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

Fatemeh mehmandoost

M. Sc. Student of food science and technology,

Islamic Azad University, Shahre Kord Branch

Isfahan, Iran

Fateme.mehmandoost@yahoo.com

Mohammad Hojjatoleslamy[2], Javad keramat[3]

[2] Assist. Prof. Food Sci. and Tech. Department,

Islamic Azad University, Shahre Kord Branch

Shahre Kord, Iran

mohojjat@iaushk.ac.ir

[3] Assist. Prof. Food Sci. and Tech. Department, Isfahan Univ. of Technology, Isfahan, Iran.

***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.**

Key words- rheological property; sodium alginate; methylcellulose; shear thickenin; polymers

I. 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 [1]. 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 [2,3,4]. 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 [5].

Sodium alginate and sodium salts of alginic acid extracted from the cellular walls of brown algae. Sodium alginate form gel ionotropically at constant temperature upon addition of divalent cations, such as Ca^{2+}, Sr^{2+}, and Cu^{2+} [6-11]. 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 [12].

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 [13]. The most widely used compound is MC.

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.

II. Materials And Method

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). 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. 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.

III. 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[2,3,4].

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

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

$$\sigma = K(\dot{\gamma})^{n} + \sigma_{\circ}$$
(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, $\sigma_{\circ}$ 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).

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. The results summarized in table I. All of samples showed high conformity with the three models, and in all treatments the regression coefficient, r2, was not lower than 0.87, but curves were adjusted to the Herschel-Balkly model (Eq. (2)) by the best-fit regression.

a. Analysis of Results for sodium alginate control group

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 (Fig. 1). 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 [14].

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 [15]. 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[14].

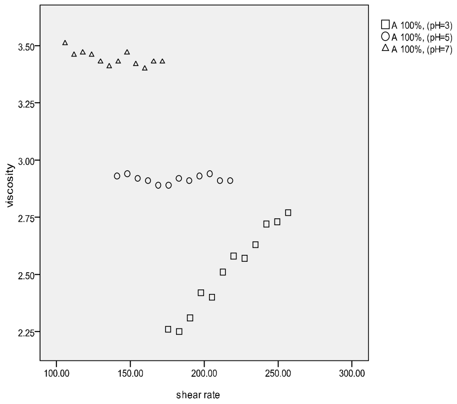

Fig 1. Viscosity as a function of shear rate of Alg solutions at pH 3,5 and 7.

In general, contained sodium alginate gum solutions show shear pseudoplastic behavior with decrease in shear rate, which is consistent with previous studies.

b. 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 [16]. 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 [17]. 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 [18]. Flow index analysis for solutions shows that flow index for all tested samples were 1.00 or higher which is evidence to Newtonian behavior or dilatant behavior (Table I). Fig. 1 shows that behavior of these solutions.is shear thickening specially solutions at pH 5 and 7.

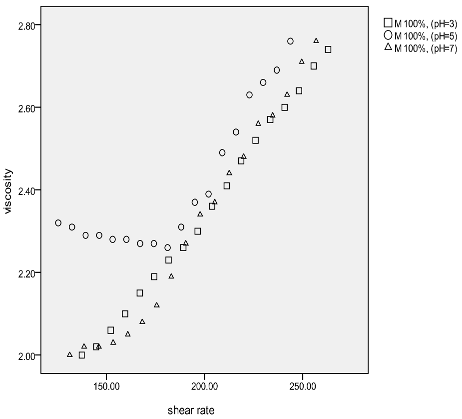

Fig 2. Viscosity as a function of shear rate of MC solutions at pH 3,5 and 7.

c. *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 I). 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.

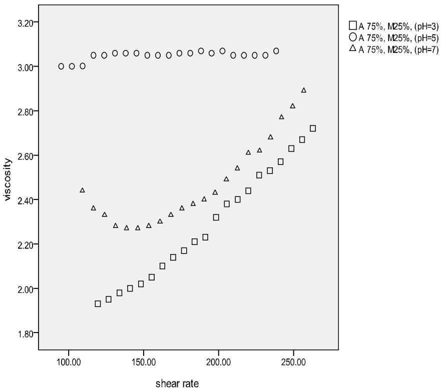

Fig 3. Viscosity as a function of shear rate of (75%)Alg-(25%)MC mixture solutions at pH 3,5 and 7.

