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ORIGINAL PAPER

Shear-thinning and viscosity synergism in mixed solution of guar gum and its etherified derivatives

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Abstract The flow properties of mixed solution of guar gum and carboxymethyl guar gum, including shear-thinning and viscosity synergism, have been studied at different mixed ratios, shear rates and temperatures using rheometer. The results show that addition of carboxymethyl guar gum enhances shear-thinning behavior and increases viscosity in guar gum solution at a given range of mixed ratios. The temperature-dependence of the mixed solution is markedly different from a single solution. The activation energy of blends with 50 and 75% of guar gum were determined to be 11.02 and 10.39 kJ mol^{-1}, respectively, lower than that of a single solution. These results indicate that the network structure of viscous solution has been changed because carboxymethyl groups branched in galactomannans had changed the interaction among macromolecular chains.

Keywords GG · CMG · Shear-thinning · Viscosity synergism

Introduction

Guar gum is a natural macromolecule extracted from endosperm of the legume (*Cyamopsis tetragonolobus*). It belongs to the galactomannans family, and consists of a linear backbone of β(1–4)-lined D-mannose residues partially substituted α(1–6) linked D-galactose residues, with an average ratio of 2 mannose to 1 galactose [1]. Its derivatives are obtained by suitable chemical modifications, for example, etherification, esterification and oxidation [2–7]. Since the derivatives of guar gum may compensate the disadvantages of natural guar gum, they have increasingly been

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a part of major research and development. For example, a carboxymethyl derivative may increase the hydrophilicity and solution clarity of the galactomannans and make it better soluble in aqueous solution. Therefore, the carboxymethyl derivative, whose structural characteristic is that the H atom of hydroxyl group in the D-galactose units and D-mannose units are partially substituted by –RCOOH, is one of objects to be investigated in this work. Its structure is shown in Fig. 1.

Guar gum and its derivatives, as a series of water-soluble polymers, are attributed to their special structure with a large number of –OH in molecular chains. They are able to bind up H_2O with hydrogen bonding. Meanwhile, numerous molecular chains entangle each other, and thus, a strong network forms eventually in this system. Therefore, they are able to produce a high viscous aqueous solution, even at a low concentration, which is slightly affected by pH, ions and temperature [8]. At present, they have been extensively used as thickening and stabilizing agents in many industrial sectors such as food industry, paper-making, pharmacy, ceramic industry and oil industry. Because many commercial applications of such plant gums are primarily based on their ability to modify flow properties of a system, namely rheology, knowledge of the rheological behavior of guar gum and its derivatives is essential in meeting end-user requirements. Generally speaking, a study on rheology is carried out with measurement of viscosity behavior. Many factors including the concentration of gums, temperature, electrical charge and mechanical treatments may affect their viscosity properties. In this regard, guar gum and its derivatives have been extensively studied, respectively [2, 9–14].

It is amazingly found during the course of investigation that the rheological behavior of the galacomannans solution changed when the galactomannans with different structures are mixed. Generally speaking, as comparing with a system with a single component, a system with appropriate compound components help to optimize the property of the system. In particular, the multi-system is of advantage to improve quality and broaden the range of applications. Thus, the mixed system of guar gum and other galactomannans has attracted an extensive attention. The mixture of xanthan and guar gum shows a higher combined viscosity than each separate gum [15]. Guar gum at high concentrations demonstrates a better synergism when used with salep. It was observed that the *K* of the power law model increased [16]. The property of synergistic viscosity was also found in the mixed

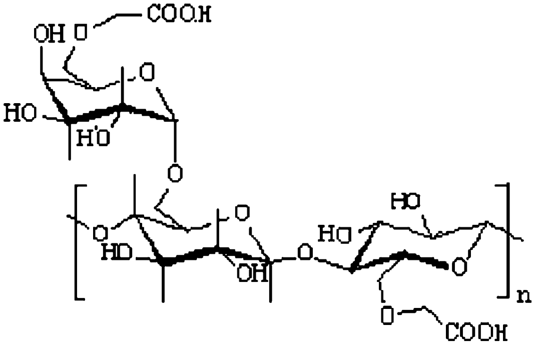

Fig. 1 The molecular structure of carboxymethyl guar gum

polysaccharide solution of two derivatives of guar gum [17]. Xanthan and Guar gum may change the rheological property of cationic tapioca starch, and guar gum was more effective than xanthan gum in terms of increasing peak viscosity due to increasing the swelling power and solubility index [18]. The mixture of rice starch and guar gum, or locust bean gum, shows high shear-thinning feature with high Casson yield stress, which is similar to a weak gel-like feature in respect of rheology [19]. From these results, it is not difficult to find that the binary or multiple galacomannans solution show a change of pseudo-plastic feature and an increase of viscosity.

