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A Numerical Approach on New Constitutive Model for Thixotropic Substances

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Abstract. The thixotropic substances can be found in different industrial sectors, such as chemical, biomedical, manufacturing and oil. These substances show a rheological time-dependent behavior, dependent of their structural level. Generally, a constitutive model for the thixotropic substances is composed by a pair of coupled equations: the constitutive equation (based on viscoelastic models) and the rate equation (that describes the structural evolution). In many works presented in the specialized literature, the shear modulus and viscosity dependencies with the structural nature are not formally considered in the dynamical principles from that the constitutive equation is originated. In the present work, a new, thermodynamically consistent, constitutive model for thixotropic substances, where such dependences are considered, is presented and some rheological tests are analyzed in a numerical simulation point of view (code developed in MATLAB). The constitutive model is based on Jeffreys' model and the coagulation theory of Smoluchowsky.

Introduction

The thixotropic fluids (structured fluids) are characterized by rate-dependent properties associated to their structural level. The behavior of these substances under rheological tests have been analyzed in many scientific works ([1,2,3,4,5]), where a qualitative explanation of the breakdown and build-up processes of the structure is presented. Although, there is still some uncertainties related to how it proposes a rheological consistent constitutive model for the thixotropic substances.

In many models proposed in the literature ([2,5,6,7,8,9,10]), the structural nature of the thixotropic fluids is described by a single scalar variable (structural parameter λ). The evolution of λ, via the rate equation, represents the structural level behavior of the substance. The structural and viscoelastic natures of the thixotropic fluids are connected, in terms of models, by a coupled pair of equations: the constitutive equation and the rate equation. There are several difficulties related to this coupled time-dependent description, in a rheological and numerical sense. It is important to point out that a real thixotropic fluid exhibits two distinguished phenomena/behavior, structural and viscoelastic, and they are intimately related.

The constitutive equation (relationship), based on viscoelastic models, and it can be expressed in a general form as

$$\tau = \tau\left(\lambda, \dot{\gamma}\right) \tag{1}$$

Where the stress τ is a function of the shear rate $\dot{\gamma}$ and λ. In many works ([11,12,13,14,15]) the explicit form of Eq. 1 is directly based on linear viscoelastic models (Maxwell, Jeffreys or Kelvin-Voigt for instance) or a simple combination of these models. These models does not take into account the time/structural dependence of the shear modulus and/or viscosity in the dynamical considerations, in a evident disagreement with the expected behavior of thixotropic substances.

The theory of viscoelasticity has been development advances from the continuum mechanics viewpoint ([16, 17]), and some works ([18, 19, 20]) has studied anisotropic fluids (fluids with a preferred flow orientation).

The rate equation describes the structural evolution $\dot{\lambda}$ in terms of the structural parameter λ and the shear rate $\dot{\gamma}$, as it follows

$$\dot{\lambda} = \dot{\lambda}\left(\lambda, \dot{\gamma}\right). \tag{2}$$

It is important to comment that the single structural parameter approach can be easily extended to more than one structural parameter approach.

The proposed model presented in this work is based on the hypothesis that the fully structured fluid is a system composed by a long continuous chain element of particles. When this system is under shear load, the continuous element can be decomposed into smaller chain structures called “flocs”. If the shear loads continues, these flocs can be decomposed into isolated particles (fully unstructured fluid). This process is called structural breaking/degeneration. However, due to Brownian motion and/or laminar regime, the collisions between these particles can produce the coalescence of them, this process is known as structural building up.

In the next sections, a formal description of the constitutive model is presented in terms of the constitutive equation and the structural nature of the material. The restrictions and ideas associated with the formulation are also commented.

Constitutive Equation

The adopted approach to characterize the thixotropic system is based on Jeffreys model (a Maxwell element in parallel with a viscous element). The interaction between these elements is dependent of the structural level. In this sense, the physical fluid model is presented as shown in Fig. 1.

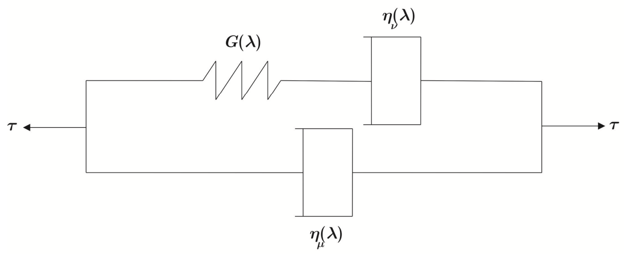

Fig.1 Sketch of the modified Jeffrey’s model.

