A Viscosity Function for Viscoplastic Liquids

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ABSTRACT

A viscosity function for highly-shearthinning or yield-stress liquids such as pastes and slurries is proposed. This function is continuous and presents a low shear-rate viscosity plateau, followed by a sharp viscosity drop at a treshold shear stress value (yield stress), and a subsequent power-law region.

INTRODUCTION

Viscoplastic or yield-stress liquids are materials that have an yield stress below which they behave as a high viscosity liquid, and above which they behave as a shear-thinning liquid. At the yield stress, an often dramatic drop of the viscosity level is observed.

Most of the viscoplastic materials that appear in processes of interest are viscoplastic liquids. A few examples of viscoplastic liquids are: cement slurries, drilling muds and heavy oils in the petroleum industry; mayonnaise, butter, creams, pastes and many dairy products in the food and cosmetics industries; clay, mud and other concentrated suspensions in nature.

With the technological advancement in rheometry, high (but finite) viscosity plateaus at low shear rates have been observed in most viscoplastic materials of interest. A comprehensive discussion on this subject is found in [1].

VISCOSITY FUNCTIONS FOR VIS-COPLASTIC LIQUIDS

Overview of the Available Viscosity Functions

Perhaps the viscosity function that is the most often employed to fit viscosity data of viscoplastic materials is the Herschel-Bulkley viscosity function [2]. The shear stress corresponding to this function is given by

$$\begin{cases} \tau = \tau_{\rm o} + K \dot{\gamma}^n, & \text{if } \tau > \tau_{\rm o}; \\ \dot{\gamma} = 0, & \text{otherwise.} \end{cases}$$
(1)

where τ is the shear stress, τ_o is the yield stress, $\dot{\gamma}$ is the shear rate, K is the consistency index, and n is the behavior (or power-law) index. When n = 1, it reduces to the traditional Bingham plastic function,

$$\begin{cases} \tau = \tau_{\rm o} + \mu_{\rm p} \dot{\gamma}, & \text{if } \tau > \tau_{\rm o}; \\ \dot{\gamma} = 0, & \text{otherwise.} \end{cases}$$
(2)

where $\mu_{\rm p}$ is the plastic viscosity. Both equations predict an infinite viscosity at the limit of zero shear rate. This behavior is not compatible with the conservation equations that govern many complex flows [3]. Moreover, the prediction of an infinite vicosity yields rather poor curve fittings to data pertaining to viscoplastic liquids.

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τ₀ = 5000 Pa 10 η_{\circ} = 5000 Pa.s $K = Pa.s^{n}$ 10³ n = 0.5 η 10¹ 10-1 Papanastasiou Modified Biviscosit 10-3 10⁻¹ 10 10 10³ 10 10⁶ 10 au

Figure 1: The qualitative behavior of the Carreau and Cross functions.

One alternative when the low shear rate range is not of interest is to discard the data in the plateau region, but then the dilemma of which data points to exclude comes into play. The quality of the fitting and, more importantly, the value obtained for τ_0 are typically strongly affected by this subjective decision. It is rather frustrating to observe such an arbitrariness in determining a parameter such as τ_0 , which has a clear physical meaning.

Possible choices when no shearthinning is observed beyond the yield stress are the Cross model [4],

$$\eta = \eta_{\infty} + \frac{\eta_o - \eta_{\infty}}{1 + (\lambda \dot{\gamma})^{n-1}} \tag{3}$$

and the Carreau model [2],

$$\eta = \eta_{\infty} + \frac{\eta_{o} - \eta_{\infty}}{\left[1 + (\lambda \dot{\gamma})^{2}\right]^{\frac{1-n}{2}}}$$
(4)

where $\eta \equiv \tau/\dot{\gamma}$ is the viscosity function, and λ is a curve-fitting parameter with dimension of time. The two viscosity functions above are commonly used for pseudoplastic liquids with a zero-shearrate plateau (η_{o}), a power-law region that

Figure 2: The qualitative behavior of the Papanastasiou viscosity function and the modified version of the bi-viscosity function.

begins at $\dot{\gamma} \simeq 1/\lambda$, and an infinite-shearrate plateau (η_{∞}) . In the limit of a very steep power-law region $(n \to 0)$, these two equations yield the behavior illustrated in Fig. 1.

For shear-thinning viscoplastic liquids, that is, viscoplastic liquids that shearthin at shear stresses larger than the yield stress, a regularized Herschel-Bulkley function was proposed by Papanastasiou [5] for usage in finite-element flow simulations, namely,

$$\tau = (1 - \exp(-a\dot{\gamma}))\tau_o + K\dot{\gamma}^n \qquad (5)$$

where a is the regularizing parameter. As $a \rightarrow 0$, Papanastasiou's function approaches the Herschel-Bulkley function, with the important advantage of holding uniformly in yielded and unyielded regions. The shear stress as given by Eq. (5) results in the viscosity function plotted in Figure 2 as a function of the shear stress. Unfortunately, the Papanastasiou function is unable to predict a finite viscosity plateau in the limit of zero shear rate for shearthinning viscoplastic liquids, as illustrated in Fig. 2.