The objects of the present work are the aqueous solutions of guar gum, of carboxymethyl guar gum and of their blends. Our aim is to observe the change of galacomannans in viscosity, in order to see how carboxymethyl group affects the flow feature, and see if a regular feature could be establish for theirs. A special attention is paid to two aspects of rheological feature, shear-thinning and viscosity synergism. The former describes the main character of pseudo-plastic flow, and the latter suggests a method improving thickening power.

Experimental

Materials

Guar gum (GG) and carboxymethyl guar gum (CMG) were obtained from Beijing Natural Plant Gum Development Center, BGRIMM. Both of them were commercial products. For the GG sample, the moisture content and pH of aqueous solution (0.6%) at 30 °C were determined to be 9.0% and 6.5, respectively, and for CMG, the two figures were 10.0% and 7.5, respectively.

Methods

Preparation of solutions

Individual GG and CMG solution with the same concentration of 0.6% was prepared, respectively by adding the given powdered GG or CMG gradually into the appropriate amount of distilled water at room temperature, under continuous stirring in a Waring blender at 7,200 rpm for 5 min. To ensure complete dissolution and remove any entrapped air bubble, the solution was kept at 30 °C in a water bath for 4 h. A series of mixed GG/CMG solutions with the same concentration (0.6%) were prepared, respectively in the same method. For these solutions, seven weight fractions of GG (Φ_G) in the blends were considered as follows: 0.20, 0.25, 0.33, 0.50, 0.67, 0.75 and 0.80.

Viscosity measurement

The viscosity measurement was performed with the help of a controlled stress rheometer (RS75, Haake, Germany), using a concentric cylinder geometry

(MS-DIN 53019). The viscosity properties under various conditions were investigated, such as various shear rates (six values from 3.0 to 600.0 s^{-1}), components (as followed above) and temperatures (25, 30, 40, 50, and 60 °C).

Results and discussion

Shear-thinning behavior

The flow curves, at 30 °C, for 0.6%GG and 0.6%CMG solutions under various shear rates from 3.0 to 600 s^{-1}, are shown in Fig. 2. The viscosity is found to decrease drastically when the shear rate increases at a constant temperature. In other words, each of GG and CMG solutions exhibits markedly shear-thinning feature. These results substantiate the entanglement theory proposed by Graessley [20]. According to his theory, the interpenetration of polymer chains in concentrated solutions gives rise to a dynamic entangled network. With increasing shear rate, the cross-link density of the network is depleted and viscosity is reduced.

As far as the degree of shear-thinning is concerned, the viscosity of GG solution decreases more quickly than that of CMG solution. This can be explained by the change of network structure, which results from the change of molecular structure. Many carboxymethyl groups, branched the chains of galactomannans, give rise to space insistence which partly block the freedom of movement of polymer chains caused by an outside force.

Similar behaviors are observed in the mixed solution of GG and CMG. As shown in Fig. 3, the apparent viscosity for the mixed solution with various Φ_G under the shear rates from 3.0 to 600.0 s^{-1} is determined. Obviously, it can be explained by

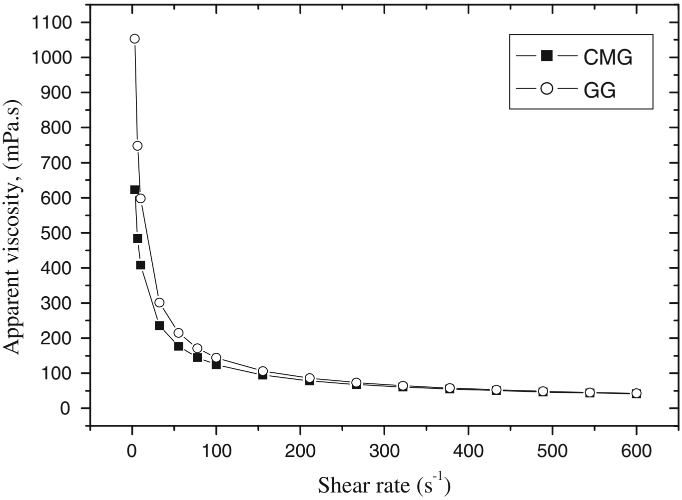

Fig. 2 Apparent viscosity versus shear rate for aqueous solution of GG and CMG, respectively. Total polymer concentration is 0.6% (30 °C)

