

## Physical Meaning of the Rheological Coefficients in the Generalized Casson Model

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**Abstract**—The coefficients of the previously proposed generalized flow model of structured systems have been interpreted. The cohesive force between particles in disperse systems has been calculated from rheological data. The number of aggregated particles in a disperse system is estimated using the kinetic equation method.

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The new rheological model proposed in [1, 2] allows one to describe flow curves of different disperse systems and relates one of the rheological coefficients to the volume concentration of a dispersed phase. Inasmuch as we used equations for smooth cylinders, it is necessary to show the meaning of the calculated coefficients for real aggregated systems.

The proposed model is valid when the energy dissipation in the system of model cylinders is the same as the dissipation energy in a real disperse system of particles prone to aggregation. The generalized Casson equation has two terms:

$$\tau^{1/2} = \frac{\tau_c^{1/2}}{1 + \chi/\dot{\gamma}^{1/2}} + \eta_c^{1/2} \dot{\gamma}^{1/2}.$$

The first term can be attributed to energy losses associated with the motion of aggregates, and the second term is due to energy losses associated with the motion of separate particles.

If a system is composed of only aggregates of medium size, the energy dissipation will be

$$\dot{E}_2 = \frac{\tau_c \dot{\gamma}}{(1 + \chi/\dot{\gamma}^{1/2})^2}.$$

If a system is composed of only separate particles, the energy dissipation will be

$$\dot{E}_1 = \eta_c \dot{\gamma}^2.$$

It follows from the generalized Casson equation that the total energy dissipation by viscous flow is determined by the formula

$$\dot{E} = \dot{E}_2 + \dot{E}_1 + 2\sqrt{\dot{E}_2 \dot{E}_1}.$$

The presence of the geometric mean term ( $2\sqrt{\dot{E}_2 \dot{E}_1}$ ) can be explained by the fact that a real system is char-

acterized by some size distribution of aggregates, from the maximal size to the size of a separate particle.

The coefficients  $\tau_c^{1/2}$  and  $\eta_c^{1/2}$  as a function of the volume concentration  $\Phi$  are described for ideal cylinders as

$$\eta_c^{1/2} = \eta_0^{1/2} \left[ \frac{1}{1 - k_1 \Phi} \right]^{A_1}, \quad (1)$$

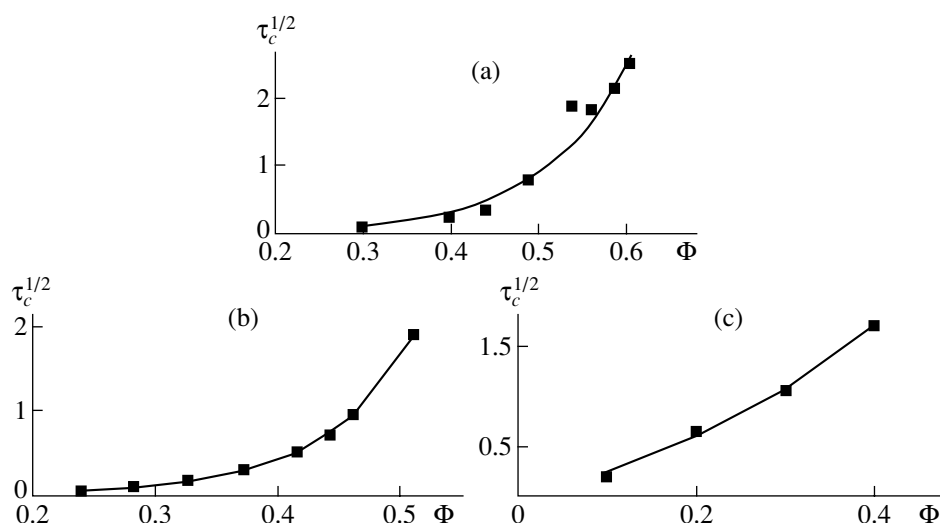
$$\tau_c^{1/2} = \tau_{0c}^{1/2} \left[ \left( \frac{1}{1 - k_2 \Phi} \right)^{A_2} - 1 \right], \quad (2)$$

