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ORIGINAL CONTRIBUTION

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Aqueous polysaccharide blends based on hydroxypropyl guar gum and carboxymethyl cellulose: synergistic viscosity and thixotropic properties

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Abstract Aqueous polysaccharide blends, formed from 2.5% (*w*/*v*) solution of hydroxypropyl guar gum (HPG) and 2.5% (*w*/*v*) solution of carboxymethyl cellulose (CMC) according to different blending ratios, were investigated at 20 °C in terms of their shear-dependent viscosity and thixotropic properties. The Cross viscosity equation was found to fit the shear-dependent viscosity data with reasonable accuracy. When the HPG solution with the mass fraction (f_{HPG}) of 0.87 was mixed, the zero shear viscosity (η_o) of the corresponding blend was found to be 168.5753 Pa s, while the η_o values of component HPG and CMC solutions were found to be 3.3859 and 98.6525 Pa s, respectively. For the aqueous HPG/CMC blends investigated, the resulting zero shear viscosity was observed to be much greater than the combined zero shear viscosity of the component polysaccharide solutions, showing a synergistic viscosity property. The quantitative determination of the hysteresis loop area, developed during viscometer tests on shear rate–shear stress reverse paths, was used to describe the thixotropic behavior. When compared with aqueous solutions of the component polysaccharides, these polysaccharide blends could afford enhanced thixotropic property. Maximum thixotropy synergism was observed for the HPG/CMC blend with the f_{HPG} of 0.67.

Keywords Aqueous polysaccharide blends · Hydroxypropyl guar gum · Carboxymethyl cellulose · Zero shear viscosity · Thixotropy · Synergistic behavior

Introduction

During the last decades, aqueous polysaccharide blends have extensively been studied with respect to their viscosity or rheological properties. This is due mainly to their intrinsic scientific interest and possible pharmaceutical, biotechnological, and industrial applications. Zhang [1] investigated viscosity properties of aqueous carboxymethyl cellulose (CMC)/hydroxyethyl cellulose blends at different blending ratios, shear rate, and temperatures and found that such blends exhibited viscosity synergism at all blending ratios, as well as improved shear and temperature stability. Casas and Garcia-Ochoa [2] measured the viscosity of aqueous xanthan/locust bean gum blends and observed a dramatic increase in these blends in comparison with the combined viscosity of the separated polysaccharide solutions. On the other hand, Florjanci et al. [3] studied the rheological properties of aqueous sodium CMC/xanthan under destructive and nondestructive shear conditions and evaluated the synergistic/ono-synergistic effects of these polysaccharide systems. Pai and Khan [4] examined the rheological behavior and synergistic character of aqueous xanthan/enzyme-modified guar blends and found that the extent of synergism in terms of the gel elastic modulus and yield stress increased with increasing extent of enzymatic modification. Moreover, aqueous polysaccharide blends composed of galactomannan and other biopolymers, such as xanthan [5], starch [6], or k-carrageenan [7], were also studied for their rheological characteristics. Recently, Chaisawang and Suphantharika [8] investigated the effects of guar gum and

xanthan gum additions on physical and rheological properties of cationic tapioca starch and found that guar gum was more effective than xanthan gum in terms of increasing peak viscosity due to its ability to increase the swelling power and solubility index. Yoo et al. [9] studied the rheological properties of rice starch–galactomannan mixtures at different concentrations of guar gum and locust bean gum in steady and dynamic shear, and found that such mixtures showed high shear-thinning flow behaviors with high Casson yield stress. In particular, the synergistic behavior found in aqueous polysaccharide blends is commercially valuable because it often leads to new desirable physicochemical properties or the development of new textures, which could not be resulted from aqueous solutions of the component polysaccharides [10, 11].

In the present work, new polysaccharide blends based on aqueous solutions of hydroxypropyl guar gum (HPG) and CMC were investigated by means of a rotating viscometer for their shear-dependent viscosity and thixotropic properties. For the comparison, the component solutions of two polysaccharide derivatives were also investigated in a similar way.

