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Effect of pH and calcium salt on rheological properties of sodium alginate -methyl cellulose mixtures

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Abstract

In this study, rheological properties of two gums, sodium alginate (Alg) and methylcellulose (MC) in 5 concentration levels were studied. Total concentration of gums in solution was 0.1% (w/v) and different gums ratios (100% (Alg), 75% (Alg) and 25% MC, 50% (Alg) and 50% (MC), 25% (Alg) and 75% (MC), and 100% (MC)) were prepared. Measurements were carried out at 25˚C. Consequently the synergistic effect of these gums in different pH values (3, 5 and 7) in 0.1%(w/v) concentration was investigated. Obtained data indicated that dispersions which contain these polymers showed shear thickening behavior as mention in the text.

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Introduction

Gums are hydrophilic biopolymers with high molecular weight and widely used in food industry to control functional properties of food products. The most important properties of a solution made from a gum are water binding and viscosity in terms of gelling and thickening. In addition to those functions, they are also used in food formulations for emulsion stabilization, prevention of ice recrystallization and sensory attributes. There are many types of gums available in the market which are of plants, seaweeds, microbial or synthetic base. They are also obtained by chemical or enzymatic treatment of starch or cellulose (Dikinson, 2003). Many factors including the concentration of gums, temperature, dissolution, electrical charge, previous thermal and mechanical treatments and presence of electrolytes may affect the rheology of containing gums food in liquid form (Marcotte *et al.*, 2001; Rao & Anatheswarn, 1982; Rao & Kenny, 1975). The use of two or more gums in the formulation of a single food is a common practice in the food industry for creating synergistic effect of the combined use. Product quality could be improved by synergism of gums and economical benefit may be gained from the use of mixed gums as they can impart better rheological properties to the product which may also result in cost reduction during manufacturing (Walkenström *et al.*, 2003).

Sodium alginate and sodium salts of alginic acid extracted from the cellular walls of brown algae (3). Sodium alginate form gel ionotropically at constant temperature upon addition of divalent cations, such as Ca^{2+}, Sr^{2+}, and Cu^{2+} (6-9), (3), (23,25).(Wang *et al.*, 1994; Liu *et al.*, 2003; Liu *et al.*, 2003 ; de Kerochov, 2007; Wells & Sheardown, 2007; Skjåk-Bræk *et al.*, 1989).

Matsumoto and Mashiko investigated the influence of added salts on the viscoelastic properties of aqueous alginate and metal cations which did not work as the cross-linking points (10).

Recently there has been increased interest in self-associated polymer systems based on natural polymers, which are environmentally safe and biodegradable. It is known that a number of cellulose derivatives, in particular, methyl cellulose (MC), hydroxypropyl cellulose (HPC), hydroxypropyl methyl cellulose (HPMC), and methyl ethyl cellulose (MEC), form physical thermally reversible gels in aqueous solutions. These cellulose derivatives are widely used as gelling agents, thickeners, stabilizers, and emulsifiers in food industry, cosmetic products, and perfumery (1). The most widely used compound is MC. Gums are hydrophilic biopolymers with high molecular weight and widely used in food industry to control functional properties of food products and detection Effect of pH and calcium salt on rheological properties of sodium alginate -methyl cellulose mixtures are very important.

The aim of this research was to study the influence of different pH values, different amounts of salts and different ratios of these polymers on their rheological behavior.

Materials and method

Materials

Samples of Alginic acid-sodium salt (medium viscosity, lot x092N76322) and methyl cellulose (lot T64590283F72) were purchased from Sigma (Sigma-Aldrich, St. Louis, MO, USA).

Methods

The stock solutions (0.1% m/w) were prepared by mixing 0.1 g of dry sample with deionized distilled water while continuously stirring at ambient temperature. The gum solutions were continuously stirred with a magnetic stirrer for 2 h at ambient temperature. The solutions were refrigerated over night (16 h) to completely hydrate the gums. To study rheological properties of gums amalgamation, the following treatments were considered: sodium alginate 100%, sodium alginate 75%-MC 25%, alginate sodium 50%-MC 50%, alginate sodium 25%-MC 75%, MC 100%. Stock solutions were stirred at room temperature. Prepared sodium alginate and MC solutions were mixed at 25°C, and were measured at neutral and acidic (5 and 3) pH values. To adjust pH, pH meter (Metrohm, France) and 0.1 N HCl solution were applied for adjusting pH values. To study the effect of salt on the polysaccharide solutions, the appropriate amounts of calcium chloride were added to the prepared solutions and were completely dissolved to obtain final concentrations of 10 and 5 mM $CaCl_2$. For rheological properties determination Brookfield rheometer (Brookfield engineering, INC, Middle Boro, MA02346 USA.(LV DV III)) equipped by ULA (ULA_EY UL Adaptor) and rheocalc (Rheocalc V3.2 Build 47_1) software were used. All rheological measurements were carried out at 25˚C by using a temperature-controlled circulating water bath (Brookfield engineering, TC 502). All the solutions were allowed to stand for 2 h at room temperature before rheological data were obtained.

