Shear stress during the flow of thixotropic and rheopex suspensions

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Abstract

A semi-empirical equation is derived that describes the dependence of shear stress on shear rate during the flow of a one-component thixotropic and rheopex suspension. The suspension is considered as consisting of two fractions: single grains and their dimers, and the dimerization of single grains is considered as a reaction characterized by a constant rate constant, and the decomposition of dimers is considered as a reverse reaction with a rate constant that linearly increases with shear rate. The equation is based on the Krieger formula generalized to the case of multicomponent suspensions.

The equation needs experimental verification.

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Introduction

In previous work [1], an equation was derived that describes the dependence of shear stress on shear rate during the flow of concentrated suspensions. This equation was based on the Krieger formula [2][3] generalized in our work [4] to the case of multicomponent suspensions:

$$\eta = \eta_0 \left(1 - \frac{\varphi}{\bar{\varphi}_0} \right)^{-[\bar{\eta}]\bar{\varphi}_0} \qquad (1)$$

Here $[\eta]$ and φ_0 are the parameter values averaged over all solid components:

$$\begin{cases} [\bar{\eta}] = \dfrac{\Sigma \left[\eta_i\right]\varphi_i}{\varphi} \\[2em] \bar{\varphi}_0 = \dfrac{\varphi}{\Sigma \varphi_i/\varphi_{0,i}} \end{cases} \qquad (2)$$

where φ is the total volume fraction of all solid components, $\left[\eta_i\right]$ is the characteristic viscosity of the i-th component, φ_i and $\varphi_{0,i}$ are its volume fraction and limiting concentration, respectively.

In work [1] it was shown that the generalized Krieger formula (1-2) can be used to describe the dependence of the shear stress σ on the shear rate $\dot{\gamma}$ if the following assumptions are made:

1. A one-component suspension can be considered as a system consisting of two fractions: single grains of the suspension and their dimers, whereby single grains and their dimers correspond to different values of the parameters $[\eta]$ and φ_0;
2. Dimerization of single grains can be considered as a reaction with a rate constant k_1, decomposition of dimers as a reaction with a rate constant k linearly dependent on the shear rate $\dot{\gamma}$: $k = k_2 + k_3\dot{\gamma}$. Here k_2 is the rate constant of the reverse reaction in the absence of flow, k_3 is the rate of change of this constant with increasing of shear rate.

It was shown that the derived equations describe well the flow of both pseudoplastic and dilatant suspensions.

However, in that work it was tacitly assumed that the equilibrium between single grains and their dimers established instantly.

This work is a continuation and further elaboration of the approach developed in[1] and its extension to the nonequilibrium case, when the achievement of equilibrium lags behind the change in shear rate (i.e., relaxation effects take place – thixotropy or rheopexy).

Theory of calculations

So, let consider the suspension as consisting of two components: single grains (we denote their volume fraction in the suspension as φ_1) and their dimers (the volume fraction φ_2)

Let there be n grains of the solid phase per unit volume of the suspension, and let the average grain volume be v. Then the volume fraction φ of the solid phase is equal to $\varphi=nv$. At a given shear rate $\dot{\gamma}$, an equilibrium is established between single grains and dimers: $2n_1 \rightleftarrows n_2$, and $n_1 + 2n_2 = n$. Multiplying the left and right sides of the last equality by v, we obtain:

$$\varphi_1 + \varphi_2 = \varphi. \qquad (3)$$

Let the rate constants k_1 of dimerization be constant and reverse reaction (dimer dissociation) constant k depend linearly on the shear rate $\dot{\gamma}(t)$, which is some function of time: $k = k_2 + k_3\dot{\gamma}(t)$. Therewith, the reaction kinetics is described by a system of two differential equations:

$$\begin{cases} \dfrac{d\varphi_1}{dt} = -k_1\varphi_1^2 + \left(k_2 + k_3\dot{Y}\right)\varphi_2 \\ \\ \dfrac{d\varphi_2}{dt} = k_1\varphi_1^2 - \left(k_2 + k_3\dot{Y}\right)\varphi_2 \end{cases}, \qquad (4)$$