Experimental

Materials

Commercial-grade HPG was kindly provided by China Agency Office of Economy Polymers and Chemicals Company of USA. Its intrinsic viscosity (η) was determined to be 931.5 ml/g at 30±0.02 °C by applying Huggins equations [12]: $\eta_{sp}/C_p=[\eta]+k_H[\eta]^2C_p$, where η_{sp} is the specific viscosity, C_p is the HPG concentration, and k_H is the Huggins constant. The CMC used in this study was purchased from Hoechst in Germany. It has a weight-average molecular weight of 5.0×10^5 g/ml according to the product information provided by the supplier. Figure 1 shows the structure of repeat units of HPG and CMC.

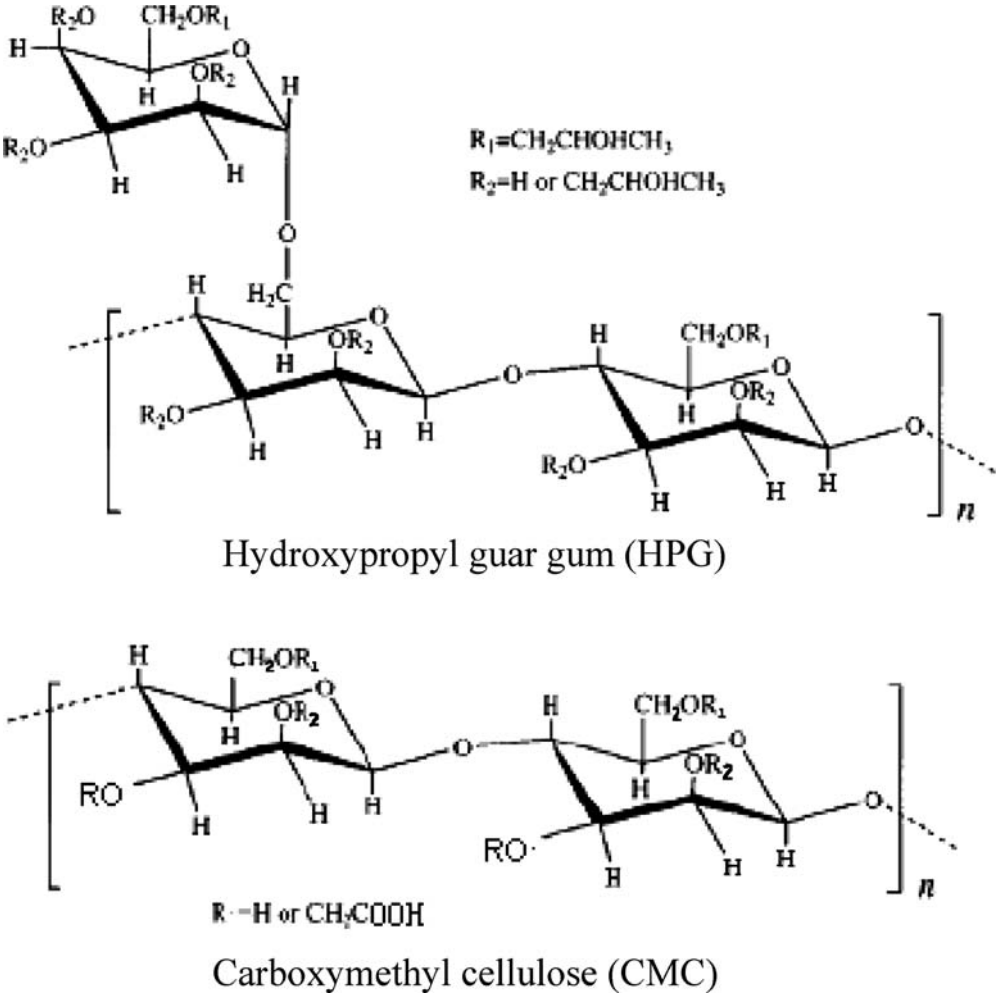

Fig. 1 The structure of repeat units of HPG and CMC

Preparation of the solutions

First, individual HPG and CMC solutions with the same concentration of 2.5% (*w*/*v*) were prepared by respectively dissolving 2.5 g dried HPG or CMC sample in 100 ml distilled water at room temperature. To ensure complete dissolution, each component solution was stirred at 300 rpm for 24 h. Then, aqueous HPG/CMC blends with various mass fractions (f_{HPG}) of HPG were prepared by adding the required mass of HPG solution into the required mass of CMC solution under agitation (pH 6.0~7.0). For this investigation, four mass fractions of HPG in the blends, corresponding to four blending ratios, were considered to be 0.33, 0.50, 0.67, and 0.83. Unaided and microscopic visual inspections on these polysaccharide blends investigated did not reveal any sign of phase separation.

