A new constitutive model for time-dependent fluids

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ABSTRACT

Many fluids found in our daily lives and in industry are time-dependent, such as daily care products, coatings, paints, etc. These fluids response varies with time even for a constant imposed load. In the current work, a general model to predict the behaviour of time-dependent fluids is proposed. This easy-to-understand and -to-fit model can be applied to either thixotropic or anti-thixotropic fluids and is a function of both load (either stress or shear rate) and time-dependent properties. The time-dependent materials dealt in this work are those in which an equilibrium is reached within an observable time after a constant load (stress or shear rate) is applied. This model is based on a kinetic equation derived from the equilibrium condition. A viscoelastic constitutive equation based on the Jeffrey's model is used in step-up change simulations to exemplify the model potential. While the common stress overshoot is obtained in shear rate controlled experiment, the avalanche effect found in yield stress materials is noted in creep tests.

INTRODUCTION

Many fluids found in our daily lives and in industry are time-dependent, such as daily care products, coatings, paints, drilling muds, starches, different kind of gels, suspensions, polymer solutions, polymer melts, ketchup, mayonnaise, canned baby foods, grease, melts, etc. These fluids response varies with time even for a constant imposed shear rate or stress. The knowledge of the flow behaviour of these kinds of fluids is quite important either for industrial applications (eg. What is the pumping pressure to move a fluid from place to place?) or for our everyday life use (eg. How easy is it to push toothpastes from customer tubes?).

Some of these fluids are classified as viscoelastic because elasticity causes time-dependency[1] and some others as thixotropic or anti-thixotropic (rheopetic) since the change on the material structure produces the time response. There are still some more complex materials that encompass simultaneously viscoelasticity and change on the material structure[2]. Larson[3] called the purely thixotropic materials as ideal thixotropic once they have instantaneous stress relaxation upon cessation of flow and the materials that include both viscoelasticity and thixotropy as nonideal thixotropic.

Purely viscoelastic materials are those in which their properties, such as viscosity and/or elastic modulus, are constant (linear viscoelasticity) or load dependent (non-linear viscoelasticity) but are not time-dependent, so that the material properties vary immediately after any load change. If the structure of this kind of material change with the imposed load, the time for breaking or building up the structure is much smaller than the viscoelastic relaxation or retardation times. On the other hand, the structure dependent materials, either ideal thixotropic (viscoplastic-thixotropic) or nonideal thixotropic (viscoelastic-thixotropic), are those in which their properties are both load and time-dependent, so that the properties do not change immediately after load variations. Notably, the non-linear viscoelastic materials are a particular case of viscoelastic-thixotropic materials.

How can thus a viscoelastic fluid be distinguished from either a viscoplastic-thixotropic or a viscoelastic-thixotropic material if their responses are all time-dependent? A controlled shear rate test can be used to differentiate them. Figure 1 illustrates the stress response of purely viscous, viscoelastic, visco-thixotropic (ideal thixotropic) and viscoelastic-thixotropic materials to a step-up change of shear rate. As shown, the stress response: for purely viscous fluids rises immediately to the equilibrium; for viscoelastic fluids increases gradually to the steady state; for visco-thixotropic fluids reaches immediately a large value decreasing steadily to the equilibrium and; for viscoelastic-thixotropic fluids gradually increases exceeding the equilibrium and then returns to the final value. Two time constants play a role on the behaviour of the viscoelastic-thixotropic material: the relaxation time, λ, that is related to viscoelasticity and the structure time constant, t_{eq}, that depends on how fast the structure of the material changes. The other three materials are particular cases of the viscoelastic-thixotropic material, depending on the magnitude of these two time constants in comparison to the experiment time scale, t_{exp}, that in the current case can be characterized as the inverse of the experiment shear rate. For a very slow experiment ($t_{exp} >> \lambda \sim t_{eq}$), the material appears to be purely viscous. While a viscoelastic material is the one with a very small structure time constant and large relaxation time, the visco-thixotropic has a tiny relaxation time and large structure time constant in comparison to the experiment time scale. For viscoelastic-thixotropic materials, the experiment time scale is on the same order of magnitude of the two time constants. Table 1 shows the materials classification according to these two time constants.

