# New Equation for Fitting Rheological Data of Bingham Materials

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### SYNOPSIS

In this article we propose a new equation that combines behaviors of Bingham and Williamson pseudoplastic materials. We compare this equation with other ones, and in the Appendix, we consider its theoretical foundation. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Many technically important materials, such as polymer suspensions,[1] $\gamma$-iron oxide (III) suspensions,[2] fermentation broths,[3] and polymer melts and solutions,[4] exhibit viscoplastic properties, characterized by the existence of initial shear stress.

To describe flow curves of such materials, in the case of linear viscoplasticity, the Bingham–Shvedov equation is usually used[5]:

$$\tau = \tau_0 + \eta\dot{\gamma} \tag{1}$$

and in the case of nonlinear viscoplasticity, the Herschel–Balkley equation[5]:

$$\tau = \tau_0 + k\dot{\gamma}^n \tag{2}$$

where $\tau$ is shear stress; $\dot{\gamma}$, shear rate; and $\tau_0$, $\eta$, $k$, and $n$ are constants selected from experimental data.

Wide application of eqs. (1) and (2) is due to the fact that they are useful not only to fitting rheological data but also are best suited when calculating viscoplastic material flows in different devices. However, eq. (2) frequently does not describe adequately the rheological curves of nonlinear viscoplastis materials, for most of which the shear stress–shear rate relation becomes linear with increasing $\gamma$.

For such materials, Kuin proposed the following empirical equation[2]:

$$\tau = A + B\dot{\gamma} + A[1 - \exp(-C\dot{\gamma})] \tag{3}$$

which transforms into a linear equation at large $\gamma$[2]:

$$\tau = (A_1 + A_2) + B\dot{\gamma} \tag{4}$$

where $A_1, A_2, B$, and $C$ are coefficients selected from experimental data.

Because of the presence of the exponent, eq. (3) is considered unsuitable both for selected coefficients from experimental data and for calculated flows. For this reason, the problem of an adequate description of nonlinear viscoplasticity admittedly cannot be solved.

## NEW EQUATION AND ITS COMPARISON WITH OTHER ONES

As in eq. (2), this combines behaviors of Bingham and pseudoplastic materials characterized by the de Waele–Ostwald power law. One may propose to combine the behaviors of the Bingham and Williamson pseudoplastic materials[6] as in the following equation:

$$\tau = \tau_0 + a\dot{\gamma}\left[1 + \frac{b}{c + \dot{\gamma}}\right] \tag{5}$$

where $\tau_0$, $a$, $b$, and $c$ are coefficients selected from experimental data.

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Equation (5), as shown in Ref. 7, can be considered as a semiempirical equation because it is a special case of the Denny–Brodkey kinetic equation (see the Appendix). In practice, this equation is superior to eqs. (2) and (3) in respect to adequate experimental data representation. As to use of flow calculations, eq. (5) is more complicated than is eq. (2), but as mentioned below, no unsurmountable problems arise.

As an example of the curve-fitting of flows of nonlinear viscoplastic materials, consider data[1] on the shear stress $\tau$ (dyn cm$^{-2}$)–shear rate $\dot{\gamma}$ (s$^{-1}$) relation for coagulated PMMA sol with a mean particle size equal to 250 nm in a 31.2% glycerol/water medium. The experimental data and the results of their processing by eq. (2), (3), and (5) are presented in Table I. The coefficients of these equations have been obtained by the method of least squares using a nonlinear regression program given in Ref. 8.

An absolute value of a mean relative error of calculated data by eq. (2) is 1.025%; by eq. (3), 0.632%; and by eq. (5), 0.597%. Therefore, eqs. (3) and (5) are found to be almost equal, but significantly superior to eq. (2) concerning the accuracy of data representation.

