Effect of pH and calcium salt on rheological properties of xanthan gum-carboxymethyl cellulose blends.

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ABSTRACT

Effect of Calcium salt ($CaCl_2$ 1,5mM) and pH (3, 5 and 7) on rheological properties of xanthan-carboxymethyl cellulose blend solutions have been investigated. Gum solutions in all ratios showed shear thinning flow behavior that was adjusted to the Herschel–Bulkley model. Salt addition and pH decreasing cause apparent viscosity reduction .

INTRODUCTION

The term ‘hydrocolloids’ refers to a range of polysaccharides and proteins that are nowadays widely used in a variety of industrial sectors to perform a number of functionsincluding thickening and gelling aqueous solutions, stabilising foams, emulsions and dispersions, inhibiting ice and sugar crystal formation and the controlled release of flavours, etc.[10]

Xanthan gum is an extracellular polysaccharide secreted by the micro-organism *Xanthomonas campestris*. Xanthan is widely used as a food gum. which makes it unique among food gums. The unusual and very useful properties of xanthan undoubtedly result from the structural rigidity and extended nature of its molecules, which in turn result from its linear, cellulosic backbone, which is stiffened and shielded by the anionic trisaccharide side chains.[1]

Carboxymethylcellulose (CMC) is widely used in many application areas such as food, pharmaceutical, personal care, paper, paint and milling industry.[6]

The rheological properties of gums are particularly important when they are used in the formulation of any food for its effect on the textural attributes. The rheological properties of fluid food should be carefully taken into account for designing and modeling purposes. [14]

There are several studies on rheological properties of gum solution blends in the presence of salts. Molecular conformation of the complex of xanthan–LBG was assessed by the power law and the Huggins equations. Higiro et al.(2006) showed that addition of the salts reduced significantly the intrinsic viscosity and elastic component of the xanthan gum-LBG blends, with a pronounced effect from divalent ions, compared with monovalent ions.[4]

Khouryieh et al. demonstrated that intermolecular interaction has occurred between xanthan and guar mixtures in water and 2 mM NaCl, but may not occur in 40 mM NaCl.[5]

In previous works, effect of pH on rheological prpoerties of gum solutions in the presence of salts, didnt investigated.[2,3,4,5,6,8,9,13 and 14]

In this study effect of Calcium salt ($CaCl_2$ 1,5mM) and pH (3, 5 and 7) on rheological properties of xanthan-carboxymethyl cellulose blend solutions have been investigated.

MATERIALS AND METHOD

Xanthan gum and carboxymethyl cellulose were purchased from Sigma (Sigma–Aldrich, St. Louis, MO). The stock solutions (0.1% m/v) 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 and were heated for 1 h at 80 ˚C in a water bath to completely hydrate the gums. The solutions were refrigerated for one night (16 h) to completely hydrate the gums. To study rheological properties of gum blends, the following treatments were considered: xanthan 100%, xanthan 75%–CMC 25%, xanthan 50%–CMC 50%, xanthan 25%–CMC 75%, and CMC 100%. Stock solutions were stirred at room temperature. Prepared xanthan and CMC solutions were mixed at 25 ˚C, and were stirred with a magnetic stirrer for 10 min. To study the effect of pH ,the rheological properties were measured at neutral and acidic (5 and3) pH values. A pH meter (Metrohm, France) and 1N 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 of and were completely dissolved to obtain final concentrations of 1 and 5 mM $CaCl_2$. For rheological properties determination Brookfield rheometer[1] (LV DV III) equipped by ULA[2] and rheocalc[3] software were used. All Rheological measurements were carried out at 25 ˚C by using a temperature-controlled circulating water bath[4].

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 fluid food (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 and12]

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

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

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

where σ (d/cm^2) 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 and8]

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

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1- Brookfield engineering. INC,Middle Boro, MA02346 USA.