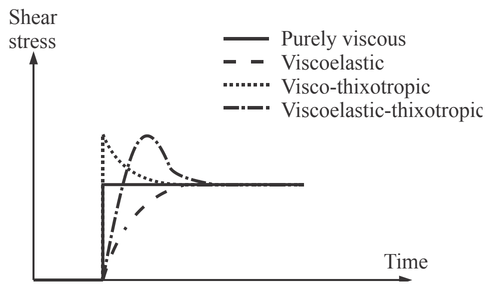

Figure 1. Shear stress response of different materials to a step-up change of shear rate.

Table 1 – Classification of materials according to relaxation and structure time constants.

Time constants	**Type of material**
$t_{exp} >> \lambda \sim t_{eq}$	Purely viscous
$t_{eq} << t_{exp} \leq \lambda$	Viscoelastic
$\lambda << t_{exp} \leq t_{eq}$	Visco-thixotropic
$t_{exp} \leq \lambda \sim t_{eq}$	Viscoelastic-thixotropic

Several works have developed constitutive equations to predict the behaviour of thixotropic materials[2,4,5]. Most of them are based on a structure parameter that describes the level of material structure and use a kinetic equation to predict the change of the material structure with time[6]. Usually, the structure parameter varies from 0 to 1, meaning the fluid is totally unstructured and completely structured, respectively. Some thixotropy models do not include elasticity[7,8] and some others consider it in the material structure[4,9,10]. Despite the large amount of models available, a general model has not yet been able to describe appropriately the thixotropic or rheopetic behaviour of these materials.

The kind of time-dependent materials dealt in this work are those in which an equilibrium is reached within an observable time after a constant load (stress or shear rate) is applied. Besides, the process is said to be completely reversible as only one equilibrium condition is allowed for a constant load. Materials such as waxy crude oils in which the flow curve may depend on the shear and thermal history[11–13] are not considered here.

In this work, a general model for time-dependent materials, either thixotropic or rheopetic, is proposed. This model, however, is not based on a structure parameter but rather, on time-dependent properties computed from a kinetic equation derived from the equilibrium condition.

MATHEMATICAL MODEL

A constitutive equation usually correlates the shear stress tensor to the material response and can generally be written as:

$$\tau_{ij} = F_1\left(\dot{\gamma}_{ij}, \ddot{\gamma}_{ij}, \dot{\tau}_{ij}, \theta_1, \theta_2, \ldots, \theta_n\right) \quad (1)$$

where τ_{ij} is the shear stress tensor that is a function of the shear rate, $\dot{\gamma}_{ij}$, of the rate of the shear rate, $\ddot{\gamma}_{ij}$, and of the shear stress rate, $\dot{\tau}_{ij}$, tensors. θ_1, θ_2 and θ_n are time dependent properties of the material, such as, viscosity, elastic modulus, etc. Those material properties can be dependent only on the load (shear stress or shear rate), for time-independent properties, or dependent on both load and time, for time-dependent properties. A general form of a time-dependent property can be written as a function of the load and of time:

$$\theta_k = \theta_k\left(L, t\right) \quad (2)$$

where L is an invariant of the load - either shear stress, τ_{ij}, or shear rate, $\dot{\gamma}_{ij}$, tensors - and t is the time. For time-independent property fluids, a change on the load (shear rate for instance) causes an immediate change on the property that, of course, depends on the time scale of the change.

If a constant load (shear rate or shear stress) is imposed to the material, its properties tend to the equilibrium. According to Eq. 2, the equilibrium properties can then be written as:

$$\theta_{k,e}\left(L\right) = \theta_k\left(L, t \to \infty\right) \quad (3)$$

where $\theta_{k,e}$ is the equilibrium counterpart of θ_k that depends only on the load.

