

A FRACTIONAL MODEL FOR TIME-VARIANT NON-NEWTONIAN FLOW

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This work applies a fractional flow model to describe a time-variant behavior of non-Newtonian substances. Specifically, we model the physical mechanism underlying the thixotropic and anti-thixotropic phenomena of non-Newtonian flow. This study investigates the behaviors of cellulose suspensions and starch-milk-sugar pastes under constant shear rate. The results imply that the presented model with only two parameters is adequate to fit experimental data. Moreover, the parameter of fractional order is an appropriate index to characterize the state of given substances. Its value indicates the extent of thixotropy and anti-thixotropy with positive and negative order, respectively.

Key words: *fractional calculus, time-dependent, thixotropic, anti-thixotropic, modeling, non-Newtonian flow*

Introduction

In the past few decades, the time-dependent rheological phenomena have been a major research topic. In particular, time-variant non-Newtonian substances attract great attention. However, advances in these areas are quite limited and many problems remain opening. The thixotropic and anti-thixotropic behaviors are often encountered in many areas, such as chemical industry [1], biomedical [2, 3], civil [4], and food engineering [5]. Thus, accurate mathematical models are highly demanded by research communities and industries. They play important roles in enhancing productivity, reducing the waste of resource, and improving product quality. As of today, the existing models are far from satisfying real-world demands.

The main purpose of this study is to seek appropriate strategies for constructing unified and practical models for thixotropic and anti-thixotropic behaviors. Firstly, we discuss the basic concepts of thixotropy [6, 7] by describing a time-dependent continuous decrease of the viscosity under shear. Notably, this effect is reversible when the flow is stopped. In contrast, an anti-thixotropy is that the viscosity increases under shear, but it is usually irreversible [8].

Different approaches have been proposed to incorporate thixotropic and anti-thixotropic phenomena into rheological models. Some models adopted empirical equations. For example, the Weltman model [9], the first-order stress decay models [10, 11], and the models presented in Joye and Poehlein [12] and Tiu and Boger [13] which is based on rate conception.

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However, the *memory* characteristics in the given substance is neglected. Since material parameters typically vary in time, these models encounter great difficulty to depict the memory essence of such phenomena.

Our proposed model is based on fractional derivative. The fractional calculus is a branch of mathematic that defines precise non-integer integrals or derivatives. The applications of fractional calculus are quickened profoundly due to the fact that fewer parameters are required to achieve precise approximation of the rheological experimental data. Its inherent time-dependent and path-dependent features enhance its applications in various fields, such as signal processing [14], viscoelastic mechanics [15], anomalous diffusion [16], electromagnetic [17], and *etc.* Several techniques have also been proposed to solve fractional derivative models [18, 19]. However, to our best knowledge, developing a constitutive relationship of time-variant non-Newtonian substances by means of fractional calculus is not yet available. This paper attempts to adopt a fractional derivative model to investigate the viscosity and shear stress vs. shearing time for time-variant non-Newtonian substances.

Mathematical model

Basics of fractional order derivative

Several definitions exist for fractional derivative, such as the Riemann-Liouville, the Caputo, the Grunwald-Letnikov, and others less common definitions [20]. In our context, the Riemann-Liouville definition is adopted because it is highly related to obtain the fractional flow model for time-variant non-Newtonian substances.

We evaluate the Riemann-Liouville fractional derivative of the Heaviside function $H(t)$. For any c in R , we have [20]:

$$\frac{d^\alpha}{dt^\alpha}[cH(t)] = \frac{c}{\Gamma(1-\alpha)}t^{-\alpha}, \quad (t > 0, \quad \alpha \in R) \quad (1)$$

Fractional flow model

Elastic materials obey the Hooke's law $\tau(t) - \varepsilon(t)$, whereas purely viscous materials obey the law of Newton internal friction, $\tau(t) - d^1\varepsilon(t)/dt^1$ for shear stress, τ , and shear strain, ε . In our fractional derivative approach, the intermediate viscoelastic materials are modeled [21]:

$$\tau_\alpha(t) = E\theta^\alpha \frac{d^\alpha \varepsilon(t)}{dt^\alpha}, \quad 0 \leq \alpha \leq 1 \quad (2)$$

where the fractional order, α , is invariable during deformation, and the parameters E and θ are material constant. Equation (2) has been successfully applied to geomaterials and polymers [22, 23].