The constitutive equation is obtained from the following dynamic considerations

$$\tau = \tau_m + \tau_v,\quad \dot{\tau} = \dot{\tau}_m + \dot{\tau}_v,\quad \dot{\gamma} = \dot{\gamma}_m = \dot{\gamma}_v \text{ and } \dot{\gamma}_m = \dot{\gamma}_v = \dot{\gamma}_e, \tag{3}$$

Where the properties with subindexes $(\cdot)_v$ and $(\cdot)_m$ refer to the viscous element and to the Maxwell element, respectively. Considering the Maxwell element, $(\cdot)_v$ represents a viscous property and $(\cdot)_e$ an elastic property. Thus, supposing the material is under shear load (τ), it can be written for the Maxwell element, that

$$\tau_m = 2\eta_v\dot{\gamma}_v \quad\text{and}\quad \dot{\tau}_m = G\dot{\gamma}_e + \dot{G}\gamma_e \tag{4}$$

And, with respect to the viscous element, one has

$$\dot{\gamma}_v = \frac{\tau_v}{2\eta_\mu} \quad\text{and}\quad \dot{\tau}_v = 2\eta_\mu\ddot{\gamma} + 2\dot{\eta}_\mu\dot{\gamma}. \tag{5}$$

From some algebraic manipulation of the equations (3), (4) and (5), the following constitutive equation is obtained

$$\frac{2\eta_v}{G}\dot{\tau} + \left(1 - \frac{2\eta_v\dot{G}}{G^2}\right)\tau = \left[2\eta_v + 2\left(1 - \frac{2\eta_v\dot{G}}{G^2}\right)\eta_\mu + \frac{4\eta_v\dot{\eta}_\mu}{G}\right]\dot{\gamma} + \frac{4\eta_v\eta_\mu}{G}\ddot{\gamma} \tag{6}$$

It is important to comment that the time/structural dependence of the shear modulus $G = G(\lambda)$ and viscosity coefficient ($\eta_v = \eta_v(\lambda)$ and $\eta_\mu = \eta_\mu(\lambda)$) are taken into account in constitutive equation (6). Note that this consideration is in agreement with the expected behavior for a thixotropic fluid ([21,22]). In the next section, some aspects of the structural nature are analyzed.

Structural Nature

This section is didactically divided in three main ideas (the structural destruction, construction and the combined effect – the rate equation expression). In terms of structural destruction, consider a unique continuous chain of particles under shear load. The linkage between these particles are stretched and if the shear load continue, these linkages can be broken (originating flocs structures and/or single particles). In this sense, from the generalized Gibbs equation and the reptation model ([23]), one has

$$\dot{N} = \frac{\left(K_\psi N\theta\ddot{\gamma} + \tau\right)N\dot{\gamma}}{\zeta}, \tag{7}$$

Where N is the number of linkages, θ is temperature, ζ is the chemical potential and K_ψ is a constant that incorporates some bulk effect of the structural nature.

The shocks between flocs and/or single particles, due to Brownian motion and/or laminar flow regime, can produce the structural construction by the coalescence of these types of structures. In this sense, some flocs can be reunited to form a bigger floc (can be reached the complete rebuilding of the continuous structure). In this process, a floc of size x coalesces with a floc of size y to form another floc of size $x+y$ ($x, y \to x+y$). The cases of the coalescence of more than two flocs simultaneously are not common [24] and were disregarded.

In this work, the structural rate equation is obtained from some hypothesis: (i) the coagulation process occurs according with the law of mass action [25,26] and (ii) that the reaction rate is proportional to the reactive substances concentration. In this sense, the factor of proportionality which characterizes the coalescence process ($x, y \to x+y$) is defined as

$$K(x,y) = k_0\left(e^{-px\left(\frac{\beta}{2}-1\right)}n(x,t)^{\left(\frac{\beta}{2}-1\right)}\right)\left(e^{-py\left(\frac{\beta}{2}-1\right)}n(\mathrm{y},t)^{\left(\frac{\beta}{2}-1\right)}\right), \tag{8}$$

Where $n(\cdot,t)$ is the continuous density distribution of probability for size particles$(\cdot)$, β is a positive constant and k_0 represents a potential related with some additional possible linkage.

Following similar steps presented in [13] with some additional considerations related to the Smoluchowski equation, it can be shown that the rate of structural construction can be represented by

$$\frac{d}{dt}N(\mathrm{t}) = \frac{1}{2}k_0\left(N_0 - N(\mathrm{t})\right)^\beta, \tag{9}$$

Where $2\left(N_0 - N(\mathrm{t})\right)$ represents the potential of formation of linkage pair.