Substituting equality (3) into the first equation of the system of equations (4), we obtain:

$$\frac{d\varphi_1}{dt} = \left(k_2 + k_3\dot{Y}\right)\left(\varphi - \varphi_1\right) - k_1\varphi_1^2. \qquad (5)$$

As the initial condition, we take the equilibrium concentration of single grains, which is established in the absence of shear, i.e.

at $\dot{Y} = 0$ and $\dfrac{d\varphi_1}{dt} = 0$. Then $k_2\left(\varphi - \varphi_1\right) - k_1\varphi_1^2 = 0$, whence

$$\varphi_1^{init.} = \frac{\sqrt{k_2^2 + 4k_1k_2\varphi} - k_2}{2k_1} \qquad (6)$$

Unfortunately, equation (5) is the Riccati-equation, which in the general case is not integrated in quadratures[5][6] and even in the simplest case $f(t) = const$ is expressed in terms of Bessel functions, which is of little use for practical calculations. Therefore, in this work, Eq. (5) was solved numerically using the Euler method with correction for the second derivative: the iterative formula

$$\varphi_{n+1} = \varphi_n + \dot{\varphi}_n\Delta t + \frac{\ddot{\varphi}_n}{2}\Delta t^2,$$

with

$$\dot{\varphi}_n = \left(k_2 + k_3\dot{Y}\right)\left(\varphi - \varphi_n\right) - k_1\varphi_n^2,$$

whence for the case when $\dot{Y}$ increases or decreases uniformly (what is realized in experiments on a rotational viscometer), i.e. when $\dot{Y} = c_1 \pm c_2 t$,

$$\ddot{\varphi}_n = c_2 k_3\left(\varphi - \varphi_n\right) - \left(k_2 + k_3\dot{Y}\right)\dot{\varphi}_n - 2k_1\varphi_n\dot{\varphi}_n.$$

The result of the numerical solution will be denoted as $\varphi_1(t)$.

The Krieger formula for a two-component suspension has the form[1]

$$\tau = \tau_0 + \eta_0\dot{Y}\left(1 - \frac{\varphi_1}{\varphi_{10}} - \frac{\varphi_2}{\varphi_{20}}\right)^{-\frac{[\eta_1]\varphi_1 + [\eta_2]\varphi_2}{\varphi_1/\varphi_{10} + \varphi_2/\varphi_{20}}}, \qquad (7)$$

where τ is the shear stress, τ_0 is the yield stress, η_0 is the viscosity of the dispersion medium, $\dot{Y}$ is the shear rate, φ_1 is the volume fraction of single grains (the result of solving equation (5)), φ_2 is the volume fraction of dimers

$\left(\text{in accordance with (3) } \varphi_2 = \varphi - \varphi_1\right)$, φ_{10} and φ_{20} are the corresponding limiting concentrations, $\left[\eta_1\right]$ and $\left[\eta_2\right]$ are the corresponding intrinsic viscosities.

Having a numerical solution $\varphi_1(t)$ of the differential equation (5), it is possible to calculate the shear stress using formula (7).

Results and discussion

To compare the obtained equations with experiment, a rotational viscometer (Thermo Haake) with a measuring cell with a cone-plane geometry and a controlled shear rate, as well as two concentrated suspensions, one thixotropic and one rheopex, are required. For each suspension, it is necessary to carry out two series of measurements: with an increase in the shear rate and with its decrease. Unfortunately, the author has no longer the opportunity to perform experiments.

And preliminary – the simulation.