2- ULA-EY UL Adaptor

3- Rheocalc V3.2 Build 47-1

4- Brookfield engineering, TC 502

the best model to predict accurately the behavior of xanthan-CMC 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 behaviour of xanthan–CMC blends in all ratios at pH 7, 5 and 3 befor and after adding calcium salt (1,5 mM). The results were summarised 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. In neutral pH and without adding salt, solutions exhibited shear-thinning behavior. Salt addition and pH decreasing induced newtonian behavior and apparent viscosity reduction. An increase in CMC concentration resulted in lower values of σ_0 and apparent viscosity, and a shift to newtonian behavior.

Table 1. Rheological parameters of the Casson (C), Power-law (PL) and Herschel–Bulkley (HB) models for description of Rheological behaviour of xanthan gum solutions.(X(100%))

Sample	Model	σ_0(d/cm^2)	K(cP)	Plastic Viscosity	n	R2
pH 3, without salt	C	0.01		2.69		0.997
	PL		4.08		0.93	0.989
	HB	0.15	2.79		1.00	1.000
pH 3, 1 mM Ca	C	0.01		2.49		0.997
	PL		3.51		0.93	0.987
	HB	0.15	2.51		1.01	1.000
pH 3, 5 mM Ca	C	0.01		2.31		0.996
	PL		3.39		0.94	0.987
	HB	0.17	2.03		1.03	1.000
pH 5, without salt	C	0.04		6.23		0.994
	PL		12.70		0.87	0.992
	HB	0.02	12.10		0.89	1.000
pH 5, 1 mM Ca	C	0.02		3.43		0.998
	PL		6.31		0.90	0.990
	HB	0.09	5.00		0.95	1.000
pH 5, 5 Mm Ca	C	0.01		2.57		0.997
	PL		4.17		0.92	0.988
	HB	0.14	2.87		0.99	1.000
pH 7 without salt	C	0.03		8.92		0.994
	PL		15.70		0.89	0.996
	HB	0.00	16.30		0.89	1.000
pH 7, 1 Mm Ca	C	0.02		3.89		0.998
	PL		6.81		0.91	0.991
	HB	0.09	5.42		0.95	1.000
pH 7, 5 Mm Ca	C	0.01		2.56		0.997
	PL		3.74		0.94	0.988
	HB	0.12	2.61		1.01	0.999

Table 2. Rheological parameters of the Casson (C), Power-law (PL) and Herschel–Bulkley (HB) models for description of Rheological behaviour of CMC solutions.(CMC(100%))

Sample	Model	σ_0(d/cm^2)	K(cP)	Plastic Viscosity	n	R2
pH 3, without salt	C	0.00		2.57		0.989
	PL		2.29		1.01	0.984
	HB	0.35	0.72		1.22	0.995
pH 3, 1 mM Ca	C	0.01		2.60		0.979
	PL		1.88		1.04	0.967
	HB	0.67	0.12		1.54	0.990
pH 3, 5 mM Ca	C	0.06		2.79		0.965
	PL		1.22		1.11	0.946
	HB	0.83	0.02		1.90	0.993
pH 5, without salt	C	0.00		3.18		0.997
	PL		3.47		0.98	0.992
	HB	0.10	2.64		1.04	1.000
pH 5, 1 mM Ca	C	0.00		3.18		0.997
	PL		3.47		0.98	0.992
	HB	0.10	2.64		1.04	1.000
pH 5, 5 mM Ca	C	0.01		2.52		0.980
	PL		2.07		1.02	0.967
	HB	0.58	0.20		1.44	0.992
pH 7 without salt	C	0.01		7.97		0.997
	PL		10.60		0.95	0.997
	HB	0.00	10.50		0.95	1.000
pH 7,	C	0.00		4.03		0.997

1 mM Ca	PL		4.78		0.97	0.991
	HB	0.08	3.87		1.01	1.000
pH 7, 5 mM Ca	C	0.00		2.53		0.985
	PL		2.20		1.01	0.979
	HB	0.47	0.38		1.33	0.989

