Rheological behaviour of gum solutions and their interactions after mixing

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ABSTRACT

The rheological behaviour of three gum mixtures (X/G, X/LBG and G/CMC) has been investigated and compared using steady and oscillatory shear measurements. The strong synergism was found in all systems with strongly dependence on gum ratio. The different interactions may exist which are discussed in the text.

INTRODUCTION

To date, the synergistic properties between mixed polysaccharides are in great interests. The study of rheology on mixed gums which promote high solution viscosity and stability were conducted interestingly from many researchers with expectation to apply in food product, e.g. emulsions. But the investigation are still less and mostly focused on xanthan and galactomannans synergism.

Even now the understanding over the intermolecular interaction between xanthan and galactomannans is still controversial, and different models have been proposed. The first model was proposed by Dea et al.[1] and Morris et al.[2], who reported that the intermolecular binding may occur between the ordered xanthan, rod-like conformation and unsubstituted or poorly substituted regions of the galactomannan backbone. After, Tako et al.[3] has been proposed at which the sidechains of the xanthan are inserted into adjacent unsubstituted regions of the galactomannan backbone, which adopts an ribbon-like conformation. The others[4-6] also supported these two theories or proposed another models until now.

However, most of them demonstrated mainly the gelling properties between locust been gum and xanthan. Less of them were investigated interactions but non-gelation solutions between guar and xanthan gums[7-9]. Even more the study of rheological properties on their synergistic and in other types of mixed gums is in a lesser extent.

Therefore, the aims of this research were to determine the rheological properties on mixed gum solutions between xanthan and galactomannans, both from guar and locust been. The more extent would be the investigation on another type of mixed polysaccharides as guar and sodium carboxymethylcellulose which the differences in interaction binding mechanism may observe.

MATERIALS AND METHODS

Gums studied were kindly donated by respective companies. Xanthan gum type 402 (E 415), guar gum (E 412) and locust been gum (E 410) were obtained from Loryma GmbH, Germany. High molecular weight sodium carboxymethylcellulose (Walocel® CRT 40,000 PA) was obtained from Wolff Cellulosics GmbH & Co. KG, Germany.

Preparation of gum solutions

To study the interaction of three gum mixtures (xanthan/guar, xanthan/locust been gum and guar/sodium carboxymethyl cellulose), 100 gram of gum solutions were prepared by thoroughly dispersing the desired amount of premix gum powders in distilled water at room temperature except

the samples containing locust been gum which required high temperature (80 − 85 °C) to fully disperse. All gum solutions were continuously stirred under the same conditions with a glass propeller for 10 min at 600 rpm. Samples were then stored overnight in refrigerator (4 °C) before rheological measurements. The total polysaccharide concentration was kept constant at 1 wt% with the gum ratio ranged from 15:85 to 85:15.

Rheological measurement

All rheological measurements were performed using a Physica UDS 200 rheometer (Universal Dynamic Spectrometer) equipped with a Z3 DIN rotational cylinder. Measurements were carried out with controlling temperature at 20 °C.

Steady state flow curves were obtained measuring in three loops: (1) shear rate was increased from 0.1 to 100 /s in 1 min, (2) the constant shear rate were controlled for 1 min, and then the downward curve were measured by decreasing shear rate from 100 to 0.1 /s in 1 min. The data for upward and downward curves were collected every 1 sec. Only data from downward curves were used to calculate rheological parameters and effective viscosity (η_{eff}) at $\dot{\gamma}_{max}$ = 100 /s using Power law models. The flow behavior was explained according to Ostwald-de Waele (see eq. 1),

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

and Herschel-Bulkley equations (see eq. 2).

$$\tau = \tau_{0HB} + K \cdot \dot{\gamma}^{n} \qquad (2)$$

Where τ is shear stress (Pa), $\dot{\gamma}$ is shear rate (1/s), K is consistency factor (Pas^{n}), n is flow index and τ_{0HB} is yield point (mPa).

Viscoelastic properties were performed by determining the storage (G′) and loss (G″) moduli at a constant strain rate of 0.001 in the frequency range from 0.1 to 50 Hz.

The complex modulus |G*| in Pa is defined when G′ > G″ as

$$|G*| = \sqrt{(G')^{2} + (G'')^{2}} \qquad (3)$$

Where G′ is storage modulus and G″ is loss modulus. The complex modulus is related to the rigidity of samples.