Results and discussion

Several models have been used to characterize the flow behavior of gum solutions and among them Power law model has been frequently used for the determination of rheological properties of the food in liquid form (Eq. (1)). In addition, Casson equation (Eq. (2)) and Herschel–Bulkley model (Eq. (3)) have been also used for the characterization of some gum solutions (7,11, and 12).

$$\sigma = K(\dot{\gamma})^{n} \quad (1)$$

$$\sigma^{0/5} = K_1(\dot{\gamma})^{0/5} + \sigma_0^{0/5} \quad (2)$$

$$\sigma = K(\dot{\gamma})^{n} + \sigma_0 \quad (3)$$

Where σ (d/cm2) is shear stress, K (cP) is the consistency coefficient, $\dot{\gamma}$ (s^{-1}) is the shear rate and n (dimensionless) is the flow behavior index, σ_0 is the yield stress and K_1 is plastic viscosity. Several authors have employed the power law model (Eq. (1)) to describe the viscosity of gum solutions (3, 4 and 8). Other authors have used the Casson model (Eq. (2)) for rheological description of some gum solutions and in other studies Herschel–Bulkley model has been used (3 and 8).

Table 1. Rheological parameters of the casson (C), Power-law (PL) and Herschel-Balkly (HB) models for description of rheological behavior of sodium alginate 100%.

Sample		Treatment	Rheological model	σ.(d/cm²)	K(cP)	K_1	N	Co.F	R²
Sodium alginate 100%	pH=3	No Salt	Caccon	0.07±0.07		6.26±0.49		87.50	0.875
			Power Law		1.12±0.17		1.33±0.04	98.60	0.986
			Herschel-Bulkley	1.21±0.37	0.01±0.00		1.93±0.41	99.70	0.997
		5 mmol Ca	Caccon	0.04±0.02		7.68±0.32		97.70	0.977
			Power Law		7.67±1.74		0.91±0.03	1.00	1.00
			Herschel-Bulkley	0.00±0.19	2.88±2.00		0.90±0.05	1.00	1.00
		10 mmol Ca	Caccon	0.01±0.20		7.75±0.11		98.10	0.981
			Power Law		6.54±0.90		0.91±0.00	1.00	1.00
			Herschel-Bulkley	0.18±0.10	4.00±0.85		0.95±0.06	1.00	1.00
	pH=5	No Salt	Caccon	0.00±0.02		6.70±0.92		94.30	0.943
			Power Law		5.65±0.41		1.00±0.00	99.80	0.998
			Herschel-Bulkley	0.21±0.12	0.09±0.05		1.05±0.07	99.80	0.998
		5 mmol Ca	Caccon	0.01±0.01		7.91±0.24		98.10	0.981
			Power Law		6.83±0.84		0.92±0.02	1.00	1.00
			Herschel-Bulkley	0.08±0.10	3.94±0.65		0.94±0.07	1.00	1.00
		10 mmol Ca	Caccon	0.02±0.01		9.27±0.62		98.80	0.988
			Power Law		6.63±0.20		0.93±0.01	1.00	1.00
			Herschel-Bulkley	0.14±0.06	2.65±0.32		0.96±0.02	1.00	1.00
	pH=7	No Salt	Caccon	0.01±0.04		5.37±0.06		93.80	0.938
			Power Law		4.14±0.42		0.96±0.01	99.80	0.998
			Herschel-Bulkley	0.00±0.00	1.37±0.24		0.95±0.35	99.80	0.998
		5 mmol Ca	Caccon	0.08±0.03		7.89±0.27		98.10	0.981
			Power Law		10.00±2.00		0.91±0.02	1.00	1.00
			Herschel-Bulkley	0.06±0.04	0.95±1.90		0.92±0.08	1.00	1.00
		10 mmol Ca	Caccon	0.02±0.01		7.59±0.32		98.30	0.983
			Power Law		6.14±0.53		0.92±0.01	1.00	1.00
			Herschel-Bulkley	0.26±0.13	2.94±0.42		0.98±0.08	1.00	1.00

