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# CONSTITUTIVE RELATION FOR THIXOTROPIC FLUIDS CALIBRATED TO A LAPONITE SOLUTION

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***Abstract.*** *Understanding thixotropic fluids is a major concern of the oil industry, since waxy crudes exhibit a time dependent behavior that is usually modeled as thixotropy. These materials also exhibit an elasto-viscoplastic behavior, which is still a challenge to be modeled mathematically. In the current work, a mathematical model is employed to predict the flow start-up of a Laponite RD solution, a thixotropic material with yield stress. The model computes the evolution of the material properties from their value in steady state, rather than using a microstructural parameter. Also, the simplest evolution equations for this model were used, to verify their prediction capability. The material flow curve and start-up experiments were developed in order to accomplish the model fitting. Numerical simulations were conducted in order to compare the experimental and numerical results. The main qualitative characteristics of the start-up were successfully predicted by the mathematical model, i.e., an initial linear increase on the shear stress as a function of the strain, followed by an overshoot and then relaxation until reaching steady state. The overshoot shear stress value, the most relevant parameter to be predicted, was also quantitatively well predicted by the model.*

***Keywords:*** *Thixotropy, Mathematical model, Laponite, Start-up.*

## 1. INTRODUCTION

Thixotropy is a characteristic that can be found in many materials, such as paints, bentonite and laponite solutions, drilling fluids, starch pastes and even the human blood (Barnes, 1997; Chhabra and Richardson, 2008; Apostolidis et al., 2015). Thixotropic materials are characterized by a continuous decrease in the apparent viscosity when submitted to shear from rest, with complete recovery of the viscosity when shear is removed (Mewis, 1979; Barnes, 1997). The prediction of a thixotropic behavior through mathematical modeling is complex, as the material can exhibit not only thixotropy, but also viscoelasticity and viscoplasticity. The difficulty is reflected in the many mathematical models developed for thixotropic fluids (Sestak et al., 1987; Santos and Negrão, 2017; de Souza Mendes et al., 2018; Wei et al., 2018). One of the main challenges of these models is to fit the parameters. As the complexity of the models increased over the years, the number of parameters to be fit increased as well. In addition, sometimes parameters without physical meaning are present, which increases the difficulty of fitting.

Many of the mathematical models for thixotropic fluids rely on a scalar structural parameter (usually denoted by $\lambda$) (de Souza Mendes, 2011; Ahmadpour e Sadeghy, 2014; Guo et al., 2015), which is responsible for dictating the structural level of a thixotropic material by an indirect way (de Souza Mendes and Thompson, 2012). It is not simple to correctly predict the fluid behavior using this parameter, since it is not easily measurable and a homogeneous structure for all the material has to be assumed, which can be an unreal condition.

The mathematical model proposed by Santos and Negrão (2017) aims to avoid this problem, by not using a structural parameter in their formulation. The model is based on measurable properties of the material, which may assist a rheologist on the fitting. In this sense, the objective of the current paper is to fit the proposed model to the rheological data of a thixotropic fluid, a Laponite RD solution, and then to verify if the model correctly predicts the material response during an experimental flow start-up process.

## 2. MATERIALS AND METHODS

### 2.1 Fluid formulation and Experiments

An aqueous solution of Laponite RD 2% wt was formulated. NaOH was added in order to increase the pH to 10 and stabilize the solution (Tanaka et al., 2004). $10^{-3}$ mol/l of NaCl were added to the solution in order to increase the yield stress of the fluid, since it increases the van der Waals attraction between particles, overcoming electrostatic repulsion and forming a stronger gel (Tanaka et al. 2004).

The Anton Paar MCR 702 TD rheometer was employed for the experiments. The tests were performed under ambient temperature (around 25 °C) using cross-hatched (for the lower shear rates, in order to avoid fluid slippage on the geometry) and sandblasted (for the higher shear rates, to avoid secondary flows) parallel plates geometries with 35 mm of diameter each. A pre-shear of $10^3$ s$^{-1}$ was imposed to the sample for 10 minutes prior to each test in order to ensure a homogeneous state and to erase the shear history of the material. Shear rate-controlled experiments were performed in order to obtain the material flow curve and start-up results. For the flow curve, the equilibrium shear stresses for the shear rates of 800, 600, 100, 10 and 1 s$^{-1}$ were measured, whereas for the start-up results, the material was left to rest for 10 minutes under a zero-shear stress condition after the pre-shear, and then, a constant shear rate of 1 s$^{-1}$ was imposed in order to start-up the flow. The zero-shear stress time is required to ensure a material structure build-up, in order for the start-up experiment to be successful.