Rheological measurements

Rheological measurements for aqueous HPG/CMC blends with various blending ratios as well as 2.5% component solutions of HPG and CMC were undertaken with the help of a rotational rheometer (Rheotest 2, 50 Hz, type RV 2) using a cylinder measuring system (S/S_1, 25 ml) at 20 °C. The temperature of the thermostat was controlled within a range of ±0.5 °C. The rheological data were calculated from the following equations:

$$\tau = \Phi \times \alpha \tag{1}$$

$$\eta = \tau/\dot{\gamma} \tag{2}$$

where Φ is the cylinder constant, α is the instrument reading, τ is the shear stress, $\dot{\gamma}$ is the shear rate, and η is the apparent viscosity.

For the investigation of the thixotropic property of aqueous HPG/CMC blends and their component solutions, the flow curves were measured by increasing the shear rate from a minimum of 3.0 s^{-1} to a maximum of 1,312 s^{-1} and then decreasing the shear rate in the same equal steps. The duration of shear at each step was about 15 min. This method is similar to that adopted by Saunders [13] when he studied the thixotropic behavior of thickened polystyrene latexes. If the polysaccharide system investigated exhibits the thixotropy, a hysteresis loop could be obtained from these "upward" and "downward" curves developed during round-trip shear stress–shear rate paths, and the corresponding enclosed area could be used to evaluate the magnitude of the thixotropy.

