

# THE CAPILLARY VISCOMETER METHOD FOR THE RHEOLOGICAL CHARACTERIZATION OF THERMOPLASTIC CERAMIC PASTES

WILLI PABST, JIŘÍ HAVRDA, EVA GREGOROVÁ

*Department of Glass and Ceramics, Institute of Chemical Technology,  
Technická 5, 166 28 Prague*

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*A variant of the well-known capillary viscometer method is described which is able to measure the rheological behavior of thermoplastic ceramic pastes in dependence of the temperature. The construction of the heated viscometer is shown, the principle of measurement is explained and for a selected paste (an alumina paste with 66 vol.% solid content designed for injection-molding) at two distinctly different temperatures the complete evaluation procedure is demonstrated. Attention is also paid to the assumptions underlying the evaluation procedure, especially the Mooney-Rabinowitsch correction, and the accuracy of the method is discussed where possible.*

## INTRODUCTION

In a recent paper [1] we have worked out the theoretical background for the mathematical modelling of ceramic injection molding based on the formalism used in rational thermodynamics. A simple but nevertheless practically important flow geometry, viz unidirectional Poiseuille tube flow, was chosen for illustration and the possibilities of material modelling were assessed for this onedimensional case. It was pointed out that the material model for materials without memory, i.e. in cases where effects of viscoelasticity (stress-relaxation, die-swell etc.) and time-dependence (thixotropy, rheopexy) are negligible, can be given in an explicit form by constitutive equations of the differential type and coincides with the well-known model of generalized Newtonian fluids (liquids), whenever normal stress effects are out of interest. The behavior of these materials in a fairly wide class of flows (so-called viscometric flows [1]) can be uniquely characterized by one viscometric function, intimately related to the so-called apparent viscosity (i.e. the quotient of shear stress and shear rate at a certain shear rate value), which is accessible from standard viscometric measurements. The present paper introduces the instrumental equipment used for such measurements at elevated temperatures and deals with the practical aspects of determining flow curves of thermoplastic ceramic pastes in principle. A subsequent paper will consider the rheology of ceramic injection-molding feedstocks with various solid contents systematically and in more detail [2].

Capillary viscometry (also called capillary tube viscometry or capillary extrusion viscometry) is one of the well-known standard methods for the rheological characterization of ceramic pastes and other materials with high apparent viscosities [3, 4, 5]. Together with rotational or cone-and-plate viscometry (but in contrast to

many empirical methods used e.g. in production control) it belongs to the methods, by which rheological data of scientific and engineering value can be obtained, because the measurements can be performed under precisely defined conditions and evaluated on a sound theoretical basis, which enables shear stress and shear rate to be determined at the same point (namely, at the wall). Basic construction principles of capillary viscometers have been described e.g. by Skelland [6], who also cites most of the classical references. The two basic types used in routine measurements (gas- or piston-driven viscometers) can have very different degrees of sophistication depending on the application intended. While the gas-driven instruments usually need a lot of special devices (gas supply, pressure regulators, valves, manometers etc.), piston-driven instruments are constructionally simpler and can be used in connection with a universal testing machine, which belongs to the standard equipment of each ceramic laboratory. Although standard for room-temperature measurements (dissipative heating being neglected), great care has to be taken when this method is to be used for measurements at higher temperatures. The crucial question is whether the instrument can or cannot guarantee conditions that can be considered as isothermal to the desired degree of accuracy. In some cases the selection of new construction materials turns out to be necessary as well. The construction suggested by Bowen [7] for isothermal measurements, where the capillaries are turned upside down (i.e. the entry surrounded by the paste inside the material chamber and the exit being at one level with the reservoir cylinder bottom) has the disadvantage, that only a very small volume of the material chamber (reservoir cylinder, barrel) can be effectively used for the measurement itself and furthermore this volume depends on the length of the capillaries used, see also [8]. Therefore in the present work a traditional modular

system has been used, consisting in a material chamber of constant effective volume with exchangeable capillaries at its bottom. It is clear that in this case the capillary needs an extra external heating and realistic estimates of the temperature differences from the entry to the exit must be at hand.