### 2.2 Mathematical Model

The mathematical model was based on the one developed by Santos and Negrão (2017). It uses a modified Jeffreys constitutive equation, which can be written as follows:

$$\tau + \left( \frac{\eta_v + \eta_\infty}{G} \right) \dot{\tau} = \eta_v \left( \dot{\gamma} + \frac{\eta_\infty}{G} \ddot{\gamma} \right) \tag{1}$$

where $\tau$ is the second invariant of the shear stress tensor, $\eta_v$ is the structural viscosity, $\eta_\infty$ is the viscosity plateau corresponding to the completely unstructured material, $G$ is the elastic modulus, $\dot{\tau}$ is the rate of change of the second invariant of the shear stress tensor, $\dot{\gamma}$ is the second invariant of the shear rate tensor and $\ddot{\gamma}$ is the rate of change of the second invariant of the shear rate tensor.

The structural viscosity and the elastic modulus are load and time dependent. Their evolution equations are modeled, respectively, as:

$$\frac{d\eta_v}{dt} = \frac{\eta_{v,eq} - \eta_v}{t_{eq}} \tag{2}$$

$$\frac{dG}{dt} = \frac{G_{eq} - G}{t_{eq}} \tag{3}$$

where the subscript $eq$ stands for the property at equilibrium and $t_{eq}$ is the characteristic time for the material build-up.

It is interesting to note that, as mentioned earlier, Eqs. (2) and (3) do not require a structural parameter to compute the evolution of the properties, being also rather simple equations. In addition, it is worth mentioning that in this formulation, the characteristic times for both equations are considered the same. This is the simplest case, since different characteristic times could be employed for each property.

The equilibrium viscosity, $\eta_{v,eq}$, is modeled by a Herschel-Bulkley equation with the Papanastasiou's (1987) regularization and a constant plateau for when the shear rate tends to the infinity, $\eta_\infty$:

$$\eta_{v,eq} = \eta_\infty + \left[ 1 - \exp\left( -\frac{\eta_0 \dot{\gamma}}{\tau_0} \right) \right] \left( \frac{\tau_0}{\dot{\gamma}} + k \dot{\gamma}^{n-1} \right) \tag{4}$$

where $\eta_0$ is the regularization parameter, meaning the completely structured material viscosity, $\tau_0$ is the yield stress, $k$ is the consistency index and $n$ is the power-law index.

In summary, the model contains 8 parameters to be found: $\eta_0, \eta_\infty, \tau_0, k, n, G_0, G_{eq}$ and $t_{eq}$.

## 3. RESULTS AND DISCUSSION

### 3.1 Flow Curve

The flow curve of the Laponite solution was obtained experimentally, and then the parameters from Eq. (4) were fit to the curve. The comparison between the experimental results and the modified Herschel-Bulkley model are shown in Figure 1. The fitting parameters are shown in Table 1. It is worth mentioning that the maximum difference between the experimental and computed results was of 0.3% at 10 $s^{-1}$.

**Table 1 - Parameters for the numerically adjusted flow curve.**

| Parameter | Value |
|---|---|
| $\eta_\infty$ [Pa.s] | $4.7\times10^{-3}$ |
| $\eta_0$ [Pa.s] | 45.0 |
| $\tau_0$ [Pa] | 4.58 |
| $k$ [Pa.s$^n$] | 0.605 |
| $n$ [-] | 0.293 |

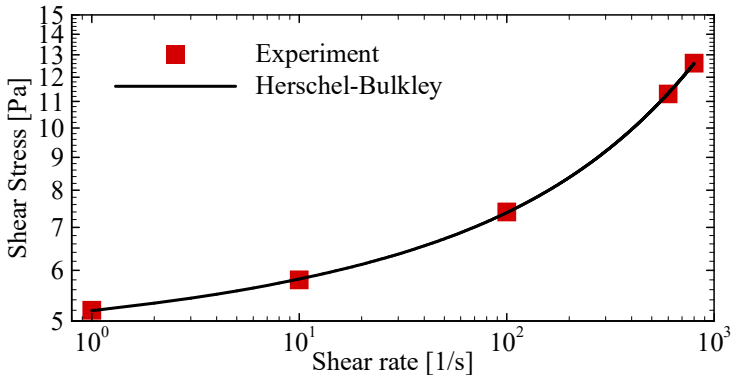


**Figure 1 - Experimental and numerical flow curves of the Laponite solution.**

### 3.2 Characteristic time and elastic modulus

The fitting of the characteristic time was obtained from the start-up experimental results. The strain corresponding to the maximum shear stress was considered as the critical strain. Once this strain was found, the characteristic time was fit to the following equation:

$$t_{eq} = \frac{\gamma_c}{\dot{\gamma}} \tag{5}$$

where $\gamma_c$ is the critical strain and $\dot{\gamma}$ is the imposed shear rate for the start-up test.

The initial elastic modulus, $G_0 = G(t=0)$ was fitted to the Hooke's law (Hearn, 2000):

$$\tau = G\gamma \tag{6}$$

where $\gamma$ is the strain.

Figure 2 shows the shear stress as function of the strain for the start-up experiment with a constant shear rate of 1 $s^{-1}$. In this figure, the dashed vertical line represents the critical strain $(\gamma_c = 0.88)$, and the full circle depicts the elastic region to be represented by Eq. (6).

In order to find $G_{eq}$, once the start-up experiment reaches steady state (400 s on the example above), a higher shear rate of 10 $s^{-1}$ was imposed, and then the linear region was used once more to find the new elastic modulus. With these simple experiments, the values found for the elastic modulus were: $G_0 = G(t=0) = 23.2$ Pa and $G_{eq} = 1.9$ Pa.

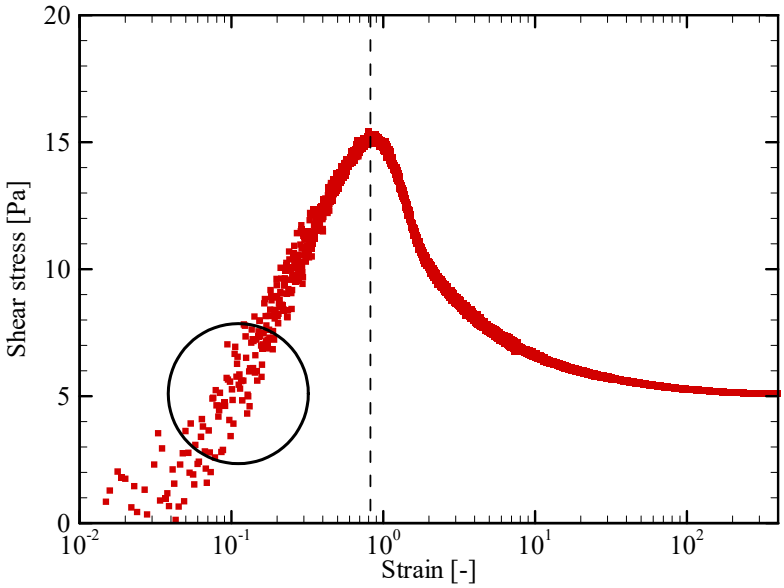


**Figure 2 - Start-up experiment showing the critical strain (vertical dashed line) and the region for the linear shear stress adjust to find the elastic modulus (full circle).**

It is interesting to note that the value of $G_0$ is higher than $G_{eq}$, which is a rather intuitive response. When the material is gelled and at rest, the behavior is mainly elastic. However, when the steady state is reached after the start-up, the response is predominantly viscous. This means that the expected elastic response is much smaller that the viscous one, resulting in a lower value of $G$.

As mentioned earlier, for this case, the equilibrium time, $t_{eq}$ was considered the same for both the structural viscosity and the elastic modulus, in order to show a simple model. However, different equilibrium times could be used for each property. The elastic modulus characteristic time could be found via an oscillatory experiment, for example.

### 3.3 Comparison Between Experimental and Numerical Results

Using the parameters found in the previous section, numerical simulations were conducted and then compared to the experimental results. This comparison can be seen on Figure 3, where the shear stress response of the material is shown as a function of the strain.

