Rheological Properties of Zodo Gum Exudates as a Function of Concentration, Temperature, pH, Salt and Sucrose

H. Reza Mozafari[1*] and G. Hossein Mohebbi[2]

[1]*Young Researchers and Elite Club, Shahrekord Branch, Islamic Azad University, Shahrekord, Iran*
[2]*Department of Marine Toxinology, the Persian Gulf Marine Biotechnology Research Center, Bushehr University of Medical Science, Bushehr, Iran*
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ABSTRACT

The growing demand for hydrocolloids with the specific functional properties and the use in the food industry lead to the introduction of new sources of gums. The purpose of this study was to investigate the flow behavior of Zodo exudate gum as an easily accessible source of hydrocolloid compared with imported gums. Gum solutions with concentration of 1-3% Zodo gum, 0-30% sucrose, 100-500 mM sodium chloride and 5-100 mM calcium chloride at pH = 4, 7 and 10 were prepared and then the effect of shear rate (4.8–85 s^{-1}) was assessed on the flow behavior of gum solutions at temperature of 5-85 ˚C using the power law model with Viscometer Brookfield LV DV-III. All samples except for the 1% Zodo gum solution showed non-Newtonian and shear thinning behavior at 85 ˚C. Increase in gum concentration and decreased temperature led to increased viscosity and consistency index (K), and decreased flow index (n). Both salts led to decreased viscosity, consistency index, and increased flow index. Furthermore, the highest viscosity and the lowest flow index were obtained at pH 7 (P≤0.05).

Keywords: Zodo gum, Flow behavior, viscosity, consistency index, flow index.
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INTRODUCTION

Hydrocolloids are highly water absorbent polymers and they are polysaccharide from the chemical point of view (Arabic gum, guar gum, Carboxy methylcellulose, carrageenan, starch, pectin), or protein (gelatin) [1]. Polysaccharides are good stabilizer agents due to the hydrophilic property, high molecular weight gel property behavior, the prevention of macromolecular accumulation in emulsions by increasing the viscosity of the water phase and controlling rheological properties [2, 3]. Many today`s known polysaccharides were experimentally used in food industry such as pectin (regulatory factor of jam tissue) and starch (thickening agent of soups and sauces) in the distant past [4]. Considering the high price and, in some cases, lack of access to conventional stabilizers, the tendency has growingly risen to use a new native polysaccharide. In this regard, multiple studies have been conducted concerning the rheological characteristics of food hydrocolloids because of many applications in various fields of food industry [1, 5-7]. Following increased shear rate, in most cases, the apparent viscosity of gum solutions has declined, showing a shear thinning behavior. Power law model is generally employed to determine this behavior [8]. Zodo gum, also known as Zedo and Angum is a transparent exudate gum taken from *Amygdalus scoparia spach* [9]. This gum comes in white, red, and yellow. Its white color consists of chemical compounds including 0.21% protein, 12.08% humidity, and 1.67% ash [10]. Compared with Arabic gum, its lower price, accessibility to large quantities in Iran, potential applications in industries in particular food industry, and lack of information regarding its functional properties make more studies essential in order to know this gum. Few studies

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have been conducted in this field. Most studies conducted in this filed have focused on its compounds, chemical and physical properties, and performance characteristics such as emulsifiers properties, thermal behavior, and viscosity [10, 11]. This study aims to evaluate the effect of other chemical and physical properties such as temperature, shear rate, concentration, pH, salt and sucrose on behavioral characteristics of Zodo gum solution using power law equation.

EXPERIMENTAL SECTION

Zodo gum preparation
Zodo gum is taken from *Amygdalus scoparia spach* in forest areas near mountains in Kazeroun, Fars province, Iran. Prior to the test, it was ground and then sifted by laboratory sieve 200mm Wire Mesh in order to obtain a fine and uniform powder. All chemical materials were of analytical grade purchased from Merck Company.

Temperature dependence of the Zodo gum solution
After dissolving essential amount of powder in deionized distilled water (1-3% concentration), Zodo gum solutions were constantly and steadily mixed for 2 hours. The viscosities of hydrocolloid solutions reach their maximum over time; therefore all samples were tested after an overnight incubation at room temperature and full hydration. Viscosity and shear stress were measured at 5-85 ˚C (±0.1accuracy). Brookfield hot tubs were used for this purpose.

