. (2011), the ionized groups on gum structure will be neutralized at the higher contents of salt, hence its structure was more compact.

**Influence of Sugars**

Figure 2 demonstrates the flow behaviour curves of QSM (0.25% w/w) at the presence of two selected sugars (glucose and sucrose) and at different concentrations (10, 20, and 30 % w/w). It can be seen that all samples exhibited the shear-thinning behaviour. Yousefi et al. (2016) also reported similar results for the effect of sugars on the flow behaviour of sage seed gum. They found a rapid decrease in the viscosity at 10-50 s⁻¹ shear rates. As shown in Figure 2, the sugars had a synergistic influence on the viscosity of QSM dispersion. The apparent viscosity increased by enhancing the sugars concentration. Sucrose had considerable influence on the viscosity increment in comparison with the glucose. The viscosity of control sample was the lowest. The viscosity enhancing of 30% w/w glucose and sucrose compared to the control at 100 s⁻¹ were 165.48 and 192.50%, respectively. The n values of the all samples were lower than 1, which proved the shear-thinning behavior of the QSM in the presence of sugars (Table 1). The n values of QSM dispersion were decreased by increasing the concentration of sugars. The type and concentration of sugars also influenced k value, so, increment in the k value was observed when the sugar concentration was increased (from 0.185 to 0.433 Pa sⁿ for glucose and from 0.244 to 0.629 Pa sⁿ for sucrose). The yield stress of QSM dispersion increased as the sugar concentration increased from 10 to 30% w/w and the sucrose had more prominent effect on τ₀ (Table 1).

By adding sucrose-glucose into the polysaccharide network, the density of QSM
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dispersion noticeably increased, which subsequently resulted in increase in viscosity. Moreover, the sugar in the solution could bind to the polysaccharide structure of the QSM via hydrogen bonding and then promoting the cross-linking strength of the polysaccharide network (Lei et al., 2001, 2001; Richardson and Norton, 1998), which also causes the viscosity increment. Salehi and Kashaninejad (2014) mentioned that the competition between the sugar and basil seed gum for water-binding will enhance by the increase in sugar concentration. Chenlo et al. (2011) proposed that the polymer-polymer interactions are influenced by the sugars and hydrogen bonds created among the hydrocolloid and hydroxyl groups of the sugar, which could increase the number of junction zones and stabilize the polymer chain associations. Finally, these interactions result in structural changes.

A number of researches have reported the positive effect of sugars on the viscosity of other hydrocolloids such as oat gum (Cancela et al., 2005), cress seed gum (Behrouzian et al., 2013), Balangu seed gum (Salehi and Kashaninejad, 2015) and sage seed gum (Yousefi et al., 2016). According to Chenlo et al., (2011), the viscosity of guar gum was enhanced by adding sucrose and glucose, which was related to the interactions between the polymer and sugars. As reported by Wu et al. (2015), the addition of high concentration of sucrose (30 mg mL$^{-1}$) had the comprehensive influence on the flow behaviour of tara gum solution. They concluded that by adding sucrose, a compact conformation of tara gum appeared.

According to Capitani et al. (2015), the addition of sugar to aqueous dispersion of chia mucilage leads to decrease in the pseudoplastic behaviour. Other researchers also observed similar results by adding sugar into the hydrocolloid solution (Salehi et al., 2014 in case of glucose; Yanes et al., 2002 in case of sucrose; Galmarini et al., 2010; Bayari et al., 2004 and Sato et al., 2004). In contrast, some authors explained that the flow behavior index ($n$) of hydrocolloid decreased in the presence of sugar (Elfak et al., 1980; Salehi et al., 2014 for sucrose; Yousefi et al., 2016). Moreover, the additive concentrations and compositions are the main factors influencing the rheological properties of particular hydrocolloid.

### Time-Dependent Rheological Properties of QSM

#### Influence of Salts

After initial shearing, the viscosity of dispersions attained a constant value corresponding to a steady-state just about 350 s. When a polymer solution is exposed to shearing, the rearrangement or breakdown of links among polymer chains could happen, which is related to the thixotropy (Mao and Chen, 2006). This behavior proved that the QSM chains have the possibility to create a three-dimensional structure and shearing force could change the polysaccharide configuration. Other researchers concluded similar trends for Balangu seed gum, Alyssum homolocarpum seed gum and green Laver mucilage (Razavi and Karazhian, 2009; Koocheki and Razavi, 2009; Huei Chen and Yuu Chen., 2001).