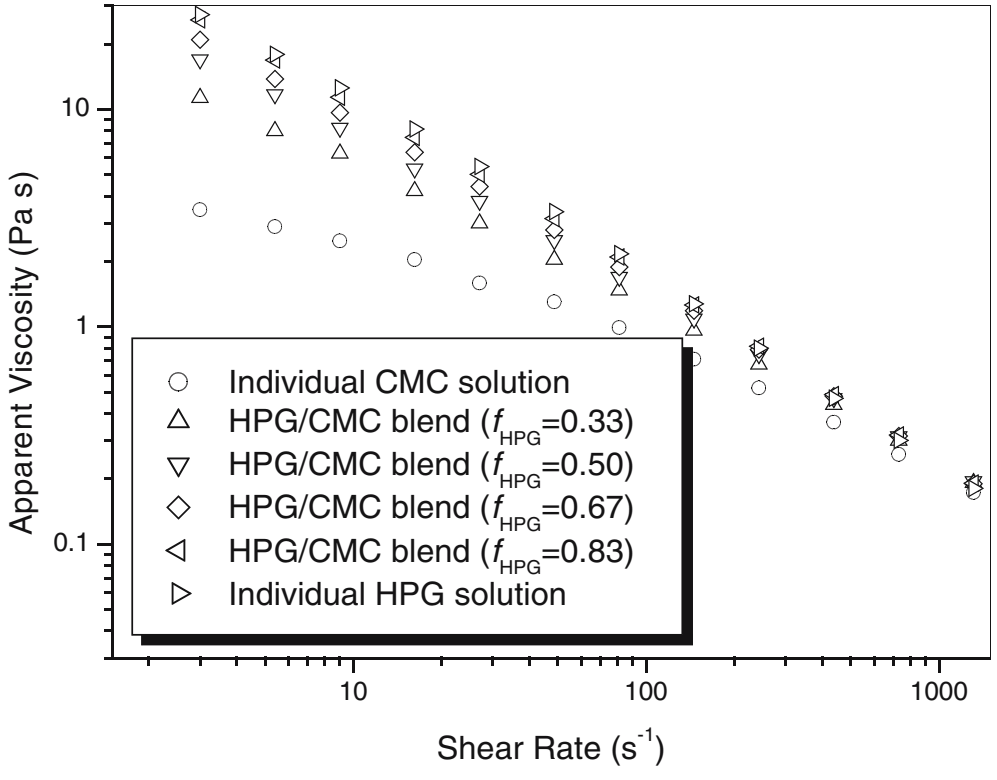

Fig. 2 Apparent viscosity vs shear rate for aqueous HPG/CMC blends with different f_{HPG} values and two component solutions (total polysaccharide concentration, 2.5%; temperature, 20 °C)

Table 1 Regressed parameter values of Cross viscosity model fitting to the flow curves for aqueous HPG/CMC blends with different f_{HPG} values and two component solutions (total polysaccharide concentration, 2.5%; temperature, 20 °C)

Sample solutions	η_o (Pa s)	η_∞ (Pa s)	λ	m	R^2
Component solutions					
2.5% CMC	3.3859	0.0114	0.0449	0.7041	0.9999
2.5% HPG	98.6525	0.0236	1.0192	0.8627	0.9997
HPG/CMC blends					
f_{HPG}=0.33	37.7001	0.0021	1.0696	0.7185	0.9992
f_{HPG}=0.50	87.4027	0.0142	1.7884	0.7650	0.9999
f_{HPG}=0.67	121.5618	0.0046	2.0357	0.7874	0.9999
f_{HPG}=0.83	168.5753	0.0083	2.2608	0.8163	0.9999

HPG Hydroxypropyl guar gum, *CMC* carboxymethyl cellulose

Results and discussion

Figure 2 gives the relationships between apparent viscosity and shear rate for aqueous HPG/CMC blends with various f_{HPG} and two component solutions. For all polysaccharide systems investigated, the apparent viscosity was observed to decrease with the increase of shear rate, showing a typical non-Newtonian shear-thinning behavior. This shear-thinning nature of individual HPG or CMC solution was also identified by Vennkataiah and Mahadevan [14] and Ghannam and Esmail [15].

As a further investigation, the experimental data shown in Fig. 1 were correlated with different rheological models suitable to describe the flow properties of non-Newtonian pseudoplastic fluids, such as Ostwald–Dewaele model [16], Carrean model [17], Quemada model [18], and Cross model [19]. As a result, the following Cross viscosity model was found to provide the best fitting so that it could be used to describe the shear-thinning behaviors of aqueous HPG/CMC blends and their component solutions:

$$\eta = \eta_\infty + (\eta_o - \eta_\infty) \Big/ (1 + \lambda \dot{\gamma}^m) \tag{3}$$

in which η_o is the zero shear viscosity, η_∞ is the infinite shear viscosity, λ is a characteristic time, and m is an exponent. Table 1 gives the values of Cross parameters obtained by nonlinear curve fittings and corresponding regression coefficients (R^2). It was noticed that when the aqueous HPG solution was added into the aqueous CMC