Table 3. Rheological parameters of the Casson (C), Power-law (PL) and Herschel–Bulkley (HB) models for description of Rheological behaviour of xanthan–CMC blends(X(75%),CMC(25%))

Sample	Model	σ_0(d/cm^2)	K(cP)	Plastic Viscosity	n	R2
pH 3, without salt	C	0.06		3.19		0.996
	PL		9.00		0.83	0.986
	HB	0.15	6.18		0.90	1.000
pH 3, 1 mM Ca	C	0.05		2.90		0.996
	PL		7.74		0.84	0.985
	HB	0.18	4.97		0.93	1.000
pH 3, 5 mM Ca	C	0.03		2.61		0.996
	PL		5.93		0.87	0.988
	HB	0.15	3.94		0.95	1.000
pH 5, without salt	C	0.14		8.08		0.992
	PL		29.10		0.75	0.989
	HB	0.10	24.60		0.79	1.000
pH 5, 1 mM Ca	C	0.08		3.91		0.995
	PL		12.10		0.81	0.992
	HB	0.10	9.66		0.86	1.000
pH 5, 5 mM Ca	C	0.05		2.84		0.996
	PL		7.65		0.84	0.984
	HB	0.17	4.02		0.92	1.000
pH 7 without salt	C	0.19		9.86		0.999
	PL		37.20		0.75	0.983
	HB	0.13	31.70		0.78	0.999
pH 7, 1 mM Ca	C	0.10		4.17		0.991
	PL		14.10		0.80	0.985
	HB	0.06	12.30		0.82	0.999
pH 7, 5 mM Ca	C	0.13		3.48		0.989
	PL		13.60		0.78	0.974
	HB	0.04	12.50		0.80	0.997

Table 4. Rheological parameters of the Casson (C), Power-law (PL) and Herschel–Bulkley (HB) models for description of Rheological behaviour of xanthan–CMC blends(X(25%),CMC(75%))

Sample	Model	σ_0(d/cm^2)	K(cP)	Plastic Viscosity	n	R2
pH 3, without salt	C	0.01		2.69		0.997
	PL		4.08		0.93	0.989
	HB	0.15	2.79		1.00	1.000
pH 3, 1 mM Ca	C	0.01		2.49		0.997
	PL		3.51		0.93	0.987
	HB	0.15	2.51		1.01	1.000
pH 3, 5 mM Ca	C	0.01		2.31		0.996
	PL		3.39		0.94	0.987
	HB	0.17	2.03		1.03	1.000
pH 5, without salt	C	0.04		6.23		0.994
	PL		12.70		0.87	0.992
	HB	0.02	12.10		0.89	1.000
pH 5, 1 mM Ca	C	0.02		3.43		0.998
	PL		6.31		0.90	0.990
	HB	0.09	5.00		0.95	1.000
pH 5, 5 mM Ca	C	0.01		2.57		0.997
	PL		4.17		0.92	0.988
	HB	0.14	2.87		0.99	1.000
pH 7 without salt	C	0.03		8.92		0.994
	PL		15.70		0.89	0.996
	HB	0.00	16.30		0.89	1.000
pH 7, 1 mM Ca	C	0.02		3.89		0.998
	PL		6.81		0.91	0.991
	HB	0.09	5.42		0.95	1.000
pH 7, 5 mM Ca	C	0.01		2.56		0.997
	PL		3.74		0.94	0.988
	HB	0.12	2.61		1.01	0.999

Table 5. Rheological parameters of the Casson (C), Power-law (PL) and Herschel–Bulkley (HB) models for description of Rheological behaviour of xanthan–CMC blends(X(50%),CMC(50%))

