Rheological Characterization and Structural Modeling of a Thixotropic Yield Stress Cosmetic Emulsion

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ABSTRACT

Due to their complex composition, cosmetic products are often shear thinning (decreasing viscosity η with increasing shear rate $\dot{\gamma}$), they may display a yield stress τ_y (no flow for stresses τ lower than τ_y) and they may also be thixotropic (time evolving viscosity under constant solicitation, due to progressive evolution of the material structure) [1]. These properties may be desired because they improve the end-use properties of the product, but in return can also cause problems during the production. While the rheology of thixotropic fluids has been fairly much investigated, their flow simulation was the object of only a few studies [2]. The objectives of this work are to characterize and model the rheological behavior of evolving fluids in order to further simulate the flow of a thixotropic yield stress fluid. The proposed model was built from the regularized Herschel-Bulkley model also called bi-viscosity model. To capture the thixotropic effects, the consistency k was made a function of λ, the time-dependent structure parameter. This parameter is governed by Moore's kinetics. The model was successfully tested in steady state and transient conditions and compared with experimental data obtained from rotational rheometry measurements (ARG2 and ARES rheometers both from TA Instruments).

INTRODUCTION AND CONTEXT

Many industrial products (cosmetics, paints, food, etc.) exhibit complex rheological behaviors such as yield stress, shear-thinning, viscoelasticity and thixotropic behaviors. In order to manufacture correctly these products and to provide them the desired end-use properties, it is necessary to understand their rheological behavior. Thixotropy is a time-dependent phenomenon manifested by a decrease in the viscosity of the material over time under constant shear. This behavior is often displayed by dispersions of particles or macromolecules within which weak interactions produce a structured three-dimensional network. Under the effect of shear, the network breaks, destructuration occurs leading to facilitated flow of the fluid and therefore to a lower viscosity. This destructuration is not instantaneous: it follows a kinetics often described by a first order differential equation [3]. A rheological behavior model may be associated to this structural kinetics, such as the Houska model [4] for thixotropic yield stress fluids.

The rheological behavior of rheologically evolving fluids is the subject of numerous studies because knowledge of their flow modalities is necessary for the optimization of many industrial processes. However, structural modeling and numerical simulation of thixotropic fluids remains a subject in full development. In the present study, the aim is first to propose a generic structural rheological model that describes a yield stress thixotropic fluid and secondly that can be easily coupled with the conservation equations of mass and momentum in computational fluid mechanics codes such as ANSYS Fluent software, in order to simulate the flow of these fluids. The paper is organized as follows. In the first part, the thixotropic nature of a cosmetic yield stress fluid will be investigated experimentally from steady state and transient studies. Then, a structural rheological model will be proposed. The model parameters will be determined from the steady state experimental data. Secondly, the rheological model will be solved to predict the transient behavior of the fluid and confronted with the experimental data in section 4. Finally, the perspectives will be presented in chapter 4

EXPERIMENTAL STUDY

A commercial Nivea body lotion of density $\rho = 1040\ kg/m^3$ were used in this study. The lotion was fed directly into the rheometers without any prior preparation. Two rotary rheometers equipped with parallel plate geometry (a stress-controlled rheometer ARG2 and a strain-controlled rheometer ARES, both from TA Instruments) were used. The model parameters are determined from experiments carried out in steady state with the ARG2 rheometer (diameter $D = 40mm$ and gap $h = 1mm$), in order to get low shear rate values and to fit the critical shear rate (see next section). It consists in applying increasing and decreasing shear rate steps to the same sample. For each applied shear rate value, the rheometer records the asymptotic value of viscosity and stress. The thixotropic behavior was investigated in transient regime. In these tests, the shear rate is suddenly reduced from a high value $\dot{\gamma}_0 = 130\ s^{-1}$ applied during $30\ min$ (preshear) to a lower value $\dot{\gamma}_1$. Different values of $\dot{\gamma}_1 = 0.1 - 1 - 10 - 100\ s^{-1}$ were applied for approximately $2h$. Transient measurements were performed with ARES strain controlled rheometer.

REGULARIZED HERSCHEL-BULKLEY MODEL AND STRUCTURAL MODELLING

The proposed rheological model was adapted from Herschel-Bulkley model

$$\begin{gathered} \eta(\dot{\gamma}) = k\dot{\gamma}^{n-1} + \frac{\tau_y}{\dot{\gamma}} \quad if \ \ \tau > \tau_y \\ \dot{\gamma} = 0 \quad if \ \ \tau < \tau_y \end{gathered} \tag{1}$$

where τ_y is the yield stress, k the consistence and n is the flow index. In order to avoid numerical issues during simulation due to tending-to-infinity viscosity, the Herschel Bulkley model was regularized. For the purpose of simulation, the Tanner-Milthrope regularization method was used. In fact, this regularization has been used in ANSYS Fluent Software to simulate yield stress fluids. This technique was first proposed by Tanner [5] for a Bingham fluid (see [3] for more information).