Figure 3 (a, b) demonstrates the time-dependent rheological characteristics of the QSM in the presence of cations (Na$^{+}$ and Ca$^{2+}$). By increasing the time of shearing, the viscosity of all samples decreased in comparison with the control, which revealed their thixotropic behavior. Basil seed gum and its fractions also showed thixotropic behavior during the shearing (Naji-Tabasi and Razavi, 2017). This behavior is also reported for the other mucilage like cress seed gum and its fractions (Karazhian et al., 2009; Razmkhah et al., 2017).

The structural kinetics model was used to describe the time-dependency of the flow behavior of QSM and the obtained data are presented in Table 2. It was found that their transient viscosity data could be fitted satisfactorily with a second order structural
Table 2. Viscosity of QSM dispersions (0.25 w/w) in the presence of salts (NaCl and CaCl$_2$) and sugars (glucose and sucrose) as a function of shearing time (shear rate 50 L s$^{-1}$).$^a$

<table>
<thead>
<tr>
<th>Salt concentration (mM)</th>
<th>$\eta_0$ (Pa s)</th>
<th>$\eta_0/\eta_\infty$</th>
<th>$K \times 10^{-3}$ (s$^{-1}$)</th>
<th>$R^2$</th>
<th>RMSE</th>
<th>SSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>45.02± 0.21$^{a}$</td>
<td>1.21± 0.03$^c$</td>
<td>12.34± 0.00$^{a}$</td>
<td>0.99</td>
<td>0.08</td>
<td>0.28</td>
</tr>
<tr>
<td>NaCl</td>
<td>22.44± 0.43$^b$</td>
<td>1.21± 0.05$^c$</td>
<td>12.30± 0.00$^{a}$</td>
<td>0.99</td>
<td>0.05</td>
<td>0.11</td>
</tr>
<tr>
<td>100</td>
<td>21.87± 0.17$^c$</td>
<td>1.22± 0.06$^c$</td>
<td>12.17± 0.01$^{ab}$</td>
<td>0.98</td>
<td>0.06</td>
<td>0.16</td>
</tr>
<tr>
<td>150</td>
<td>20.30± 0.13$^d$</td>
<td>1.26± 0.09$^b$</td>
<td>12.55± 0.01$^{a}$</td>
<td>0.96</td>
<td>0.06</td>
<td>0.15</td>
</tr>
<tr>
<td>CaCl$_2$</td>
<td>21.92± 0.19$^c$</td>
<td>1.19± 0.06$^d$</td>
<td>12.16± 0.00$^{a}$</td>
<td>0.99</td>
<td>0.06</td>
<td>0.16</td>
</tr>
<tr>
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<td>20.71± 0.11$^c$</td>
<td>1.26± 0.04$^b$</td>
<td>12.19± 0.01$^{ab}$</td>
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<tr>
<td>150</td>
<td>19.88± 0.14$^c$</td>
<td>1.77± 0.17$^a$</td>
<td>12.03± 0.01$^{a}$</td>
<td>0.98</td>
<td>0.12</td>
<td>0.59</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sugar concentrations (%) w/w</th>
<th>$\eta_0$ (Pa s)</th>
<th>$\eta_0/\eta_\infty$</th>
<th>$K \times 10^{-3}$ (s$^{-1}$)</th>
<th>$R^2$</th>
<th>RMSE</th>
<th>SSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucose</td>
<td>43.37± 0.30$^G$</td>
<td>1.14± 0.17$^D$</td>
<td>12.44± 0.00$^{a}$</td>
<td>0.98</td>
<td>0.03</td>
<td>0.26</td>
</tr>
<tr>
<td>20</td>
<td>49.26± 0.32$^E$</td>
<td>0.92± 0.64$^F$</td>
<td>12.09± 0.00$^{a}$</td>
<td>0.98</td>
<td>0.15</td>
<td>0.11</td>
</tr>
<tr>
<td>30</td>
<td>94.68± 0.39$^A$</td>
<td>1.36± 0.06$^D$</td>
<td>12.23± 0.01$^{a}$</td>
<td>0.99</td>
<td>0.06</td>
<td>0.69</td>
</tr>
<tr>
<td>Sucrose</td>
<td>63.57± 0.41$^D$</td>
<td>1.28± 0.19$^D$</td>
<td>12.11± 0.00$^{a}$</td>
<td>0.99</td>
<td>0.28</td>
<td>0.14</td>
</tr>
<tr>
<td>20</td>
<td>66.66± 0.27$^C$</td>
<td>1.10± 0.18$^C$</td>
<td>12.10± 0.00$^{a}$</td>
<td>0.97</td>
<td>0.06</td>
<td>0.96</td>
</tr>
<tr>
<td>30</td>
<td>105.20± 0.44$^A$</td>
<td>1.14± 0.14$^D$</td>
<td>12.67± 0.01$^{a}$</td>
<td>0.98</td>
<td>0.07</td>
<td>0.54</td>
</tr>
</tbody>
</table>

$^a$ (a-f) and (A-G): Different letters show significant differences (P < 0.05) (small letters for salts and capital letters for sugars), ns: Not significant.