Many have devised models for the time dependent properties based on a structure parameter[4,5,7–10] that is derived from a kinetic equation. Differently from previous works, the difference between the equilibrium and the instantaneous value of a property is stablished as the driving force for a fluid property change. A rate equation for any material property, based on the product of a load function and on a function of the property unbalance from the equilibrium, is thus proposed:

$$\frac{d\theta_k(L,t)}{dt} = F_2\left(L\right)F_3\left[\theta_{k,e}\left(L\right) - \theta_k\left(L,t\right)\right] \quad (4)$$

where $F_2(L)$ is a positive function of an invariant of an imposed load and F_3 is a function of the property unbalance. As noted, the difference in brackets is the unbalance between the equilibrium value and the instantaneous value of θ_k, which is positive if the equilibrium value is larger than the instantaneous counterpart and negative if the opposite happens. If a constant load, L, is maintained for a long period ($t \to \infty$), the variation rate tends to zero, as θ_k approaches $\theta_{k,e}$:

$$\frac{d\theta_k(L, t \to \infty)}{dt} = 0 \quad (5)$$

Considering that the breakdown is usually faster than the buildup[1], a possible function for F_2 can be defined as:

$$F_2(L) = 1 + \alpha L^{\beta} \tag{6}$$

where α and β are fitting parameters. As noted, if the load is removed, the material builds up to the equilibrium at zero load condition, $\theta_{k,e}(L=0)$. This function also allows the material break-up to be load dependent.

Many structure parameter models base the calculation on the equilibrium. Although this is equivalent to the Eq. 4, the approach proposed here is much easier to understand and perhaps to fit. It is also worth mentioning that the current model states that the driving force can be either the shear stress or the shear rate.

In order to illustrate the model potential, a thixotropy model based on the Jeffrey's equation is used as an example:

$$\tau_{ij} + \theta_1(\tau,t)\frac{d\tau_{ij}}{dt} = \eta_v(\tau,t)\left[\dot{\gamma}_{ij} + \theta_2(\tau,t)\frac{d\dot{\gamma}_{ij}}{dt}\right] \tag{7}$$

where θ_1 and θ_2 are the time-dependent relaxation and retardation times given, respectively, by:

$$\theta_1(\tau,t) = \frac{\eta_v(\tau,t) - \eta_\infty}{G} \tag{8}$$

$$\theta_2(\tau,t) = \frac{\eta_v(\tau,t) - \eta_\infty}{\eta_v(\tau,t)}\frac{\eta_\infty}{G} \tag{9}$$

where τ is the second invariant of τ_{ij}, η_v is the instantaneous viscosity that depends on τ, η_∞ is the completely unstructured state viscosity, and G is the shear modulus. The properties are assumed to be shear stress dependent rather than shear rate dependent, as suggested by Souza Mendes and Thompson[4] and Larson[3]. In order to simplify the model, G and η_∞ are assumed load and time-independent. Based on Eq. 4, a simple equation rate for the viscosity is proposed:

$$\frac{d\eta_v(\tau,t)}{dt} = \frac{\eta_{v,e}(\tau) - \eta_v(\tau,t)}{t_{eq}} \tag{10}$$

where t_{eq} is the material structure time constant. As noted in Eq. 4, F_2 is assumed to be 1.0 and F_3 as $\left[\eta_{v,e}(\tau) - \eta_v(\tau,t)\right]/t_{eq}$. According to Eq. 10, the instantaneous viscosity approaches exponentially the equilibrium viscosity for an applied constant shear stress. t_{eq} represents the time for the viscosity to reach exponentially 67% of its final value if a constant shear stress is applied to the material.

The time response of the model depends on the magnitude of the experiment time scale, t_{exp}, in comparison to the material time constant, t_{eq}. The material properties are time-independent if t_{exp} is much larger than t_{eq} and thixotropic (time-dependent) if t_{exp} is much smaller than t_{eq}.

