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SHORT COMMUNICATION

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Synergistic blends from aqueous solutions of two cellulose derivatives

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Abstract Homogeneous blends of two solutions of carboxymethylcellulose and hydroxyethylcellulose (HEC) were studied with respect to viscosity properties at different blending ratios, shear rates and temperatures. The blends exhibited viscosity synergism at all blending ratios, as well as improved shear and temperature stability. Maximum synergism was observed for the blend containing 67% of HEC. The UV and IR spectra showed that the hydrogen-bonding interaction between the blended components is the main reason for the synergism.

Key words Synergistic blend · Carboxymethylcellulose · Hydroxyethylcellulose · Viscosity · Interpolymer complexation

Introduction

Certain combinations of aqueous polymer solutions have recently attracted great interest [1–7]. It is known that macromolecules in solution often interact with each other, resulting in excluded volumes and ordered structures through the formation of interpolymer complexes [8]; therefore, such systems may possess unique properties that are different from those of the individual components and there is potential in utilizing these blends in many formulated products.

Water-soluble carboxymethylcellulose (CMC) and hydroxyethylcellulose (HEC) have a very wide range of applications in industry because of their viscosity properties in aqueous solution. They are also becoming more popular due to increasingly stringent environmental regulation. In the oil industry, for example, they can be used as viscosifiers and filtrate-loss controllers for drilling fluids, gelling agents for fracturing fluids, water-plugging/profile-modifying polymers and flooding agents for enhanced oil recovery (EOR) [9]. In food, pharmaceutical and cosmetics products, water-based paints and the textile industry, they can function as thickeners or viscosity-increasing agents [10–12]. Up to now, many studies on individual CMC or HEC solutions have been carried out [13–15]; however, there are no reports on blends of solutions of CMC and HEC. In this work, the viscosity properties of CMC–HEC blends and the interaction between the blended components were investigated.

Experimental

Materials

Commercial samples of CMC and HEC obtained from Hoechst Co., Germany, were used. The molecular weight of CMC is 1.40×10^6 (0.01 M aqueous NaCl solution, 25 °C) and the molecular weight of HEC is 4.56×10^5 (H_2O, 25 °C), determined by viscosity methods [16, 17]. These cellulose ethers were used without purification.

Methods

A solution of each cellulose ether was prepared by dissolving 1.2 g in 100 ml distilled water. Each solution was then stirred and aged for 24 h to ensure complete dissolution. Then, the CMC–HEC blends with different weight fractions of HEC, W_{HEC}, were prepared by mixing uniformly the two polymer solutions with the same concentration at room temperature under agitation (pH 6–7).

The viscosity properties were studied with the help of a rheometer (Rheotest 2, 50 Hz, type RV 2) using a cylinder measuring system (S/S_1, 25 ml, range) under various conditions. The rheological data were calculated from the following equations:

$$\tau_{\mathrm{r}} = z \times \alpha \qquad (1)$$

$$\eta_{\mathrm{a}} = (\tau_{\mathrm{r}}/D_{\mathrm{r}}) \times 100 \ , \qquad (2)$$

where z is the cylinder constant, α is the reading on the indicating instrument, τ_r is the shear stress, D_r is the shear rate and η_a is the apparent viscosity. For IR measurements, the blend ($W_{HEC} = 0.67$) was precipitated by acetone. After filtration and washing with distilled water, the precipitate was dried in an oven and was then ground. Its FTIR spectrum as well as that of CMC, HEC and their mixture ($W_{HEC} = 0.67$) were recorded on a Perkin-Elmer 1650 FTIR spectrophotometer using the KBr technique. The concentrations of the CMC solution, the HEC solution and their blend ($W_{HEC} = 0.5$) for UV/vis spectroscopy measurements were 8 g/dm^3 and the UV spectra were recorded on a Shimadzu UV-240 spectrophotometer.

Results and discussion

The observed and calculated apparent viscosity for various CMC–HEC blends at shear rates of 3.0, 9.0, 16.2, 27.0 and 48.6 s^{-1} are shown in Fig 1. The observed apparent viscosity ($\eta_{a,obs}$) is determined from Eqs. (1) and (2) by experimental measurements. The calculated value ($\eta_{a,cal}$) is determined by the following additivity rule [18, 19]:

$$\log \eta_B = \sum W_i \log \eta_i \ , \tag{3}$$

where η_i is the solution viscosity of the ith component, η_B is the solution viscosity of the polymer blend and W_i is the weight fraction of the ith component. According to the Catsiff and Hewett concept [20], for an ideal blend system, the differences between the observed and calculated values should be zero throughout. For the CMC–HEC blends, however, the $\eta_{a,obs}$ of the blends has a positive deviation with respect to its $\eta_{a,cal}$ at all shear rates and blending ratios, and the positive deviation increases with the decrease in shear rate. Obviously, there is viscosity synergism between the CMC and HEC solutions. In order to compare the degree of synergism, the relative positive deviation (RPD) is defined as follows:

