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MATHEMATICAL MODEL OF RHEOLOGICAL BEHAVIOR OF SILICA SUSPENSION IN HYDROXYPROPYL METHYL CELLULOSE SOLUTION

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Abstract. A mathematical model of rheological behavior of silica suspension in hydroxypropyl methyl cellulose solution was investigated. The model takes into account the friction between particle aggregates, particle aggregates and macromolecules in solution and the formation of well ordered layers containing solid particles with adsorbed macromolecules and macromolecules in the holes between particles in aggregates at the large shear rates. Suggested model allows to describe the rheological behavior of silica suspensions in water solution of hydroxypropyl methyl cellulose.

Key words: silica suspension, polymer, rheology, mathematical model.

1. Introduction

Dispersions of natural and synthetic materials in polymer solutions are widely used in the industry. Therefore many studies deal with the effect of polymer adsorption on the solid particles [1], the suspension flocculation by polymers and its stability [2, 3] as well as rheological behavior of suspensions in polymer solutions [4–6].

The investigation of rheological properties of silica suspensions flocculated by polyacrylamide showed [5, 6] that the elasticity of the suspension increased with the increase of adsorbed polyacrylamide amount. Rheological measurements showed [7, 8] that under small deformations the structure of suspensions is practically the same as that in their equilibrium state and under relatively large deformations, a partial or full disturbance occurs. Nonlinear relationship between shear stress and shear rate has been observed.

Rheological properties of suspensions depend on the concentration of polymer and solid particles [9, 10]. An investigation of silica suspensions in aqueous solutions of hydroxypropyl methyl cellulose (HPMC) showed that the relationship between shear rate and shear stress was linear at low silica content. At large silica concentrations one can observe three stages on the plots of steady state

shear stress against shear rate curves. Shear stress increased in the first stage till shear rate was close to 0.1 s^{-1} . Then it was constant or decreased. In the third stage, shear stress increased with the increase of shear rate and this relationship is practically linear at the shear rate more than 3 s^{-1} . Small angle neutron scattering investigations showed [11, 12] that silica dispersion has liquid-like order in equilibrium state and deformed liquid-like structure under shear rate.

We have suggested the mathematical model describing an influence of the concentration of solid particles and polymer concentration on rheological behavior of suspension.

2. Results and Discussion

The suspension contains the particle aggregates with adsorbed macromolecules and macromolecules in the holes of floccules, not chemically bounded with particles by adsorption, as well as macromolecules in solution. We suggested that adsorbed macromolecules do not break off the particles under the deformation of floccules or break up the aggregates. Macromolecules in holes of floccules can go out from particle aggregates into the solution at the floccules deformation or can enter into the holes of particle aggregates when they form the structure.

There are three friction forces in suspension under the moving: between particle aggregates, between floccules and macromolecules in solution, and between macromolecules in solution. When the particle aggregates form well ordered layers, the friction forces between particle aggregates in the layer are stronger than those between ordered layers and macromolecules in solution. Therefore, in the first approximation, the first forces do not influence the friction under the moving of suspension. In this case one can take into account only two friction forces between well ordered layers of particle aggregates and macromolecules in solution as well as between macromolecules in solution. These forces are close to each other because particle aggregates are covered with adsorbed macromolecules. Therefore, the friction occurs

between adsorbed macromolecules and macromolecules in solution.

The relationship between shear rate (γ) and shear stress (P) can be described by equation:

$$P = k_1 c_{ag} \gamma + k_2 c_M \gamma, \quad (1)$$

where k_1 is the coefficient, taking into account the friction between particle aggregates of outwardly ordered layers, c_{ag} is the volume concentration of particle aggregates, k_2 is the coefficient taking into account the friction between macromolecules in solution and between particle aggregates and macromolecules in solution, c_M is the polymer concentration in solution

$$c_{ag} = N_{ag} [n(V_p + n_a V_M) + m V_M], \quad (2)$$

where N_{ag} is the number of particle aggregates in the volume unit of suspension, n is the number of primary particles in aggregate, V_p is the volume of one primary particle, n_a is the number of macromolecules adsorbed over one primary particle, V_M is the volume of one macromolecule, m is the number of macromolecules in the holes of particle aggregate which are not adsorbed.

$$c_M = c_p - m M N_{ag} / N_A, \quad (3)$$

where c_p is the equilibrium polymer concentration in solution, M is the molecular mass of polymer, N_A is Avogadro's number.