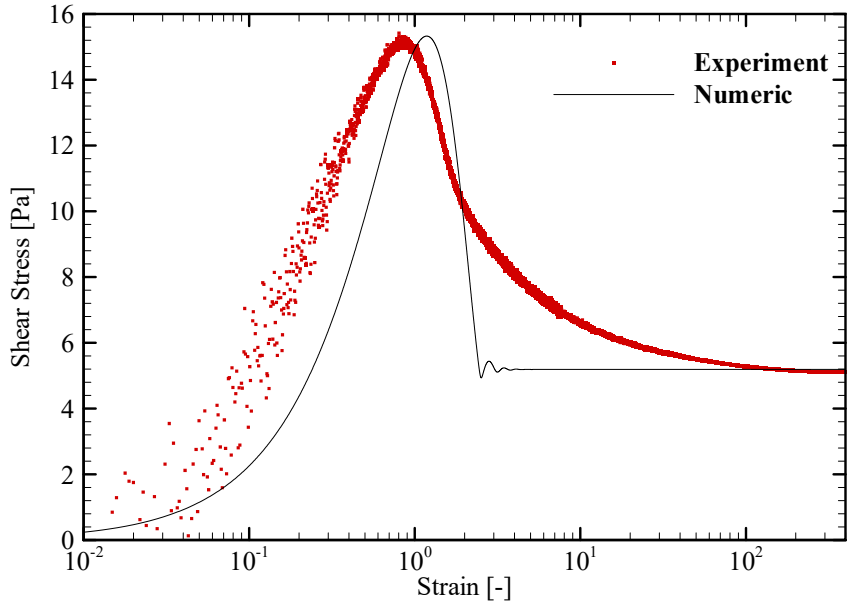


**Figure 3 - Start-up results for the experimental test and the numerical simulation of the laponite solution.**

It can be seen that the qualitative response of the numerical results is quite similar to that of the experimental ones, i.e., the linear increase of the shear stress until it gets close to the overshoot, the overshoot itself and the shear stress relaxation until reaching steady state.

The main quantitative points evaluated were the overshoot strain (or the critical strain), the value of the shear stress overshoot and the difference between the steady state values. This analysis can be seen on Table 2.

**Table 2 - Quantitative comparison between the experimental and numerical results.**

| Point evaluated | Experimental value | Numerical value | Difference |
|---|---|---|---|
| Overshoot shear stress | 15.36 [Pa] | 15.33 [Pa] | 0.20% |
| Critical strain | 0.88 [-] | 1.18 [-] | 25.42% |
| Steady state shear stress | 5.13 [Pa] | 5.19 [Pa] | 1.16% |

This table depicts that the quantitative response of the mathematical model is similar to the experimental one for both the overshoot shear stress and the steady state value. The critical strain, however, shows a non-negligible difference between the results, but with the same order of magnitude. This parameter has a direct relation to the time of the experiment, meaning that the numerical simulations are taking about 25% longer to reach the overshoot value. This difference and the one seen on the time for the steady state to be reached can be justified by the simplicity of the evolution equations chosen, Eqs. (2) and (3).

Even though there are differences on the strain (or time) for the simulations to reach the overshoot or the steady state, it must be emphasized that the most important point to be considered is the overshoot shear stress. This comes from the necessity of prediction of the overshoot shear stress in order to ensure that the pipelines that transport oil & gas are well dimensioned and will not fail. Since the difference between the experimental and numerical results for this point was of only 0.20% it can be seen that the model satisfied its purposes.

## 4. CONCLUSIONS

In this work, a mathematical model for thixotropic fluids was presented and its eight parameters were fit to a Laponite solution rheological data. This material has an elasto-viscoplastic and thixotropic behavior when sheared from rest. One of the main features of the presented model is that it does not require a structural parameter to compute the evolution of the material properties, which is an advantage in several ways. For instance, finding suitable values for the structural parameter is not an easy task, since it cannot be directly measured. The evolution equations chosen for the elastic modulus and the structural viscosity were simple and based on the assumption that they could be computed from the equilibrium state.

The flow curve of the material was experimentally found, and then the numerical adjust was done, finding five parameters of the model $\left(\eta_0, \eta_\infty, \tau_0, k, n\right)$. From the start-up experiment the other three parameters required for the numerical simulations $\left(G_0, G_{eq}, t_{eq}\right)$ were found.

Comparing the numerical and experimental results it was shown that the qualitative response from both results was rather similar. Even though differences were found for the critical strain, the overshoot shear stress was predicted with minimum differences from the experiments. This shows that this simple model is able to successfully predict the main characteristics of a start-up experiment and its parameters are easily calibrated from simple experiments.

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