where

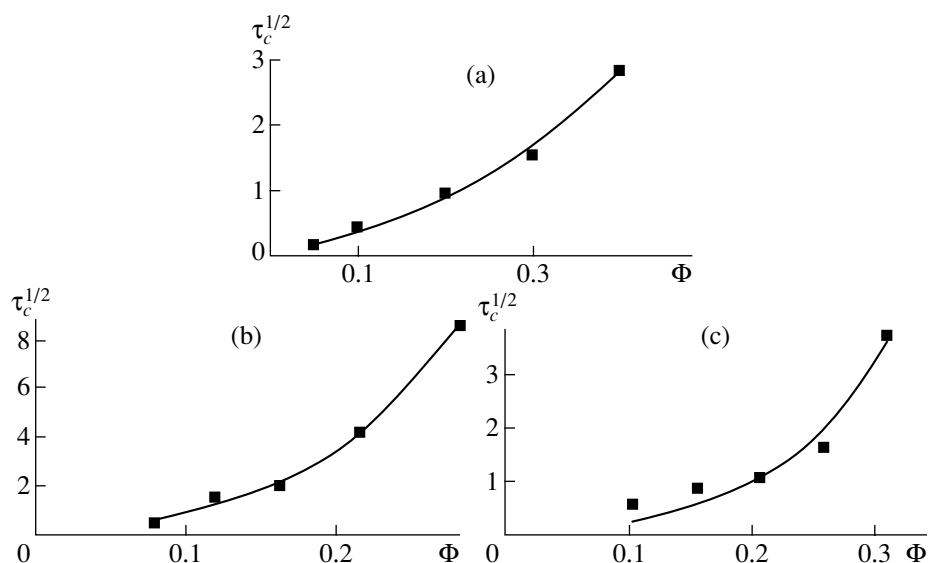
$$\tau_{0c}^{1/2} = \frac{2}{3} \left( \frac{\bar{F}_A a_2}{3} \right)^{1/2} \frac{1}{a_2 \alpha - 1}, \quad a_2 = \frac{2A_2 + 1}{\alpha}, \quad \alpha = \frac{4}{3}.$$

Here,  $\bar{F}_A$  is the force that prevents the disruption of an aggregate (it is normalized to unit area of the aggregate cross section).

In the cylinder model, the coefficients  $k$  and  $A$  in Eqs. (1) and (2) are equal; however, in real aggregated systems, they can have different values. The  $k_1$  and  $A_1$  coefficients describe the hydrodynamic interaction of separate particles in shear flow, whereas the  $k_2$  and  $A_2$  coefficients are related to the hydrodynamic interaction of aggregates and, therefore, can differ from  $k_1$  and  $A_1$ , respectively. However, we may assume that the functional dependences of the coefficients  $\tau_c^{1/2}$  and  $\eta_c^{1/2}$  on the volume concentration  $\Phi$  in a real disperse system and in a model cylinder system are identical. The  $\eta_c^{1/2}(\Phi)$  dependence has been comprehensively studied by us in [1]. It is adequately described by Eq. (1). Aggregated systems exhibit, to a greater or lesser extent, thixotropic properties [3], the deviation from the equilibrium flow state having the strongest effect on the



**Fig. 1.** Coefficient  $\tau_c^{1/2}$  vs. volume concentration: (a) GR-X latex, (b) Neopren latex, and (c) latex in silicone oil.



**Fig. 2.** Coefficient  $\tau_c^{1/2}$  vs. volume concentration: (a) deionized latex in water, (b) latex of poly(methyl methacrylate) in *n*-hexadecane, and (c) polyethylene powder in polyether resin.

$\tau_c$  value. Therefore, the dependence  $\tau_c^{1/2}(\Phi)$  is seldom a smooth monotonic function.

We selected some systems with a rather smooth  $\tau_c^{1/2}(\Phi)$  dependence. These are aqueous systems with latexes GR-X [4] and Neopren [5], sterically stabilized latex of poly(methyl methacrylate) in silicone liquid [6], deionized polystyrene latex in water [7], latex of poly(methyl methacrylate) in *n*-hexadecane [8], and polyethylene powder in unsaturated polyester resin [9]. The results are shown in Figs. 1 and 2. The solid curves were calculated by Eq. (2).

The  $\tau_{0c}^{1/2}$ ,  $k_2$ , and  $A_2$  values were calculated using Eq. (2) by the nonlinear regression method. Assuming that the aggregate decomposes through the breaking of the contact between two neighboring particles, let us introduce the cohesive force

$$F_s = \bar{F}_A \pi r^2,$$

where  $r$  is the averaged particle radius. The calculated  $\tau_{0c}^{1/2}$ ,  $k_2$ ,  $A_2$ ,  $\bar{F}_A$ , and  $F_s$  values are summarized in the table. The average size of aggregates in a real dispersion can be estimated in a similar way. In the model sys-

Coefficients  $\tau_{0c}^{1/2}$ ,  $k_2$ , and  $A_2$ ; normalized cohesive force  $\bar{F}_A$ ; and cohesion force between particles  $F_s$  for different disperse systems (SI dimension)