The material parameters of many non-Newtonian substances change with time during shearing and show dependence on shear rate and other factors. The time-dependent shear-thinning behavior is commonly referred to as the thixotropic flow behavior. Foods, such as salad dressing and soft cheese, often encounter such thixotropic behavior. In contrast, time-dependent shear-thickening behavior is known as the rheopexy, also known as anti-thixotropy [24]. These time-variant non-Newtonian substances demonstrate strong time-dependent nature, which suggests that eq. (2) can not describe the flow properties of these materials satisfactorily.

Cheng and Evans [25] and Cheny [26] proposed a pair of generalized constitutive equations:

– the state equation

$$\tau = \eta(\lambda, \dot{\gamma})\dot{\gamma} \quad (3)$$

– the equation of rate

$$\frac{d\lambda}{dt} = g_{\dot{\gamma}}(\lambda, \dot{\gamma}) \quad (4)$$

where, τ , η , $\dot{\gamma}$, λ represent the shear stress, viscosity, shear rate, and structural parameter, respectively. Note that, eqs. (3) and (4) can not be directly applied to non-Newtonian fluids without specific expression. To obtain the proper model parameters, complicated experiments must be carried out.

We proposed a time-based fractional flow model for time-variant non-Newtonian substances. The viscosity equation is represented:

$$\eta(t) = k \frac{d^{\alpha}(\dot{\gamma})}{dt^{\alpha}} \quad (5)$$

and the time-dependent flow equation:

$$\tau(t) = k\dot{\gamma} \frac{d^{\alpha}(\dot{\gamma})}{dt^{\alpha}} \quad (6)$$

can be derived by combining eqs. (3) and (5), where k is the constant consistency coefficient, and α is the fractional order. To study any time-variant non-Newtonian substance, most experiments are conducted under a constant shear rate [26]. Thus, in the following, we consider $\dot{\gamma} = cH(t)$.

Using eqs. (1) and (5), we can obtain a viscosity equation:

$$\eta(t) = kc \frac{t^{-\alpha}}{\Gamma(1-\alpha)} \quad (7)$$

Combining eqs. (1) and (6), we get a time-dependnt flow equation:

$$\tau(t) = k\dot{\gamma}c \frac{t^{-\alpha}}{\Gamma(1-\alpha)} \quad (8)$$

For simplicity, we denote $k_1 = kc$ and $k_2 = k\dot{\gamma}c$. At this point, we have a system of equations:

$$\eta(t) = k_1 \frac{t^{-\alpha}}{\Gamma(1-\alpha)} \quad (9)$$

$$\tau(t) = k_2 \frac{t^{-\alpha}}{\Gamma(1-\alpha)} \quad (10)$$

where k_1 and k_2 represent the ideal initial viscosity and ideal initial shear stress, respectively.

The value of the fractional order, α , typically varies between 0 and 1 [21], which could well describe most experimental data. However, if we restrict α in this range, the proposed model can not reflect the time-variant flow behaviors (including growth and recession) of the studied substances. Thus, we consider α between -1 and 1 .

According to eqs. (9) and (10), the viscosity and shear stress may gradually increase (or decrease) together with evolution of time when α is negative (or positive). We show the

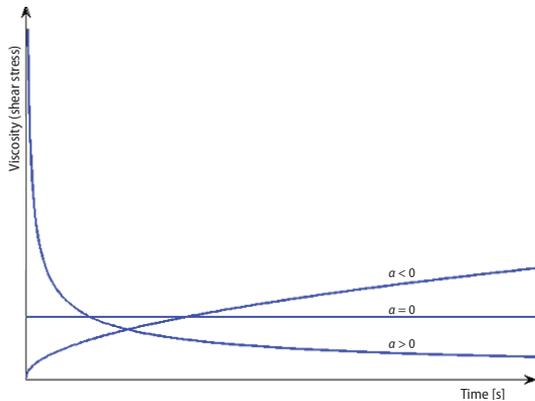


Figure 1. The $\eta-t(\tau - t)$ curves under the constant shear rate

simulated viscosity (shear stress) during a constant shear rate test in fig. 1. It can be seen that the response of this fractional flow model depends on the value of α . The viscosity and shear stress increase when $\alpha < 0$, while their values decrease when $\alpha > 0$.