## EXPERIMENTAL PART

### Viscometer Construction

The heatable capillary viscometer used in this work has been constructed at the Department of Glass and Ceramics of the Institute of Chemical Technology Prague in connection with a grant concerning bioinert alumina ceramics<sup>1</sup> in order to enable the extrusion of thermoplastic ceramic pastes designed for injection-molding and the rheological characterization of these materials. The schematic view on figure 1 shows the viscometer itself and the necessary peripheral devices. The viscometer consists of a steel cylinder (the material chamber) with a height of ca. 100 mm and an inner diameter of 50 mm (inner volume approximately 200 ml) and a Duraluminium bottom connecting this reservoir with the (exchangeable) "capillaries" or "dies", steel tubes of various lengths and different inner diameters ranging from 4 mm to 20 mm. In order to avoid or at least reduce apparent slip phenomena at the capillary walls, the capillaries are equipped with an internal thread to keep the outer shear layer of the flowing paste fixed at the walls, cf. [6, 9]. While for some liquids with low or medium (apparent) viscosities capillaries with large length to diameter ratios ( $L/D$  ratios ranging from 100 to 1000!) are recommended [6], most authors working in the field of paste rheology apply for viscometric measurements capillaries with  $L/D$  ratios ranging between approx. 1 to 20 [3,4,5]. In the present work the 4 mm-diameter capillaries were used generally for viscometric measurements ( $L/D$  ratios of 20, 12.5 and 7.5 for capillaries of length 80 mm, 50 mm and the difference length 30 mm, respectively), whereas capillaries with wider diameters were employed only exceptionally (e.g. for the wall slip test described below) or for other purposes (e.g. for flow profile visualization and the extrusion of samples under defined flow conditions, which are not subject of this paper). While for room temperature measurements a Silon (Nylon 6) piston ("ram") could be successfully employed [9, 10], measurements at elevated temperatures (60-90 °C) yielded unreproducible results, probably due to the large thermal expansion of this piston in the interesting temperature range. Therefore it has been replaced by a new Duraluminium piston in the present work, tightened against leakage by rubber bands. In addition the following modifications have been made in order to adapt

the original instrument for measurements at elevated temperatures:

- Two independent external heating systems have been added. The first system consists in a copper tube coil twisted around the material chamber and supplied by hot water pumped through the coil from a thermostatic heater. The second system consists in an electroresistant heating coil (Konstantan) embedded in an epoxy resin mantle and is controlled by a low voltage source.
- Two thermocouples are used for temperature control, one at the capillary entry, the other at its exit (Cu-Konstantan-Cu thermocouples, reference: crushed ice melting in a Dewar).

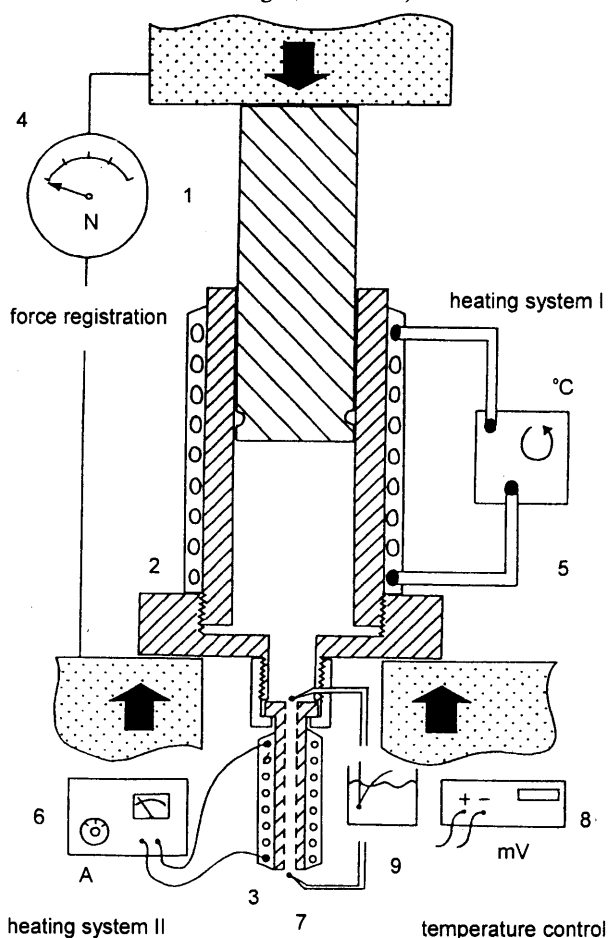


Figure 1. Schematic view of the heated capillary viscometer and peripheral devices: Piston (ram) (1), material chamber (barrel, reservoir) (2), capillary (tube, die) (3), force display of the universal testing machine (4), thermostatic heater (5), low-voltage source (6), thermocouples (at entry and exit) (7), digital voltmeter (8), thermocouple reference (9).