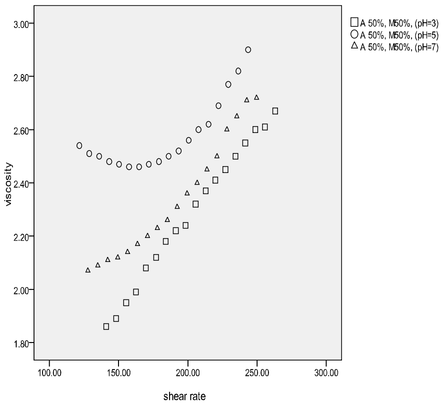

Fig 4. Viscosity as a function of shear rate of (50%)Alg-(50%)MC mixture solutions at pH 3,5 and 7.

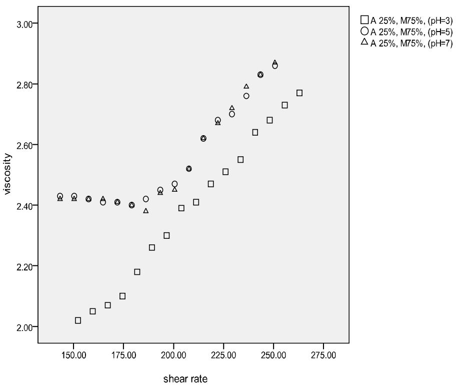

Fig 5. Viscosity as a function of shear rate of (25%)Alg-(75%)MC mixture solutions at pH 3,5 and 7.

IV. Conclusion

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 plays a fundamental role in rheology properties of final product. With regard to results obtains, 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 and some dairy products. 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 satability and thickening and viscosity behavior of foods (specifically liquid form foods).

references

[1] E. Dickinson, "Hydrocolloids at interfaces and the influence on the properties of dispersed systems," Food Hydrocolloids, vol. 17. 2003, pp. 25-39.

[2] M. Marcotte, A.T. Taherian, M. Trigui and H. S. Ramaswamy, "Evaluation of rheological properties of selected salt enriched food hydrocolloids," Food Engineering, vol. 48, 2001, pp.157-167.

[3] M. A. Rao and R. C. Anantheswaran ," Rheology of fluid in food processing," Food Technology ,vol. 36, 1982, pp 116-126.

[4] M. A. Rao and J. F. Kenny," Flow properties of selected food gums," Canadian Institue of Food science and Technology, vol. 8, 1975, pp. 142-148.

[5] P. Walkenström, S. Kidman, A. Hermansson, P. B. Resmusen, and L. Hoegh. "Microstructure and rheological behavior of xanthan/pectin mixed gels," Food Hydrocolloids, vol. 17, 2003, pp. 593-603.

[6] Z. Y. Wang," Sol-Gel transition of alginate solution by the addition of various divalent-cations- a rheological study," Biopolymers, vol. 34 (6), 1994, pp.737-46.

[7] L. Liu," Sol-gel transition in aqueous alginate solutions induced by cupric cations observed with viscoelasticity," Polym J, vol.35(10), 2003, pp.804-809.

[8] X. X. Liu 2003 "Rheology characterization of Sol-gel transition in aqueos alginate solution s induced by cupric cations observed with viscoelasticity," Polym J, vol.35 (10), 2003, pp. 804-9.

[9] A. J. De Kerchove, M. Elimelech, "Formation of polysaccharide gel layers in the presence of Ca^{2+} and K^{+} ions: measurements and mechanisms," Biomacromolecules, vol. 8(1), 2007, pp. 113-21.

[10] L. A. Wells, and H. Sheardoewn," Extended release of high pI proteins from alginate microspheres via a novel encapsulation technique," Eur J Pharm Biopharm, vol. 65: 2007, pp. 329-35.