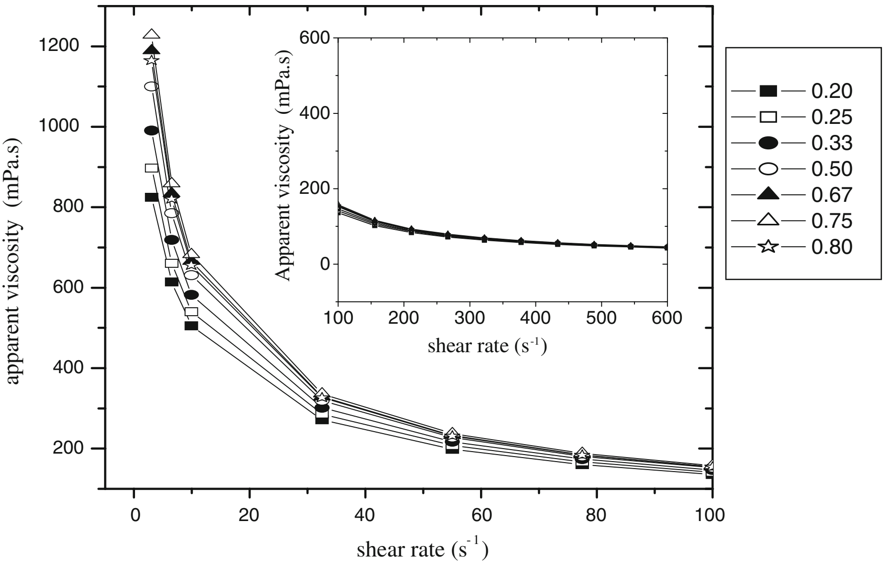

Fig. 3 Apparent viscosity versus shear rate for the mixed solution of GG and CMG with various $\Phi_G = 0.20, 0.25, 0.33, 0.50, 0.67, 0.75, 0.80$. Total polymer concentration is 0.6% (30 °C)

using the entanglement theory described above. Moreover, it has to be pointed out here that, for the mixed solution of GG and CMG, the formed network structure is different from a single component solution. The reason is that when the negative CMG molecules are added to the neutral GG solution, the interaction of electrostatic force deriving from the negative charge and the space insistence arising from carboxymethyl group can change the form of entanglement and the network structure. Eventually, the flow feature of viscous solution is influenced. In evidence, the degree of shear-thinning varies with the increase of concentration of GG, due to the decrease of carboxymethyl group in the system. But, it is noticeable that when the Φ_G is over 0.5, the flow curves tend to converge. It is illuminated that when the concentrate of carboxymethyl group is below a given value, the differentia of shear-thinning is weaken. Besides, both of Figs. 2 and 3 show that the convergence of apparent viscosity is more marked under a high shear rate, especially above 200 s^{-1}.Thus, contrasting with the strong share force, the resistance resulted from electrostatic force and space resistance may be neglected.

The effect of shear rate on the apparent viscosity of GG, of CMG and of their blends is illustrated in Figs. 2 and 3. All data can be represented satisfactorily by the following power law model.

$$\eta_a = KD_r^{n-1} \tag{1}$$

where η_a is the apparent viscosity, K is the consistency coefficient, D_r is the shear rate and n is the flow behavior index. The obtained K and n as well as the corresponding coefficients (R^2) are listed in Table 1. Similar to a solution of GG or CMG, their blends show the pseudo-plastic feature due to the fact that all values of n

Table 1 Values of K, n and the corresponding coefficients (R^2) for solutions of GG, of CMG and of their blends with various Φ_G under different shear rates

Φ_G	0.00	0.20	0.25	0.33	0.50	0.67	0.75	0.80	1.00
K	1345.1	1846.4	2026.0	2260.6	2546.6	2773.3	2871.0	2709.0	2432.0
n	0.466	0.420	0.409	0.394	0.376	0.371	0.359	0.366	0.374
R^2	0.998	0.997	0.997	0.998	0.998	0.997	0.998	0.998	0.996

Total polymer concentration is 0.6% (30 °C)