Fig. 1 shows the dependence of shear stress on shear rate, Fig. 2 – viscosity on shear rate in a thixotropic suspension. Set of parameters: $k_1 = 10$; $k_2 = 0,1$; $\varphi = 0,5$; $\varphi_{10} = 0,9$; $\varphi_{20} = 0,8$; $\tau_0 = 0$; $\eta_0 = 0,1$; $\left[\eta_1\right] = 4$; $\left[\eta_2\right] = 2,5$; $c_1 = 0$, $c_2 = 20$; the red curve corresponds to the increase of the shear rate, the blue one to its decrease.

Fig. 1. Thixotropy: shear stress vs. shear rate
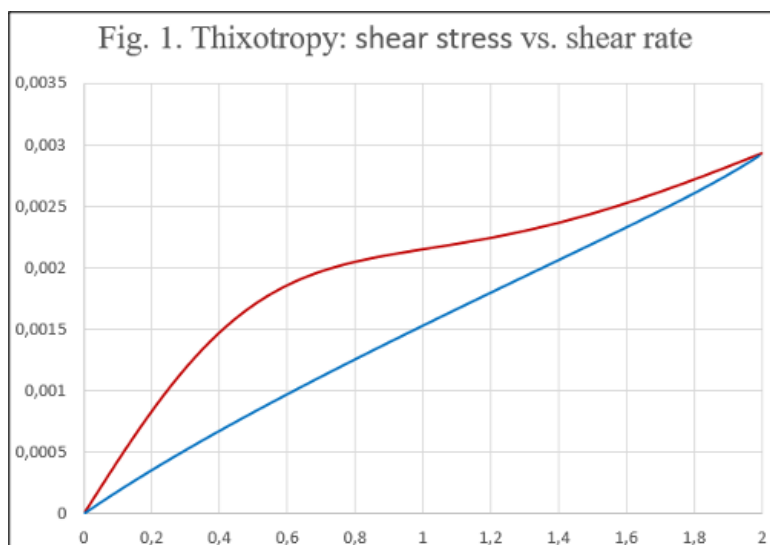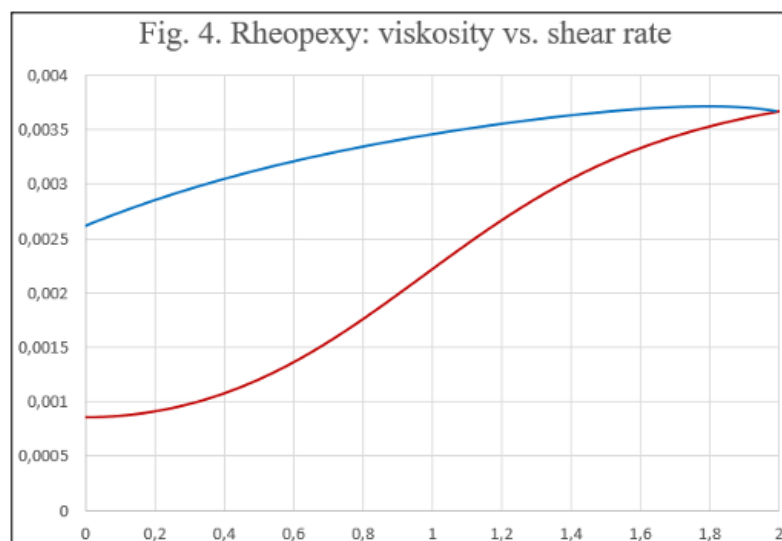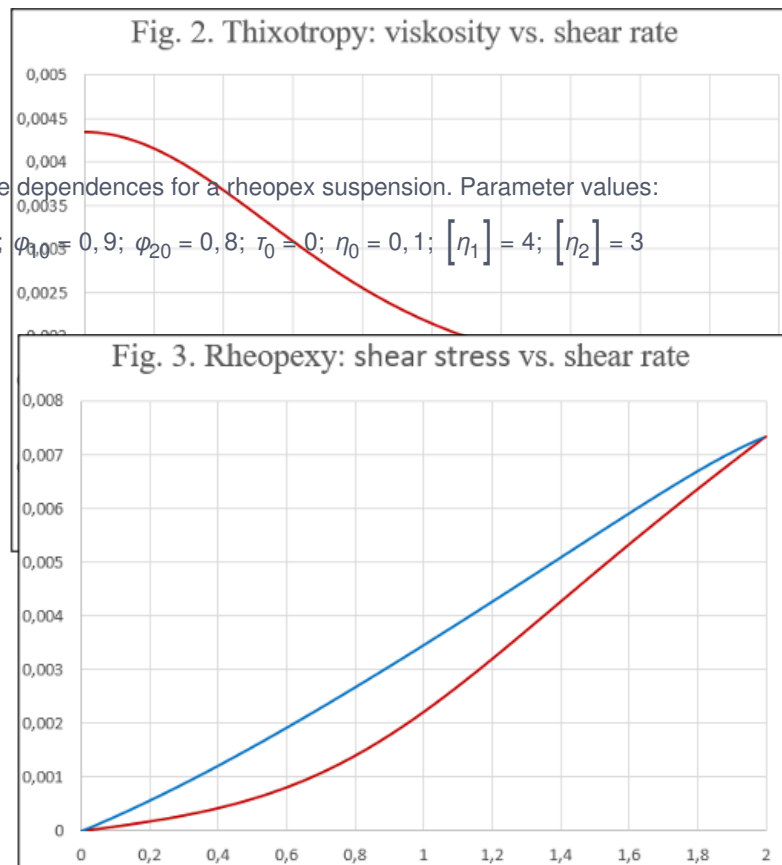
Fig. 2. Thixotropy: viskosity vs. shear rate