System	$r, \mu\text{m}$	$k_2$	$A_2$	$\tau_{0c}^{1/2}$	$\bar{F}_A$	$F_s$	$\eta_0$
Aqueous suspension of GR-X latex [4]	0.07	0.035	292.9	0.005	0.00365	$5.6 \times 10^{-17}$	$1 \times 10^{-3}$
Aqueous suspension of Neopren latex [5]	0.05	0.045	300.0	0.0018	0.0005	$7.7 \times 10^{-18}$	$1 \times 10^{-3}$
Latex of poly(methyl methacrylate) in silicone liquid [6]	0.318	0.010	293.1	0.746	2934	$9.3 \times 10^{-10}$	0.18
Deionized polystyrene latex in water [7]	0.11	0.012	293.0	0.848	3783	$1.4 \times 10^{-10}$	$1 \times 10^{-3}$
Latex of poly(methyl methacrylate) in <i>n</i> -hexadecane [8]	0.4	0.035	293.1	0.507	1352	$6.8 \times 10^{-10}$	$2.7 \times 10^{-3}$
Polyethylene powder in polyester resin [9]	20	0.073	142.9	0.146	54.3	$6.8 \times 10^{-8}$	0.939

tem, the average axial ratio of a cylinder is equal to the ratio of the half-length to the radius  $J_f = l_f/r$ , and the functional dependence of the axial ratio on structural rheological parameters has the form

$$J_f \sim \frac{F_A^{1/2}}{\eta_0^{1/2} \dot{\gamma}^{1/2} + \chi(\Phi)}.$$

We may assume that the average relative aggregate size is described analogously:

$$l_r \sim \frac{\bar{F}_A^{1/2}}{\eta_0^{1/2} \dot{\gamma}^{1/2} + \chi(\Phi)}.$$

Inasmuch as the smallest aggregate size cannot be smaller than the size of a separate particle, we can write the approximate equation

$$l_r \approx \frac{B\bar{F}_A^{1/2}}{\eta_0^{1/2} \dot{\gamma}^{1/2} + \chi(\Phi)} + 1.$$

In general, the average aggregate size decreases with an increase in the shear rate ( $\dot{\gamma}$ ) and viscosity of a disperse medium ( $\eta_0$ ) or with a decrease in the cohesion between the particles ( $F_s \approx \bar{F}_A \pi r^2$ ).

The original Casson model and the generalized flow model of structured systems are based on calculation of the energy dissipation by viscous flow. Another known approach uses equations of chemical kinetics.

In particular, Cross [10] used the number of bonds between particles ( $L$ ), rather than the concentration of a substance, and introduced the bond formation rate constant ( $k_2$ ), the spontaneous bond breaking rate constant ( $k_0$ ), and the shear flow-induced bond breaking rate

constant ( $k_1 \dot{\gamma}^n$ ). Thus, the rate of the change in the number of bonds between particles is

$$\frac{dL}{dt} = k_2 N - (k_0 + k_1 \dot{\gamma}^n) L,$$

where  $N$  is the total number of particles in unit volume, and  $L$  is the number of bonds between particles in unit volume. Under equilibrium conditions,  $dL/dt = 0$ ; hence,  $L = k_2 N / (k_0 + k_1 \dot{\gamma}^n)$ . If  $L_0$  is the number of bonds in the zero shear rate limit ( $\dot{\gamma} = 0$ ),

$$\frac{L}{L_0} = 1 + \frac{k_1}{k_0} \dot{\gamma}^n.$$

Cross [10] used an empirical expression from the polymer flow theory:  $\eta = \eta_\infty + BL$ , where  $\eta_\infty$  is the system viscosity at  $\dot{\gamma} \rightarrow \infty$  and  $B$  is a coefficient. If the maximal viscosity  $\eta(0)$  at  $\dot{\gamma} \rightarrow 0$  is introduced, then the maximal number of bonds is  $L_0 = [\eta(0) - \eta_\infty]/B$ . As a result, we obtain the known Cross equation:

$$\frac{\eta - \eta_\infty}{\eta(0) - \eta_\infty} = \frac{L}{L_0},$$

$$\frac{\eta - \eta_\infty}{\eta(0) - \eta_\infty} = \frac{1}{1 + (k_1/k_0) \dot{\gamma}^n}.$$

Analogously, let us define the number of particles in aggregates  $N_2$  (in unit volume) through the aggregation rate constant  $k_2$ , the spontaneous aggregate breaking rate constant  $k_0$ , and the rate constant of aggregate breaking under the action of hydrodynamic tensile forces ( $k_1 \dot{\gamma}^{1/2}$ ). The aggregation rate can be expressed as

$$\frac{dN_2}{dt} = k_2 N - (k_0 + k_1 \dot{\gamma}^{1/2}) N_2,$$

where  $N$  is the total number particles in unit volume, and  $N_2$  is the total number of particles in all aggregates that exist in unit volume.

