A new method of classifying rheological curves

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Abstract: A new method of comparing and classifying rheological curves on the basis of two parameters describing their shapes is presented. Using this classification system it is possible to represent each curve by a single point in a special coordinate system.

Key words: Rheological curve, empirical equation CLERD, non-Newtonian liquid, classification scheme

1. Introduction

A new method of processing, comparing and classifying rheological curves, i.e. the dependence of the shear rate \( \dot{\gamma} \) on the shear stress \( \tau \), has been devised in our institute. The first and basic requirement when devising the method was to formulate a two-parameter equation (with parameters \( a \) and \( b \)) which would well characterize the course of rheological curves of various liquids, with the exception of those with time-dependent behaviour. Once this condition is met, it is then possible to define a coordinate system in which values of the first parameter \( a \) of the equation in question are plotted on the abscissa and values of the second parameter \( b \) are plotted on the ordinate. In this system of coordinates it is then possible to represent a rheological curve as a point \( Q \) with the coordinates \( a, b \), whose position is characteristic for the curve shape.

The second requirement, formulated later, was the reconstruction of the rheological curve using the position of the point \( Q \) with coordinates \( a, b \).

The suitable equation was then formulated and designated as CLERD (Cumulative Logarithmic Equation with Ratio of Derivatives). This equation is derived from the course of the rheological curve in logarithmic coordinates. The abscissa is used for the logarithm of the shear stress (\( \ln \tau \)), and the ordinate for the logarithm of the shear rate (\( \ln \dot{\gamma} \)). The origin of the rheogram has coordinates \( T(0), \dot{\gamma}(0) \); the end point is given by coordinates \( T(M), \dot{\gamma}(M) \). The course of the rheological curves is very well characterized by the CLERD equation. Numerical values of parameters \( a \) and \( b \) are determined by linear regression. The correlation precision is characterized by the correlation coefficient \( r \) whose value for most flow curves is better than 0.999 when \( \tau \) or \( \dot{\gamma} \) vary by approximately 4 orders of magnitude.

The other requirement, i.e. reconstruction of a rheogram, is more difficult to meet. Apart from values of the parameters \( a \) and \( b \), it is necessary to know the coordinates \( T(0), \dot{\gamma}(0) \) of the starting point (origin) \( P \) and \( T(1), \dot{\gamma}(1) \) of the first point of the rheological curve. In some cases the reconstructed and original curves do not fully agree.

2. Theory

The basic form of the CLERD equation is

\[
Y(N+1) = a[X(N+1) \cdot K(N+1)]^b,
\]
where \( X(N+1) \) is the independent variable, \( Y(N+1) \) the dependent variable, \( K(N+1) \) the correction term, and \( a \) and \( b \) empirical parameters. The index \( N \) designates the sequential order of points of the rheological curve. The total number of curve points, with the exception of the starting point (origin) \( P \), is \( M \). The correction term is a ratio of derivatives of the two parameter power function in eq. (1a) in point \( N \) and point \( (N+1) \),

\[
Y = aX^b .
\]

The definition equations of the individual terms of the CLERD equation are

\[
Y(N+1) = \sum_{i=1}^{N+1} [\ln D(i) - \ln D(0)] ,
\]

\[
X(N+1) = \sum_{i=1}^{N+1} [\ln T(i) - \ln T(0)] ,
\]

\[
Y(N) = \sum_{i=1}^{N} [\ln D(i) - \ln D(0)] ,
\]

\[
X(N) = \sum_{i=1}^{N} [\ln T(i) - \ln T(0)] ,
\]

\[
K(N+1) = \frac{X(N+1) \cdot Y(N)}{X(N) \cdot Y(N+1)} ,
\]

where \( T \) is the shear stress in mPa, and \( D \) is the shear rate in s\(^{-1}\).

By substituting the definition eqs. (2 - 6) into the CLERD equation (1), carrying out algebraic arrangement and logarithmic calculation, the following equation is derived, which is suitable for linear regression:

\[
\ln Y(N+1) = R \cdot \ln \left( \frac{(X(N+1))^2 \cdot Y(N)}{X(N) \cdot Y(N+1)} \right) + \ln S .
\]

Using linear regression it is then possible to calculate auxiliary parameters \( R \) and \( S \) and using eqs. (8) and (9), the latter are used to calculate the parameters \( a \) and \( b \) as

\[
a = \exp \frac{\ln S}{1 - R} ,
\]

\[
b = \frac{R}{1 - R} .
\]

3. Use of the special coordinate system
   and reconstruction of rheograms

For these purpose it is possible to use either parameters \( a \) and \( b \) or the quantities \( N_a \) and \( N_b \), which are termed non-Newtonian deviations of the 1st and 2nd kind. They are defined by eqs. (10) and (11) and are more suitable in some cases since they linearize the definition fields for parameters \( a \), \( b \).

\[
N_a = \frac{\arctan a - 45^\circ}{45^\circ} ,
\]

\[
N_b = \ln b .
\]

Figure 1 shows nine characteristic points with different combinations of their coordinates \( a \) and \( b \) or \( N_a \) and \( N_b \). Each point corresponds to a particular shape of the rheological curve. Its position depends on the numerical values of the parameters \( a \) and \( b \) and on the values of the coordinates of the initial and final points of the rheological curve and also partly on the coordinates of each point of the rheological curve. If these quantities are known, it is possible to calculate the corresponding values of the shear rate \( D \) for selected values of the shear stress \( T \) using

Fig. 1. Characteristic points (01) – (09) with different combinations of coordinates \( a \) and \( b \) (or \( N_a \) [%] and \( N_b \)).

The location of each point corresponds to the shapes of the rheological curves shown in figure 2

Fig. 2. Characteristic rheological curves (01) – (09)