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A MATLAB-Based Software for Estimating Measurement Uncertainties in Capillary Viscometry

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The Mooney wall slip correction procedure is sometimes mandatory in the rheological characterization via capillary viscometry of certain complex fluids that have the tendency of slipping at solid walls. Besides making the measurement more complex, the Mooney procedure may give rise to measurement error amplification due to an imprecise knowledge of the capillary radius, even if the uncertainty is of the order of 0.01 mm. This error amplification may be so large that the result becomes grossly inaccurate, and in the worst case the procedure may even not produce a physically acceptable result. In this work a MATLAB-based software that can help researchers determine the maximum allowable inaccuracy on the capillary diameter that can yield feasible data for fluids characterization is devised. For best results, though, the user should know in advance the constitutive characteristics of the unknown fluid in an approximate sense.

1. Introduction

Capillary viscometry is still the most widely used experimental technique to determine viscosity of molten polymers. Despite theoretical simplicity, its correct application becomes rather cumbersome and may lead to measurement errors in some relevant cases, such as natural fiber filled polymers.[1–3] In fact, in addition to the Bagley[4] procedure to correct for entrance effects, also the Mooney[5] and the Weissenberg–Rabinowitsch[6] procedures must be performed: the former corrects for problems of slippage at solid walls, while the latter corrects for Non-Newtonian effects. Despite the Rabinowitsch procedure is clearly necessary, due to the shear thinning nature of polymers, the Mooney procedure is also needed, because of the relatively high viscosity of natural fiber filled plastics that requires usage of external lubricants in their formulation. Moreover, it is also well known that these materials may present additional difficulties in the wall slip characterization due to the flow being non-fully developed.[7]

Of all these corrections, the Mooney procedure is the most critical concerning measurement uncertainty, and this is the topic of the present work. In this paper we wish to explore issues of uncertainty propagation due to an imprecise knowledge of capillary radius that are amplified by the application of the Mooney slip correction procedure. As well known, if we indicate with Q the volumetric flow rate, P the pressure drop across the capillary, R the capillary radius, and L the capillary length, the Mooney procedure consists in performing several measurements of the apparent wall shear rate[8]:

$$\dot{\gamma}_N = \frac{4Q}{\pi R^3} \tag{1}$$

keeping the wall shear stress,[8]

$$\tau_w = \frac{PR}{2L} \tag{2}$$

constant. The measurements must be performed using different capillary radii, and the following equation,[5]

$$\dot{\gamma}_N = 4\frac{U_s}{R} + \dot{\gamma}_{ns} \tag{3}$$

is then used to obtain both the slip velocity U_s and the wall shear rate without the contribution of slip $\dot{\gamma}_{ns}$. This is finally adjusted with the Rabinowitsch correction, if the fluid that is studied is Non-Newtonian, in order to calculate the true shear rate and thus the fluid viscosity. The important consequences of Equation (3) are: i) in an apparent wall shear rate versus inverse radius plot, Equation (3) must yield straight lines, ii) the slope of these lines must be positive, as it represents the slip velocity U_s multiplied by 4, and iii) the intercept of these lines with the vertical axis must be positive as well, as it represents the shear rate $\dot{\gamma}_{ns}$.

The choice of the capillary radius as the geometrical parameter that most likely introduces measurement uncertainty is motivated by the fact that it appears with the highest power in the above equations. In fact, notice that if there was no slip and the fluid was Newtonian, viscosity η would simply be obtained as the ratio between shear stress and shear rate, therefore:

$$\eta = \frac{\pi}{8}\frac{P}{Q}\frac{R^4}{L} \tag{4}$$

in which R appears at the fourth power.