It is shown that these three models are the best models for description of rheological properties of gum solutions. In this study these three models was investigated to select the best model to predict accurately the behavior of sodium alginate-MC solutions. Rheological parameters under steady shear were measured. All of curves were adjusted to the three models and rheological parameters of the Casson (C), Power-law (PL) and Herschel–Bulkley (HB) models were investigated for description of rheological behavior of sodium alginate -methyl cellulose mixtures in all ratios at pH 7, 5 and 3 before and after adding calcium salt (10,5 mM). The results were summarized in Table 1-5. All of samples showed high conformity with the three models, and in all treatments the regression coefficient, r^2; was not lower than 0.94, But curves were adjusted to the Herschel Bulkley model (Eq. (2)) by the best-fit regression.

table 2. Rheological parameters of the casson (C), Power-law (PL) and Herschel-Balkly (HB) models for description of rheological behavior of methylcellulose 100%.

Sample	Treatment		Rheological model	σ.(d/cm^2)	K(cP)	K_1	N	Co.F	R^2
methylcellulose 100%	pH=3	No Salt	Caccon	0.05±0.12		7.80±0.73		93.30	0.933
			Power Law		0.47±0.54		1.49±0.05	99.40	0.994
			Herschel-Bulkley	0.32±0.18	0.00±0.00		1.61±0.28	99.60	0.996
		5 mmol Ca	Caccon	0.23±0.00		7.15±0.32		91.50	0.915
			Power Law		0.50±0.04		1.42±0.01	99.30	0.993
			Herschel-Bulkley	0.94±0.24	0.01±0.00		1.88±0.14	99.90	0.999
		10 mmol Ca	Caccon	0.44±0.12		7.46±0.78		92.70	0.927
			Power Law		0.19±0.11		1.52±0.03	99.80	0.998
			Herschel-Bulkley	0.00±0.00	0.01±0.00		1.46±0.06	99.90	0.999
	pH=5	No Salt	Caccon	0.02±0.02		6.33±0.48		94.70	0.947
			Power Law		3.57±0.38		1.00±0.07	99.90	0.999
			Herschel-Bulkley	0.25±0.50	0.53±0.22		1.06±0.37	99.90	0.999
		5 mmol Ca	Caccon	0.01±0.00		4.84±0.40		86.40	0.864
			Power Law		2.15±0.15		1.12±0.01	98.00	0.980
			Herschel-Bulkley	1.69±0.78	0.02±0.01		2.08±0.50	99.50	0.995
		10 mmol Ca	Caccon	0.54±0.24		7.43±0.64		93.90	0.939
			Power Law		0.20±0.01		1.52±0.02	99.90	0.999
			Herschel-Bulkley	0.00±0.00	0.02±0.01		1.35±0.07	99.80	0.998
	pH=7	No Salt	Caccon	0.03±0.01		5.13±0.47		87.00	0.870
			Power Law		1.34±0.18		1.28±0.04	98.30	0.983
			Herschel-Bulkley	1.42±	0.01±0.00		1.99±	99.80	0.998
		5 mmol Ca	Caccon	0.22±0.02		6.59±0.68		88.90	0.889
			Power Law		0.25±0.05		1.42±0.03	99.00	0.990
			Herschel-Bulkley	1.26±0.67	0.02±0.00		2.13±0.58	99.90	0.999
		10 mmol Ca	Caccon	0.10±0.05		6.90±0.54		90.60	0.906
			Power Law		0.88±0.88		1.39±0.09	99.00	0.990
			Herschel-Bulkley	1.32±0.76	0.01±0.00		2.20±0.66	99.90	0.999

Analysis of Results for sodium alginate control group

As it can be seen in figure 1, adding calcium salts to 0.1 percent sodium alginate gum solution could increase the solution viscosity which appears to be consistent with the other studies. Also it has been found that adding 5 mM calcium salt results in higher viscosification compare to 10 mM calcium salt, which may be justified by this approach that adding the salt to solutions to a specific degree cause viscosity increase for solution which is result of polymer-cation-polymer bonds in addition to polymer-polymer interactions. Therefore, when concentration of salt reaches a specific degree, this excess of salt results in inhibition of binding between polysaccharides in gum solution and number of bonds will decrease because of the inhibition attribute of salt, therefore, the apparent viscosity will decrease. No-salt sodium alginate solutions for 5 and 7 pH levels shows a behavior between Newtonian behavior and pseudoplastic behavior, while in pH value of 3 they show Newtonian behavior to dilatant behavior. The effect may be the result of polysaccharides ionization rate increase for gum solution in pH>3 to neutral pH. Therefore, polysaccharides hydrophobic interactions among polysaccharides chains decrease (because of ionized groups in gum solution). Hence, in pH=3 ionization rate is very low and insignificant. Hydrophobic interactions between polysaccharides chains are higher, therefore, polysaccharides composite have been maintained well and solutions are more viscose. In a study done by Yang *et al*, the general trend showed specific viscosity increased for lower pH values such as 3 and 4. Also in pH<3, phase separation took place by microscopic technique (Yang ,chen & Fang, 2009).

table 3. Rheological parameters of the casson (C), Power-law (PL) and Herschel-Balkly (HB) models for description of rheological behavior of sodium alginate 75%, methylcellulose 25%.

