

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.

Introduction

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

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

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

$$\begin{cases} [\bar{\eta}] = \frac{\sum [\eta_i] \varphi_i}{\varphi} \\ \bar{\varphi}_0 = \frac{\varphi}{\sum \varphi_i / \varphi_{0,i}} \end{cases} \quad (2)$$

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

In our work [1] it was shown that the generalized Krieger formula (1–2) can be used to describe the dependence of the shear stress τ 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 linearly dependent on the shear rate $\dot{\gamma}$:

$$k = k_2 + k_3\dot{\gamma}$$

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, we will 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), between which the reversible reaction $2\varphi_1 \rightleftharpoons \varphi_2$ proceeds. The total number of single grains (i.e. both single and included in dimers) $\varphi_0 = \varphi_1 + 2\varphi_2$, or

$$\varphi_2 = \frac{\varphi_0 - \varphi_1}{2}. \quad (3)$$

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

$$\begin{cases} \frac{d\varphi_1}{dt} = -2k_1\varphi_1^2 + 2(k_2 + c\dot{\gamma})\varphi_2 \\ \frac{d\varphi_2}{dt} = k_1\varphi_1^2 - (k_2 + c\dot{\gamma})\varphi_2 \end{cases}, \quad (4)$$

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

$$\frac{d\varphi_1}{dt} = (k_2 + c\dot{\gamma})(\varphi_0 - \varphi_1) - 2k_1\varphi_1^2. \quad (5)$$

As the initial condition, we take the equilibrium concentration of single grains, which is established in the absence of shear, i.e. at $\dot{\gamma} = 0$. The equilibrium constant of the reaction $2\varphi_1 \rightleftharpoons \varphi_2$ at $\dot{\gamma}(t) = 0$ is

$$\frac{\varphi_1^2}{\varphi_2} = \frac{k_2}{k_1}, \text{ or } \frac{\varphi_1^2}{\varphi_0 - \varphi_1} = \frac{k_2}{2k_1}, \text{ whence}$$

$$\varphi_1^{init.} = \frac{\sqrt{k_2^2 + 8k_1k_2\varphi_0} - k_2}{4k_1} \quad (6)$$

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 $f(t) = \text{const}$ 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

$$\dot{\varphi}_n = (k_2 + c\dot{\gamma})(\varphi_0 - \varphi_1) - 2k_1\varphi_1^2,$$

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

$$\ddot{\varphi}_n = c_2 c (\varphi_0 - \varphi_n) - (k_2 + c\dot{\gamma})\dot{\varphi}_n - 4k_1\varphi\dot{\varphi}_n.$$

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]

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

where τ is the shear stress, τ_0 is the yield stress, η_0 is the viscosity of the dispersion medium, $\dot{\gamma}$ 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 (in accordance with (3) $\varphi_2 = \frac{\varphi_0 - \varphi_1}{2}$), φ_{10} and φ_{20} are the corresponding limiting concentrations, $[\eta_1]$ and $[\eta_2]$ 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 rheopex suspension. Set of parameters: $k_1 = 20$; $k_2 = 0,2$; $\varphi = 0,4$; $\varphi_{10} = 0,5$; $\varphi_{20} = 0,8$; $\tau_0 = 0$; $\eta_0 = 0,1$; $[\eta_1] = 4,4$; $[\eta_2] = 4,5$; $c_1 = 0$, $c_2 = 1$; the red curve corresponds to the increase of the shear rate, the blue one to its decrease.