[11] G. Skjåk-Bræk, H. Grasdalen, O. SmidsrØd, Carbohydr Polym. vol. 10, 1989, pp. 31.

[12] T. Matsumoto and K. Mashiko, Biopolymers vol 29, 1990, pp. 411.

[13] A. M. Bochek, N. M. Zabivalova, V. K. Lavrent'ev, M. F. Lebedeva, T. E. Sukhanova and G. A. Petropavlovskii, "Formation of Physical Thermally Reversible Gells in Solutions of Methyl Cellulose in Water and Dimethylacetamide and Properties of Films Thereof," MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS, vol. 74, 2001, pp. 10.

[14] J. Yang, Sh. Chen And Y. Fang , "Viscosity study of interactions between sodium alginate and CTAB in dilute solutions at different pH value," Carbohydrate Pplymers, vol. 75, 2009, pp. 333-337.

[15] H. Bu, A-L. KjØriksen and B. Nyström, " Effects of pH on dynamics and rheology during association and gelation via the Ug: reaction of aqueus alginate," European Polymer Journal, vol. 41, 2005, pp. 1708-1717.

[16] J. E. Glass, Polymers in aqueous media: performance through association. Advance in chemistry series, vol. 223.

Washington, DC: American Chemical Society, 1989.

[17] C. Tandford, The hydrophobic effect. Formation of micelles and biological memberanes, New York: Wiley, 1973.

[18] L. Leibler, M. Rubinstein. and R. H. Colby, Macromolecules, vol. 24, 1991, pp.4701.

Table I. Rheological parameters of the casson (C), Power-law (PL) and Herschel-Balkly (HB) models for description of rheological behavior of sodium alginate - methylcellulose mixtures in different pH values (3,5 and 7).

sample	Treatment	Rheological model	σ.(d/cm^2)	K(cP)	K_1	N	Co.F	R^2
pH=3	100% Alg	Caccon	0.07±0.01		6.26±0.49		87.50	0.875
		Power Law		1.12±0.17		1.33±0.00	98.60	0.986
		Herschel-Bulkley	1.21±0.37	2.02±0.00		1.94±0.41	99.80	0.998
	100% MC	Caccon	0.00±0.09		6.50±0.33		88.50	0.885
		Power Law		0.60±0.55		1.45±0.03	99.40	0.994
		Herschel-Bulkley	0.73±0.31	0.00±0.00		1.76±0.16	99.90	0.999
	75% Alg, 25% MC	Caccon	0.05±0.12		7.80±0.73		93.40	0.934
		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
	50% Alg, 50% MC	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
	25% Alg, 75% MC	Caccon	0.18±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
pH=5	100% Alg	Caccon	0.00±0.02		7.00±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±0.82		1.05±0.07	99.90	0.999
	100% MC	Caccon	0.00±0.05		5.00±0.29		87.90	0.879
		Power Law		1.28±0.25		1.15±0.06	98.60	0.986
		Herschel-Bulkley	1.24±0.19	0.03±0.03		1.88±0.16	99.30	0.993
	75% Alg, 25% MC	Caccon	0.02±0.02		6.34±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
	50% Alg, 50% MC	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
	25% Alg, 75% MC	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±0.06	0.02±0.01		1.85±0.05	99.80	0.998
pH=7	100% Alg	Caccon	3.14±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
	100% MC	Caccon	0.20±0.07		7.00±0.18		89.30	0.893
		Power Law		0.64±0.41		1.44±0.03	99.10	0.991
		Herschel-Bulkley	1.02±0.51	0.00±0.00		1.98±0.37	99.90	0.999
	75% Alg, 25% MC	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	0.95±0.62	0.01±0.00		1.90±0.56	99.70	0.997
	50% Alg, 50% MC	Caccon	0.00±0.06		5.95±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	99.70	0.997
	25% Alg, 75% MC	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	1.29±0.65	0.02±0.00		1.80±0.39	99.40	0.994