The gelling properties of X/LBG mixtures were investigated by temperature sweep method. The temperature sweep test was performed by decreasing temperature from 80 to 20 °C at a cooling rate of 1 K/min with the frequency held constant at 1 Hz and the strain amplitude at 0.001.

RESULTS AND DISCUSSION

In general, gum solutions exhibited flow behavior according to power law model. Accordingly, all gum studied showed shear thinning behavior (see Fig. 1). However, the high degree of decreasing in viscosity has been shown. From Fig. 1, illustrated that at low $\dot{\gamma}$, effective viscosities (η_{eff}) of all gum solutions were relatively different and at higher $\dot{\gamma}_{max}$ of 100 /s, η_{eff} was reduced with different extent.
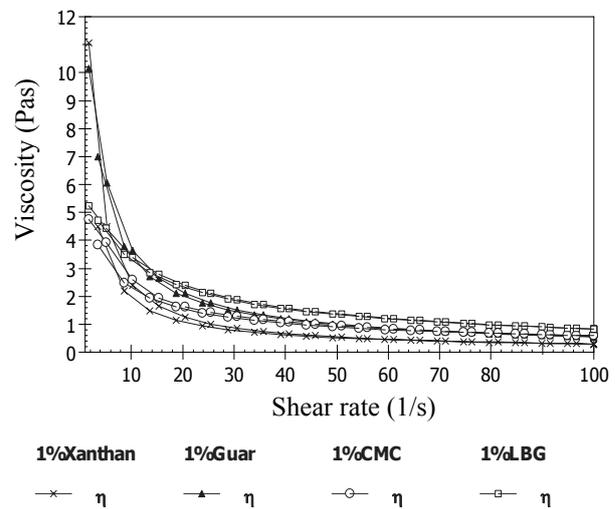

Figure 1. Viscosity depended on shear rate of various gum solutions

Table 1. Rheological parameters of pure gum solutions at 20 °C

| Sample | Ostwald-de Waele | | | | | Herschel-Bulkley | | | | | |
	K (Pas^n)	n -	r -	$\eta_{eff (100/s)}$ (Pas)		τ_0 (Pa)	K (Pas^n)	n -	r -	$\eta_{eff (100/s)}$ (Pas)	
1% Xanthan	12.460	0.186	0.9994	0.2932	X	3.712	9.227	0.222	0.9997	0.2941	√
1% Guar	17.785	0.256	0.9866	0.5780	√	-16.861	34.664	0.162	0.9974	0.5613	X
1% CMC	8.346	0.428	0.9978	0.5985	√	-0.173	8.477	0.425	0.9980	0.5973	X
1% LBG	8.641	0.519	0.9614	0.9442	√	-4.000	13.285	0.422	0.9883	0.8894	X

(√) valid; (X) non-valid parameters

Rheological parameters are given in Table 1. The results reveal that 1 % xanthan gave lower η_{eff} than other gums studied whereas 1 % Guar gum gave the highest value at shear rate of 100 /s. In addition, all gum studied exhibited flow behavior according to Ostwald-de Waele equation except xanthan gum. Only xanthan gum exhibited Herschel-Bulkley behavior because of the existence of yield point (τ_0). To compare between gums, the consistency factor (K) of xanthan and guar gums showed high values than others with lower flow index (n). Flow index indicates the degree of structure properties and stability. The structure stability decreases when n value increases. Ranking by this experiment, polysaccharides has been ranked structural stability as follow, X > G > CMC > LBG. From these results, it can be assumed that xanthan exhibits semi-solid behaviour where guar, CMC and LBG exhibit high viscous non-Newtonian fluid behaviour.

Individually, xanthan gave the lowest n value therefore induced high structural stability. It results from its rigid rod-like conformation in solution and its side chain. In solution the side chains of xanthan wrap around the cellulose backbone thereby protecting the labile β - (1→4) linkages from attack[10]. In distilled water at 25 °C, the backbone of xanthan is disordered or partly ordered (helical) in the form of a randomly broken helix but highly extended due to the electrostatic repulsions from the charged groups on the side chains[11]. High viscous solution under non-covalent bonding, principally hydrogen bond was found. Moreover, xanthan is also able to particulate or form intermolecular associations in solutions that result in the formation of a complex network of weakly bound molecules[10] and able to form time-independent interactions. This formation of a weak network results in yield-point values which induced the ability to stabilize emulsions and dispersions.