Flow properties at different pH
99% purity imidazole was used to stabilize the pH of gum solution. In order to prepare pH-7 buffer, the lowest possible compound concentration was used (0.05 grams per liter of deionized distilled water). Hydrochloric acid and 0.5 N Na OH, were employed to regulate the pH. In order to study the gum behavior at different pH, Zodo gum powder (up to 3% concentrations) was gradually and continuously added to 4, 7, and 10 pH buffers.

Flow properties at different salt concentrations
Gum solutions were prepared at 3% concentration at the presence of monovalent sodium chloride and divalent calcium chloride in 100-500 and 5-100 mM, respectively. The flow properties and viscosity were measured at 54.4 s^{-1} shear rate and 25 ˚C.

Flow properties at different sugar concentrations: 0-30% concentration sucrose was added to 3% Zodo gum. Then consistency coefficient (K) and flow behavior index (n) were measured at 54.4 s^{-1} shear rate and 25 ˚C.

Viscosity measurement
The viscosity of samples was measured by Viscometer Brookfield LV DV-III (Brookfield Engineering Laboratories. Inc. USA) equipped with spindle No. 27. As many as 20 minutes was considered to reach the desired temperatures. Viscosity and shear stress were measured at different shear rate including 4.08, 6.8, 13.6, 20.4, 27.2, 34, 40.8, 47.6, 54.4, 61.2, 68, 74.8, and 85s^{-1} and vice versa until 4.08 according to mpa.s. Measurement was repeated three times for each sample. consistency coefficient (K) and flow behavior index (n) were calculated for Zodo gums by shear rate-shear stress curves using Curve Expert V1/4 and power model ($\tau = K\gamma^{\circ n}$). In this equation, τ shows shear stress (Pa); γ° is shear rate (s^{-1}); K is consistency coefficient (pa.s^n); n is flow index (Without unit).

Statistical analysis
Results were analyzed by ANOVA using SPSS 18. Then Duncan test was employed to compare the mean and categorize them at $\alpha \leq 0.05$. Excel 2010 was employed to draw the curves.

RESULTS AND DISCUSSION

The effect of concentration, temperature, and shear rate on flow properties
R^2=0.99 in table 1 shows the suitability of the power law model to describe Zodo gum flow properties for all samples. Other studies indicate the suitability of this model to explain the flow behavior of food hydrocolloids including brown seaweeds polysaccharides [12], locust bean gum [13], hydrocolloids from monoi leaves [14], and salep [6]. Due to the lack of flow behavior index difference between Upward and Downward curves, Zodo gum rheological behavior was independent of time and it displayed the shear thinning behavior in all concentrations except for 1% concentration at 85 ˚C due to less-than-1 flow index (n=1.06).

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Table 1: Summary of regression analysis and information of power law equation for Zodo gum solution

		Upward curve				Downward curve		
concentration	Temperature(°C)	Consistency Coefficient(pa.s^n)	flow index	R^2		Consistency Coefficient(pa.s^n)	flow index	R^2
1%	5	0.03±0.0001[a]	0.813±0.0028[d]	0.99		0.028±0.0004	0.828±0.0052	0.99
	25	0.016±0.0009[a]	0.884±0.0213[e]	0.99		0.015±0.0001	0.902±0.0080	0.99
	85	0.003±0.0629[a]	1.066±0.0692[f]	0.99		0.025±0.0001	1.145±0.0288	0.99
2%	5	0.181±0.0202[c]	0.609±0.0230[b]	0.99		0.167±0.0005	0.637±0.0040	0.99
	25	0.114±0.0040[b]	0.671±0.0057[c]	0.99		0.108±0.0002	0.686±0.0028	0.99
	85	0.029±0.0003[a]	0.841±0.0005[de]	0.99		0.030±0.0004	0.832±0.0005	0.99
3%	5	0.726±0.0993[e]	0.513±0.0271[a]	0.99		0.568±0.0692	0.566±0.0306	0.99
	25	0.605±0.0344[d]	0.522±0.0098[a]	0.99		0.522±0.0011	0.554±0.0028	0.99
	85	0.186±0.0398[c]	0.624±0.0381[bc]	0.99		0.103±0.0011	0.742±0.0086	0.99

[a-e]: the same alphabets in the same column have no significant difference (p>0.05).