Sample	Treatment		Rheological model	σ.(d/cm²)	K(cP)	K₁	N	Co.F	R²
Sodium alginate 75% & MC25%	pH=3	No Salt	Caccon	0.05±0.12		7.80±0.73		93.30	0.933
			Power Law		0.47±0.54		1.49±0.05	99.40	0.994
			Herschel-Bulkley	0.32±0.18	0.00±0.00		1.61±0.28	99.60	0.996
		5 mmol Ca	Caccon	0.23±0.00		7.15±0.32		91.50	0.915
			Power Law		0.50±0.04		1.42±0.01	99.30	0.993
			Herschel-Bulkley	0.94±0.24	0.01±0.00		1.88±0.14	99.90	0.999
		10 mmol Ca	Caccon	0.44±0.12		7.46±0.78		92.70	0.927
			Power Law		0.19±0.11		1.52±0.03	99.80	0.998
			Herschel-Bulkley	0.00±0.00	0.01±0.00		1.46±0.06	99.90	0.999
	pH=5	No Salt	Caccon	0.02±0.02		6.33±0.48		94.70	0.947
			Power Law		3.57±0.38		1.00±0.07	99.90	0.999
			Herschel-Bulkley	0.25±0.50	0.53±0.22		1.06±0.37	99.90	0.999
		5 mmol Ca	Caccon	0.01±0.00		4.84±0.40		86.40	0.864
			Power Law		2.15±0.15		1.12±0.01	98.00	0.980
			Herschel-Bulkley	1.69±0.78	0.02±0.01		2.08±0.50	99.50	0.995
		10 mmol Ca	Caccon	0.54±0.24		7.43±0.64		93.90	0.939
			Power Law		0.20±0.01		1.52±0.02	99.90	0.999
			Herschel-Bulkley	0.00±0.00	0.02±0.01		1.35±0.07	99.80	0.998
	pH=7	No Salt	Caccon	0.03±0.01		5.13±0.47		87.00	0.870
			Power Law		1.34±0.18		1.28±0.04	98.30	0.983
			Herschel-Bulkley	1.42±	0.01±0.00		1.99±	99.80	0.998
		5 mmol Ca	Caccon	0.22±0.02		6.59±0.68		88.90	0.889
			Power Law		0.25±0.05		1.42±0.03	99.00	0.990
			Herschel-Bulkley	1.26±0.67	0.02±0.00		2.13±0.58	99.90	0.999
		10 mmol Ca	Caccon	0.10±0.05		6.90±0.54		90.60	0.906
			Power Law		0.88±0.88		1.39±0.09	99.00	0.990
			Herschel-Bulkley	1.32±0.76	0.01±0.00		2.20±0.66	99.90	0.999

The initial pH value for neutral alginate solution with 0.1 Wt % concentration is 6.6. It means, acid carboxylic groups have been broken in some degree. Two kinds of interactions play important role in alginate aqueous solution; first, charge repulsion between broken carboxylic groups and formation of Hydrogen bonds between acid carboxylic and ionized carboxylic groups (Bu,2005,Kjoniksen & Nystrom). Lowering pH reduces broken carboxylic groups in alginate chains, which in turn diminish the hydrophilic property of alginate to some extent. When some of the broken carboxylic groups in alginate chains gradually protonate, hydrophobic sections appear in alginate chains.(Yang ,chen& Fang ,2009).

In general, contained sodium alginate gum solutions show shear pseudoplastic behavior with decrease in shear rate, which is consistent with previous studies. Adding 10 mM of Ca^{2+} compare to 5 mM shows higher viscosity decrease. In other word, it causes more thinning in solutions.

According to table 1, the study of flow index for sodium alginate solutions shows that for pH of 3 and 5, adding salt results in decreasing flow index. The reason of this fact can be lower ionization rate for lower pH values and consequently, lower available ionized groups in solution. Therefore adding salts do not provide any significant effect on thickening of solutions.