Model fitting and results

In this section, some cellulose suspensions and the starch-milk-sugar (SMS) pastes are selected to verify our fractional flow model. The former is chosen to test the equation of viscosity as in eq. (9), while the latter is for testing the equation of shear stress in eq. (10). Subsequently, the comparison between experimental results and our model predictions will be discussed. We also discuss the effects of the fractional order α on these samples in terms of the magnitude and sign.

Araki, *et al.* [27] performed a series of rheological tests on some H_2SO_4 -treated and HCl-treated cellulose suspensions, Their experimental data are shown in figs. 2(a) and 2(b). Equation (9) is used to describe the viscosity vs. the shearing time. As shown in fig. 2(a), the H_2SO_4 -treated suspension does not exhibit time dependency. A larger value of ideal initial viscosity k_1 corresponds to a higher content of H_2SO_4 . The fractional order, α , is barely discernible because the value of α inclines to 0. The curve of viscosity-time is almost a straight line. This is because the H_2SO_4 -treated suspensions contain a large amount of strong acid groups and certain weak acid groups to form a stable system, which is hard to be destroyed by shear flow. A typical time-dependent thixotropic and anti-thixotropic behaviors can be observed in fig. 2(b), which show the same experimental data for HCl-treated suspensions. Note that, the concentration of HCl has significant effect on viscosity. When the concentration of HCl is higher than 5 g/l, the viscosity decreases with time during shearing. A higher concentration of HCl corresponds to larger values of k_1 and α . The magnitude of α can reflect the extent of thixotropy for HCl-treated suspensions. The concentration of HCl has impacts on the state of aggregation and affects

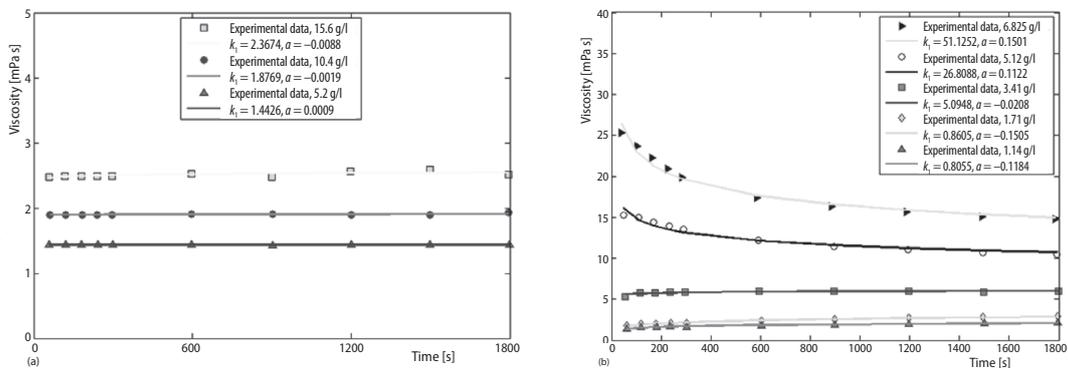


Figure 2. Comparison the viscosity of experimental observations and simulated results: (a) H_2SO_4 -treated cellulose suspensions and (b) HCl-treated cellulose suspensions (the experimental data is quoted from [27])

the strength of skeleton of the systems. When the concentrations of the dilute suspensions are less than 3 g/l, a growing trend can be observed in viscosity vs. time (anti-thixotropy) and the fractional order is negative. For such thixotropic behavior, the viscosity test also indicated that the effect is reversible. When the deformation is stopped, the viscosity could return to the initial value [27].

From figs. 2(a) and 2(b), we can see that our proposed model yields a good agreement with experimental data. The magnitude of α can reflect the effect of the concentration of acid on the cellulose suspensions. And, the sign of α is able to reveal the time-dependent behavior for the cellulose suspensions.