Figure 3. Viscosity of QSM dispersions (0.25 % w/w) in the presence of NaCl (a) and CaCl$_2$ (b), glucose (c), and sucrose (d) as a function of shearing time (shear rate 50 L s$^{-1}$).
kinetic model (n=2). Fitting the data with this model showed the highest $R^2$ and the lowest RMSE and SSE values, which proved the acceptable capability of the structural kinetic model for prediction of the time-dependent behavior of the QSM dispersion. Shear-induced breaking of internal configuration was responsible for the changes of rheological characteristics. On the other hand, breakdown rate of QSM structure during the shearing is determined by the kinetics changes of structured to non-structured state (Abu-Jdayil, 2003). Koocheki and Razavi (2009) also reported that this second-order model was the best for fitting the time-dependent viscosity of A. homolocarpum seed gum at a constant shear rate.

According to Table 2, the highest initial apparent viscosity ($\eta_0$) belonged to the control sample. This parameter declined by enhancing the salt concentration. The lowest value of initial viscosity was shown at 150 mM CaCl$_2$ sample (19.884 Pa s), which showed 55.84% reduction compared with the control. The salts had no significant impact on the breakdown rate constant (k), which shows how fast the QSM dispersions reach the equilibrium viscosity under the action of shearing. Similar results were reported by Farahmandfar and Naji-Tabasi (2020). The ratio of initial to equilibrium viscosity ($\eta_0/\eta_\infty$) can be presumed as a relative assessment of the extent of structural breakdown (Koocheki and Razavi, 2009). The result of the $\eta_0/\eta_\infty$ is given in Table 2. The ratio $\eta_0/\eta_\infty$ is a relative measure of the extent of thixotropy of the QSM dispersions. According to Table 2, the addition of salts led to increase in the $\eta_0/\eta_\infty$ values (P<0.05) and also led to enhancing the thixotropic behavior. Seemingly, the salts caused weak links among the chains of QSM structure and reduced the amount of structuring.

### Influence of Sugars

Figure 3 (c, d) present the time-dependent characteristics of QSM in the presence of glucose and sucrose (10, 20, and 30 % w/w). Increasing the shearing times resulted in the viscosity reduction, which indicated thixotropic behavior of QSM in all samples. The viscosity of QSM dispersions increased after adding sucrose and glucose (Figure 3). The rheological parameters of the structural kinetic model are summarized in Table 2. As shown, by adding 30 % w/w sucrose, the viscosity elevated (the highest value). In contrast to salt, the sugar addition had synergistic effect on the $\eta_0$ likewise, the highest amount of initial viscosity belonged to the 30% w/w sucrose (57.21% increase compared to the control). There was no significant change in case of breakdown rate constant (k), because this index was a function of ion change. In case of the ratio of initial to equilibrium viscosity ($\eta_0/\eta_\infty$), the systematic trend was not observed. Razavi and Kashaninejad, (2009) reported that k value (as a relative measure of thixotropic breakdown rate) for Balangu seed gum in shear rate of 50 s$^{-1}$ was 0.0643. They also stated that this value was independent of the shear rate. According to their research, the extent of thixotropy ($\eta_0/\eta_\infty$) at a similar shear rate was 2.44, which was higher than the data obtained for the QSM dispersions containing sugars.

### Atomic Force Microscopy (AFM)

As shown in AFM Figures (Figure 4, a-b), addition of CaCl$_2$ (150 mM) had some effect on fibrils and lengthened them to a certain direction. A tightly pack continuous network structure with some inhomogeneity was observed in the presence of CaCl$_2$. On the contrary, the direction of fibers in the QSM sample was not definite and the structure was heterogeneous. Generally, addition of cations (like calcium ions) leads to inter-helical association of the QSM chains. The degree of structural shrinkage was determined by stiffness of the polysaccharide chain (Wyatt et al., 2011). These observations were in agreement with the rheological behavior result, which thixotropic behavior increased behavior
increased after adding salt. Similar results were concluded for Gellan gum in the presence of various cations (Funami et al., 2008; 2009). They reported that the reduction of repulsion was distinguishable among cations, which explained the difference in the network formation, and the effect of CaCl$_2$ was more obvious, at least 10 times more than the other cations. Adding CaCl$_2$ promoted inter-helical association of Carageenan and formation of the network-like structures. Mean vertical height was longer than the control sample (Funami et al., 2007).