In galactomannans, yield points are not found but high viscous exhibited in solutions. In general, guar conform the ratio of mannose to galactose approximately ranges at 2:1 whereas locust been gum (LBG) consists of 4:1. This less of hairy unsubstitute of galactose side chain leads LBG to be less water soluble. In this present study, only LBG were dispersed at high temperature (80-85 °C) to obtain fully disperse. From the results, it suggested that guar gum has lower n value or higher stable than LBG. This could be reason of the more side chain in guar gum which conform a disordered, more extended random coil after dissolution in water[12]. In aqueous solution, guar immobilizes water and forms the artificial network which causes the strong hydrogen bonding within.

Normally, sodium carboxymethyl-cellulose (CMC) gave low viscosity in water. In this study, a high molecular weight type of CMC was used. So, the high viscous with odorless and transparent solution was obtained. Long CMC molecules give increase in viscosity owing to chain entanglement. From these results, it can be seen that CMC gave relatively high n value with low K which comparably to LBG.

Flow behaviour of mixed gums

To evaluate the synergistic effect of gum mixtures, all mixtures were dispersed in solution at the same total amount of mixed polysaccharides in solutions of 1 wt%. As xanthan/guar mixtures, xanthan fraction was varied from 15 to 85 wt%.

As mentioned above, pure guar solution (0:100) gave high viscous non-Newtonian fluid behaviour, where xanthan solution showed semi-solid behaviour with yield point (τ_0). When these two polysaccharides were mixed, the strong synergistic has been occurred more than expected. As shown in Table 2, rheological properties are strongly dependence on gum ratio (concentration-dependent). Considered by the rheological parameters of mixed gum solutions, two mechanisms can be seen. For the mixed gums containing xanthan 15 – 50 %, samples showed high viscous non-Newtonian fluid behaviour which are according to Ostwald-de Waele equation. On the contrary, samples containing xanthan more than 50 % had yield point and showed semi-solid behaviour which are according to Herschel-Bulkley equation. The highest interaction between X/G mixtures was found at 25:75 which has been seen by the highest value of K. The maximum viscosity was observed at a ratio of 25:75, whereas lowest n value was observed at a ratio of 50:50. The maximum yield point was observed at a ratio of 85:15.

These results show the influence of guar gum on the increase of viscosity, where the structure would dominant by xanthan.

When solutions contain xanthan more than 50 %, X/G mixtures showed yield point and higher value was found compared to pure xanthan solution. A complex network formed which influenced by the xanthan conformation. Xanthan which highly extend in solution had entanglement with network interaction and would bind with guar. Hydrogen bonding between two or more molecules of xanthan by the side chain of guar may arise. Indicating by higher in τ_0 but lower in viscosity, it suggested that xanthan would dominant the structural arrangement in the system. At high concentration of xanthan, a formation of strong network interaction between xanthan/guar mixtures would evident by the presence of yield point (τ_0) instead of the increasing of viscosity. The semi-solid with high degree of structural stability well represents for this system. In contrast, at low concentration of xanthan, the hydrophilic interaction between xanthan/guar is less. Two or more molecules of guar gave only high viscous behaviour which exhibited less n value however much higher viscosity. It can be assumed that only small amount of xanthan presented in mixtures have been binding with guar. Guar can form only weakly network between itself, highest internal friction would occur, results in lower n value. Xanthan/guar interaction molecules would immobilize water, results in higher in viscosity.

Table 2. Rheological parameters of gum mixtures

Gum ratio	Xanthan : Guar (X/G)						Guar : CMC (G/CMC)				
	τ_0 (Pa)	K (Pas^n)	n -	r -	η_{eff} (100/s) Pas	Eq.	K (Pas^n)	n -	r -	η_{eff} (100/s) Pas	Eq.
0 : 100	-	17.79	0.256	0.9866	0.5780	OW	8.35	0.428	0.9978	0.5985	OW
15 : 85	-	26.38	0.186	0.9909	0.6201	OW	10.30	0.384	0.9975	0.6042	OW
25 : 75	-	27.17	0.181	0.9941	0.6265	OW	14.70	0.345	0.9969	0.7210	OW
50 : 50	-	23.19	0.168	0.9957	0.5032	OW	21.46	0.287	0.9948	0.8053	OW
75 : 25	3.88	14.35	0.194	0.9999	0.3901	HB	23.76	0.253	0.9930	0.7625	OW
85 : 15	4.15	13.67	0.189	0.9995	0.3677	HB	33.11	0.219	0.9879	0.9075	OW
100 : 0	3.71	9.23	0.222	0.9997	0.2941	HB	17.79	0.256	0.9866	0.5780	OW