To verify the suitability of eq. (10), we compare our simulated results of SMS in [28] with the experimental data. Figure (3) shows the experimental shear stress-time data and the simulated results (solid lines). The results indicate that the temperature can significantly influence the time-dependent flow behavior of wheat starch-milk-sugar (WSMS) paste. The value of k_2 reduces from 147.17 at 95 °C to 6.20 at 75 °C. The magnitude of α changes from 0.1402 at 95 °C to 0.0787 at 85 °C. The WSMS exhibits slightly anti-thixotropic behavior with the value of $\alpha = -0.0783$ at 75 °C. Within the first 1000 seconds, the shear stress shows a sharp decrease at 95 °C and 85 °C. After a long time of shearing, the shear stresses tend to reach the same value, indicating the equilibrium structure is the same for the WSMS at 95 °C and 85 °C. On the other hand, the shear stress of WSMS shows a slight increase with time during shearing at 75 °C. The plateau stress is distinct from the stress at 95 °C and 85 °C, which implies that the equilibrium structure of paste 75 °C is different from that at the other two temperatures. This is due to that the state of the granules is different at different temperatures.

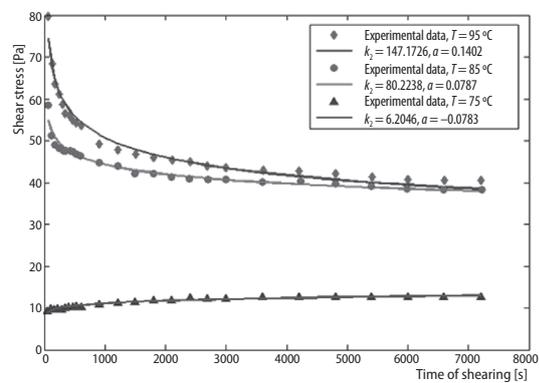


Figure 3. Comparison the experimental measured and simulated stress as a function of time of WSMS paste at $\dot{\gamma} = 47.45 \text{ s}^{-1}$, (the experimental data is quoted from [28])

The behavior of corn starch-milk-sugar (CSMS) paste is shown in fig.4. The concentration of glucose and starch in CSMS is the same as that in WSMS. In the case of CSMS, the thixotropic and anti-thixotropic behaviors also show a pronounced dependency on temperature. The value of k_2 drops rapidly from 101.08 at 95 °C to 16.57 at 75 °C. The value of α decreases from 0.075 at 95 °C to 0.046 at 85 °C. When the CSMS paste is tested at 75 °C, an obvious ascending trend in shear stress can be observed. We can see that the SMS (including WSMS and CSMS) exhibit the same anti-thixotropic behavior at 75 °C in spite of different kinds of sugar.

From the previous observations, the SMS behaves as thixotropic substances with the positive value of α at 95 °C and 85 °C. Anti-thixotropic behaviors can be observed in the SMS with the negative value of α at 75 °C. Temperature and the type of starch play an important role in determining the time-dependent feature of SMS. The type of sugar shows little effect on the paste system.

In eqs. (9) and (10), the parameters k_1 and k_2 represent the ideal initial viscosity and ideal initial shear stress, respectively. From figs. 2-4, a larger value of k_1 and k_2 corresponds a higher initial viscosity and shear stress for thixotropic behavior, which indicates that higher concentration of acid is able to strengthen the loose and unstable structure of cellulose sus-

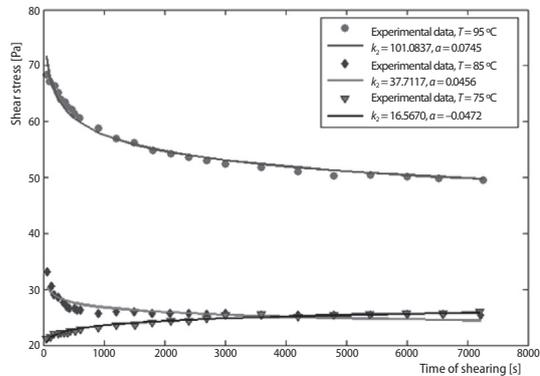


Figure 4. Comparison the experimental measured and simulated stress as a function of time of CSMS paste at $\dot{\gamma} = 47.45 \text{ s}^{-1}$, (the experimental data is quoted from [28])

that a larger absolute value of α corresponds to a more dramatic change (including growth and recession) of the viscosity or shear stress in the early stage of shearing. Thus, the value of α can indicate the extent of breakdown of the inner structure in the systems. In other words, the value of α can be an index to reflect the structure variation in the procedure of shearing. A larger absolute value of α corresponds to a more disordered and amorphous structure state. A smaller absolute value of α corresponds to a more ordered and crystalline structure state.