The c_p values have been calculated from adsorption isotherms of HPMC over silica suspension particles and may be described by linear dependence according to equation:

$$c_p/A = 1/a + b/a c_p, \quad (4)$$

where A is mass of adsorbed polymer on the silica mass unit, a and b are equation coefficients.

Fig.1 shows that these data for different silica concentrations lie on the straight line according to Eq. (4). Values of a and b are found from intercept on the ordinate axis and the slope of straight line. They are equal to 0.11 cm³/g and 1.04 cm³/g correspondingly.

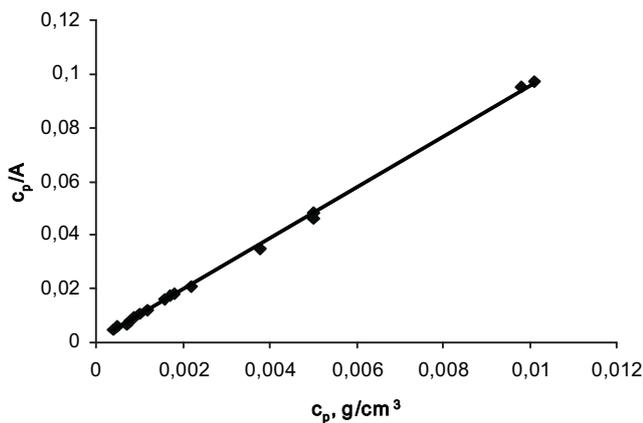


Fig. 1. Relationship between adsorption and equilibrium concentration of the polymer in HPMC adsorption solution over silica particles in suspension according to Eq. (4).

Silica concentration is changed from 0.8 to 15 g/l.

Experimental data are taken from [10].

The dependence of c_p on the initial polymer concentration (c_o) and initial silica concentration (c_s) has been calculated according to the equation:

$$c_p = -F + (F^2 + c_o b)^{1/2}, \quad (5)$$

where $F = S(1/b - c_o + a c_s/b)$, $A = (c_o - c_p)/c_s$

The data are presented in Table 1. Results show that adsorption value is practically constant at different reagent concentrations used in rheological experiments. Equilibrium polymer concentration in solution increases with the increase of initial polymer concentration in the mixture and the decrease of silica concentration. The number of macromolecules adsorbed over one primary particle of silica (n_a) is equal to 1.14.

Table 1

The values of adsorption and equilibrium polymer concentration in solution at the adsorption of HPMC on the silica suspension

Initial silica concentration c_s (g/l)	Initial polymer concentration c_o (g/l)	Equilibrium polymer concentration c_p (g/l)	Adsorption c_p/A
0.8	0.8	0.001	0.005
0.8	1.5	0.002	0.01
0.8	2.5	0.003	0.015
0.8	5.0	0.004	0.02
0.8	10.0	0.005	0.03
1.5	0.8	0.006	0.04
1.5	1.5	0.007	0.05
1.5	2.5	0.008	0.06
1.5	5.0	0.009	0.07
1.5	10.0	0.010	0.08

The number of primary particles in aggregate can be calculated according to the equation:

$$n = N_o / N_{ag}, \quad (7)$$

where N_o is the number of primary particles in the volume unit of suspension.

The Eq. (1) can be transformed into he Eq. (8) taking into account Eqs. (2), (3), and (7).

$$P = k_1 N_{ag} \{V_p + n_a V_M + m/n[V_M - k_2 M/(k_1 N_A)]\} \gamma + k_2 c_p \gamma \quad (8)$$

Fig. 2 shows that the relationship between shear stress on shear rate is really linear at large shear stress. The values of the intercepts on ordinate axis (a_1) and tangents of the slopes of straight lines (b_1) are presented in Table 2.