$$\mathrm{RPD} = 1 - \eta_{a,cal}/\eta_{a,obs} \ . \tag{4}$$

The variation of RPD with the weight fraction of HEC (W_{HEC}) is shown in Fig. 2. As shown, the RPD is a maximum for the blend with a W_{HEC} of 0.67, regardless of shear rate. This shows that maximum synergism can be obtained at this blend composition. From the rheological point of view, on the other hand, the positive deviation in viscosity indicates good blend compatibility between the two aqueous solutions of CMC and HEC [19]. Unaided and microscopic visual inspection of the blends does not reveal any signs of phase separation in the CMC–HEC blends.

Although there are other factors determining the degree of synergism, the viscosity enhancement may be mainly dependent on the development of hydrogen bonding between CMC and HEC in aqueous solution.

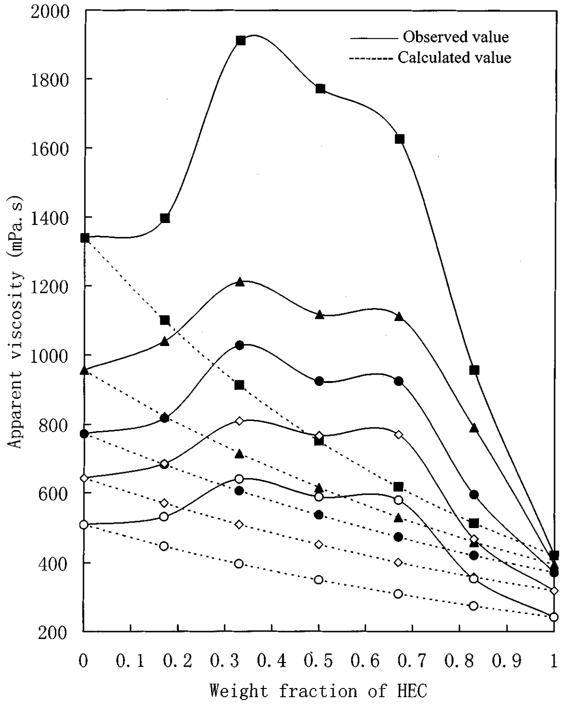

Fig. 1 Apparent viscosity of aqueous solutions of carboxymethylcellulose (*CMC*), hydroxyethylcellulose (*HEC*) and blends with different weight fractions of HEC. Shear rate: (■) 3.0, (▲) 9.0, (●) 16.2, (◇) 27.2 and (○) 48.6 s^{-1}; total polymer concentration 1.2%; 16 °C

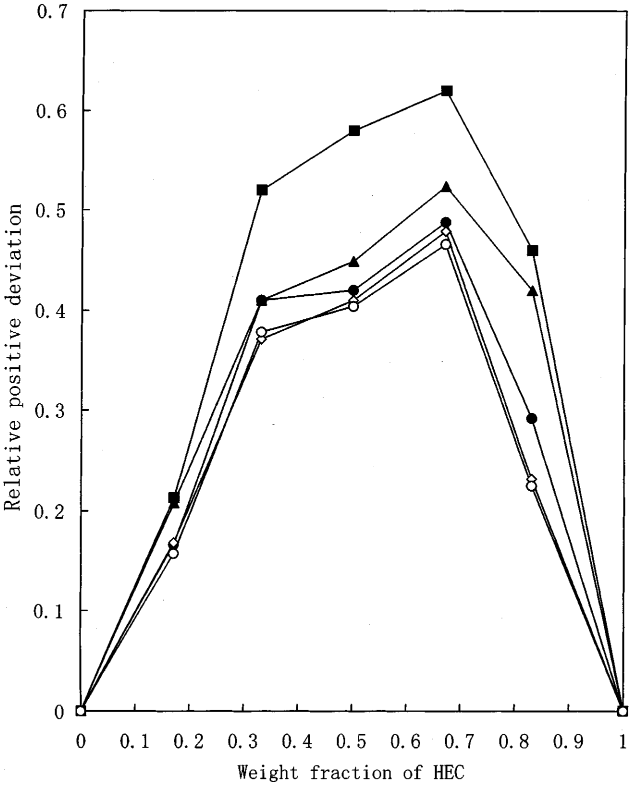

Fig. 2 Variation of relative positive deviation of apparent viscosity with the weight fraction of HEC in the CMC–HEC blends. Shear rate: (■) 3.0, (▲) 9.0, (●) 16.2, (◇) 27.2 and (○) 48.6 s^{-1}; total polymer concentration 1.2%; 16 °C