Analysis of results for MC gum samples

In general, hydrophilic polymers such as MC and HPC contain a few hydrophobic units which can form temporary hydrophobically associating network in aqueous systems in low concentration of polymer. (Glass, 1989). Main microstructure specification of these kinds of polymer systems is their ability to create hydrophobic interactions intermolecular strong to weak in aqueous solutions. Actually, hydrophobic groups which distributed along polymers chains, attach to each other to avoid exposure to water. (Tanford, 1973).

table 4. Rheological parameters of the casson (C), Power-law (PL) and Herschel-Balkly (HB) models for description of rheological behavior of sodium alginate 50%, methylcellulose 50%.

Sample	Treatment		Rheological model	σ.(d/cm²)	K(cP)	K₁	N	Co.F	R²
Sodium alginate 50% & MC 50%	pH=3	No Salt	Caccon	0.29±0.14		7.32±0.76		92.30	0.923
			Power Law		0.46±0.27		1.50±0.02	99.60	0.996
			Herschel-Bulkley	0.67±0.37	0.00±0.00		1.79±0.37	99.80	0.998
		5 mmol Ca	Caccon	0.62±0.05		7.35±0.12		92.30	0.923
			Power Law		0.06±0.04		1.59±0.02	99.80	0.998
			Herschel-Bulkley	0.00±0.03	0.02±0.01		1.53±0.09	99.80	0.998
		10 mmol Ca	Caccon	0.98±0.38		7.84±0.86		90.70	0.907
			Power Law		0.09±0.17		1.75±0.16	99.80	0.998
			Herschel-Bulkley	0.45±0.38	0.02±0.01		1.67±0.23	99.70	0.997
	pH=5	No Salt	Caccon	0.02±0.00		5.97±0.47		89.20	0.892
			Power Law		1.85±0.06		1.14±0.18	98.60	0.986
			Herschel-Bulkley	1.34±0.78	0.04±0.00		1.76±0.43	99.40	0.994
		5 mmol Ca	Caccon	0.49±0.24		6.82±0.13		91.60	0.916
			Power Law		0.05±0.40		1.56±0.04	99.80	0.998
			Herschel-Bulkley	0.00±0.09	0.00±0.01		1.41±0.11	99.80	0.998
		10 mmol Ca	Caccon	0.09±0.00		6.89±0.21		91.00	0.910
			Power Law		0.98±0.02		1.28±0.02	98.70	0.987
			Herschel-Bulkley	1.08±0.19	0.03±0.02		2.00±0.13	99.70	0.997
	pH=7	No Salt	Caccon	0.00±0.06		6.07±0.06		87.70	0.877
			Power Law		0.93±0.94		1.42±0.06	98.90	0.989
			Herschel-Bulkley	0.93±0.57	0.00±0.00		1.86±0.45	99.70	0.997
		5 mmol Ca	Caccon	0.21±0.01		6.59±0.18		87.60	0.876
			Power Law		0.37±0.03		1.42±0.03	98.80	0.988
			Herschel-Bulkley	1.20±0.50	0.02±0.01		2.00±0.49	99.70	0.997
		10 mmol Ca	Caccon	0.04±0.02		5.45±0.34		89.20	0.892
			Power Law		1.22±0.22		1.19±0.37	98.60	0.986
			Herschel-Bulkley	1.42±0.91	0.05±0.00		1.98±0.57	99.60	0.996

In commercial concentration rate, these intermolecular interactions become more significant and effective. They shape a temporary associating network which use for fortification and strengthening trapped network. The issue was studied theoretically by Leibler (Leibler, Rubinstein & Colby, 1991).

Flow index analysis for solutions show that flow index for all tested samples were 1.00 or higher which is evidence to Newtonian behavior or dilatant behavior (Table 2). Flow index dose not follow a specific role or pattern for 100% methyl cellulose solutions. Flow index in pH=3 shows that adding calcium salts with 10mM concentration results in flow index increase in contrast to control group (no salt added). Reason may be that in lower pH levels such as pH=3, ionic interaction between ionic groups is low because of lower ionization rate between gum polysaccharide chains. Therefore, adding salts to solutions results in charge impediment because of salt positive charges and repulsion between them. Hence, the cations obtain a maximum distance from each other in order to repel each other. Therefore, they locate among polysaccharide chains to use them as barrier. Therefore, adding salt, almost create a dense and arranged structure for gum contained solutions which in turn result in higher viscosity in contrast to no added salt solution. As it has been mentioned higher salt concentration is more helpful on creating this effect because it results in increase repulsive changes (Fig. 2).