Sample	Model	σ_0(d/cm^2)	K(cP)	Plastic Viscosity	n	R2
pH 3, without salt	C	0.01		2.42		0.997
	PL		3.87		0.93	0.989
	HB	0.14	2.56		1.00	1.000
pH 3, 1 mM Ca	C	0.01		2.28		0.996
	PL		3.36		0.94	0.990
	HB	0.20	1.95		1.04	1.000
pH 3, 5 mM Ca	C	0.00		2.25		0.986
	PL		2.91		0.96	0.977
	HB	0.53	0.44		1.29	0.989
pH 5, without salt	C	0.06		5.80		0.993
	PL		13.90		0.85	0.994
	HB	0.02	13.30		0.86	1.000
pH 5, 1 mM Ca	C	0.03		3.33		0.998
	PL		7.40		0.87	0.989
	HB	0.10	5.53		0.93	1.000
pH 5, 5 mM Ca	C	0.02		2.50		0.998
	PL		5.11		0.89	0.987
	HB	0.15	3.28		0.97	1.000
pH 7 without salt	C	0.05		8.85		0.992
	PL		18.80		0.86	0.996
	HB	0.00	19.80		0.85	1.000
pH 7, 1 mM Ca	C	0.03		3.65		0.997
	PL		7.99		0.87	0.991
	HB	0.09	6.40		0.91	1.000
pH 7, 5 mM Ca	C	0.02		2.53		0.997
	PL		4.78		0.90	0.986
	HB	0.13	3.18		0.97	1.000

Figs. 1–5 show the apparent viscosity (AV) values of solutions prepared with xanthan gum and CMC. The AV of solutions decreased with increasing CMC concentration. The highest AV value was observed for xanthan solutions that contained no CMC, at pH 7 without addind $CaCl_2$ salt (Fig. 1).

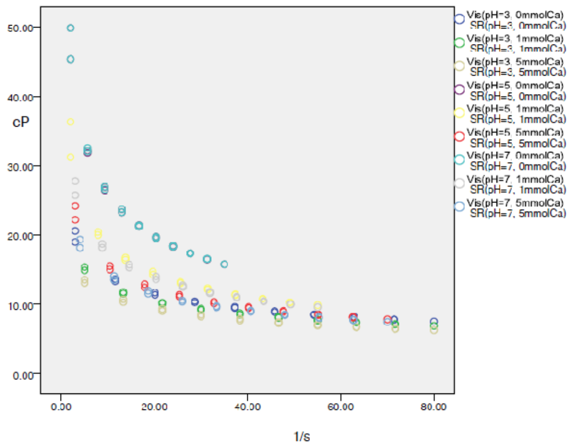

Figure 1. Viscosity as a function of shear rate of xanthan solution at pH 7, 5 and 3 without or with $CaCl_2$ (1,5 mM).

Fig. 2 shows that CMC solutions exhibit shear-thinning behaviour in low shear rates whereas at pH 3 or in the presence of 5 mM calcium ions the AV of solutions increased slightly in high shear rate values due to increasing molecular interactions in these conditions.

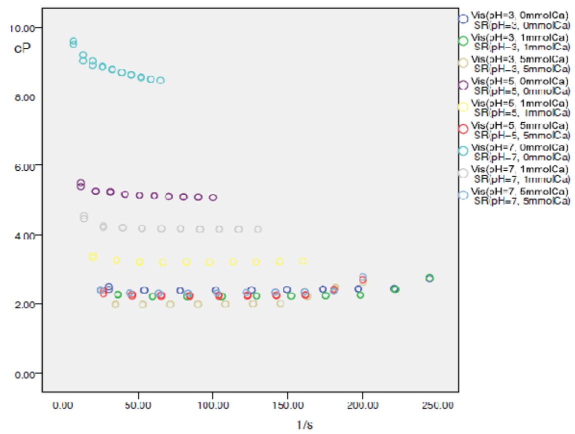

Figure 2. Viscosity as a function of shear rate of CMC solution at pH 7, 5 and 3 without or with $CaCl_2$ (1,5 mM).

Fig 3-5 show the effect of different ratios of gum solution blends on the AV of solutions in different experimental conditions. The results demonstrated that all solutions showed a non-Newtonian flow in which AV changed with shear rate. AV values of sample solutions decreased with increasing shear rate, thus solutions exhibited a shear thinning behavior. The addition of xanthan caused an increase in the AV values of the solution.