To substantiate this, spectroscopic studies were carried out. Figure 3 represents the spectra of CMC, HEC, the mixture of CMC with HEC ($W_{\mathrm{HEC}} = 0.67$) and the precipitate of the CMC–HEC blend ($W_{\mathrm{HEC}} = 0.67$). The characteristic absorption bands of CMC are located at frequencies of 3438 cm^{-1} (hydrogen-bonded O—H stretching), 2921 cm^{-1} (antisymmetric stretching of CH_2), 1616 cm^{-1} (C=O stretching in carboxyl groups) and 1058 cm^{-1} (C—O stretching), while those of HEC are located at frequencies of 3425 cm^{-1} (hydrogen-bonded O—H stretching), 2879 cm^{-1} (C—H stretching in methylene groups), 1637 cm^{-1} (H_2O molecules in non-crystalline cellulose) and 1063 cm^{-1} (C—O stretching). The spectrum of the mixture displays absorption bands at frequencies that represent the characteristic absorption bands of the individual components of the mixture. In contrast, the spectrum of the blend precipitate shows similar spectral features but the band maxima corresponding to bonded O—H groups, the C=O in carboxyl groups and the C—O ether groups appear with different intensities and, at shifted positions of 3356, 1600 and 1035 cm^{-1}, respectively. Similar phenomena were observed by Moharram et al. [7] when they used IR spectroscopy to study the interpolymer complexation of poly(acrylic acid) with polyacrylamide and they reported that hydrogen bonding is the primary mechanism of interaction between the two polymers. Thus, it is inferred that these differences in positions and intensities of the absorption bands may be attributed to the formation of an interpolymer complex resulting from the interaction between CMC and HEC at pH 6–7, most probably through hydrogen bonding. The existence of such an interaction is confirmed by the UV spectra shown in Fig. 4. In the range 190–220 nm, there is no maximum UV absorption ($\lambda_{\max}$) for the CMC solution and $\lambda_{\max}$ of the HEC solution is 199.4 nm, while $\lambda_{\max}$ of the blend ($W_{\mathrm{HEC}} = 0.5$) is 204.3 nm. According to Zhang et al. [21], the red shift of $\lambda_{\max}$ for the blend results from the hydrogen-bonding interaction. Therefore, the viscosity synergism of the CMC–HEC blends may be attributed to the hydrogen-bonding interaction between the blended components, which leads to a more-expanded conformation and a larger hydrodynamic radius.

The effect of shear rate on the apparent viscosity of aqueous solutions of CMC, HEC and their blends with different blending ratios is illustrated in Fig. 5. All data can be represented satisfactorily by the following power-law equation [22]:

$$\eta_a = KD_r^{n-1} , \qquad (5)$$

where K is the consistency index and n is the flow-behavior index. The values obtained for the rheological parameters, K and n, as well as the corresponding

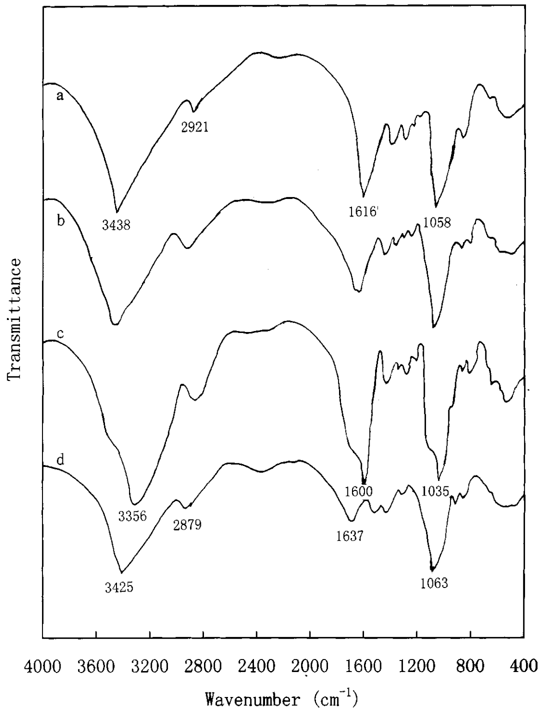

Fig. 3 FTIR spectra of *a* individual CMC, *b* the mixture of CMC with HEC ($W_{\mathrm{HEC}} = 0.67$), *c* the precipitate of CMC-HEC blend ($W_{\mathrm{HEC}} = 0.67$) and *d* individual HEC