Table 2 Values of K, n and the corresponding coefficients (R^2) for the mixed solutions of GG and CMG ($\Phi_G = 0.75$) with various temperatures

T (°C)	25	30	40	50	60
K	2914.6	2871.0	2627.9	2214.3	1818.2
n	0.361	0.359	0.363	0.380	0.404
R^2	0.998	0.998	0.998	0.998	0.997

are less than 1.00. Moreover, the n of the mixed solutions are smaller than that of the single component solution, especially when Φ_G is greater than 0.5. This means that the mixed system has stronger shear-thinning characteristics. It has to be mentioned here that the K value of the mixed solution with the appropriate mixed ratio is larger than that of a single component solution. It is suggested that the mixed system has a good viscosity synergism, which will be discussed at the following part. In addition, as shown in Table 2, it is found that K is decreased with the increasing of the temperature, while the opposite trend is observed with n. This fact implies that the increasing of temperature weakens the properties of both thickening and shear-thinning of the aqueous solution of galactomannan.

The obtained results in the present investigation are generally in a good agreement with the results reported for other galactomannans, including both a single component and a multi-components solution [21, 22].

Synergistic viscosity behavior

As said above,when Φ_G is over 0.5, the K of two component solution are greater than a single component solution, which indicates the synergistic viscosity feature of the mixed solution. To further study this, the apparent viscosity of two component solutions, supposed that they are the ideal mixed solution that ignores the interaction of molecules, is calculated by the following equation [23].

$$\mathrm{Log}\eta_c = \Phi_G \log\eta_{GG} + (1 - \Phi_G)\log\eta_{CMG} \tag{2}$$

where η_c is the viscosity of the mixed solution, Φ_G is the weight fraction of the GG solution, η_{GG} and η_{CMG} is the viscosity of the GG and CMG solution, respectively. As listed in Table 3, it is interesting to find that the measured viscosity (η_m) of the mixed solution has a positive deviation with respect to its calculated viscosity (η_c) at

Table 3 The measured viscosity (η_{m}, mPa.s) and the calculated viscosity (η_c, mPa.s) of GG solution, CMG solution and their mixed solutions reflectively with various Φ_G under different shear rates

Shear rate (s^{-1})		Φ_G								
		0	0.2	0.25	0.33	0.5	0.67	0.75	0.8	1.0
3.0	η_m	622.3	824.7	897.2	990.7	1100.0	1189.0	1228.0	1165.0	1053.0
	η_c		691.3	709.8	740.3	809.5	885.2	923.3	947.9	
10.0	η_m	407.8	505.5	540.6	582.2	630.9	665.3	682.7	655.5	597.7
	η_c		440.2	448.7	462.2	493.7	526.9	543.2	553.7	
32.5	η_m	235.0	271.4	286.2	301.5	319.3	328.9	336.0	326.5	301.4
	η_c		247.0	250.1	255.1	266.1	277.6	283.2	286.8	
72.5	η_m	144.7	160.1	167.1	173.7	181.0	184.4	188.0	183.7	170.9
	η_c		149.6	150.8	152.9	157.3	161.8	163.9	165.3	
155.6	η_m	94.6	102.0	105.8	109.1	112.6	113.7	115.7	113.5	106.1
	η_c		95.6	97.4	98.3	100.2	102.2	103.1	103.7	
433.3	η_m	50.2	52.4	53.8	54.9	55.8	55.8	56.6	55.7	52.7
	η_c		50.6	50.8	51.0	51.4	51.8	52.0	52.1	

Total polymer concentration is 0.6% (30 °C)

all shear rates and mixed ratios. As expected, there exists viscosity synergism in the mixed solution of GG and CMG.

The positive deviation means the enhancement of viscosity, which is the expected result. This behavior can be demonstrated by the change of network structure which is mainly responsible for the enhancement of viscosity. Most carboxymethyl groups, branched the molecular chains of galactomannan, change the regular network structure which is formed by the entanglement of galactomannan molecules. The form of network structure may be basically dependent on the interaction of molecules, especially hydrogen bonding in this system [24]. Adding of carboxymethyl group helps to enhance the effect of hydrogen bonding. The oxygen atom of carboxyl group has a larger contribution to hydrogen bonding than that of hydroxyl group due to the larger electronegativity. Thus, with the quantitative change of carboxymethyl group, the new formed network is modulated, and the degree of viscosity enhancement will be also varied.