The equilibrium viscosity of the fluid is based on the model proposed by Blackwell and Ewoldt[14]:

$$\eta_{v,e}(\dot{\gamma}) = \eta_\infty + \frac{\eta_0}{1 + a\dot{\gamma}} \tag{11}$$

where η_0 is the viscosity of the completely structured material, a is a positive parameter that controls the curve slope and $\dot{\gamma}$ is the second invariant of $\dot{\gamma}_{ij}$. As noted, the equilibrium viscosity changes from $\eta_\infty+\eta_0$ (maximum) to η_∞ (minimum) as the shear rates varies from 0 to ∞, respectively. As the current model requires the properties being shear stress dependent rather than shear rate dependent, Eq. 11 is rewritten as:

$$\eta_{v,e}(\tau) = \frac{1}{2}\Big\{(\eta_\infty + \eta_0) - a\eta_\infty\tau + \sqrt{\left[a\eta_\infty\tau - (\eta_\infty + \eta_0)\right]^2 + 4a\eta_\infty\tau}\Big\} \tag{12}$$

which is the only root of the second order equation that provides a positive value for the viscosity.

In order to evaluate the model, the above equations are written in the dimensionless form as:

$$\tau^* + \left(\eta_v^* - 1\right)\frac{d\tau^*}{dt} = \eta_v^*\left(\dot{\gamma}^* + \frac{\eta_v^* - 1}{\eta_v^*}\frac{d\dot{\gamma}^*}{dt}\right) \tag{13}$$

$$\dot{\eta}_v^*\left(\tau^*, t^*\right) = \frac{\eta_{v,e}^*\left(\tau^*\right) - \eta_v^*\left(\tau^*, t^*\right)}{t_{eq}^*} \tag{14}$$

$$\eta_{v,e}^*\left(\tau^*\right) = \frac{1}{2}\left\{\left(1+\eta_0^*\right) - a^*\tau^* + \sqrt{\left[a^*\tau^* - \left(1+\eta_0^*\right)\right]^2 + 4a^*\tau^*}\right\} \tag{15}$$

where $\tau^* = \tau/(\eta_\infty \dot{\gamma}_{ref})$, $\eta_v^* = \eta_v/\eta_\infty$, $\eta_0^* = \eta_0/\eta_\infty$, $t^* = t(G/\eta_\infty)$, $\dot{\gamma}^* = \dot{\gamma}/\dot{\gamma}_{ref}$, $t_{eq}^* = t_{eq}(G/\eta_\infty)$ and $a^* = a\dot{\gamma}_{ref}$. Notably, the relaxation time η_∞/G is used as a reference for the dimensionless time, so that t_{eq}^* is the ratio of the structured material time constant, t_{eq} and of η_∞/G. If the structured material time constant tends to zero, the properties change immediately and consequently, a viscoelastic response is observed. As t_{eq}^* increases, the variation of the properties is not instantaneous, and the response is the one of a viscoelastic-thixotropic fluid.

It is worth mentioning that the proposed model is represented by only three dimensionless parameters, t_{eq}^*, a^* and η_0^*.

RESULTS AND DISCUSSION

In order to demonstrate the model potential, this section presents results obtained from the solution of Eqs. 13, 14 and 15 for shear rate and shear stress controlled tests. The initial condition for these flows is of a fully relaxed fluid, $\tau^* = 0$, at rest, $\dot{\gamma}^* = 0$. Consequently, the initial viscosity is $\eta_v^*(t=0) = \eta_0^* + 1$. All the simulations were performed with the following set of parameters: $a^* = 10^5$ and $\eta_0^* = 10^6$.

Shear rate controlled test

For these tests, a constant shear rate, $\dot{\gamma}_f^*$, is imposed to the material at $t = 0$. Figure 2 presents the shear stress as a function of time for different imposed shear rates and $t_{eq}^* = 1$.