Coefficients of eqs. (2) and (3) proved to be equal: $\tau_0 = 6.2714$; $\eta = 0.68776$; $n = 0.68594$; $A_1 = 8.5769$; $B = 0.05474$; $A_2 = 21.343$; and $C = 0.00471$; and for eq. (5), $\tau_0 = 7.1533$; $a = 0.05032$; $b = 663.02$; and $c = 230.8$. Equations (2) and (5) are not sensitive to the selection of initial approximations by choice of coefficients, whereas for eq. (3), initial approximations had to be selected on the "Eureka" program[9] and then calculated by a nonlinear regression program.[8]

## OTHER EXAMPLES AND DISCUSSION

These inferences were confirmed by more extensive statistical materials. Therefore, on processing the flow curves of 16 samples of magnetic lacquer [20% $\gamma$-iron (III) oxide suspension with mean particle size 600 nm in 12% epoxy resin solution in mixed organic solvent: toluol (15%), cyclohexanon (24%), ethylcellosolve (15%), and isoforon (10%) with other additives] by eq. (5), for five samples, one performed simultaneously, a choice of coefficients were available for eq. (3). For all these samples, the residual sum of difference squares of observed and calculated values of shear stress by eq. (5) was two or more

**Table I   Experimental Values of Shear Stress $\tau$ (dyn cm$^{-2}$) as a Function of Shear Rate $\dot{\gamma}$ (s$^{-1}$) by Experimental Data[1] and Calculated Values by Eqs. (2), (3), and (5)**

| $\dot{\gamma}$ | $\tau$ | Eq. (2) | Eq. (3) | Eq. (5) |
|---|---|---|---|---|
| 50 | 15.70 | 16.337 | 15.796 | 15.612 |
| 100 | 22.20 | 22.464 | 22.074 | 22.274 |
| 175 | 30.50 | 30.042 | 30.146 | 30.351 |
| 216.5 | 34.20 | 33.777 | 34.080 | 34.200 |
| 267 | 37.80 | 38.032 | 38.474 | 38.488 |
| 308 | 41.60 | 41.301 | 41.784 | 41.728 |
| 358 | 45.40 | 45.109 | 45.570 | 45.458 |
| 400 | 48.10 | 48.180 | 48.578 | 48.443 |
| 425 | 51.00 | 49.960 | 50.306 | 50.166 |
| 484 | 53.60 | 54.034 | 54.235 | 54.105 |
| 525 | 57.40 | 56.774 | 56.422 | 56.752 |
| 566 | 60.20 | 59.447 | 59.422 | 59.340 |
| 616 | 63.00 | 62.626 | 62.477 | 62.427 |
| 700 | 67.50 | 67.791 | 67.450 | 67.475 |
| 750 | 70.25 | 70.772 | 70.353 | 70.413 |
| 790 | 72.20 | 73.112 | 72.649 | 72.734 |
| 835 | 75.00 | 75.701 | 75.211 | 75.317 |
| 875 | 77.60 | 77.966 | 77.472 | 77.591 |
| 915 | 79.50 | 80.198 | 79.721 | 79.850 |
| 1000 | 84.30 | 84.843 | 84.468 | 84.589 |
| 1100 | 89.80 | 90.151 | 90.014 | 90.092 |
| 1250 | 98.20 | 97.839 | 98.285 | 98.266 |

times less than by eq. (3).[10] In both cases, to select coefficients, the "Eureka" program was used.[9]

The simplicity of an algebraic equation for experimental rheological data representation is of particular importance in its further applications when calculating flows in different devices. In this respect, eq. (2) is simpler. However, it is significantly inferior to eq. (5) on processing rheological data. For example, in the above-mentioned case (see Table I and Fig. 1), a mean relative error of data representation by eq. (2) is 1.7 times more than by eq. (5). A significant discrepancy may occur, especially when the flow curve has an extended section outside its linear regime. Therefore, the processing of flow curves for current conductive inks[4] by eq. (2) according to the program of Ref. 8 is characterized by a mean relative error of 7.05%, whereas this error by eq. (5) amounts 0.732% (see Fig. 2).

Hence, when calculating viscoplastic fluid flows, eq. (5) should be used as eq. (2) does not give sufficient accuracy of experimental data representation. Equation (3) is not superior to eq. (5) in this regard and has a complicated algebraic structure resulting in a transcendental equation relative to shear rate.