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2. Analytical Procedure

In order to highlight the measurement uncertainty amplification due to the Mooney procedure, we will use the following steps. We will first suppose that each capillary radius that is used has a certain known error indicated with δ:

$$R = \hat{R} + \delta \tag{5}$$

Since the measurement uncertainty u is the upper bound of the measurement error, we have that:

$$|\delta| \leq u(R) \tag{6}$$

In the remainder of this paper all quantities with a superscript hat are intended to be measured, i.e., in exact quantities. True quantities will have no superscript. As wall shear stress depends on capillary radius, we have:

$$\hat{\tau}_w = \frac{P\hat{R}}{2L} \tag{7}$$

therefore, combining (7) with (2) we have

$$\hat{\tau}_w = \frac{\hat{R}}{R}\tau_w \tag{8}$$

thus, true and measured wall shear stress will be different and depend on the ratio between measured and true radius. Next, a particular constitutive equation comprising a slip law will be assumed, as follows:

$$\begin{cases} \tau = k\dot{\gamma}^n \\ U_s = h\tau_w^{1/n} \end{cases} \tag{9}$$

Equation (9) is a power law both for shear stress τ and for slip velocity U_s, with the exponent for the slip velocity being equal to the reciprocal of the one for shear stress. The power law for the shear stress is used very often and is in general agreement with the mechanical behavior of polymeric fluids at high shear rate.[9] The power law for wall slip velocity has been first proposed by Brochart-Wyart and De Gennes[10] and is also in agreement with many experimental observations.[7] The constitutive Equation (9) can be used to solve for the special case of flow through a capillary tube, using standard methods.[6] Taking into account that Mooney procedure will be applied at constant measured wall shear stress, rather than true shear stress, we have that the apparent wall shear rate is:

$$\hat{\dot{\gamma}}_N i = \frac{4n}{3n+1}\left(\frac{\hat{\tau}_w}{k}\right)^{\frac{1}{n}}\left(\frac{R_i}{\hat{R}_i}\right)^{3+\frac{1}{n}} + \frac{4h}{\hat{R}_i}\hat{\tau}_w^{\frac{1}{n}}\left(\frac{R_i}{\hat{R}_i}\right)^{2+\frac{1}{n}} \tag{10}$$

3. Results and Discussion

As a consequence of Equation (10), the apparent shear rate versus inverse radius lines will not be necessarily straight. Indeed, curved Mooney plots are quite common for complex fluids, and can display both upward and downward curvatures.[11,12] Notice also that the non-linearity depends on the material constants, in particular the power law exponent n. Moreover, due to measurement uncertainties, it is not obvious that by forcing a linear regression through the experimental points, the resulting line would have positive slope and intercept. We have thus programmed a MATLAB-based software that on the basis of the measurement uncertainties in the capillary radii is able to calculate the uncertainties in the determination of the apparent shear rate, the intercept, and slope of the Mooney lines. Moreover, the software yields also the probability that such intercepts and slopes are negative. The software can then be used to predetermine the required uncertainty in the capillary radii in such a way that Mooney correction procedure has low probability to yield unphysical results and the uncertainty in the determination of the wall shear rate is low enough. For this goal, the material constants have to be known in advance, but in an approximate sense. The probabilities are calculated by discretizing the measurement uncertainty range for all inverse radii and estimating the slope and intercept by linear regression.

Table 1. Input data for the MATLAB based software.

Variable type	Input variables
Constitutive parameters	Power law index n
	Consistency k
	Slip parameter h
Capillary geometry	Measured capillary diameters $2\hat{R}$
	Diameter uncertainties $u(2R)$
Testing conditions	Measured shear stress $\hat{\tau}_w$

The software requires as input the data that are reported in **Table 1**. The results that are calculated are displayed in tabular form as well as graphical: possible Mooney plots are shown using error bars representing the bandwidth, within which the possible Mooney line would be comprised. A screenshot of the program is pictured in **Figure 1**. The software has been run for a few cases of interest that are reported in **Table 2**.

For simplicity, the cases reported in Table 2 are all relative to three capillary diameters, i.e., 0.5, 1, and 2 mm. These are indeed the most common diameters that are used in capillary viscometry. The uncertainty has been chosen to be equal to 0.01 mm for all capillary sizes.

As can be seen from the results of Table 2, relatively high uncertainties and high probabilities of negative intercepts are possible for higher values of the consistency k, i.e., for fluids that possess larger viscosity, for high slip constants h, and for lower values of the power law exponent n. Slope, i.e., slip velocity, on the other hand can become difficult to evaluate for smaller consistencies and slip constants.