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Practical details and general advices concerning the measuring procedure under ambient temperature conditions have been published elsewhere [3, 6, 9] and will not be repeated here. Most of what has been said there applies here as well, with the only difference that additionally the temperature has to be precisely controlled.

### Measurement Principle and Evaluation Procedure

The viscometer is placed into a universal testing machine and the forces necessary to sustain a constant piston velocity (i.e. a constant volumetric flow rate) are recorded in dependence of time (or, equivalently, piston displacement). Figure 2 shows such a force-time plot schematically, cf. similar plots in [3]. After an initial process phase (I) with a force maximum a steady-state situation is achieved in the case of isothermal measurements of the whole material volume at one selected temperature (constant-temperature measuring mode, "CT-mode"). In this steady-state phase (II) the force remains more or less constant, until "dead volume effects" become significant (when the piston reaches the stagnant or eddying material in the bottom corners of the material chamber beside the capillary entry) and the forces undergo a steep increase indicating the final process phase (III). Under certain conditions (small capillary diameters and medium to high extrusion velocities) the (usually very material- and time-consuming) CT-mode measurements can be performed more economically by using a single viscometer filling for measuring the corresponding force while the temperature of the material is slowly decreasing (decreasing-temperature measuring mode, "DT-mode").<sup>1</sup> In this case the process is never really in a steady state and after the initial phase the force is steadily increasing (see figure 2), a linear range (II') being followed by the strongly nonlinear range of the steep increase indicating again the near end of the process (III').

As soon as the forces have been measured for capillaries of at least two different lengths and various mean velocities in the relevant temperature range, a  $\tau_w - \gamma_a$  - plot, i.e. the graphical representation of the wall shear stress against the mean shear rate (both quantities directly accessible from the measurements), can be set up for each temperature in question: The force or pressure differences between two capillaries of different length can easily be transformed into wall shear stresses  $\tau_w$  according to the equation

$$\tau_w = \frac{D\Delta p}{4\Delta L}, \quad (1)$$

where  $D$  is the diameter of the capillaries used,  $\Delta L$  the length difference between both capillaries and  $\Delta p$  the difference between the two pressure drops in the longer

( $L_1 = 80$  mm) and the shorter ( $L_2 = 50$  mm) capillary. Using this difference procedure and verifying (a posteriori) that the velocity profile is fully developed within a distance small compared to the length of the shorter capillary (i.e. verifying that the entrance length is well below 50 mm), the wall shear stress differences correspond to values in which the so-called Bagley correction for entry and exit effects [4, 6] is implicitly included. On the other hand the (preselected and easily measurable) mean velocities are straightforwardly transformed into mean shear rates  $\gamma_a$  ("apparent wall shear rate") according to the equation

$$\gamma_a = \frac{8\bar{v}_z}{D}, \quad (2)$$

where  $\bar{v}_z$  is the mean velocity in the (axial) flow direction (denoted  $z$  for cylindrical coordinates).