Flow calculations using eq. (5) are certainly complicated as compared to using eq. (2), but in so doing, insurmountable problems do not arise. Consider, for example, a steady-state flow of viscoplastic fluid between two parallel plates under a pressure gradient

$\Delta P$. If the longitudinal coordinate of flow is designated as $z$ and the transverse coordinate as $x$, shear stress may be written as follows[5]:

$$\tau_{xz} = \frac{\Delta P}{L} \cdot x \qquad (6)$$

where $L$ = the length of the plate.

To find the fluid velocity distribution, $dV_z/dx$, consider the distance from the symmetry plane of the problem with coordinate $x = 0$ up to the plate with coordinate $+B$. Over the distance $0 \leq x \leq B$, two flow regions exist: one for which $dV_z/dx = 0$ is within the limits $0 \leq x \leq X_0$, where $X_0 = \tau_0 L / \Delta P$, and, second, the plastic flow region, $0 \leq x \leq B$.[5] The substitution of eq. (5) into eq. (6) for the plastic flow region yields

$$\tau_0 + a \frac{dV_z}{dx} \left[ 1 + \frac{b}{c + \frac{dV_z}{dx}} \right] = \frac{\Delta P}{L} \cdot x \qquad (7)$$

Equation (7), after simple transformations, can be reduced to a second-degree equation relative to $dV_z/dx$:

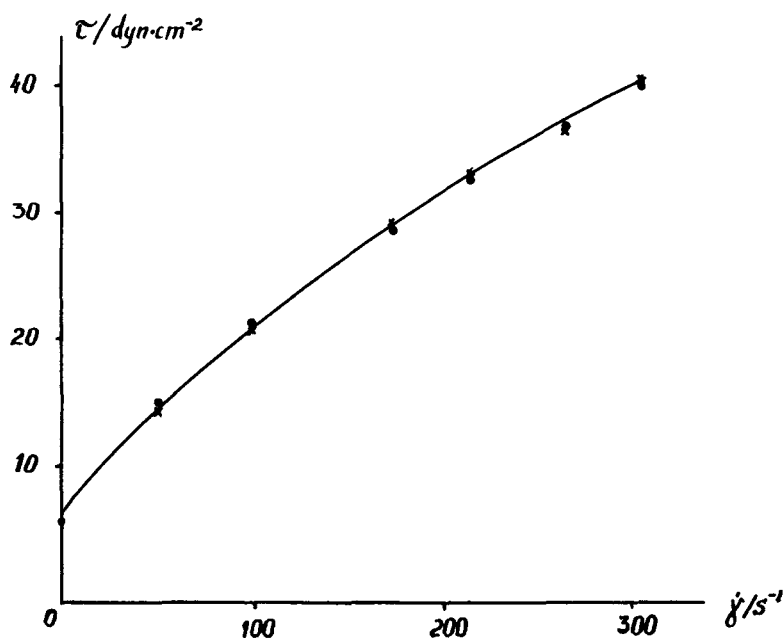$$\left( \frac{dV_z}{dx} \right)^2 + 2P(x) \frac{dV_z}{dx} + Q(x) = 0 \qquad (8)$$



**Figure 1** Shear stress vs. shear rate data for a PMMA suspended in a water–glycerol media: (x) experimental points[1]; (·) calculated points by eq. (2); (———) calculated line by eq. (5).
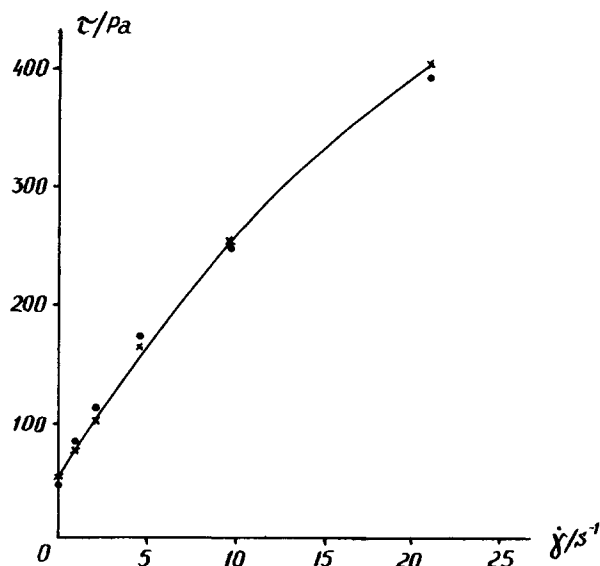
**Figure 2** Shear stress vs. shear rate data for a conductive ink: (x) experimental points[4]; (·) calculated points by eq. (2); (———) calculated line by eq. (5).