We adapted this regularization to the case of a Herschel-Bulkley fluid. The viscosity is governed by two different functions according to the value of the shear rate. At high shear rate, the viscosity is that of the classical Herschel-Bulkley equation for $\tau > \tau_y$. At low shear rate, the viscosity is very high but finite and a function of the applied shear rate

$$\begin{cases} \eta(\dot{\gamma}) = k(\lambda)\dot{\gamma}^{n-1} + \frac{\tau_y}{\dot{\gamma}} \quad if \quad \dot{\gamma} \geq \dot{\gamma}_c \\ \eta(\dot{\gamma}) = \frac{\tau_y}{\dot{\gamma}_c}\left(2 - \frac{\dot{\gamma}}{\dot{\gamma}_c}\right) + k(\lambda)\dot{\gamma}_c^{n-1}\left((2-n) + (n-1)\frac{\dot{\gamma}}{\dot{\gamma}_c}\right) \quad if \quad \dot{\gamma} < \dot{\gamma}_c \end{cases} \quad (2)$$

This bi-viscous model is continuous and so is its derivative.
In order to capture the thixotropic effects, the Herschel-Bulkley consistency k was replaced by a structural consistency $k(\lambda) = k(1 + \lambda^b)$, where, λ is the structure parameter. It assumes that all interactions are averaged into a single scalar λ that describes the structural state of the fluid, and which varies from 1 to 0. These two values correspond to a completely structured state $(\dot{\gamma} \to 0)$ and a totally unstructured state $(\dot{\gamma} \to \infty)$, respectively. Here, λ is supposed to evolve according to Moore's kinetic equation [6]:

$$\frac{d\lambda}{dt} = -k_1\dot{\gamma}\lambda + k_2(1 - \lambda) \quad (3)$$

with kinetic coefficients k_2 for structure build-up and $k_1\dot{\gamma}$ for structure break-down.

RESULTS AND DISCUSSION

Equation (2) and (3) were solved both in steady state and in transient regime. The model parameters were obtained by fitting the model with steady state experimental data. The adjustment was performed with Matlab by minimizing the least square difference between the experimental and the predicted shear stress $\tau(\dot{\gamma}) = \eta(\dot{\gamma})\dot{\gamma}$. As illustrated in **FIGURE 1**, good agreement was obtained between the model and the experiment. The optimal model parameters are listed in **TABLE 1**