Conclusion

Thixotropy and anti-thixotropy are important phenomena in rheology and can be observed in many materials. The physical mechanisms behind these behaviors vary with the material system. We present a phenomenological model to capture the time-dependent thixotropic and anti-thixotropic behaviors of non-Newtonian flows. By adopting fractional derivatives, our model is simple in the sense that it only contains two parameters. Our simulated results reveal that the proposed model is adequate to describe the experimental measured viscosity and shear stress change as a function of time during constant shear rate test. The value of parameter k_1 and k_2 can imply the initial state of the cellulose suspensions and the SMS pastes. The sign of the fractional order, α , can reflect whether a given sample is thixotropic or anti-thixotropic, which depends on test conditions, such as, temperature, concentration, *etc.* The magnitude of α indicates the extent of thixotropy and anti-thixotropy. Further research should focus on the influence of external factors such as pressure and humidity on the constitutive relationship.

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Nomenclature

c – constant, [–]
 d^α/dt^α – fractional derivative, [–]
 E – elastic modulus, [Pa]
 $g_\dot{\gamma}$ – rate equation, [–]

pensions at the initial stage. In contrast, a smaller value of k_1 and k_2 corresponds to a lower initial viscosity and shear stress for anti-thixotropic behavior, which implies that the lower concentration of acid has little effect on the structure. The contribution of acid to the structure can be reflected by the value of k_1 and k_2 . Also, based on the values of k_1 and k_2 , researchers are able to predict the equilibrium value of the viscosity and shear stress. It is noting that the values of k_1 and k_2 are not equal to the initial viscosity and initial shear stress due to the environmental factors and error in measurement.

The value of fractional order α can reflect the change in viscosity and shear stress with shearing time. From figs. 2-4, it is obviously

$H(t)$ – Heaviside function, [–]
 k – coefficient defined by eq. (5), [Pa·s³]
 k_1 – coefficient defined by eq. (9), [Pa]
 k_2 – coefficient defined by eq. (10), [Pa·s⁻¹]

R – rational number, [–]

T – temperature, [°C]

t – time, [s]

Greek symbols

α – fractional derivative order, [–]

Γ – gamma function, [–]

$\dot{\gamma}$ – shear rate, [s⁻¹]

ε – shear strain, [–]

η – viscosity, [Pa·s]

θ – material coefficient, [–]

λ – structural parameter, [–]

τ – shear stress, [–]