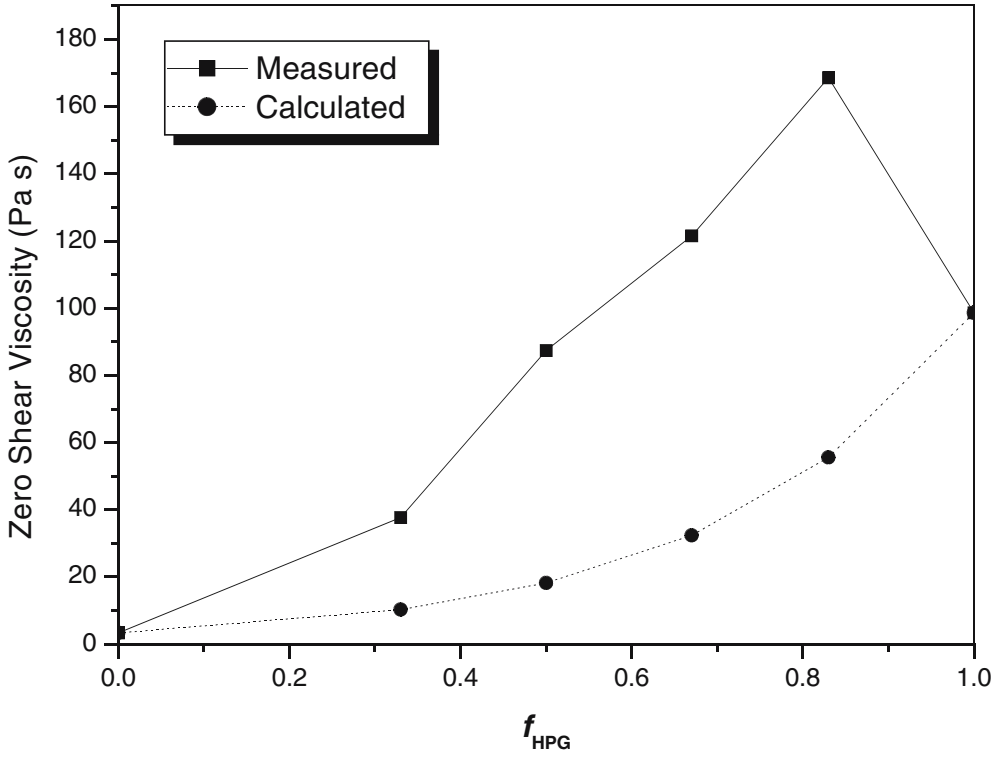

Fig. 3 The measured and calculated zero shear viscosities for aqueous HPG/CMC blends with different f_{HPG} values (total polysaccharide concentration, 2.5%; temperature, 20 °C)