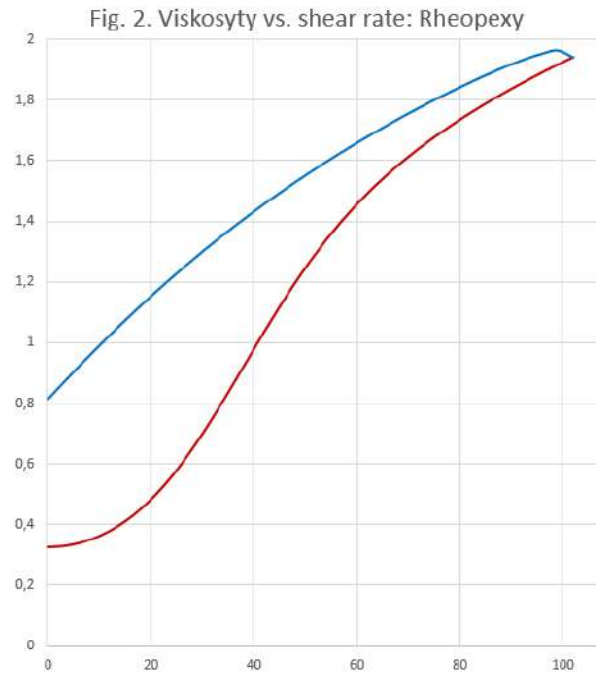
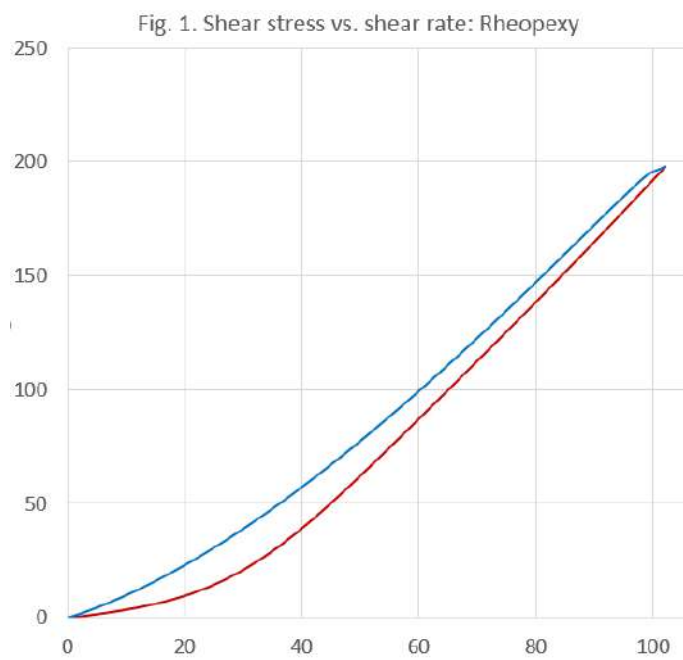
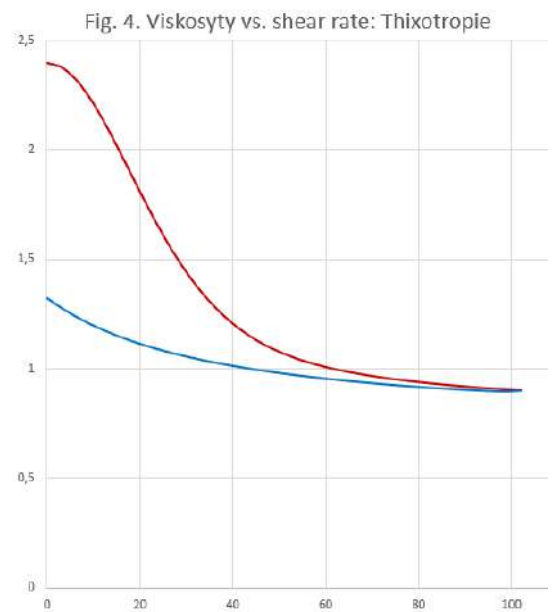
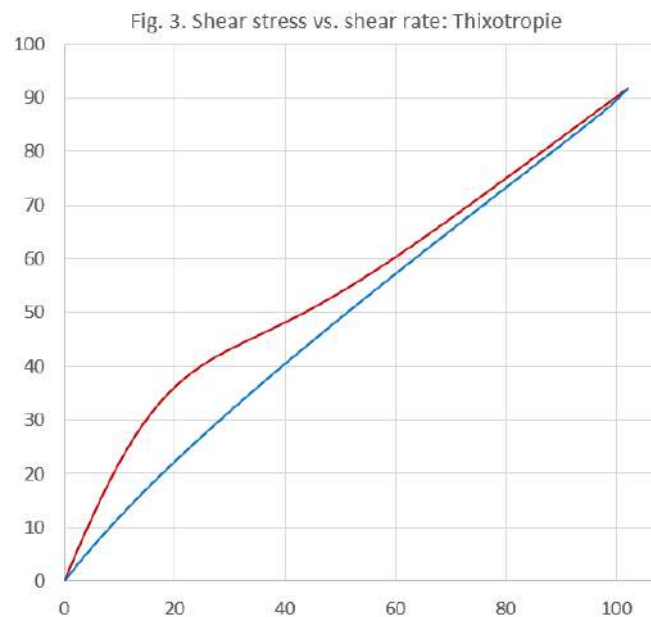


Fig. 3 and 4 show the same dependences for a thixotropic suspension. Parameter values:

$k_1 = 20$; $k_2 = 0,2$; $\varphi = 0,4$; $\varphi_{10} = 0,5$; $\varphi_{20} = 0,3$; $\tau_0 = 0$; $\eta_0 = 0,1$; $[\eta_1] = 2,5$; $[\eta_2] = 10$



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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