For pH=5, adding salts, result in flow index decreases. The reason can be explained as: increase in pH and shear rate, result in increase of gum structure ionization rate in addition to possibility for polysaccharide structure change and breaking down of polysaccharide chain. Therefore salt causes hydrophobic interaction and binding among chains with ionized anion groups, which decrease hydrodynamic volume of gum chains, and also cause that polymer chains become dense to repel other charges and solutions contain salts show more shear-thinning compare to control group (no salt added). For pH=7, the issue is also true and only exception is for adding 5 mM of calcium salt, which increase flow index compare to control group. Therefore shear-thinning effect for pH=7 in this sample was lower. It can be explained that; for MC gum in pH=7, gum molecules that have maximum distance because to high anion groups ionization and their repelling force among them is high and as concentration decreases, their weak molecular configurations disturb, and reaction sites position in gum adjacent gum chains which results in viscosity increase. Calcium salts assist the action, and 5 mM concentration of calcium salt is more effective versus 10mM of the salt.

table 5. Rheological parameters of the casson (C), Power-law (PL) and Herschel-Balkly (HB) models for description of rheological behavior of sodium alginate 25%,methyl cellulose 75%.

Sample	Treatment		Rheological model	σ.(d/cm²)	K(cP)	K_1	N	Co.F	R²
Sodium alginate 25% & MC 75%	pH=3	No Salt	Caccon	0.14±0.07		7.48±0.86		90.30	0.903
			Power Law		0.71±0.50		1.44±0.02	99.10	0.991
			Herschel-Bulkley	0.88±0.10	0.00±0.00		1.84±0.06	99.90	0.999
		5 mmol Ca	Caccon	0.23±0.02		7.13±0.58		89.50	0.895
			Power Law		0.59±0.07		1.43±0.04	99.30	0.993
			Herschel-Bulkley	0.73±0.38	0.01±0.00		1.74±0.25	99.70	0.997
		10 mmol Ca	Caccon	0.06±0.03		5.20±0.32		87.30	0.873
			Power Law		0.43±0.50		1.27±0.05	98.30	0.983
			Herschel-Bulkley	0.95±0.47	0.05±0.01		1.54±0.23	99.20	0.992
	pH=5	No Salt	Caccon	0.02±0.01		5.34±0.12		88.50	0.885
			Power Law		1.81±0.77		1.15±0.03	98.40	0.984
			Herschel-Bulkley	1.41±0.42	0.02±0.01		1.85±0.19	99.50	0.995
		5 mmol Ca	Caccon	0.15±0.01		6.23±0.48		89.60	0.896
			Power Law		0.72±0.06		1.38±0.03	99.00	0.990
			Herschel-Bulkley	1.17±0.07	0.01±0.00		1.97±0.06	99.70	0.997
		10 mmol Ca	Caccon	0.10±0.08		6.23±0.18		89.70	0.897
			Power Law		0.29±0.27		1.41±0.07	98.90	0.989
			Herschel-Bulkley	0.97±0.70	0.01±0.01		1.89±0.57	99.60	0.996
	pH=7	No Salt	Caccon	0.03±0.00		5.54±0.36		88.40	0.884
			Power Law		1.61±0.11		1.22±0.03	98.40	0.984
			Herschel-Bulkley	1.28±0.65	0.02±0.00		1.80±0.39	99.40	0.994
		5 mmol Ca	Caccon	0.06±0.14		6.64±0.29		89.60	0.896
			Power Law		0.19±0.58		1.46±0.03	99.30	0.993
			Herschel-Bulkley	0.95±0.62	0.00±0.00		1.91±0.56	99.70	0.997
		10 mmol Ca	Caccon	0.00±0.07		5.78±0.39		88.20	0.882
			Power Law		2.95±1.38		1.24±0.00	98.60	0.986
			Herschel-Bulkley	2.94±1.48	0.00±0.02		1.30±0.37	99.50	0.995

Analysis of results for samples of sodium alginate-MC mixture

comparing flow index (n) for 100% MC solution and 100% sodium alginate solution exclusively, and a mixture of both show that flow index is higher for aqueous mixture compare to solution of single gum (Table 3,4,5). Therefore, it can be concluded clearly that with mixing two gums, thickening behavior increases for mixture compare to solution with a single gum and as MC ratio increase, with increase on shear rate, shear thickening bahavior increases (Figs. 3, 4, 5). But, changes in flow rate with change in pH varied for various mixing ratios. However, the general pattern was: for pH increase from 3 to 7, adding salt results in flow behavior and flow rate increases for solution, which may be explained by solvency of gums with pH increase and higher hydrophobic interactions for solution, in addition to higher resistance among cation-sodium alginate bond for decrease in concentration.