Indeed, there are differences in the degree of viscosity synergism because of various shear rates and mixed ratios. As shown in Fig. 4, the positive deviation increases with the decrease of the shear rate. It indicates that the shear stress overcomes the resistance with effecting on the interaction of the molecular chains. In order to compare the degree of synergism, the relative positive deviation (RPD) is defined as follows:

$$\mathrm{RPD} = 1 - \eta_c/\eta_m \tag{3}$$

with the concentration of GG, the change of RPD is shown in Fig. 5. Note that a maximum value of RPD varies with the change of shear rate. At low shear rate, it reaches the maximum value when Φ_G is 0.5. However, while the shear rate increases, the value of RPD for $\Phi_G = 0.75$ increases gradually. And eventually the

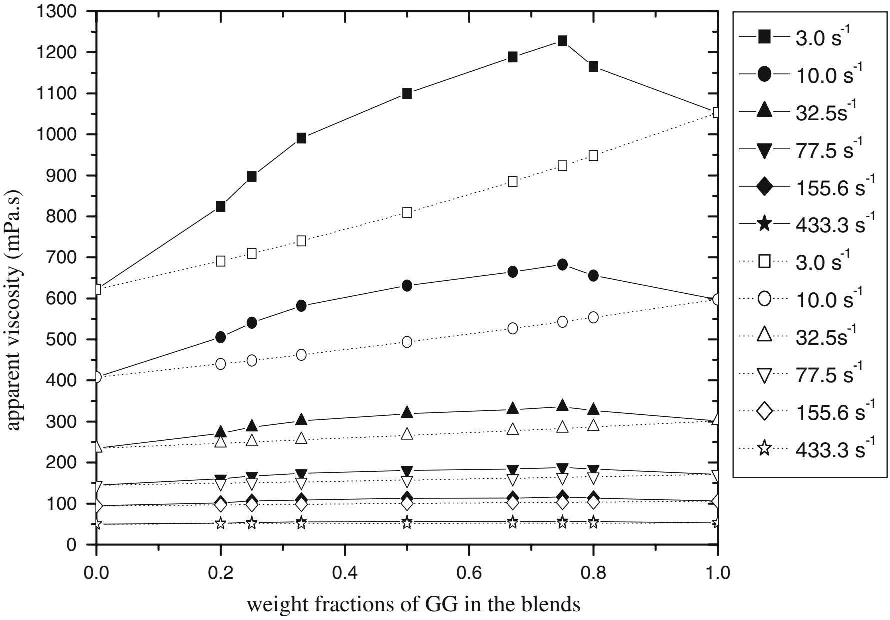

Fig. 4 Apparent viscosity of the mixed solution of GG and CMG with various Φ_G under different shear rates. Total polymer concentration is 0.6% (30 °C). The *empty symbols* are the calculated value

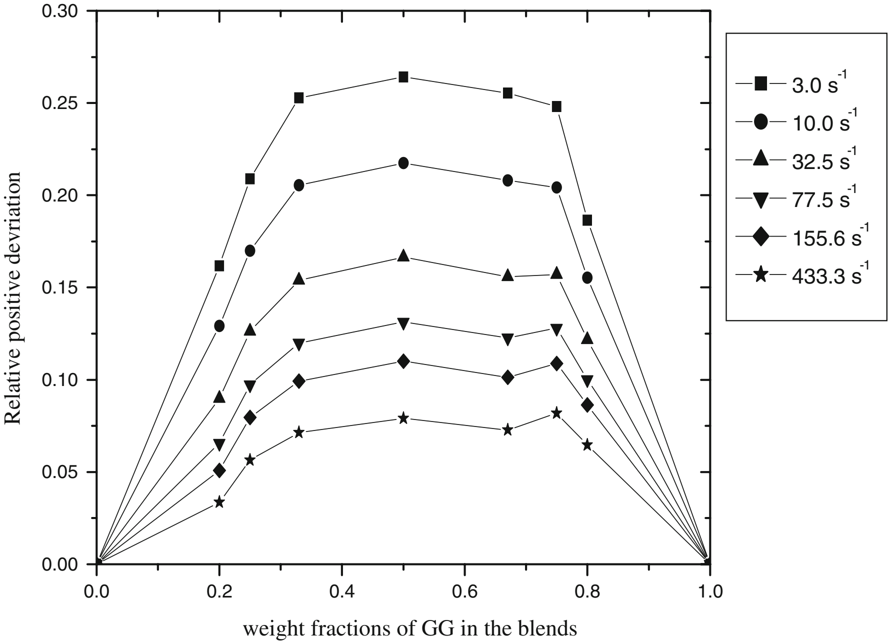

Fig. 5 The change of relative positive deviation (RPD) with the various Φ_G under the different shear rates. Total polymer concentration is 0.6% (30 °C)