The analysis of information in table 1 shows that flow index and consistency coefficients are significantly different at various temperatures and concentrations (p≤ 0.05). Considering 5-85 °C, consistency coefficients declined from 0.03 to 0.003 pa.s^n for 1% gum, from 0.181 to 0.029 pa.s^n for 2% gum, and from 0.726 to 0.186 pa.s^n for 3% gum. Considering the same temperature range, flow index increased from 0.813 to 1.06 for 1% gum, from 0.609 to 0.841 for 2% gum, and from 0.513 to 0.624 for 3% gum. Despite this behavior, the pseudo-plastic behavior increased by increased Zodo gum concentration due to reduced flow index (n or n'). Increased consistency coefficient, due to increase in gum concentration, is associated with Zodo power rise in connection with water [15]. Hui and Huang also linked viscosity dependence and Taro gum concentration with multiple branch structure of gum [16]. That is why Zodo gum might have such structure due to high viscosity dependence on concentration. Reduced viscosity and increased flow behavior index in Fig. 1 show the tendency of Zodo gum behavior to close-to-Newtonian behavior at high temperatures. This behavior is related to increased kinetic energy of the molecules, reduced interaction of molecules with each other, and thus less resistance to flow [8, 14, 17]. Zodo gum pseudo-plastic behavior is higher of pectin at similar concentrations and temperatures. In contrast, Zodo gum with flow behavior index which is higher than Xanthan, it has lower pseudo-plastic behavior. Compared with Xanthan and Carrageenan gums, Zodo gum has lower consistency coefficient at a similar concentration [8]. Low pseudo-plastic behavior and flow index of Zodo gum are highly regarded to help a good sense such as mouth feel and flavor release and high viscosity in foods [18]. In this regard, 3% Zodo gum showed less-than-0.6 flow index at 5 and 25 °C and various pHs [4, 7, 10). This is an important factor in feeling evaluation of food items. Fig. 2 shows the effect of shear rate and concentration at 25 °C on apparent viscosity.
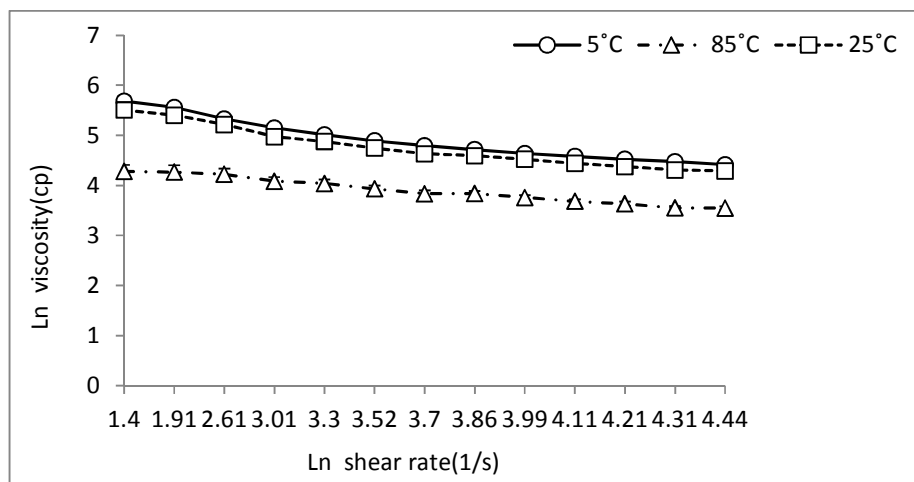

Fig. 1: Apparent viscosity logarithm versus 3% Zodo gum solution shear rate at 5-85 °C

Apparent viscosity (at 54.4s^{-1} and 25 °C) increased by 188% and 766% when the concentration increased from 1% to 2% and 1% to 3%, respectively. The apparent viscosity declined by 12% and 20% when shear rate increased from 54.4s^{-1} to 68 and 85s^{-1}, respectively. As shear rate rises, the behavior of reduced apparent viscosity of Zodo gum solutions is associated with the behaviors observed for many hydrocolloid solutions including cress seed [7],