* OW means according to Ostwald-de Waele equation
  HB means according to Herschel-Bulkley equation

As guar/CMC mixtures, samples exhibited substantially increased in η_{eff} but no yield point. It suggested that only hydrophilic interaction has been occurred with no network conformation. The high viscous non-Newtonian fluid is well described for this system. All mixtures promoted significantly high consistence factor (K) and effective viscosity (η_{eff}) but lower n value. Higher amount of guar in mixtures increased unexpectedly viscosity. At a ratio of 85:15, sample gave the highest K and η_{eff} with lowest n values which means the strongest synergistic effect has been observed. It seems that guar would dominant the structural arrangement in this system, indicating by the tendency of high value of K and low value of n similar to pure guar gum solution. The results also suggested that hydrophilic interaction may occur where guar take water from CMC which leads to the increasing in viscosity.

In comparison to X/G mixtures, G/CMC mixtures had higher viscosity but lower stability properties, indicating by higher value of n. The results suggested that the best organized system would found in xanthan/guar mixtures according to its stability system. The structural analysis of mixed gum was further supported by the viscoelastic measurements.

Viscoelastic properties of gum mixtures

Viscoelasticity of gum mixtures were described using G′, G″, |G*| and tan δ. The results revealed that only xanthan/locust been gum promoted gel properties even at the low fraction of xanthan. In contrast, xanthan/guar and guar/CMC mixtures promoted non gelling property, instead, exhibited particle system.

The gelling phenomenon between X/LBG mixtures was evident by the reduced of tan δ less than 1 (see Fig. 2). When xanthan fraction in mixtures increased, the tan δ obviously decreased.

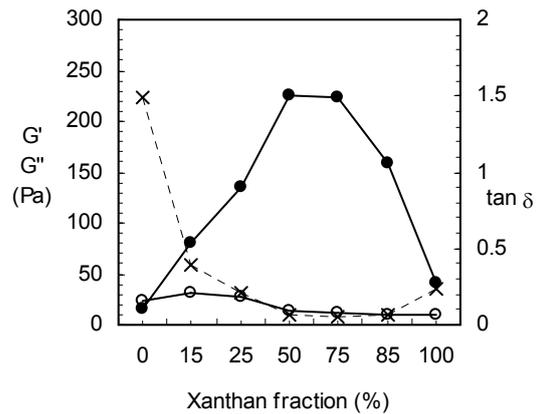Figure 2. G′, G″ variations as a function of X/LBG ratio (●, G′; ○, G″; x, tan δ; frequency at 1 Hz).

The decreasing of tan δ was influenced by the substantially increased of storage modulus (G′). Noticed that loss modulus (G″) is independence on xanthan fraction. From Fig. 2 and 3, the results showed that xanthan enhanced gel property with increasing storage (G′) and complex |G*| moduli when the fractions of xanthan increased. A strongest synergism was observed with the xanthan fraction of 0.5 - 0.75 %. The intermolecular interaction between xanthan and LBG seems to exhibit the stronger binding when the ratio is appropriate.
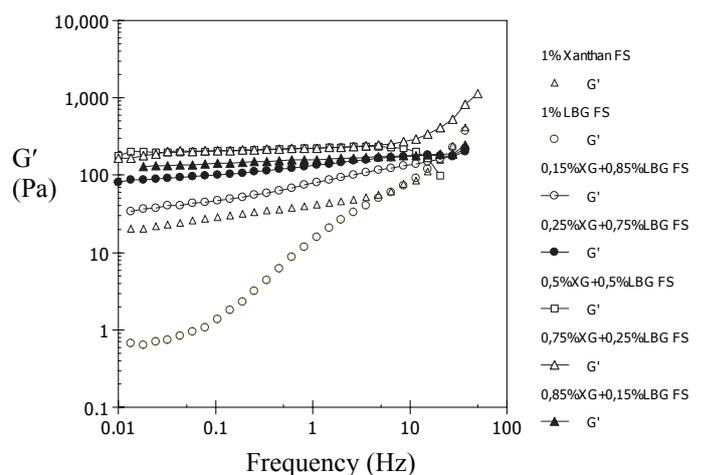
Figure 3. Storage modulus (G′) variation as a function of oscillating shear.