Fig. 3 and 4 show the same dependences for a rheopex suspension. Parameter values:

$k_1 = 10$; $k_2 = 0,1$; $\varphi = 0,5$; $\varphi_{10} = 0,9$; $\varphi_{20} = 0,8$; $\tau_0 = 0$; $\eta_0 = 0,1$; $\left[\eta_1\right] = 4$; $\left[\eta_2\right] = 3$

Fig. 3. Rheopexy: shear stress vs. shear rate

Fig. 4. Rheopexy: viskosity vs. shear rate

It is also of interest to look at the dependency of the viscosity on time at a constant speed of shear rate $\dot{\gamma}$ (including a special case $\dot{\gamma} = 0$). The corresponding diagrams are shown in figures 5 and 6.

Fig. 5. Thixotropy: viskosity vs. time
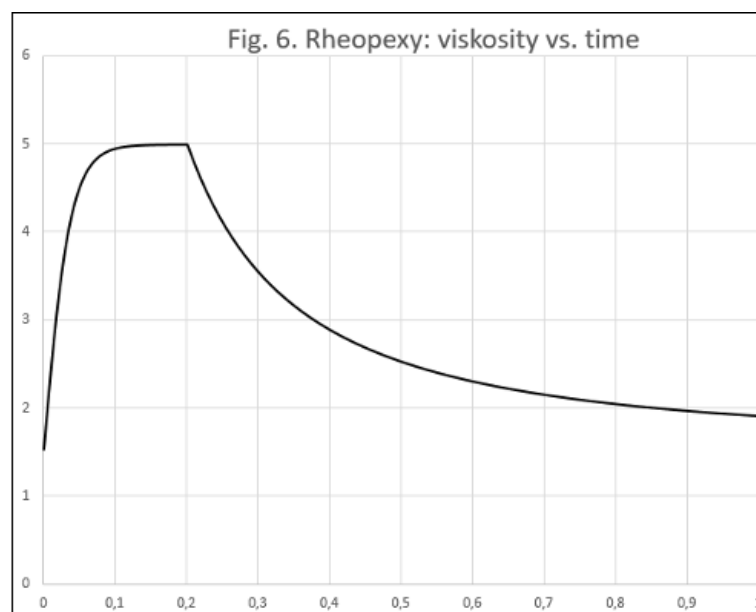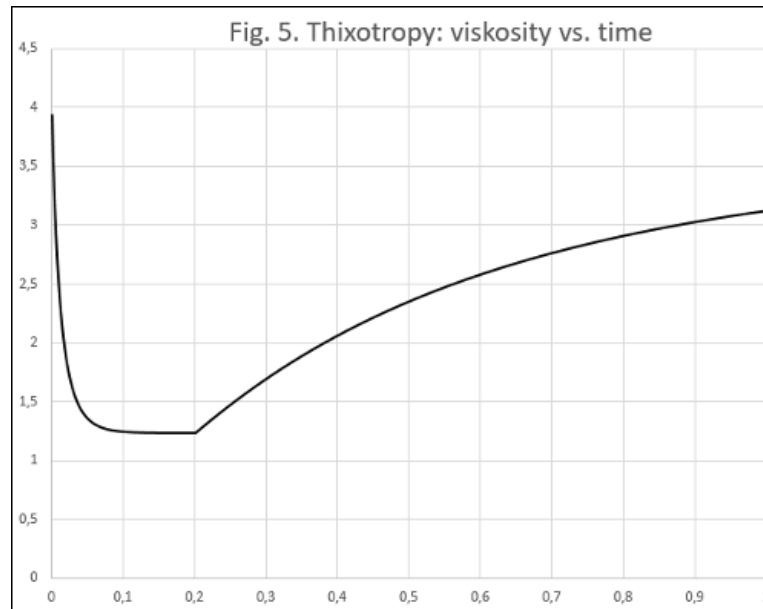

Fig. 6. Rheopexy: viskosity vs. time

Fig. 5, 6: The parameters values are the same as in the corresponding figures 1–4.

Fig. 5 and 6 shows that the viscosity changes from the equilibrium value (appropriate for the absence of the flow), asymptotically approaching the stationary value, which complies with a certain constant flow rate. Then, at a certain time point, the flow drops to zero, at that the viscosity curve has a break and changes in the opposite side, asymptotically approaching the original equilibrium value.

It is easy to see that, as expected, the derived equations describe hysteresis, which is a consequence of relaxation processes – thixotropy and rheopexy.

It is necessary to check the quantitative agreement of the derived equations with the real experiment. Unfortunately, the data published in the literature are not complete enough: there are graphs of the dependence of viscosity η and shear stress τ on shear rate $\dot{\gamma}$, but they are not tied in time, i.e. the speed at which $\dot{\gamma}$ was scanned is not indicated, and it is not clear whether this speed was constant. Nevertheless, such a comparison with the experimental data published in [7] (suspensions of nanodiamonds in polydimethylsiloxane) was performed; the results are shown in Figure 7. At that a constant scanning speed was assumed.