References

- [1] Chang, C., et al., Isothermal Start-Up of Pipeline Transporting Waxy Crude Oil, *Journal of Non-Newtonian Fluid Mechanics*, 87 (1999), 2-3, pp. 127-154
- [2] Martinez, J. E., et al., Rheological Properties of Vinyl Polysiloxane Impression Pastes, *Dental Materials*, 17 (2001), 6, pp. 471-476
- [3] Liu, C., et al., Rheological Properties of Concentrated Aqueous Injectable Calcium Phosphate Cement Slurry, *Biomaterials*, 27 (2006), 29, pp. 5003-5013
- [4] Wallevik, J. E., Thixotropic Investigation on Cement Paste: Experimental and Numerical Approach, *Journal of Non-Newtonian Fluid Mechanics*, 132 (2005), 1-3, pp. 86-99
- [5] Mleko, S., Foegeding, E. A., pH Induced Aggregation and Weak Gel Formation of Whey Protein Polymers, *Journal of food science*, 65 (2000), 1, pp. 139-143
- [6] Barnes, H. A., Thixotropy – a Review, *Journal of Non-Newtonian Fluid Mechanics*, 70 (1997), 1-2, pp. 1-33
- [7] Mewis, J., Wagner, N. J., Thixotropy, *Advances in Colloid and Interface Science*, 147-148 (2009), Mar.-June, pp. 214-227
- [8] Mewis, J., Thixotropy-a General Review, *Journal of Non-Newtonian Fluid Mechanics*, 6 (1979), 1, pp. 1-20
- [9] Weltmann, R. N., Breakdown of Thixotropic Structure as Function of Time, *Journal of Applied Physics*, 14 (1943), 7, pp. 343-350
- [10] Figoni, P. I., Shoemaker, C. F., Characterization of Time Dependent Flow Properties of Mayonnaise Under Steady Shear, *Journal of Texture Studies*, 14 (1983), 4, pp. 431-442
- [11] Hahn, S. J., et al., Flow Mechanism of Thixotropic Substances, *Industrial & Engineering Chemistry*, 51 (1959), 7, pp. 856-857
- [12] Joye, D. D., Poehlein, G. W., Characteristics of Thixotropic Behavior, *Transactions of the Society of Rheology*, 15 (1971), 1, pp. 51-61
- [13] Tiu, C., Boger, D. V., Complete Rheological Characterization of Time-Dependent Food Products, *Journal of Texture Studies*, 5 (1974), 3, pp. 329-338
- [14] Monje, C. A., et al., *Fractional-Order Systems and Controls: Fundamentals and Applications*, Springer-Verlag, London, 2010
- [15] Schiessel, H., et al., Generalized Viscoelastic Models: Their Fractional Equations with Solutions, *Journal of Physics A: Mathematical and General*, 28 (1995), 23, pp. 6567-6584
- [16] Sun, H. G., et al., Variable-Order Fractional Differential Operators in Anomalous Diffusion Modeling, *Physica A: Statistical Mechanics and its Applications*, 388 (2009), 21, pp. 4586-4592
- [17] Jesus, I. S., Machado, J. A. T., Implementation of Fractional-Order Electromagnetic Potential Through a Genetic Algorithm, *Communications in Nonlinear Science and Numerical Simulation*, 14 (2009), 5, pp. 1838-1843
- [18] Hristov, J., Approximate Solutions to Time-Fractional Models by Integral Balance Approach, in: *Fractional Dynamics* (Eds. C. Cattani, H.M. Srivastava, Xia-Jun Yang), De Gruyter Open, Warsaw, 2015, pp. 78-109
- [19] Baleanu, D., Fractional Calculus Models and Numerical Methods, in: *Complexity, Nonlinearity and Chaos* (Ed. Albert C. J. Luo), World Scientific, Boston, Mass., USA, 2012, pp. 41-138
- [20] Podlubny, I., *Fractional Differential Equations: an Introduction to Fractional Derivatives, Fractional Differential Equations, to Methods of Their Solution and Some of Their Applications*, Academic press, San Diego, Cal., USA, 1999
- [21] Yin, D. S., et al., Fractional Time-Dependent Bingham Model for Muddy Clay, *Journal of Non-Newtonian Fluid Mechanics*, 187-188 (2012), Nov., pp. 32-35

- [22] Yin, D. S., *et al.*, Fractional Order Constitutive Model of Geomaterials Under the Condition of Triaxial Test, *International Journal for Numerical and Analytical Methods in Geomechanics*, 37 (2013), 8, pp. 961-972
- [23] Di, P. M., *et al.*, Visco-Elastic Behavior Through Fractional Calculus: an Easier Method for Best Fitting Experimental Results, *Mechanics of Materials*, 43 (2011), 12, pp. 799-806
- [24] Rao, M. A., *Rheology of Fluid and Semisolid Foods: Principles and Applications*, Springer, New York, USA, 2010
- [25] Cheng, D. C.-H., Evans, F., Phenomenological Characterization of the Rheological Behaviour of Inelastic Reversible Thixotropic and Antithixotropic Fluids, *British Journal of Applied Physics*, 16 (1965), 11, pp. 1599-1617
- [26] Cheng, D. C.-H., A Differential Form of Constitutive Relation for Thixotropy. *Rheologica Acta*, 12 (1973), 2, pp. 228-233
- [27] Araki, J., *et al.*, Flow Properties of Microcrystalline Cellulose Suspension Prepared by Acid Treatment of Native Cellulose, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 142 (1998), 1, pp. 75-82
- [28] Abu-Jdayil, B., Mohameed, H. A., Time-Dependent Flow Properties of Starch-Milk-Sugar Pastes, *European Food Research and Technology*, 218 (2004), 2, pp. 123-127