4. Conclusions

In this paper a MATLAB-based software has been developed to estimate an upper limit acceptable inaccuracy on the capillary diameter to obtain reasonable results for rheological characterization. The only limitation is that the material con-

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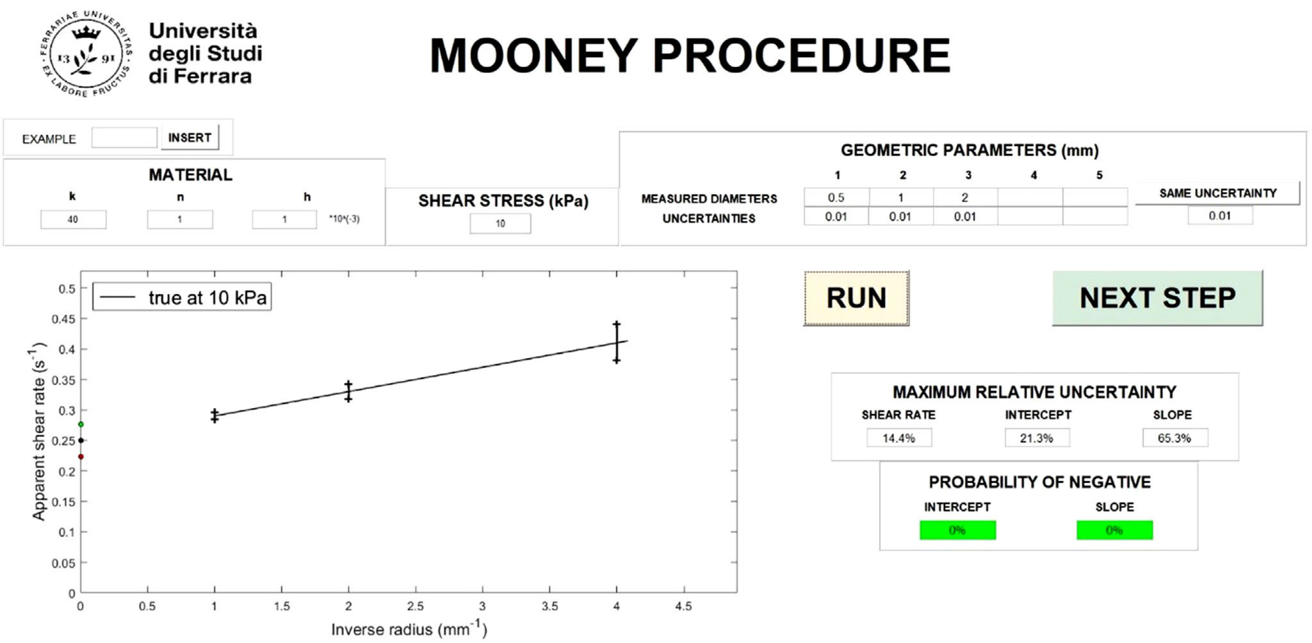

Figure 1. A screenshot of the MATLAB based software of this paper.

Table 2. Results of the software: a selection of cases of interest.

K [kPa s^n]	n	h	Maximum relative uncertainty [%]			Probability of negative [%]		Example
		[mm s^{-1} kPa$^{-1/n}$]	Shear rate	Intercept	Slope	Intercept	Slope	
100	1	1	13.5	29.2	37.4	0	0	1
10	1	0.1	15.9	16.1	1876.6	0	42.1	2
0.1	1	10	15.9	16.1	1876.6	0	42.1	3
100	1	100	12	1336	19	40.9	0	4
10000	1	1	12	1336	19	40.9	0	5
10	0.5	100	16	2221	25.3	45.3	0	6
100	0.5	1	16	2221	25.3	45.3	0	7
1	0.5	1	19.9	20.2	1883.5	0	41.7	8
10	0.5	0.01	19.9	20.2	1883.5	0	41.7	9

stants of the fluid that is intended to be characterized must be known in terms of their order of magnitude.

The application of the Mooney wall slip correction procedure may lead to very remarkable measurement errors. These are particularly relevant in the case of Non-Newtonian fluids, especially fluids displaying high shear thinning behavior. Understandably, viscosity determination is quite difficult in fluids that are highly viscous, while slip velocity determination is more challenging for fluids that possess higher fluidity: the former ones are more prone to slip at the wall in the capillary viscometry experiments, thus they will show lower deformation rate; the latter ones will show a higher deformation rate, thus they will likely slip very little.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

measurement accuracy, Mooney procedure, power law fluid, wall slip

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