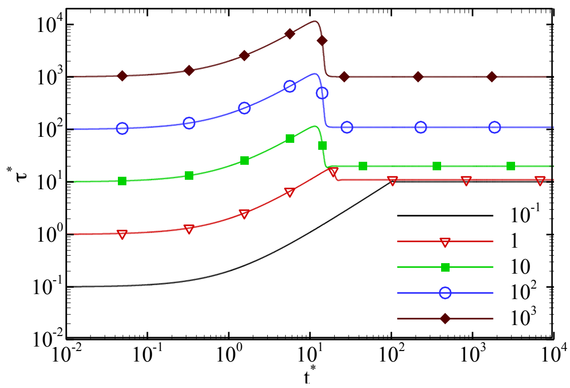

Figure 2. Shear stress as a function of time for constant shear rates of 10^{-1}, 1, 10, 10^2 and 10^3.

As shown by Souza Mendes and Thompson[4], the initial shear stress is $\tau_i^* = \dot{\gamma}_f^*$. After the shear rate is imposed ($t > 0$), there is a linear increase in the shear stress as a result of an elastic response. An overshoot is then noted, indicating a transition from an elastic dominant region to a viscous predominant region. After that, the material relaxes and the shear stress decreases to the equilibrium. The smaller the shear rates the smaller is the overshoot and the higher is the time to reach it, as the experiment time scale reduces with the shear rate increase. For a shear rate of 10^{-1}, the overshoot is not observed, indicating that the material structure time constant is small in comparison to the experiment time scale and consequently showing only the material viscoelastic behaviour.

Shear stress controlled test

In this test, t_{eq}^* is set to 100 and a constant shear stress, τ_f^*, is imposed at t = 0. Figure 3 presents the results of the shear rate as a function of time for different shear stresses.

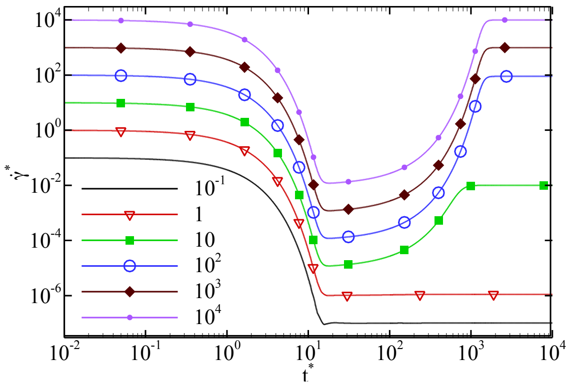

Figure 3. Shear rate as a function of time for constant shear stress of 10^{-1}, 1, 10, 10^2, 10^3 and 10^4.

As shown by Souza Mendes and Thompson[4], the initial shear rate is $\dot{\gamma}_i^* = \tau_f^*$. After the shear stress is imposed, the initial shear rate reduces slightly and then decreases significantly. After that, the shear rate is maintained at very slow values or increases rapidly to a steady-state value. This fast increase is well documented in the literature[4,15,16] and is known as avalanche effect. As noted for the lower shear stress imposed (10^{-1} and 1), there is no avalanche effect, because the equilibrium viscosity for the imposed stress is significantly high. Since the viscosity almost does not change under these conditions, it can be assumed that the material does not flow.

CONCLUSIONS

In this work, a general model to predict the behaviour of time-dependent materials was devised. The time-dependent properties are computed from a rate equation that is based on the equilibrium property condition.

The Jeffrey's model and an equilibrium viscosity equation proposed by Blackwell and Ewoldt[14] were employed to show the model potential. The final model has only three dimensionless parameters, a number significantly smaller than that observed in literature[4,7,9,10].

The results for shear rate and shear stress controlled tests presented the key features of the model. In the constant shear rate test, the stress response showed a linear elastic increase and a stress overshoot which were expected for viscoelastic-thixotropic materials. As for the constant shear stress test, the avalanche effect was observed for high-imposed stresses and the material did not yield for low shear stresses.

It can be concluded that the proposed model has shown the main features of time-dependent materials as other more complex models[4,9].

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