Taking into account $b_1 = P/\gamma$, Eq. (9) obtained from Eq. (8) has to be linear if m/n is constant for different initial concentrations of polymer and silica.

$$P/(\gamma N_{ag}) = k_1 \{V_p + n_a V_M + m/n[V_M - k_2 M/(k_1 N_A)]\} + k_2 c_p / N_{ag} \quad (9)$$

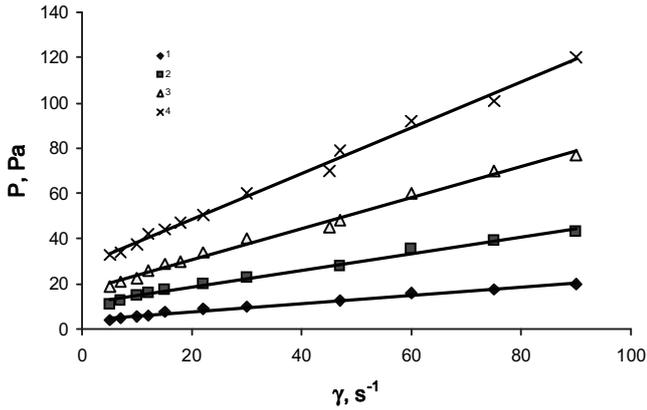


Fig. 2. Relationship between shear stress and shear rate for silica suspension in HPMC water solution for large shear rates. Silica concentration is 0.075 g/cm³, polymer concentrations are 0.02 (1), 0.0175 (2), 0.015 (3) and 0.0125 g/cm³ (4). Experimental data are taken from [10].

Table 2

Correlation coefficients and a_i and b_i values for linear relationship between shear rates and shear stress at large shear rates

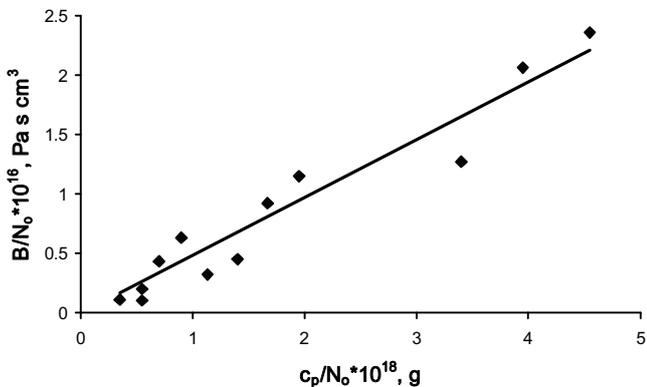
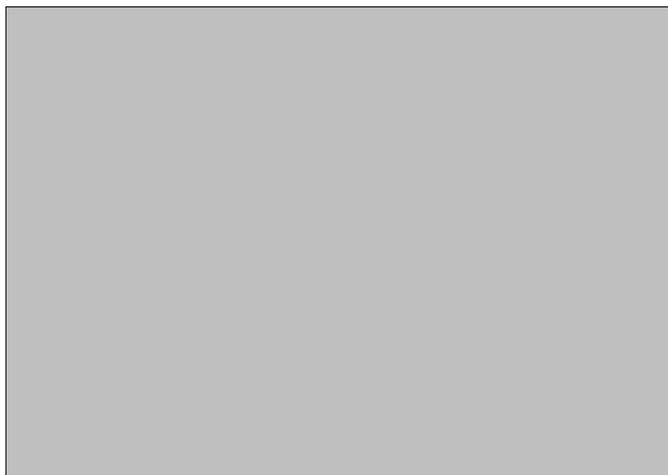


Fig. 3. Relationship between b_i/N_o and equilibrium concentration of polymer in solution calculated according to Eq. (9) at large shear rates.

Really the experimental data of the dependence of shear stress on shear rate at large shear rates lie on the straight lines according to Eq. (9) (Fig. 3). The k_2 value is close to $51 \pm 4 \text{ Pa} \cdot \text{s} \cdot \text{cm}^3 \cdot \text{g}^{-1}$. The intercept on the ordinate axis is close to zero. It is possible only if particle aggregates form the well ordered layers taking into account that the concentration of adsorbed polymer is close to the equilibrium polymer concentration in solution at the experiment. In such a case volume concentration of dispersed phase is large enough.

Really the value of

$$Y_1 = (P/\gamma - k_2 c_p) / N_{ag}, \quad (10)$$

where $Y_1 = k_1 \{V_p + n_a V_M + m/n [V_M - k_2 M / (k_1 N_A)]\}$, decreases till zero when shear rate increases at the low shear rates (Fig. 4). Therefore, the increase of shear rate leads to the increase of the concentration of particle aggregates in well ordered layers. The aggregate concentration out of the layers decreases. The a_i value in Table 2 evidently describes the properties of well ordered layers.