Under equilibrium flow conditions, the number of aggregated particles remains unaltered; hence,

$$dN_2/dt = 0, \quad \frac{N}{N_2} = \frac{k_2}{k_1\dot{\gamma}^{1/2} + k_0}.$$

In the limiting cases, we obtain the following relationships:

$$\dot{\gamma} \rightarrow 0, \quad N_2 \rightarrow N_2(0),$$

$$\frac{N_2(0)}{N} = \frac{k_2}{k_0},$$

$$\dot{\gamma} \rightarrow \infty, \quad N_2 \rightarrow (0).$$

Let us introduce the following equation for effective viscosity:

$$\eta^{1/2} = \eta_{\infty}^{1/2} + BN_2.$$

Hence,

$$\frac{\eta^{1/2} - \eta_{\infty}^{1/2}}{\eta^{1/2}(0) - \eta_{\infty}^{1/2}} = \frac{N_2}{N_2(0)}.$$

Substituting the formulas for  $N_2$  and  $N_2(0)$  into this equation, we obtain

$$\frac{\eta^{1/2} - \eta_{\infty}^{1/2}}{\eta^{1/2}(0) - \eta_{\infty}^{1/2}} = \frac{1}{(k_1/k_0)\dot{\gamma}^{1/2} + 1}.$$

Previously, it was shown that the generalized Casson equation can be expressed through the limiting viscosities:

$$\eta^{1/2} = \eta_{\infty}^{1/2} + \frac{\eta_{(0)}^{1/2} - \eta_{\infty}^{1/2}}{1 + (1/\chi)\dot{\gamma}^{1/2}}.$$

Comparison of these equations makes it possible to determine the physical meaning of the coefficient  $\chi$ , namely,  $\chi = k_0/k_1$ .

Thus, the coefficient  $\chi$  is the ratio between the spontaneous aggregate breaking rate (caused by thermal motion of particles or gravity forces) and the rate of aggregate breaking caused by hydrodynamic tensile forces.

The ratio of the number of particles in the aggregates to the total number of particles can be described by the following relationships:

$$\frac{N_2}{N} = \frac{k_2}{k_0} \left[ \frac{1}{1 + (1/\chi)\dot{\gamma}^{1/2}} \right],$$

$$\frac{N_2}{N} = \frac{k_2}{k_0} \left[ \frac{\eta^{1/2} - \eta_{\infty}^{1/2}}{\eta^{1/2}(0) - \eta_{\infty}^{1/2}} \right],$$

$$\frac{N_2}{N} = \left( \frac{k_2}{k_1\dot{\gamma}^{1/2}} \right) \left[ \frac{1}{1 + \left( \frac{k_0}{k_1\dot{\gamma}^{1/2}} \right)} \right].$$

Thus, the relative number of aggregated particles is determined (1) by the interplay between the processes of aggregation (due to Brownian motion or collisions in the course of flow) and shear-induced aggregate failure (due to hydrodynamic tensile forces),  $k_2/k_1\dot{\gamma}^{1/2}$ , and (2) by the proportion between the spontaneous and shear-induced aggregate breaking,  $k_0/k_1\dot{\gamma}^{1/2}$ .

## REFERENCES

1. Matveenko, V.N., Kirsanov, E.A., and Remizov, S.V., *Vestn. Mosk. Univ., Ser. 2: Khim.*, 2006, vol. 47, p. 393.
2. Kirsanov, E.A., Timoshin, Yu.N., Novoselova, N.V., and Matveenko, V.N., *Vestn. Mosk. Univ., Ser. 2: Khim.*, 2006, vol. 47, p. 387.
3. Kirsanova, E.A., Remizov, S.V., Novoselova, N.V., and Matveenko, V.N., *Vestn. Mosk. Univ., Ser. 2: Khim.*, 2006, vol. 47 (in press).
4. Maron, S.N. and Fok, S.M., *J. Colloid Sci.*, 1955, vol. 10, p. 482.
5. Maron, S.N. and Pierce, P.E., *J. Colloid Sci.*, 1956, vol. 11, p. 80.
6. Krieger, I.M. and Choi, G.N., *Proc. 4th Int. Congress on Rheology*, Mexico, 1984, vol. 2, p. 641.
7. Krieger, I.M. and Eguiluz, M., *Trans. Soc. Rheol.*, 1976, vol. 20, p. 29.
8. Groucher, M.D. and Milkie, T.H., *Faraday Discuss. Chem. Soc.*, 1983, vol. 76, p. 261.
9. Lem, K.W. and Han, Ch.D., *J. Rheol.*, 1983, vol. 27, no. 3, p. 263.
10. Cross, M., *J. Colloid Sci.*, 1965, vol. 20, p. 417.