An interesting alternative that has a more suitable qualitative behavior for viscoplastic liquids is the so-called modified bi-viscosity function [6, 7], which equation for shear stress is given by

$$\begin{cases} \tau = \tau_{\rm o} + K\dot{\gamma}^n, & \text{if } \dot{\gamma} > \dot{\gamma}_{\rm o}; \\ \eta_{\rm o}\dot{\gamma}, & \text{otherwise.} \end{cases}$$
(6)

where $\dot{\gamma}_{\rm o} = \tau_{\rm o}/(\eta_{\rm o} - K\gamma_{\rm o}^{n-1}) \simeq \tau_{\rm o}/\eta_{\rm o}$ is the yield shear rate, usually very low. Figure 2 shows the plot of the corresponding viscosity function as a function of the shear stress. This viscosity function involves two different expressions, each one applicable to a different shear-rate range. These ranges are delimited by the yield shear rate, which is to be determined in the curve-fitting procedure itself. These characteristics, together with its discontinuous derivative (Fig. 2), cause severe practical problems that typically prevent goodquality fittings of Eq. (6) to viscosity data of viscoplastic liquids.

The Proposed Viscosity Function

We now propose and briefly discuss the properties of the following function:

$$\tau = (1 - \exp(-\eta_{\rm o}\dot{\gamma}/\tau_{\rm o}))(\tau_{\rm o} + K\dot{\gamma}^n) \quad (7)$$

This function is plotted in Fig. 3 for illustration purposes. The physical meaning of the parameters that appear in Eq. (7), namely, η_o , τ_o , K, and n, are also illustrated in this figure. The zero-shear rate viscosity is just equal to the ratio $\tau/\dot{\gamma}$ provided τ is smaller enough than τ_o to ensure that $\dot{\gamma}$ is within the zero-shear rate plateau region. The yield stress becomes evident in the $\tau \times \dot{\gamma}$ plot, because of the plateau that occurs at τ_o . The behavior index n is the slope of the power-law region in the log-log plot of $\tau \times \dot{\gamma}$. The intercept of the extrapolated power-law-region straight



Figure 3: Shear stress as a function of shear rate as predicted by Eq. (7).



Figure 4: Viscosity as a function of shear stress for the function given by Eq. (7).



Figure 5: Derivative of shear stress with respect to shear rate as a function of shear stress for the function given by Eq. (7).

line with the vertical line at $\dot{\gamma} = 1 \, \mathrm{s}^{-1}$ occurs at $\tau = K$. This information can be used to generate good initial guesses for the curve-fitting parameter values in leastsquares fitting procedures. In Fig. 4 we can observe the qualitative behavior of the viscosity function corresponding to Eq. (7). The zero-shear rate plateau is followed by a sharp drop at $\tau = \tau_0$, and then it follows a power-law region. This behavior is quite similar to the one presented by the bi-viscosity function (Fig. 2), except that there is no discontinuity in the curve derivative at $\tau = \tau_{o}$. A good feature of Eq. (7) is that it predicts a viscosity function such that

$$\lim_{\dot{\gamma} \to 0} \eta = \eta_{\rm o} \tag{8}$$

in contrast to the Papanastasiou function, which predicts an unbounded viscosity function in the limit of zero shear rate.

Often the data do not present a viscosity drop as sharp as predicted by Eq. (7). For these cases, the exact yield stress value is not so evident, and one possible procedure to avoid subjectivity is to define $\tau_{\rm o}$ as the shear stress corresponding to the minimum derivative of the shear stress with



Figure 6: Flow curve of a Carbopol aqueous solution.

respect to the shear rate, as illustrated in Fig. 5. This derivative for a given set of data can be easily evaluated by central differences and then plotted as a function of τ :

$$\frac{d\tau}{d\dot{\gamma}}\Big|_{i+1} \simeq \frac{\tau(\dot{\gamma}_{i+1}) - \tau(\dot{\gamma}_i)}{\dot{\gamma}_{i+1} - \dot{\gamma}_i}$$

$$\tau_{i+1} = \frac{1}{2} \left[\tau(\dot{\gamma}_i) + \tau(\dot{\gamma}_{i+1})\right]$$
(9)

where $\tau(\dot{\gamma}_i)$ is the measured shear stress at $\dot{\gamma} = \dot{\gamma}_i$, and $\dot{\gamma}_i$, i = 1, 2, ..., m is the monotonically increasing series of m shear rate values at which measurements were made.

FITTINGS TO SOME REPRESENTA-TIVE DATA

We now illustrate the fitting capability of Eq. (7) to data of a few viscoplastic liquids that appear in industrial applications. All data presented in this paper were obtained in our laboratory with the aid of a commercial rotational rheometer (ARES, Rheometric Scientific). The tests were conducted in strain-rate-controlled mode. The geometry employed was a home-made four-blade vane [8].



Figure 7: Flow curve of a drilling mud.



Figure 9: Flow curve of mayonnaise.



Figure 8: Flow curve of an oil/water emulsion with surfactant.



Figure 10: Flow curve of a paper coating formulation.

In these figures we can observe that the fittings are generally of good quality, because the qualitative behavior of Eq. (7) throughout the whole range of shear rate is essentially the same as the one of the data. Therefore, there is no need to discard data pertaining to the low-shearrate range, which is undesirable because often the parameter values obtained in the curve-fitting procedure depend strongly on the choice of the data to be discarded.

FINAL REMARKS

A viscosity function for yield-stress liquids is proposed. It is continuous and has continuous derivatives, as it is convenient for numerical simulations and curve-fitting procedures. Its qualitative behavior is the same as the one observed for most viscoplastic liquids of interest, i.e., a highviscosity plateau at low shear rates, followed by a sharp drop of the viscosity level, and then a power-law region.

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