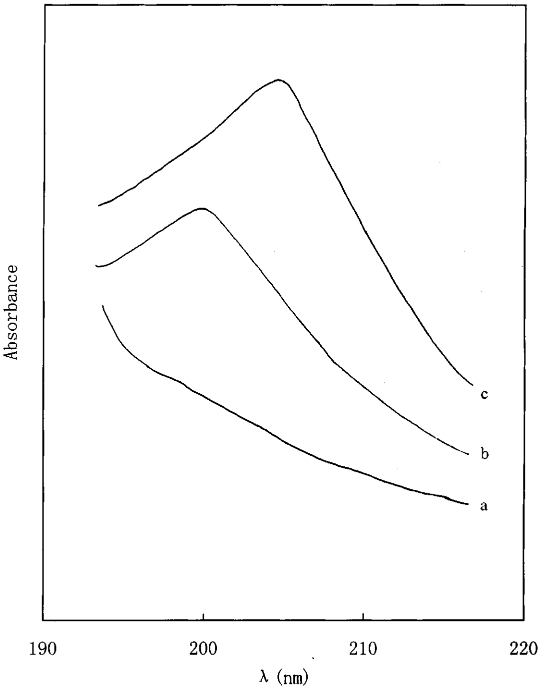

Fig. 4 UV spectra of *a* individual CMC solution, *b* individual HEC solution and *c* the blend ($W_{\mathrm{HEC}} = 0.50$)

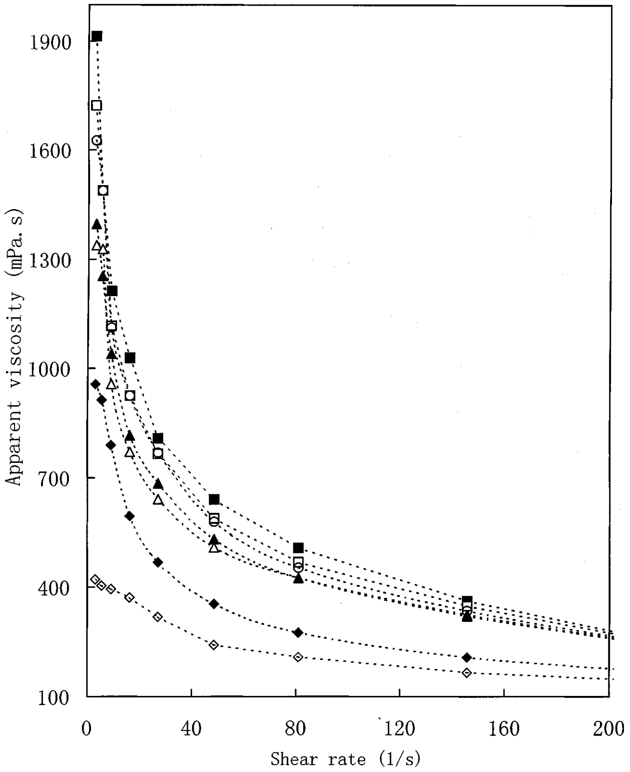

Fig. 5 Apparent viscosity versus shear rate for aqueous solutions of: CMC (△), HEC (◇) and the blends with HEC weight fractions (W_{HEC}) of 0.17 (▲), 0.33 (■), 0.50 (□), 0.67 (○) and 0.87 (◆). Total polymer concentration 1.2%; 16 °C

Table 1 Values of K and n for solutions of carboxymethylcellulose (*CMC*), hydroxyethylcellulose (*HEC*) and their blends and the corresponding determination coefficient R^2 (16 °C, total polymer concentration = 1.2%)

Sample solution	K	n	R^2
CMC	2.23	0.62	0.995
CMC–HEC blends:			
W_{HEC}			
0.17	2.57	0.59	0.999
0.33	3.09	0.58	0.995
0.50	2.97	0.58	0.998
0.67	3.06	0.56	0.997
0.83	2.07	0.54	0.998
HEC	0.94	0.70	0.995

determination coefficient R^2 are listed in Table 1. As shown, the n values are less than 1, indicating the pseudoplastic behavior of CMC, HEC and their blends. Compared with individual CMC and HEC solutions, the blends have smaller n values at all blending ratios, showing stronger non-Newtonian nature and better shear stability. In addition, greater K values were observed for the blends with W_{HEC} of 0.17, 0.33, 0.50 and 0.67, suggesting good viscosity synergism.