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Lepidium perfoliatum seed gum [19], and wild sage seed gum due to the location of high molecular weight chains in flow direction. In other words, following the creation of shear rate, hydrogen bonding and non-covalent links (van der Waals bonds and electrostatic forces) are weakened in intertwined polysaccharide molecules and the accumulation in the lost solution and chains in line with the flow [20].
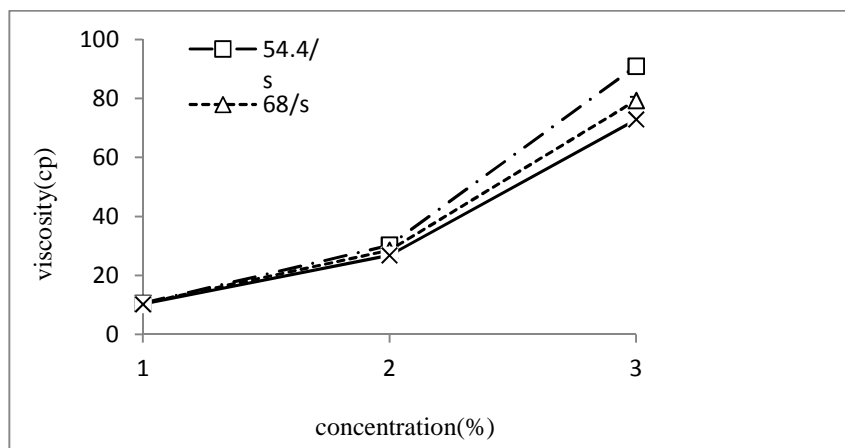

Fig.2: the effect of gum concentration on apparent viscosity at various shear rate (25˚C)

The effect of pH

Table 2 shows the effect of pH on parameters of the flow behavior and viscosity of 3% Zodo gum at 54.4 s^{-1} shear rate and 25 ˚C. Maximum consistency coefficient was observed at 7-pH. When pH increased from 4 to 7, the consistency coefficient and viscosity rose by 29.5% and 20%, respectively. At low pH, spiral state of chains and acidic shape of carboxyl groups of gum may eliminate the charge and form smaller structure of polymer chains. Increased pH leads to the ionization of carboxyl groups. Consequently, the spirals become farther due to charge repulsion, leading to an increased viscosity [17]. In contrast, in alkaline conditions, 32% reduction in consistency coefficient and viscosity at concentration in test might be related to de-alkaline polymer reactions [21].

Table 2: summary of regression analysis for power law equation and apparent viscosity (54.4 s^{-1}) for 3% Zodo gum under different pHs (25 ˚C)

	Upward curve				Downward curve		
pH	Consistency Coefficient(pa.s^n)	flow index	R^2	Viscosity(pas)	Consistency Coefficient(pa.s^n)	flow index	R^2
4	0.467±0.0011[a]	0.542±0.0028[ab]	0.99	0.075±0.0011[a]	0.419±0.0161	0.572±0.0040	0.99
7	0.605±0.0346[b]	0.522±0.0213[a]	0.99	0.090±0.0015[b]	0.522±0.0011	0.554±0.0028	0.99
10	0.410±0.0779[a]	0.577±0.0375[b]	0.99	0.076±0.0027[a]	0.386±0.0565	0.589±0.0346	0.99

[a-b]: *the same alphabets in the same column have no significant difference (p>0.05).*

The effect of salt

Studying the effect of type and concentration of salt on flow behavior is important for Zodo gum solution in order to determine the polyelectrolyte nature of hydrocolloid molecules and to identify the functional properties. The effects of salts were significant on consistency coefficient, flow index, and apparent viscosity (54.4 S^{-1}) (Table 3). Consistency coefficient of 3% Zodo gum was declined by 73% when 100 mM sodium chloride was added. It also declined by 77% when 5mM calcium chloride was added. Flow behavior index increased by 26% when 100mM sodium chloride was added. It also increased by 29% when 5mM calcium chloride was added. Generally, positive ions by reducing the repulsive force in negatively charged molecules leads to dramatic reduction in viscosity [22]. A more significant difference was achieved by salt concentration rise (p≤0.05). In this regard, Mazza and Biliaderis justified the reduced viscosity of flaxseed mucilage after adding Sodium Chloride with the increased two-way link between ions and polymer molecules as well as reduced electrostatic repulsion of charged groups on polymer chains[23]. Achi and Okolo also showed that salt leads to viscosity reduction by structural changes and increased flexibility of Prosopisa fricana gum [24]. As stated earlier, adding calcium chloride displayed more significant effect on flow properties and apparent viscosity. Higher effect of calcium chloride on consistency coefficient, flow behavior index, and apparent viscosity might be related to the creation of polysaccharide molecules with a minimum

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contract structure by Ca^{2+} ion, while Na^+ create medium contractile properties. The proximity of gums to metal ions depends on the ionic radius to charge ratio. It means that small ions with high charge are stronger to link to the chain. Therefore, $Ca^{2+}=2.1$ and $Na^+=1$ratio, the interaction of Zodo gum is higher with Ca^{2+} than Na^+ (21). Reduced viscosity of *hsian-tsao* leaf gum was higher when divalent cations were more such as Zodo gum [25].