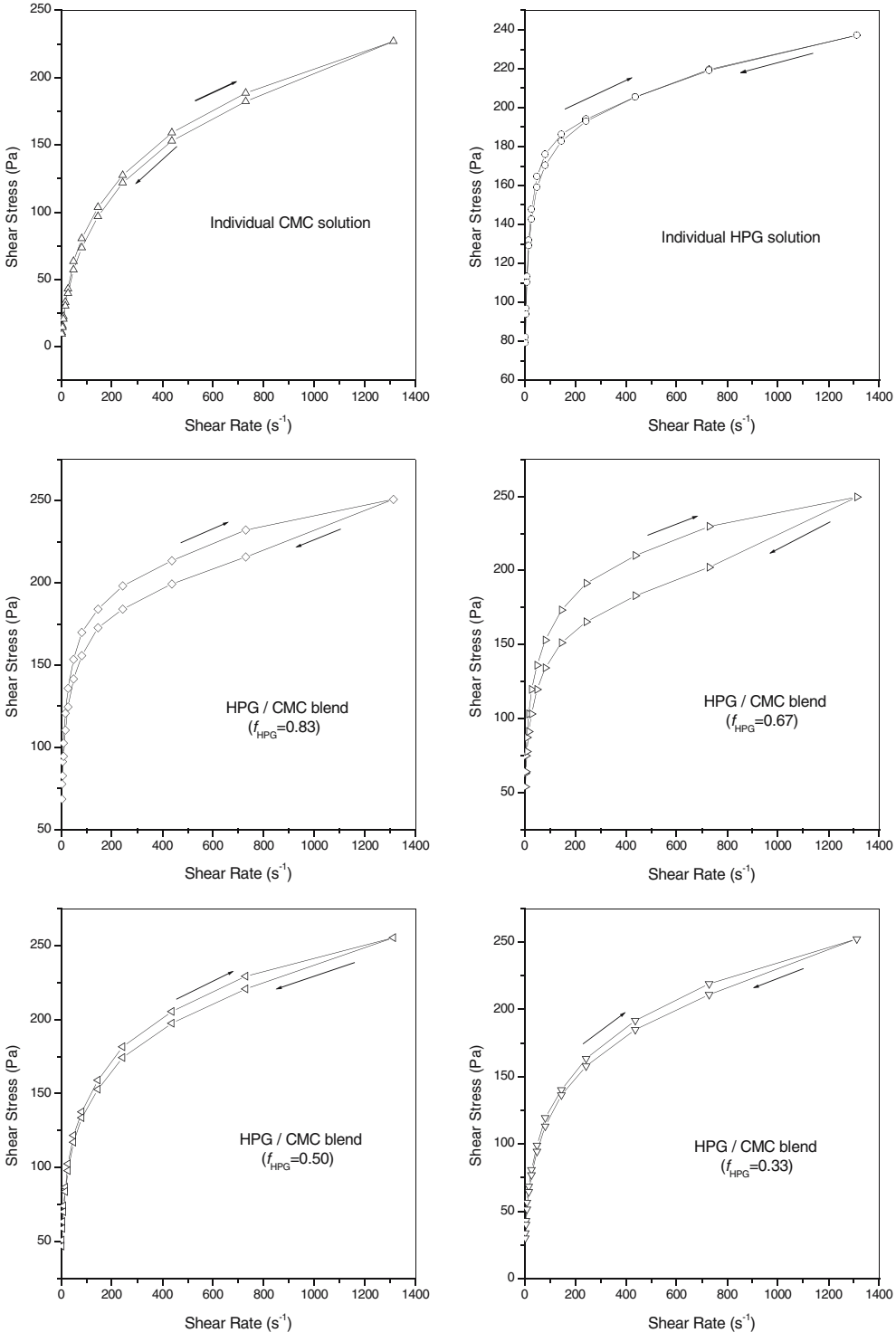

Fig. 4 Thixotropic response of aqueous HPG/CMC blends with different f_{HPG} values and their component solutions (total polysaccharide concentration, 2.5%; temperature, 20 °C)

solution, both the zero shear viscosity η_o and the characteristic time λ obtained for corresponding polysaccharide blends had an increase in comparison with those obtained for pure CMC solution. In some cases, the η_o and λ values of aqueous HPG/CMC blends were greater than those of two component polysaccharide solutions.

In a blend, the constituent polymers may be either thermodynamically compatible or incompatible. It was known [20, 21] that compatible blends with specific

interactions lead usually to the positive deviation in rheological properties, such as viscosity, modulus, die swell, etc. According to the additivity rule for an aqueous ideal blend without any interactions [22], the additive value ($\eta_{o,calculated}$) of zero shear viscosity for aqueous HPG/CMC blend could be obtained using the following equation:

$$\ln\eta_{o,calculated} = f_{HPG}\ln\eta_{o,HPG} + (1 - f_{HPG})\ln\eta_{o,CMC} \quad (4)$$

where f_{HPG} is the mass fraction of the HPG in aqueous HPG/CMC blend, and $\eta_{o,HPG}$ and $\eta_{o,CMC}$ are the measured zero shear viscosity of aqueous HPG and CMC component solutions, respectively. Figure 3 gives the measured and calculated zero shear viscosities for aqueous HPG/CMC blends with various mass fractions (f_{HPG}) of HPG. It is interesting to find that the measured value ($\eta_{o,measured}$) is higher than the $\eta_{o,calculated}$ value for aqueous HPG/CMC blend, regardless of the blending ratios, showing a positive deviation in the zero shear viscosity. This fact demonstrated that there was a synergistic effect when aqueous HPG solution was blended with aqueous CMC solution. This synergistic viscosity property was also found for other aqueous polysaccharide blends [1–3]. It is reasonable to consider that the formation of interpolymer complex between the mixed HPG and CMC components, which leads to excluded volumes and network structures, may be attributed to the viscosity synergism.