If one suggests that the concentration of particle aggregates outwardly ordered layers is inverse proportional to shear rate, Eq. (11) can be obtained from Eq. (9).

$$Y_2 = k_1 \{V_p + n_a V_M + m/n [V_M - k_2 M / (k_1 N_A)]\} / (\gamma_0 + \gamma) \quad (11)$$

where γ_0 is the shear rate at the formation of well ordered layers.

At the first approximation we suggested that the m/n value is constant in the whole range of shear rates. The Eq. (11) may be calculated by iteration when the γ_0 value is changed from 10^{-6} to 10.

Fig. 5 shows that the experimental data are plotted on the straight lines according to Eq. (11). The correlation coefficients and $k_1 \{V_p + n_a V_M + m/n [V_M - k_2 M / (k_1 N_A)]\}$ values are presented in Table 3.

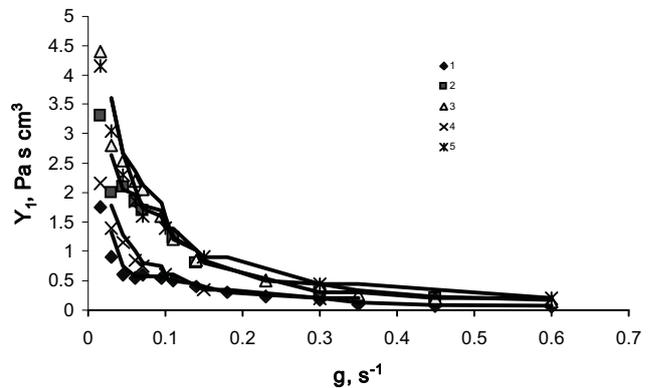


Fig. 4. Change of Y_1 at low shear rates. Silica concentrations are: 0.05 (2, 3) and 0.075 g/cm³ (1, 4-6); polymer concentrations are: 0.0125 (1), 0.02 (2), 0.0225 (3), 0.015 (4), 0.0175 (5) and 0.02 g/cm³ (6).

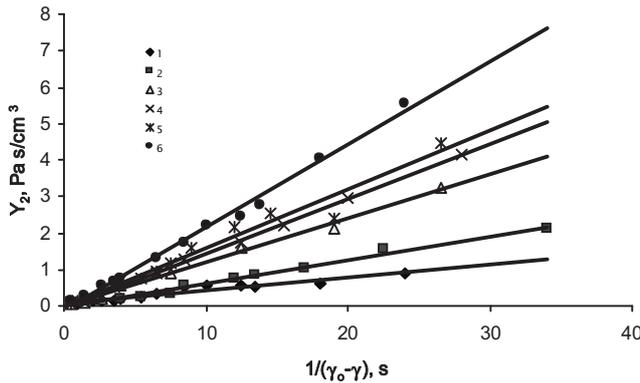
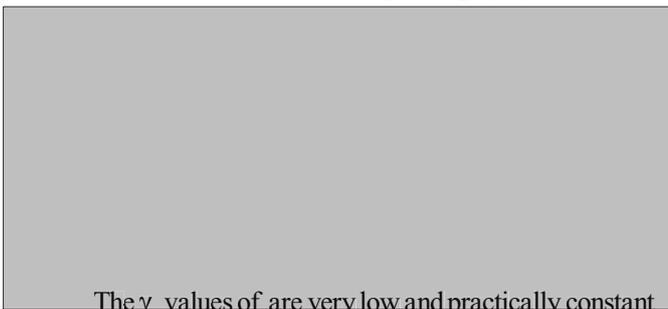


Fig. 5. Dependence of Y_2 on shear rate calculated according to Eq. (11). Silica concentrations are: 0.05 (2, 4) and 0.075 g/cm³ (1, 3, 5, 6); polymer concentrations are: 0.0125 (1), 0.02 (2, 6), 0.015 (3), 0.0225 (4) and 0.0175 g/cm³ (5).

Table 3

Correlation coefficients and the values of γ_0 and $K_1 = k_1 \{V_p + n V_M + m/n [V_M - k_2 M / (k_1 N_A)]\}$ calculated according to Eq. (11)



The γ_0 values of are very low and practically constant for different concentrations of polymer and silica. The γ_0 value increases with the increase of initial concentration of silica. It can be connected with the change of the m/n value at different reagent concentrations.