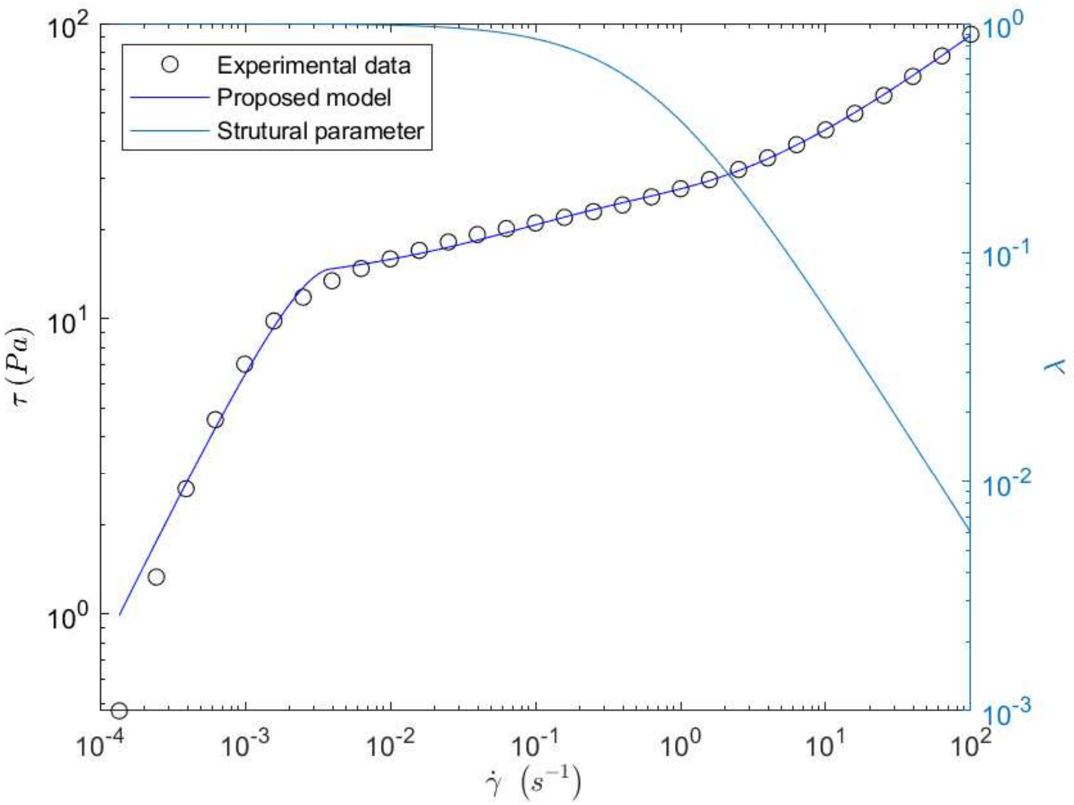

FIGURE 1: Model adjustment with experimental flow curve in steady state regime.

TABLE 1: Optimal model parameters

$\tau_y\ (Pa)$	$k\ (Pa.s^{-n})$	$\dot{\gamma}_c\ (s^{-1})$	$\frac{k_1}{k_2}$	b	n
12.26	12.05	0.00384	1.66	1.34	0.41

Then, the model was used to predict the fluid behavior in transient test (stepwise change in shear rate). The stress τ was normalized by τ_{eq} (the steady state stress) and plotted against time for each build-up kinetic, corresponding to different values of the shear rate. At low shear rate a good agreement is observed between the model end the experimental data. At high shear rates the experimental kinetic is slightly faster than that predicted by the model. It should be a result of shear driven aggregation in the system that increase the build-up kinetics. This is not taken into account by Moore's kinetic model used here. Nevertheless, the prediction of the fluid behavior in transient regime from the adjustment of the model in steady regime is satisfactory. The build-up kinetics is correctly described over different shear rate values. The shear-thinning and the yield stress behavior are well taken into account by the model. This structural model can be easily integrated within ANSYS Fluent or other CFD codes to simulate yield stress, thixotropic and reactive fluid flows in different complex geometries.

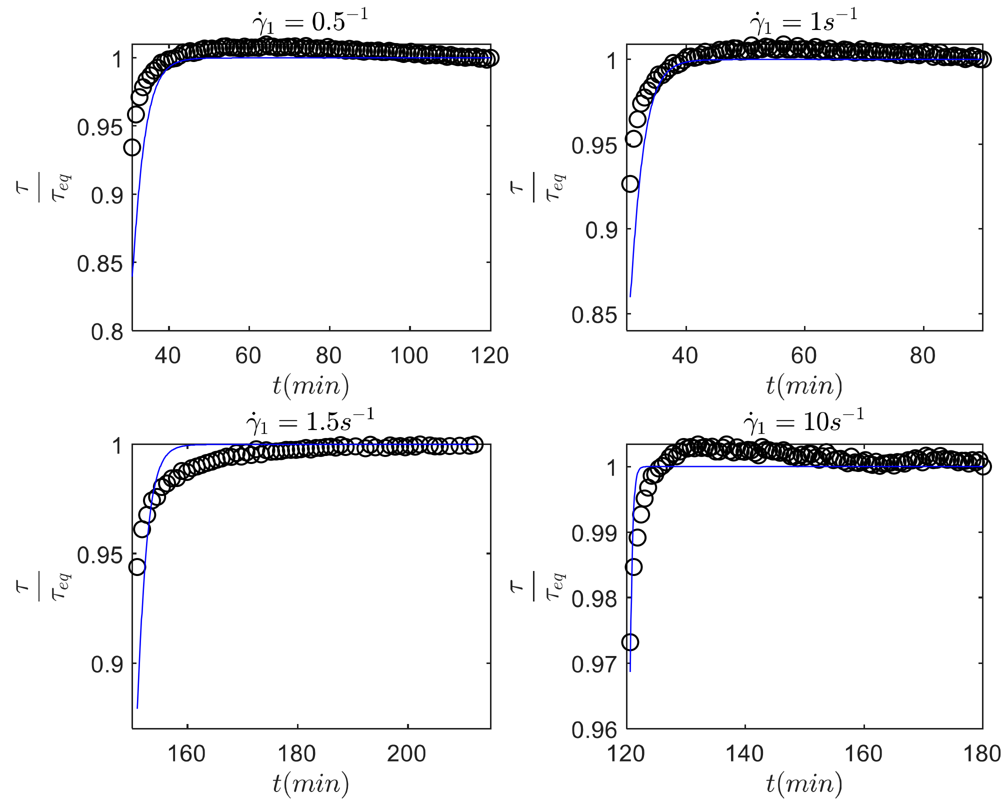

FIGURE 2: Model prediction compared to experimental results for different shear rates from a step rate wise changes from $\dot{\gamma}_0 = 130s^{-1}$ to $\dot{\gamma}_1 = 0.5 - 1 - 1.5 - 10s^{-1}$.

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