Table 3: summary of regression analysis for power law equation and apparent viscosity (54.4 s⁻¹) for 3% Zodo gum under different salts (Calcium Chloride, Sodium Chloride) (25 ˙C)

salt	Upward curve				Downward curve		
	Consistency Coefficient($pa.s^n$)	flow index	R^2	Viscosity(pas)	Consistency Coefficient($pa.s^n$)	flow index	R^2
Without salt	0.605±0.0346[e]	0.522±0.0098[a]	0.99	0.090±0.0015[g]	0.522±0.0011	0.554±0.0028	0.99
Nacl							
100mM	0.161±0.0034[d]	0.660±0.0080[b]	0.99	0.041±0.0002[f]	0.157±0.0011	0.669±0.0057	0.99
200mM	0.063±0.0069[c]	0.760±0.0213[d]	0.99	0.024±0.0005[c]	0.058±0.0022	0.785±0.0069	0.99
300mM	0.053±0.0018[a]	0.788±0.0040[e]	0.99	0.023±0.0003[b]	0.049±0.0007	0.811±0.0011	0.99
500mM	0.043±0.0059[a]	0.814±0.0277[f]	0.99	0.020±0.0004[a]	0.040±0.0014	0.834±0.0046	0.99
Cacl₂							
5mM	0.139±0.0075[c]	0.675±0.0127[b]	0.99	0.038±0.0001[e]	0.132±0.0075	0.693±0.0115	0.99
25mM	0.108±0.0005[b]	0.709±0.0040[c]	0.99	0.034±0.0004[d]	0.100±0.0000	0.726±0.0040	0.99
50mM	0.060±0.0042[a]	0.770±0.0132[de]	0.99	0.024±0.0003[bc]	0.056±0.0015	0.790±0.0017	0.99
100mM	0.053±0.0006[a]	0.787±0.0005[e]	0.99	0.023±0.0000[b]	0.047±0.0027	0.810±0.0098	0.99

a-e: the same alphabets in the same column have no significant difference (p>0.05).

The Effect of Sucrose on Viscosity
Fig. 3 shows the effect of sucrose on apparent viscosity of 3% Zodo gum at 54.4 s⁻¹ shear rate at 25 ˚C. In this Figure, the apparent viscosity increased with increasing concentrations of sucrose. Feng et al. showed that a similar trend was obtained to increase apparent viscosity of *Mesona Blumes* gum at various sucrose concentrations [17]. Increased viscosity in κ-Carrageenan solution containing sucrose have been attributed to expand and increase the number of hydrogen bonds and connection points [26]. Chenlo obtained similar findings to increase the apparent viscosity by adding sucrose and glucose associated with the interaction between polymer and sugar.
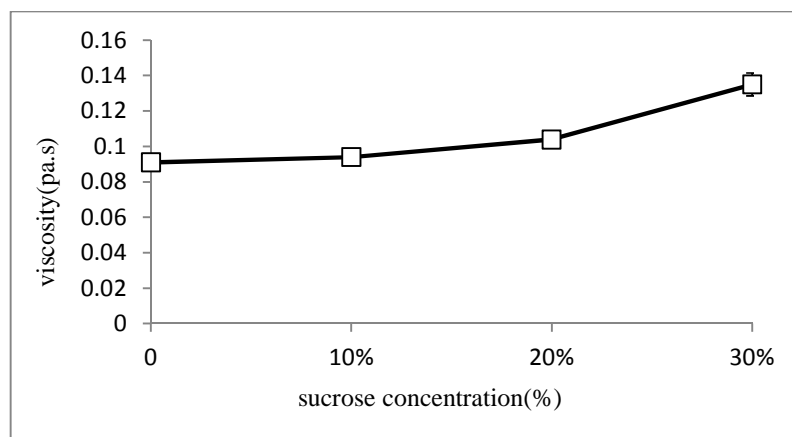
Fig. 3: the effect of sucrose on apparent viscosity (54.4s⁻¹) for 3% Zodo gum at 25 ˙C

CONCLUSION

Zodo gum has a Pseudo-plasticity behavior under different concentrations, temperature and pH conditions, and at presence of sodium and calcium salts, and sucrose (except for the 1% Zodo gum solution at 85 ˚C). Results show that Zodo gum is a negatively charged polyelectrolyte molecule so that its negative charges expand the molecule by creating intermolecular repulsion at zero ionic power or without ion cation. This might explain the high viscosity of deionized distilled water. This gum can be used as a new stabilizer instead of imported ones.

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