Finally, from discussions presented in above paragraphs and defining the structural parameter by $\frac{N(\mathrm{t})}{N_0}$, it follows that when the material is fully structured, λ is unit and if the material is composed only by isolated particles (pure viscous behavior), λ is zero. This definition yields the final form of rate equation

$$\frac{d\lambda}{dt} = \frac{1}{t_f}\left[k_0^*(1-\lambda)^\beta - \frac{\left(K_\psi^*\lambda\ddot{\gamma} + \tau\right)\lambda\dot{\gamma}}{\zeta}\right], \tag{10}$$

Where $k_0^* = \frac{k_0}{2}N_0^{-(\beta+1)}$ and $K_\psi^* = K_\psi N_0\theta$.

The Constitutive Model

Aiming a general description of the consistent rheological behavior of thixotropic fluids (in agreement to the functional forms restrictions stated on [13] and the thermodynamic consistency), the constitutive model is presented immediately below

$$\frac{2\eta_v}{G}\dot{\tau}+\left(1-\frac{2\eta_v\dot{G}}{G^2}\right)\tau=\left[2\eta_v+2\left(1-\frac{2\eta_v\dot{G}}{G^2}\right)\eta_\mu+\frac{4\eta_v\dot{\eta}_\mu}{G}\right]\dot{\gamma}+\frac{4\eta_v\eta_\mu}{G}\ddot{\gamma} \tag{6}$$

$$\frac{d\lambda}{dt}=\frac{1}{t_f}\left[k_0^*\left(1-\lambda\right)^\beta-\frac{\left(K_\psi^*\lambda\ddot{\gamma}+\tau\right)\lambda\dot{\gamma}}{\zeta}\right] \tag{10}$$

$$G=G_0\exp\left(m\lambda^{-1}\right) \tag{11}$$

$$\eta_\mu=\eta_0\exp\left(\alpha_2\lambda\right) \tag{12}$$

$$\eta_v=\eta_0\exp\left[\left(\alpha_1+\alpha_2\right)\lambda\right]-\eta_\mu \tag{13}$$

Note that the model has ten positive parameters: η_0, α_1, α_2, ζ, k_0^*, β, m, K_ψ^*, G_0 and t_f. The form of the equation (21) is based on Prony's series ([27,28,29]). The shear modulus increases monotonically as λ decreases ([12,30]), this fact is in agreement to the idea of purely viscous behavior when the substance is in a completely unstructured state ($\lambda=0$).

Numerical Examples

Aiming an appropriate analysis of the model, three rheological examples are presented in this section, in a computational simulation sense. The first example is an equilibrium curve, the second is a constant shear rate test and the third is a constant shear stress test. The parameters used were $\eta_0=0.08$, $\alpha_1=5$, $\alpha_2=0.5$, $\zeta=1000$, $k_0^*=1$, $\beta=5$, $m=0.000001$, $K_\psi^*=0.001$, $G_0=5$ and $t_f=1$.

Equilibrium curve. The equilibrium is shown at Fig. 2 .

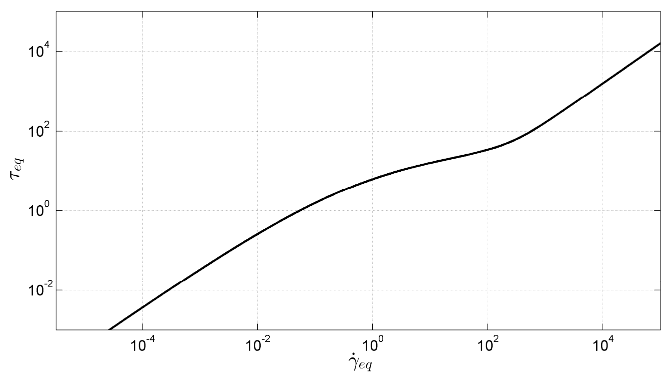

Fig.2 Steady state

This example evidences the fact that the response of the model is in accordance with the expected rheological behavior of a thixotropic fluid.

Constant shear rate test. In this test is considered as initial condition that the material is fully structured. Suddenly an constant shear rate is applied, i.e., $\dot{\gamma}=H\left(t\right)\dot{\gamma}_0$, where $\dot{\gamma}_0$ is the applied shear rate, t is the time variable and $H\left(t\right)$ is the Heaviside function. The result is shown at Fig. 3.