Fig. 6 Effect of temperature on the viscosity of GG (*black invert triangle*), of CMG (*black square*) and of the blends [$\Phi_G = 0.5$ (*black circle*), 0.75 (*black triangle*)], total polymer concentration is 0.6% and the shear rate is 10 s^{-1}

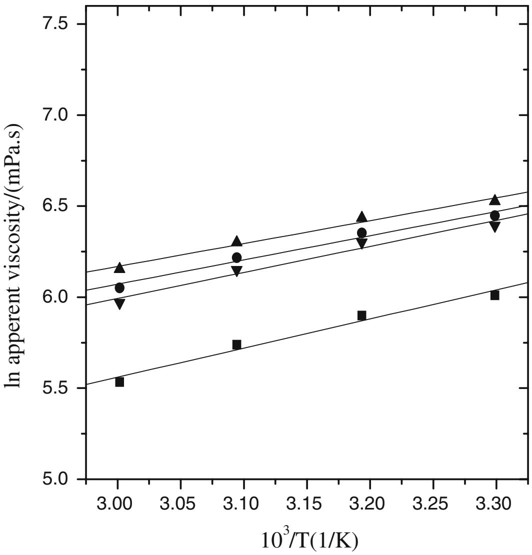

Table 4 The activation energy of the solution of GG, of CMG and of the blends ($\Phi_G = 0.5$, 0.75) under shear rate is 10 s^{-1}

Sample	E_a (kJ mol^{-1})	R^2
CMG solution	13.23	0.981
The blend ($\Phi_G = 0.5$)	11.02	0.992
The blend ($\Phi_G = 0.75$)	10.39	0.995
GG solution	11.80	0.989

value of RPD reaches the peak when the shear rate is 433.3 s^{-1}. It is clear that the network structure varies with the shear rate.

The temperature-dependence of viscosity synergism can be described by the simple Arrhenius-type equation.

$$\eta = A \exp\left(\frac{E_a}{RT}\right) \tag{4}$$

The pro-exponential factor A is the viscosity limit value for T_∞, if no other thermal processes were to occur at high temperature, R is the gas constant, and E_a is the activation energy for viscous flow.

Figure 6 shows the plots of ln η versus $1/T$ for the solution of GG, of CMG and of the blends ($\Phi_G = 0.5$ and $\Phi_G = 0.75$) taken as examples. Though the viscosity decreases with increasing the temperature for these samples, the viscosity of the blends is greater than that of single component solution. E_a reflects the sensitivity of the viscous solution toward the temperature, and its values are listed in Table 4. Note that the E_a of the blends has smaller value than that of the single component solution. It is indicated that the suitable mixed ratio of GG and CMG can improve the temperature tolerance of either GG or CMG solution. Therefore, in the course of application, the disadvantage of resisting temperature for CMG can be improved. It is the main reason for the modification of macromolecular chains.

Conclusions

Firstly, this study indicates that the solution of guar gum, of carboxymethyl guar gum and of their blends with various mixed ratios exhibits evidently shear-thinning feature. The flow curves are satisfactorily fit for the power law model. And, at the mixed system, with the addition of carboxymethyl guar gum, the degree of shear-thinning is weakened, especially when the weight fraction of carboxymethyl guar gum is greater than 0.5. Moreover, the increase of temperature weakens both thickening and shear-thinning properties of the aqueous solution of galactomannan. Secondly, the viscosity synergism is observed in the mixed solutions, and is modulated with the change of ratio of components, shear rates and temperatures. At the same temperature, there exists the maximum viscosity when Φ_G is 0.75 at low shear rate. However, the maximum increasing degree of viscosity is observed at the 0.5 of Φ_G. When the shear rate is increased gradually, the result is the opposite of that. In addition, the suitable mixed ratio of GG and CMG can improve the temperature tolerance of either GG or CMG solution, because the E_a of the mixed solution (for example, Φ_G is 0.5 or 0.75) is less than that of a single component solution. In a word, these obtained results are mainly attributed to the effect of carboxymethyl group branched the galactomannan, which include the interaction of electrostatics force and space resistance.

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