It is known [13] that the thixotropy of a polymer solution is quantified by the solution ability to regain its gel structure when the solution is allowed to rest for a longer period of time, which is usually attributed to the breakdown/alignment of the polymer chains or segments. To characterize the thixotropic property of aqueous HPG/CMC blends with different f_{HPG} values and their component solutions, the "upward" and "downward" curves developed during round-trip stress–shear rate paths were presented in Fig. 4, and the areas of the corresponding hysteresis loops were determined in Fig. 5. As can be seen, the hysteresis areas of four HPG/CMC blends studied are greater than those of the two component polysaccharide solutions, showing synergistic thixotropic property. In particular, maximum thixotropy synergism was observed for the HPG/CMC blend with the f_{HPG} of 0.67. To our knowledge, such thixotropic behavior has not been revealed for other aqueous polysaccharide blends.

Conclusions

Aqueous HPG/CMC blends behaved as non-Newtonian shear-thinning fluids. Their shear-dependent viscosity behavior could be described using Cross viscosity model with reasonable accuracy. The resulting zero shear viscosity was found to be greater than the calculated zero shear viscosity determined by the additivity rule for ideal two-component solution mixture. Moreover, the hysteresis areas of all HPG/

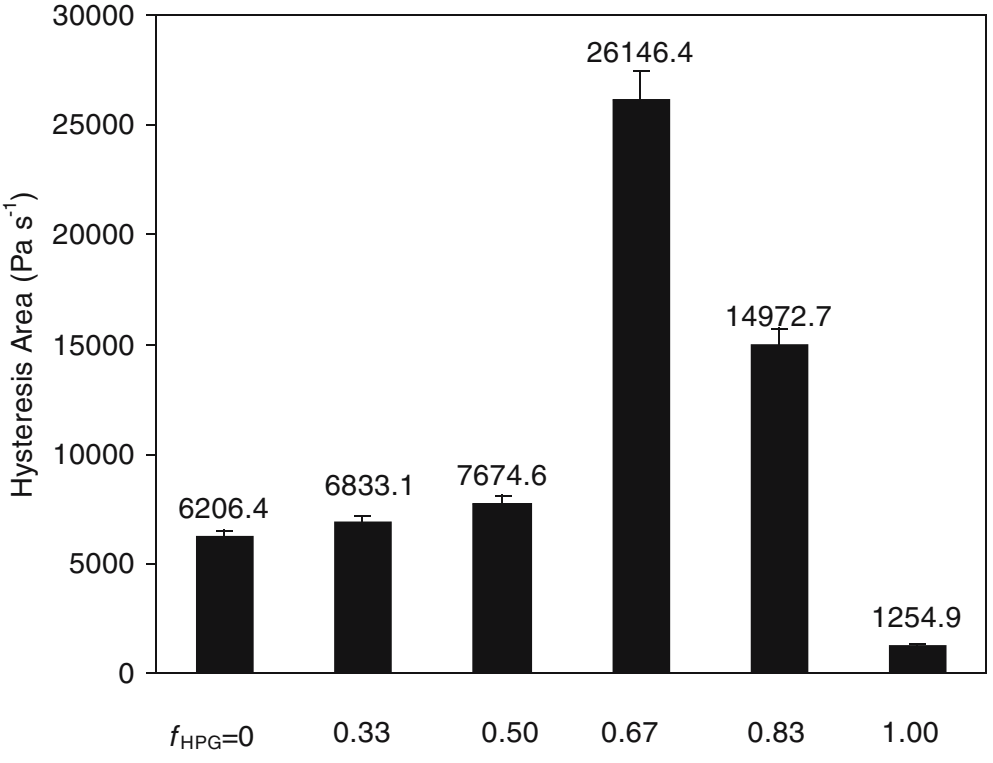

Fig. 5 Hysteresis areas of aqueous HPG/CMC blends with different f_{HPG} values and their component solutions (total polysaccharide concentration, 2.5%; temperature, 20 °C)

CMC blends studied are greater than those of the two component polysaccharide solutions. These facts indicated that HPG could interact synergistically with CMC in aqueous solutions, which resulted in synergistic viscosity and thixotropic properties with commercial importance.

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