The effect of temperature on the apparent viscosity for aqueous solutions of CMC, HEC and their blend (W_{HEC} = 0.33) is given in Table 2. Though η_a decreases with increasing temperature for all sample solutions investigated, the η_a of the blend is greater than that of individual CMC or HEC at a given shear rate and temperature. An example of the plots of ln η_a versus T^{-1} is presented in Fig. 6 and it is found that such plots give

Table 2 Effect of temperature on the apparent viscosity for aqueous solutions of CMC, HEC and their blend (W_{HEC} = 0.33) at three shear rates (total polymer concentration = 1.2%)

T (K)	Sample solution	D_r (s^{-1}) = 48.6	81.0 η_a (mPa s)	145.8
289	CMC–HEC blend	640	507	362
	CMC	508	425	325
	HEC	242	209	166
306	CMC–HEC blend	399	326	253
	CMC	342	283	223
	HEC	237	198	157
315	CMC–HEC blend	299	254	199
	CMC	248	213	169
	HEC	207	182	149
338	CMC–HEC blend	224	188	146
	CMC	153	117	98
	HEC	103	86	67

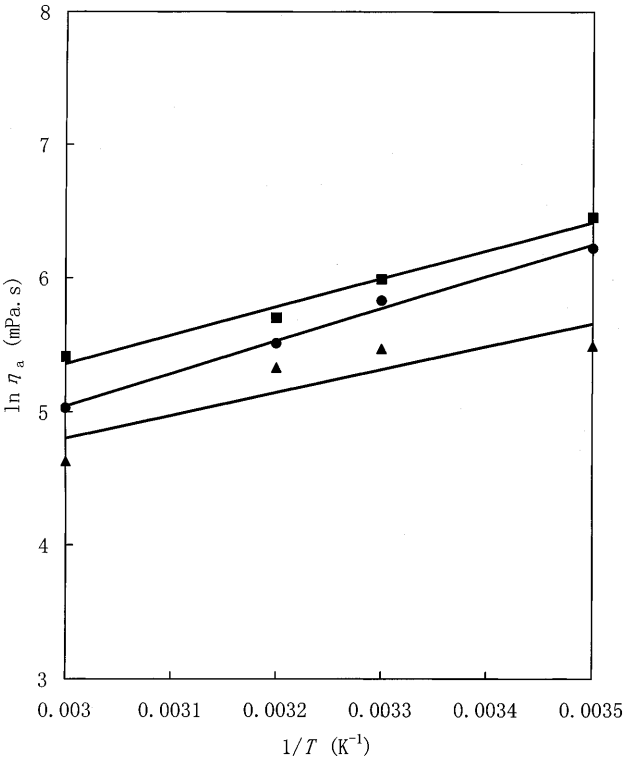

Fig. 6 Plots of ln η_a versus $1/T$ for 1.2% aqueous solutions of CMC (●), HEC (▲) and the blend (■) (W_{HEC} = 0.33). Shear rate = 48.6 s^{-1}

Table 3 Viscous flow activation (E_a) for aqueous solutions of CMC, HEC and their blend (W_{HEC} = 0.33) at three shear rates (total polymer concentration = 1.2%)

Sample solution	D_r (s^{-1}) = 48.6	81.0	145.8
		E_a (kJ mol^{-1})	
CMC–HEC blend	17.64	16.72	15.28
CMC	20.21	21.59	20.11
HEC	14.40	14.23	14.93

straight lines in all cases ($R^2 > 0.9$). This shows that the temperature effect can be explained better by an Arrhenius-type equation [23]:

$$\eta_a = A_0 \exp[E_a/(RT)] , \tag{6}$$

where E_a is the activation energy and A_0 is a pre-exponential parameter. E_a, which reflects the sensitivity of the solutions towards temperature at different shear rates, is given in Table 3. Regardless of shear rate, E_a of the CMC–HEC blend is lower than that of the individual CMC solution. This indicates that solution complexation of CMC with HEC can improve the temperature tolerance of CMC.

Conclusions

Homogeneous blends of solutions of CMC and HEC can give rise to substantially increased solution viscosity compared to solutions of the individual cellulose derivatives at the same total polymer concentration. Maximum viscosity synergism was observed for the blend with a W_{HEC} of 0.67. The blends behave as typical non-Newtonian shear-thinning fluids with a characteristic *n* parameter lower than 1 and have stronger non-Newtonian nature. Compared with CMC solution, the viscous flow activation energy of the blend is lower. Strong hydrogen bonding between the carboxyl groups along the CMC chain and the hydroxyl groups along the HEC chain effectively enhance the apparent viscosity of the blend. Such blends may be utilized to provide improved mobility control solutions for EOR in oilfields and for numerous other applications.

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