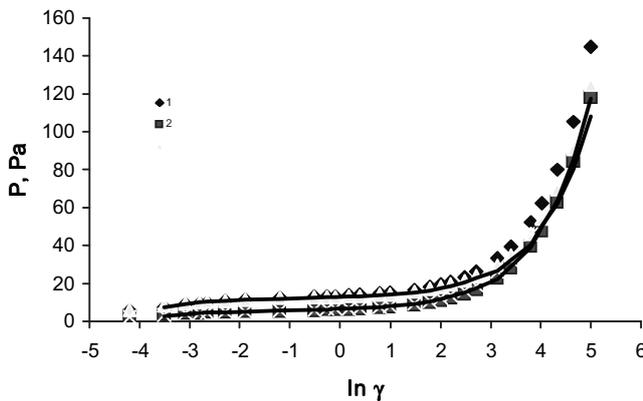


Fig. 6. Relationship between shear stress and shear rate for silica suspension in HPMC water solution. Silica concentration is 0.05 g/cm³; polymer concentrations are: 0.0225 (1) and 0.02 g/cm³ (2). Theoretical curves are calculated according to Eq. (12). Experimental data are taken from [10].

The relationship between shear rate and shear stress has been calculated according to the equation:

$$P = k_1 N_{ag} \{V_p + n V_M + m/n [V_M - k_2 M / (k_1 N_A)]\} \gamma / (\gamma_0 + r) + k_2 c_p \gamma \quad (12)$$

Figs. 6 and 7 show that the theoretical curves describe experimental data quit well. The difference between them can be explained by the change of m/n with the increase of shear rate.

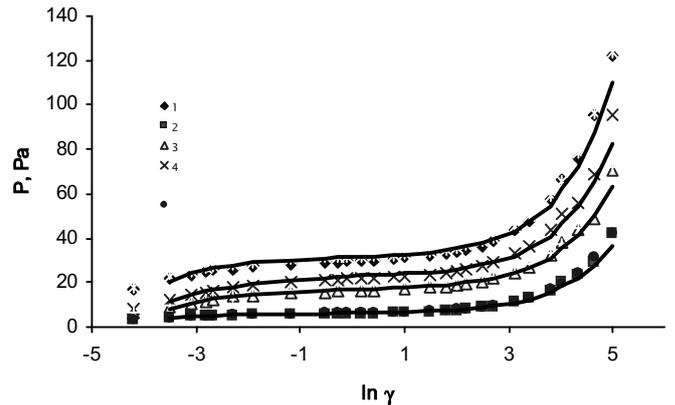


Fig. 7. Relationship between shear stress and shear rate for silica suspension in HPMC water solution. Silica concentration is 0.075 g/cm³; polymer concentrations are: 0.02 (1), 0.0175 (2), 0.015 (3) and 0.0125 g/cm³ (4). Theoretical curves are calculated according to Eq. (12). Experimental data are taken from [10].

3. Conclusions

Thus, shear stress increases rapidly as the result of friction between particle aggregates at low shear rates. The increase of shear rate leads to the formation of well ordered layers and shear stress is constant or decreases in this stage. In the third stage shear stress increases proportionally to shear rate as the result of friction between the well ordered layers of particles and macromolecules in solution as well as between macromolecules in solution.

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**МАТЕМАТИЧНА МОДЕЛЬ
РЕОЛОГІЧНОЇ ПОВЕДІНКИ СУСПЕНЗІЇ
АЕРОСИЛУ В РОЗЧИНІ
ГІДРОКСИПРОПІЛМЕТИЛЦЕЛЮЛОЗИ**

Анотація. Запропонована математична модель реологічної поведінки суспензії аеросилу в розчині

гідроксипропілметилцелюлози. Модель враховує тертя між агрегатами частинок, агрегатами частинок та макромолекулами в розчині і утворення впорядкованих шарів, які містять агрегати частинок з адсорбованими макромолекулами і макромолекулами в порах агрегатів між первинними частинками при великих швидкостях зсуву. Запропонована модель дає змогу описати реологічну поведінку суспензії аеросилу у водному розчині гідроксипропілметилцелюлози.

Ключові слова: суспензія аеросилу, полімер, реологія, математична модель.