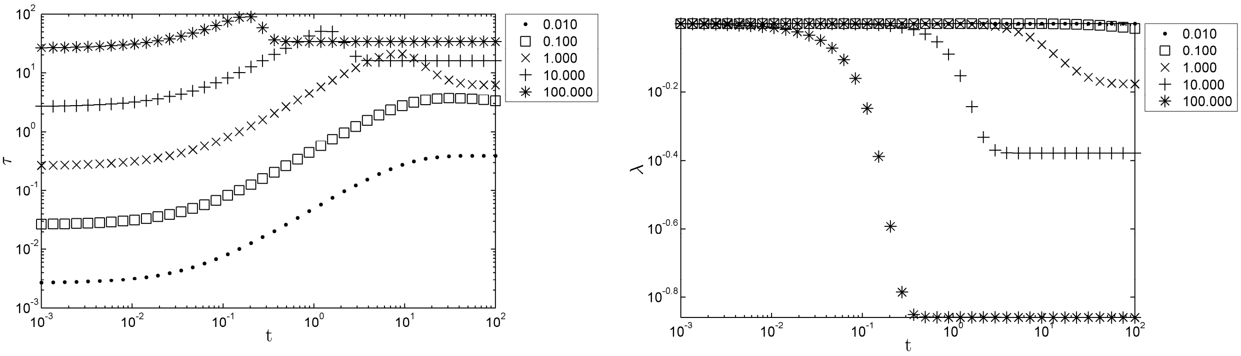

Fig.3 Cauchy stress vs. time (a) and λ vs time (b) ((a) left side, (b) right side).

The material starts to flow and several material linkages of the continuous structure are broken, generating the floc structures. However, as soon as the breaking process begins the building up process begins too, due to collisions from the laminar flow regime or/and Brownian motion. These effects can be seen in the Fig. 3(a), where it is shown the numerical response of the model, using finite difference method. Note that, there is a maximum stress point in each curve. At this point, the structural construction part of the rate equation is enhanced. However, after that point the material linkages are severely damaged and the tendency of the material tends to reach the steady state (an equilibrium state between breaking and building up processes). These effects can be seen by the use of the Figure 3(b), where the structural parameter (λ) is plotted as a function of time (t). The Fig. 4 emphasizes the importance in to take into account the shear modulus ($\dot{G}$) and viscosity ($\dot{\eta}_\mu$) time rates in the constitutive equation (6).

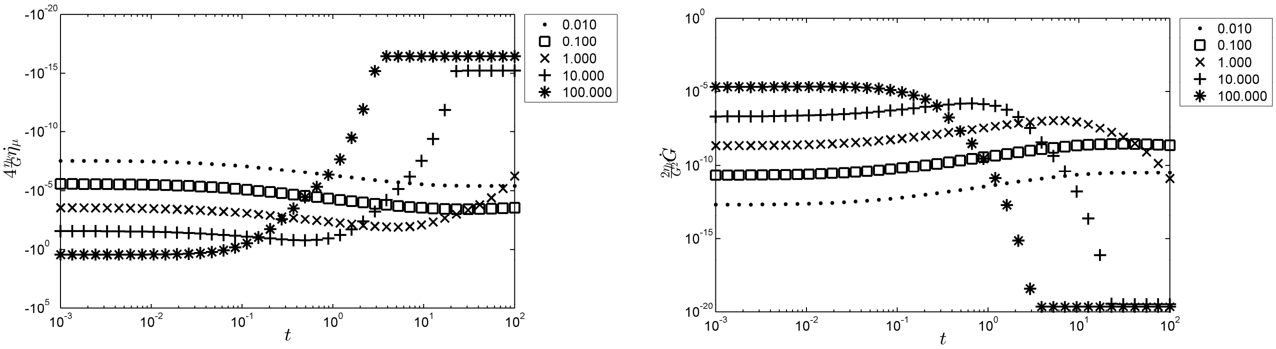

Fig.4 $\dot{\eta}_\mu$ (a) and $\dot{G}$ (b) terms behavior ((a) left side, (b) right side).

Constant shear stress test. In a similar manner as presented above, the material fully structured is the initial condition of this test, when suddenly a constant shear stress (τ_0) is imposed, i.e., $\tau = H\left(t\right)\tau_0$. The Fig. 5 shows the results of the test simulation.