QSM molecules, as the polyelectrolyte (opposite charges), were in the extended form in dispersion, so the fibrils were shown in the different directions in AFM images (Figure 4-a). The presence of a high concentration of sucrose (30% w/w) decreased considerably the water available for hydration, so, it had an impact on the flow behavior of mucilage. Moreover, by dissolving the sucrose into the polysaccharide network, density of solution increased. The sucrose also could bridge among the QSM chains via hydrogen bonds and strengthened the QSM network (Lei et al., 2001; Richardson and Norton, 1998), which condensed the molecular structure. The fibrils were not imaged clearly due to the surface roughness (Figure 4-C). These results were in agreement with those reported by Yanbei et al. (2015) for tara gum.

**CONCLUSIONS**

In this research, the impact of different kinds of salt (NaCl and CaCl$_2$) and sugar (glucose and sucrose) on the time-dependent and time-independent rheological characteristics of QSM were studied. It was found that the Herschel-Bulkley model was appropriate for characterizing the rheological properties of QSM as a function of the type and concentrations of the selected salts and sugars. The consistency coefficient ($k$) value of QSM dispersion was higher in the presence of NaCl compared to CaCl$_2$. In comparison with the control, the salt addition caused increase in the flow behavior index ($n$) and reduction in yield stress ($\tau_0$) and $k$ value. Typically, the impact of Ca$^{2+}$ on the rheological characteristics...
was stronger than Na⁺. By increasing the concentration of glucose and sucrose, the viscosity was increased. The structural kinetic model showed the acceptable ability to fit the time-dependent data. The data obtained by this model proved that the rate of thixotropic breakdown was higher in presence of CaCl₂. The viscosity of salty solution decreased by increasing the time of shearing. There were no systematic trends in the ratio of the initial to equilibrium viscosity in the presence of sucrose and glucose. The AFM results demonstrated the mechanism of QSM chains interactions in the presence of salt and sugar that justify the viscosity changes. According to the results of this work, the rheological characteristics of QSM dispersions were strongly influenced by the type and concentration of salts and sugars. Hence, adjusting the salt and sugar content could change the rheological properties of food products. The rheological and sensory properties of mucilage applied in the food products are determined by its microstructure and the degree of interactions. This issue is prominent, especially in the development of food formulations with proper sensory, functional, and rheological properties.

REFERENCES

15. Funami, T., Noda, S., Nakauma, M., Ishihara, S., Takahashi, R., Al-Assaf, S.


Shear Rheology. *Food Hydrocoll.*, **67**: 243-250.

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چکیده

ارث برخی نمک و قندها بر رفتار رئولوژیکی موسرلاژ دانه به

اتر خاص حلال/ حل و قندها در ساختار غذایی بی‌نتیجه نمی‌باشد. در این پژوهش، اثر غلظت‌های مختلف دو طرف (ساکارز و گلوکز در 10، 20 و 30 درصد وزنی-وزنی) و دو نمک (کلرید کلسیم و کلرید سدیم در غلظت‌های 0.50 و 150 میلی‌مولار) بر ویژگی‌های رئولوژیکی موسرلاژ دانه به‌ازای‌گیری گردید. موسرلاژ به‌متغیّرات با ویسکوزیته و تنظیم تنظیم (τn) با تأثیر کردن به‌بیان نوع و غلظت نمک و فنون بود. نمک‌ها با تغییر برهم کش میان نرخ‌های موسرلاژ منجر به‌کاهش ویسکوزیته حلول شدن. افزایش غلظت نمک گلوکزر منجر به افزایش ویسکوزیته حلول شدن، به‌طوری که افزایش غلظت قند، ویسکوزیته بالاتری حاصل شد. افزایش رفتار جریان وابسته به زمان‌نگه نمک داد که مدل کنیکی ساختاری به‌تنهایی توصیف را برای داده‌ها ارائه می‌دهد. کاهش غلظت به‌هم کنش‌های نرخ‌های موسرلاژ و تغییرات رفتار جریان بود. با استفاده از (AFM) نشان داده بزرگ‌ترین تأثیر را بر خواص رئولوژیکی موسرلاژ به نشان داد.