The 3D network was formed which efficiency promoted when the amount of X/LBG in solution was equal or have some more sufficient amount of xanthan. As shown in Fig. 3, the G′ increased with increasing xanthan. But no more increasing was observed over 50 % of xanthan fraction added in mixtures. It means that the G′ of gel was less when small amount of xanthan presented. Instead, high amount of xanthan would be an appropriate ratio to combine with LBG. It is clear that at low concentration of xanthan in mixture the system was less organized with higher value of tan δ (see Fig. 4). Again, it tell us that the intermolecular interaction between X/LBG mixture depended strongly by the concentration of xanthan in mixture.

Temperature sweep was also used to investigate the sol-gel transition of X/LBG mixture. The similar result was observed which all fractions had the same gelation temperature of 45 - 47 °C. However, the gel strength represents by tan δ depended on xanthan fraction. The maximum tan δ of gel obtained from the samples containing xanthan of 0.5 - 0.75 %.
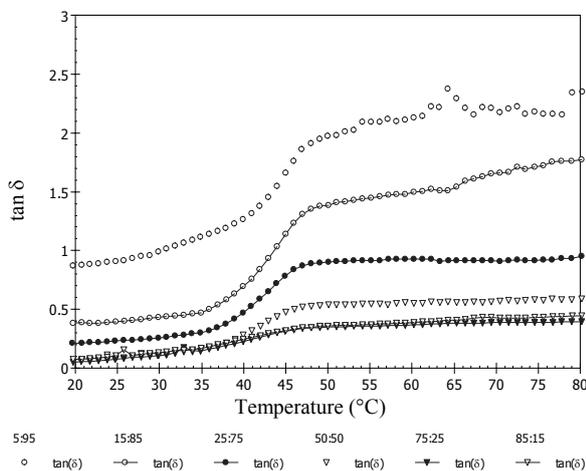

Figure 4. Temperature sweep curves of 1 wt% X/LBG mixtures at different ratio.

As X/G mixtures, viscoelastic properties has been shown in Fig. 5a,b. Considering G′ and G″, it was clearly observed that mixed gum exhibited the same behavior as xanthan. The G′ and G″ values are quite similar to those of xanthan. These results show the dominant of xanthan in X/LBG mixed gum structure. Within frequency range studied, X/G mixtures presented the semi-solid with particle system, non-gelling properties where G′ always more than G″ which supposed to reflecting that the best organized system was induced by adding xanthan. The |G*| also indicated that even small amount of xanthan presented in mixtures |G*| would increased.

As G/CMC mixtures, no gelling properties were found. Only the high viscous particle structure was presented as a cross over of G′ and G″ curves. The results demonstrated that G/CMC mixtures exhibited the same behavior as guar with the similar value of G′ and G″ as guar system (see Fig. 5c) which reflecting that guar would dominant the structure in this system. Moreover, when the amount of guar in G/CMC mixtures increased, |G*| also gradually increased (see Fig. 5d). The strongest synergism was obtained at a ratio of 75:25 where the G′ was highest and tan δ was lowest (data not shown).