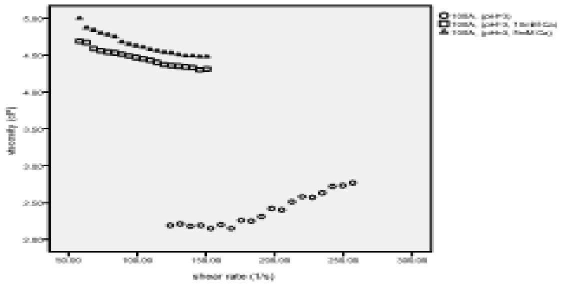

Fig. 1. A(pH=3), B(pH=5), C(pH=7).

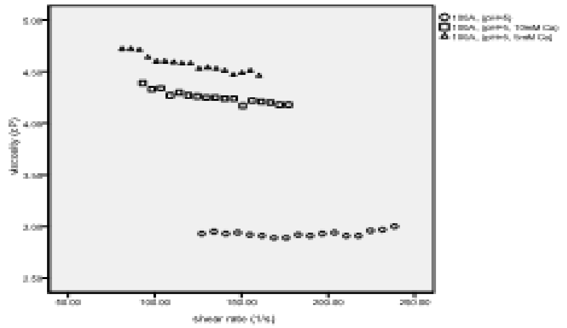

Fig. 2. A(pH=3), B(pH=5), C(pH=7)

It is predicted that for higher pH values to neutral pH, cation-polymer interaction in aqueous mixtures is mostly related to sodium alginate in mixture. Specifically, as ratio of sodium alginate is higher, effect of salts on sodium alginate polymer is more than methyl cellulose, because as it has been mentioned in previous studies, sodium alginate in present of metal cations form gel, therefore it has an effect on viscosity increase of aqueous mixtures and flow index increase.

Changes in pH and shear rate, when MC ratio is higher in mixture, results in MC primarily structure change. Therefore hydrophobic role and cation-polymer interaction for aqueous mixtures is more prominent and flow rate increases.

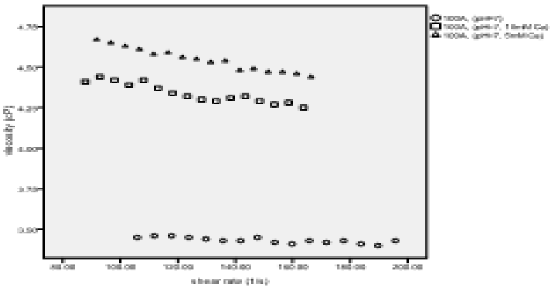

Fig. 3. A(pH=3), B(pH=5), C(pH=7).

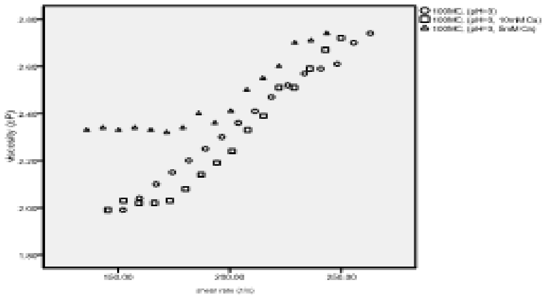

Fig. 4. A(pH=3), B(pH=5), C(pH=7).

In lower pH values (pH=3), with regard to lack of anion groups ionization, cations are not able to form bonds with them and adding salts causes weakening in hydrophobic bonds. On the other hand, as sodium alginate ratio in solution is higher, cations bind more with sodium alginate gum. Therefore, because of decrease hydrodynamic volume, sodium alginate apparent viscosity decreases which is consistent with previous studies.

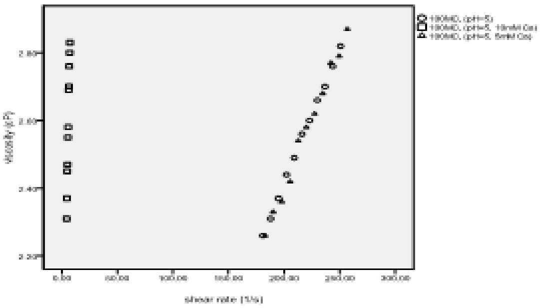

Fig. 5. A(pH=3), B(pH=5), C(pH=7)

Conclusion

Analysis of results for samples shows that cations with regard to related gum structure cause change in gum and mixture rheological prosperities. As a result viscosity of tested a single gum solutions increases with increasing cations and flow index and thickening increase with cations increase. However for MC solutions it can be mentioned that in pH>3, adding salt results in decrease on flow index (n) in contrast to control group (no salt added). For sodium alginate solutions, effective concentration of salt for increasing apparent viscosity was 5mM. For methyl cellulose solutions in pH=3, adding calcium salts with 10mM concentration had higher effect on appearance viscosity increase. For pH=5 adding salt cause decrease in flow rate and in pH=7 adding only 5mM of calcium salt caused increase in flow index.