where $P(x) = (\tau_0 + ac + ab - (\Delta P)/L \cdot x)/2a$ and $Q(x) = (\tau_0 c - (\Delta P)/L \ x)/a$. Equation (8) can be formally integrated and results in

$$V_z = \int_{x_0}^{x \leq B} [-P(x) + \sqrt{P^2(x) - Q(x)}\,] \, dx \quad (9)$$

The integral on the right side of eq. (9) should be calculated by the numerical method.

Other more complicated flow calculations also lead to a standard problem of numerical integration. Thus, the use of eq. (5) does not raise doubts to this end.

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## APPENDIX: DERIVATION OF EQ. (5) FROM DENNY–BRODKEY KINETIC MODEL[7]

Denny and Brodkey proposed to consider structured fluid flows as a chemical reaction proceeding in direct (rupture of bonds) and opposite (reduction of bonds) directions.[11] Taking that the number of bonds remaining unbroken are proportional to fluid viscosity $\eta$, they derived the following

kinetic equation that describes viscosity–time ($t$) variations:

$$\left(\frac{1}{\eta_0 - \eta_\infty}\right)\left(-\frac{d\eta}{dt}\right)$$
$$= k_1\left(\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty}\right)\dot\gamma^p - k_2\left(\frac{\eta_0 - \eta}{\eta_0 - \eta_\infty}\right)^m \quad (A.1)$$

where $\eta_0$ and $\eta_\infty$ are limiting values of viscosity at $\dot\gamma \to 0$ and $\gamma \to \infty$; $k_1$ and $k_2$, the rate constants of rupture and formation of bonds, respectively; and $n$ and m, the order of forward and reverse reactions, respectively.

For steady-state flow, when $d\eta/dt = 0$, according to eq. (A.1), we have

$$k = \frac{k_1}{k_2} = (\eta_0 - \eta)^m/(\eta - \eta_\infty)^n\dot\gamma^p(\eta_0 - \eta_\infty)^{m-n} \quad (A.2)$$

Equations (A.1) and (A.2) are not widely used because they contain too many empirical coefficients: $\eta_0$, $\eta_\infty$, $k_1$, $k_2$, $n$, $m$, and $p$. However, one may well realize models with a reduced number of coefficients.

Consider, for example, the steady-state flow of structured fluid based on simple physically significant assumptions $m = n = p = 1$. In this case, eq. (A.2) can be written as follows:

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{1 + k\dot\gamma} \quad (A.3)$$

Proceeding to shear stress through relation $\eta = (\tau - \tau_0)/\dot\gamma$ according to eq. (A.3), one obtains

$$\tau = \tau_0 + \eta_\infty\dot\gamma\left\{1 + [(\eta_0 - \eta_\infty)/k\eta_\infty]/\left[\left(\frac{1}{k}\right) + \dot\gamma\right]\right\} \quad (A.4)$$

At large values of $\gamma$, the slope asymptote of the plot of function (A.4) exists:

$$\tau = [\tau_0 + (\eta_0 - \eta_\infty)/k] + \eta_\infty\dot\gamma$$

Equation (A.4) agrees with eq. (5) mentioned in the basic text, if the following reductions are used:

$$\eta_\infty = a; \quad (\eta_0 - \eta_\infty)/k\eta_\infty = b; \quad 1/k = c$$

As noted above, the existence of a slope asymptote to the flow curve is a characteristic property of a large number of Bingham materials.

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