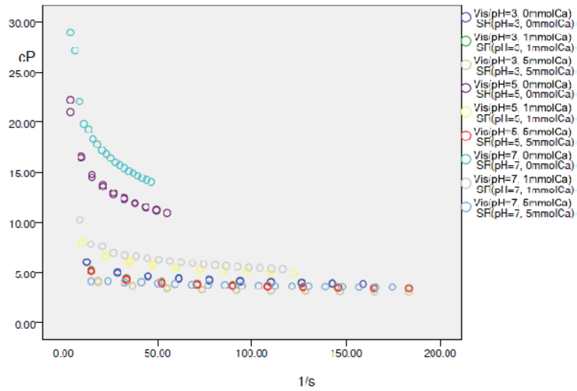

Figure 3. Viscosity as a function of shear rate of xanthan- CMC solutions (75/25) at pH 7, 5 and 3 without or with $CaCl_2$ (1,5 mM).

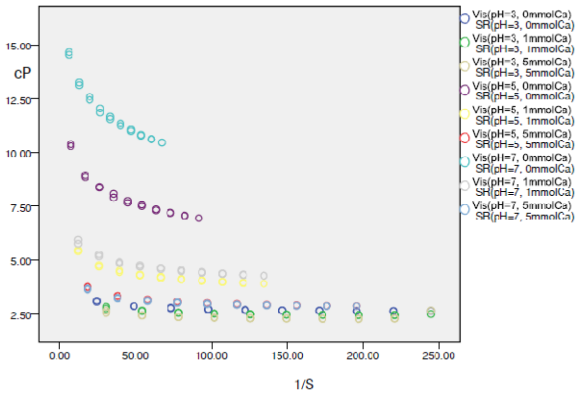

Figure 4. Viscosity as a function of shear rate of xanthan- CMC solutions (50/50) at pH 7, 5 and 3 without or with $CaCl_2$ (1,5 mM).

The results demonstrated that when salt is added, charge screening causes the side chains to collapse down to the backbone, hence giving the xanthan molecule a rod-like shape and reducing the hydrodynamic volume. Similar results have been reported by others. [3,4, 5 and 10]

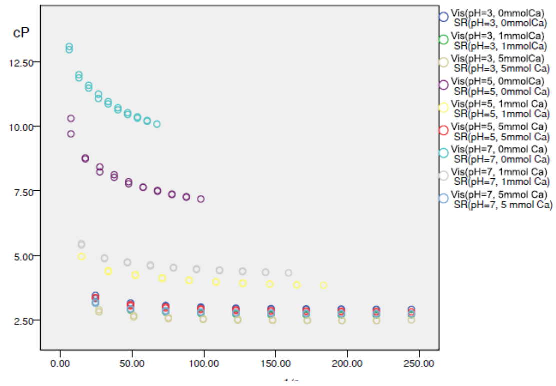

Figure 5. Viscosity as a function of shear rate of xanthan- CMC solutions (25/75) at pH 7, 5 and 3 without or with $CaCl_2$ (1,5 mM).

The more pronounced effect of the calcium ions on the intrinsic viscosity, was possibly due to molecular crosslinking between xanthan and calcium ions, which resulted in a greater extent of molecular contraction.[4]

CONCLUSIONS

Xanthan-carboxymethyl cellulose blends in all ratios showed shear thinning flow behavior at 25˚C. As the pH value of solutions decreased, a significant decrease in viscosity values was observed. Salt addition in different pH values cause apparent viscosity reduction. Adding salt cause a significant decrease in viscosity values for solutions with higher pH values, due to molecular crosslinking between xanthan and calcium ions. Gum solutions in all ratios showed shear thinning flow behavior that was adjusted to Casson, Power Law and Herschel–Bulkley models. The results demonstrated that Herschel–Bulkley model is the best model for description of rheological behaviour of xanthan-carboxymethyl cellulose blends in different under study conditions.

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