Fig. 7. Suspension: nanodiamons in polydimethylsiloxan.
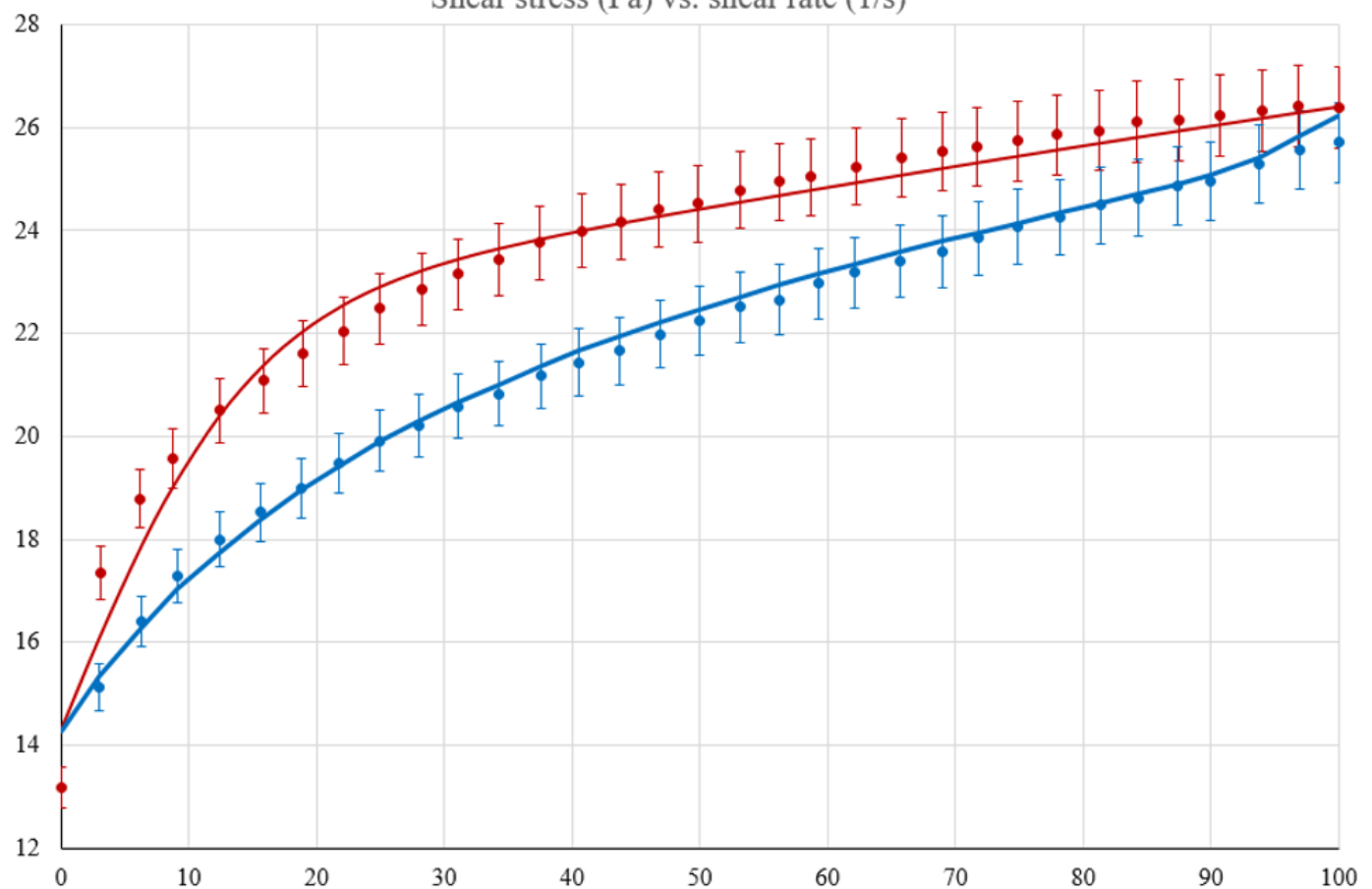Shear stress (Pa) vs. shear rate (1/s)

Fig. 7. Points - experiment according to the data[7] (error indicator shows an error of 3%), solid curves - calculations using the derived equations, red curve and points - increase in shear rate, blue - decrease. Parameter values:

$k_1 \approx 53,03;\ k_2 = 2,486;\ k_3 = 1,331;\ \tau_0 \approx 14,27;\ \varphi \approx 0,370;\ \varphi_{10} \approx 0,553;\ \varphi_{20} \approx 0,372;\ \eta_0 \approx 0,0558;\ \left[\eta_1\right] \approx 2,650;\ \left[\eta_2\right] \approx 5,981$

The standard deviation of the curves from the experimental points is (1.5% of the average shear stress value).

It is easy to see that the derived equations are in good agreement with the experiment, and the parameters of the equations take realistic values. However, it would be useful to carry out the systematic experiments with the purpose of comparing the derived equations with them.

The author hopes that this article will attract the attention of interested experimenters for the experimental verification of the derived equations.

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