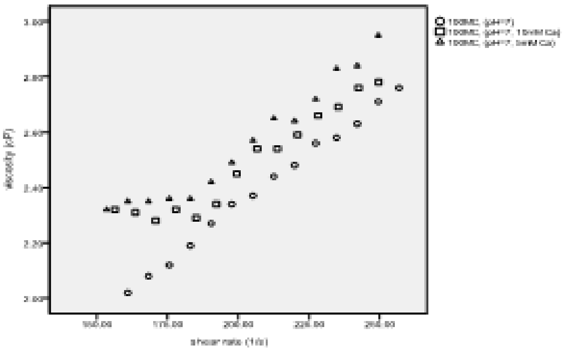

Fig. 6. A(pH=3), B(pH=5), C(pH=7).

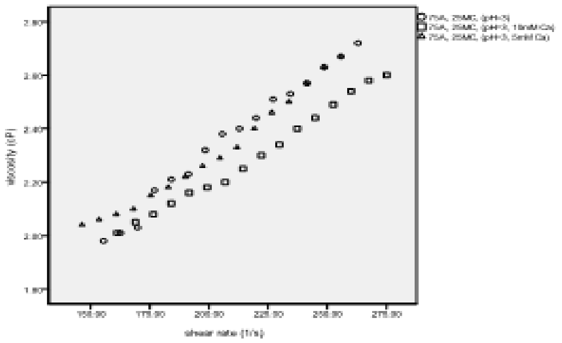

Fig. 7. A(pH=3), B(pH=5), C(pH=7)

It has been found that, sodium alginate- methyl cellulose gums mixing can create more viscose solution compare to sodium alginate solution alone or methyl cellulose by itself. However, as MC ratio in mixture increases, viscosity increases. Therefore, in overall we can tell that gums mixing are very profitable way for obtaining desirable high viscosity compare to sodium alginate solution alone. In other words, adding gums to sodium alginate gum can provide synergistic effect. Therefore gum structure in food formulation with various pH values and different type of minerals plays a fundamental role in rheology properties of final product.

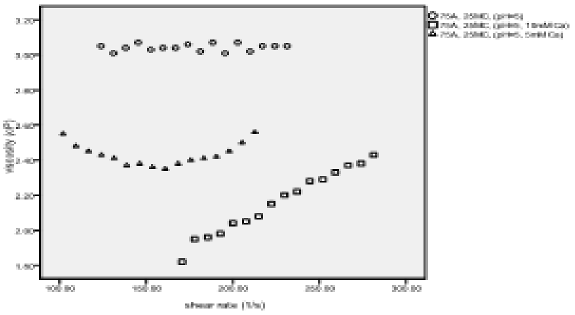

Fig. 8. A(pH=3), B(pH=5), C(pH=7).

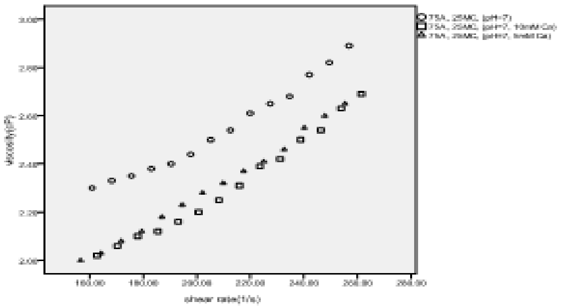

Fig. 9. A(pH=3), B(pH=5), C(pH=7).

With regard to results obtains, through cation, the higher viscosity will be achieved with use of sodium alginate-MC gums mixture in foods with neutral pH values and lower pH values (5 to 7) such as milk, flavored milk, some dairy products and calcium rich foods. Also, it causes change in rheological behavior and creating new rheological effects. In dairy products, which use of sodium alginate gum is common, applying a mixture of methyl cellulose causes change in viscosity from lightness to thickness and with more increase to pH=7 causes stability in viscosity. Hence, sodium alginate-MC gums solution behavior for all pH values and for all concentration ratios show thickening effect, it can be concluded that use of these gums for all products with various pH values is applicable. Therefore, sodium alginate-MC gum mixtures use in wide range in food industry and results in satiability and thickening and viscosification behavior of foods (specifically liquid form foods).

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