CONCLUSIONS

For pure gum itself, only xanthan exhibited semi-solid behaviour whereas the other gums (G, CMC, LBG) exhibited high viscous non-Newtonian behaviour. When mixed, various structure systems occur according to the intermolecular interaction between gums. The strong synergistic phenomena were found which strongly dependence on types and gum ratio. All gum mixtures gave much higher η_{eff}, K and lower n values than pure gum solutions at the same total concentration.
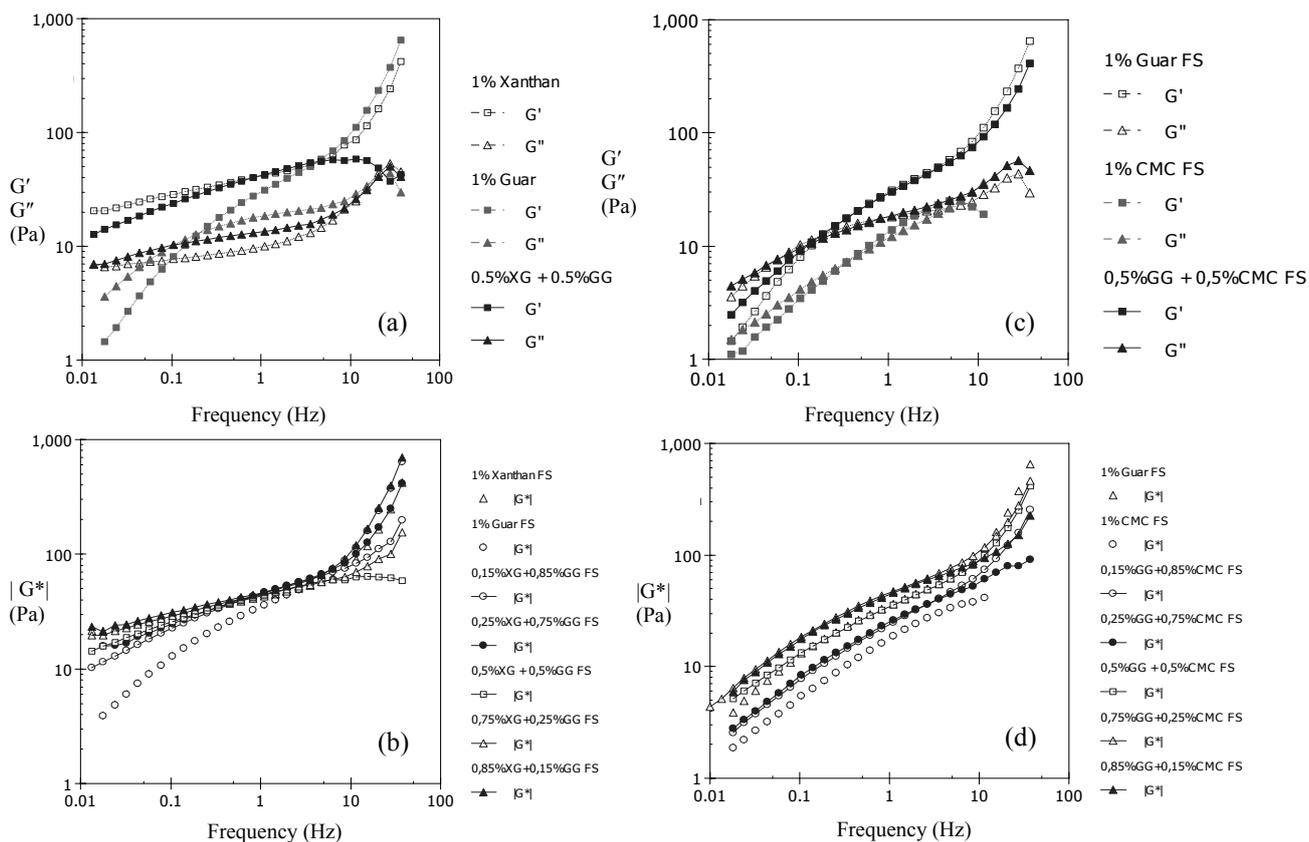
Figure 5. Viscoelastic parameters as a function of oscillating shear
for X/G mixtures (a,b) and G/CMC mixtures (c,d)

As xanthan/guar mixtures, xanthan induced the best organized system. A strong network was formed, where the mixtures promoted the network structure according to the dominant of xanthan whereas exhibited the viscosity level according to guar gum. At high concentration of xanthan in X/G mixture, the semi-solid with particle system has been presented. As guar/CMC mixtures, samples exhibited only high viscous non-Newtonian fluid behaviour with substantially increased in η_{eff}. The hydrophilic interaction may occur between them. Viscoelasticity of gum mixtures revealed that only xanthan/locust been gum promoted gel properties even at the low fraction of xanthan.

As results, it has been evidenced that xanthan would dominant the structure arrangement and rheological properties of xanthan/galactomannan systems whereas guar gum play a major role in guar/CMC mixed gum solutions.

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