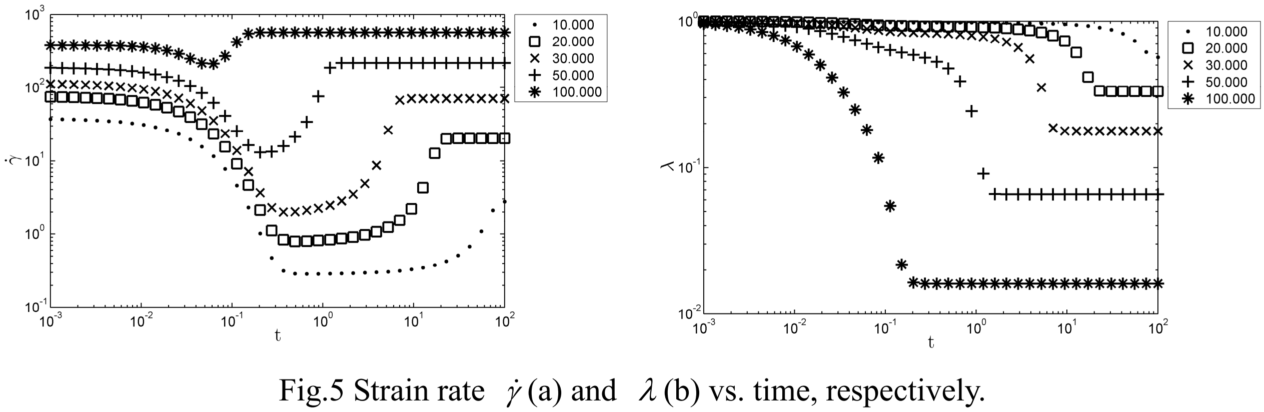

Fig.5 Strain rate $\dot{\gamma}$ (a) and λ (b) vs. time, respectively.

Note that the material starts to flow and the linkages begin to break down. The characteristic behavior of the thixotropic material is emphasized, in some imposed stress values, when the shear rate decrease (the structure level increase and resists the imposed shear stress) till a specific point when the structure does not resist anymore, and the shear rate turns to grow up and the steady state is reached. This effect is well-known in the specialized literature and is called “Avalanche effect”. The Fig. 6 presents the behavior’s influence of the terms $\dot{G}$ and $\dot{\eta}_{\mu}$ along this rheological test.

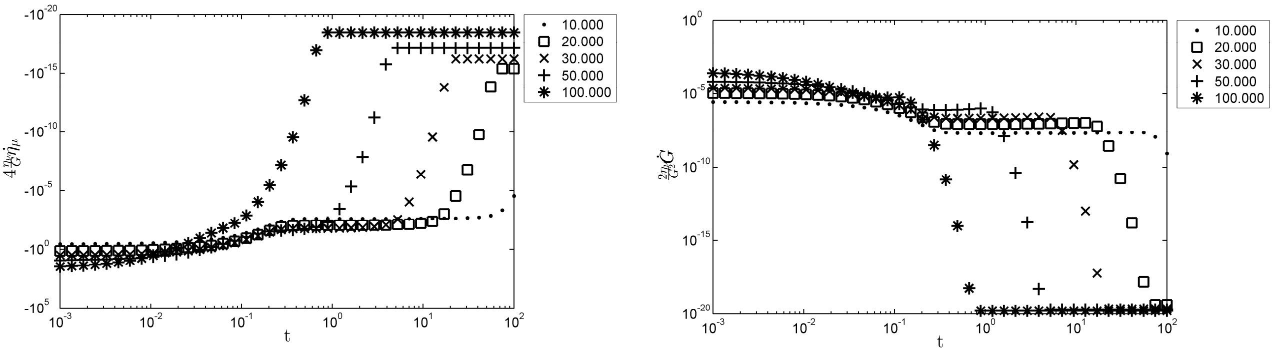

Fig.6 $\dot{\eta}_{\mu}$ (a) and $\dot{G}$ (b) terms behavior ((a) left side, (b) right side.

Conclusion

The main idea of this work was to present a new constitutive model and show the potential of this model for the adequate representation of the behavior/properties of thixotropic materials.

The proposed new constitutive model incorporates, in your dynamical principles, the sensibility of the time changes in shear modulus and viscosity. The relationship between the structural changes and constitutive equation (considering the influence of the shear modulus and the viscosity time rate) was formally described under some rheological constraints.

The rate equation development was based on two well-established physical principles, the Smoluchowski coagulation theory and the Reptation (De Gennes) model. This equation shows to be efficient to represent the microstructural behavior of a thixotropic substance, in a theoretical point of view.

Finally, the numerical analysis of some rheological tests showed an excellent agreement between the proposed model responses and the expected responses from a thixotropic substance.

Acknowledgments

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