The graph of measured points  $\tau_w(\gamma_a)$  (the "apparent flow curve") is a viscometric plot which gives preliminary and orientational information about the flow behavior of the material, but in order to obtain the flow curve proper<sup>2</sup> it is necessary to relate the wall shear stress  $\tau_w$  to the true shear rate at the wall  $\gamma_w$  (and not to the above

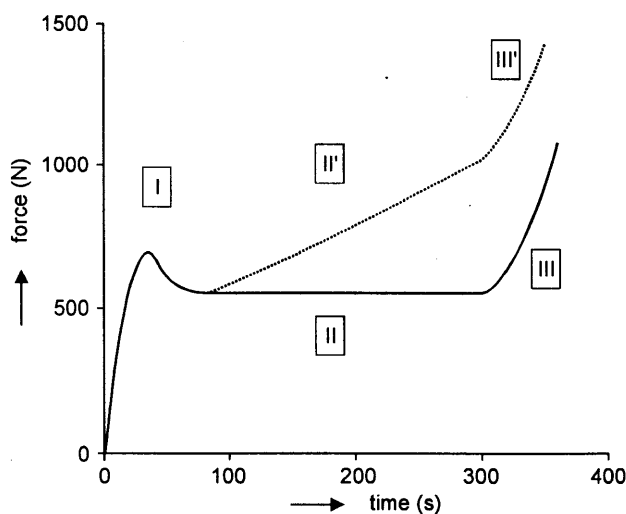


Figure 2. Force registration plot (schematic); after an initial phase (I) the flow can be considered as steady and the force is constant (II) or linearly increasing (II') for the CT- and DT-mode, respectively, followed by a steep force increase due to "dead volume effects" (III and III').

— CT mode, - - - DT mode

<sup>1</sup> It needs no special emphasis that in this case great care is needed to ensure a spatially uniform temperature decrease (in time) in the whole capillary, i.e. temperature decrease without significantly increasing the temperature gradient from the capillary entry to the capillary exit.

<sup>2</sup> I.e. graph  $\tau(\gamma)$ , where  $\tau \equiv \tau_{rz}(r)$  is the shear stress and  $\gamma \equiv dv_z(r) / dr$  the shear rate, which in cylindrical coordinates corresponds to the radial gradient of the axial velocity component.

mean shear rate which is directly accessible from the mean velocity). For the steady, laminar, fully developed flow of time-independent incompressible fluids in the absence of wall slip it is standard to perform the necessary correction by the well-known Mooney-Rabinowitsch equation [6, 11]:

$$\gamma_w = \frac{3n'+1}{4n'} \gamma_a \quad (3)$$

where  $n'$  is generally defined as

$$n' = \frac{d \log \tau_w}{d \log \gamma_a} \quad (4)$$

and has to be determined principally for each shear rate value from the tangent slope of a  $\log \tau_w - \log \gamma_a$  - plot. In many cases however, especially for power-law and Herschel-Bulkley fluids,  $n'$  does not change very much with the mean shear rate and can be determined in a straightforward way by linear regression of the  $\log \tau_w - \log \gamma_a$  - plot or, alternatively, by nonlinear regression with fit equations of the form (5) or (6), respectively.<sup>1</sup>

The graphical representation of the wall shear stress  $\tau_w$  against the ("true", i.e. Mooney-Rabinowitsch corrected) wall shear rate  $\gamma_w$  is identical with the required flow curve  $\tau(\gamma)$  and can be fitted by nonlinear regression with an appropriately chosen model in order to obtain definite values for the parameters characterizing material behavior. For power-law fluids without yield stress (pseudoplastic liquids), which can be described by a constitutive equation of the form (Ostwald-DeWaele model):

$$\tau = K\gamma^n, \quad (5)$$

there are two material parameters, namely  $K$  (called "coefficient of consistency") and  $n$  (called "flow index" or "power-law index"), and the fitting procedure can be reduced to a linear regression problem in a log-log plot. For Herschel-Bulkley fluids, for which power-law behavior sets in only after a certain stress value has been exceeded, the constitutive equation contains a third parameter  $\tau_0$  (the "yield stress") in addition to the two above mentioned ones:

$$\tau = \tau_0 + K\gamma^n. \quad (6)$$

In this case the three material parameters have to be determined either by reading (extrapolating)  $\tau_0$  from the flow curve and applying linear regression to the  $\log(\tau - \tau_0) - \log \gamma$  - plot or directly by nonlinear regression. The latter possibility has been preferred in this work.

Since the deduction of the Mooney-Rabinowitsch equation is based on a series of assumptions (steady, laminar, fully developed flow of a time-independent incompressible<sup>2</sup> fluid with the boundary condition of no wall slip) it is advisable to discuss their validity for the individual material and flow situations considered.

#### Validity of Assumptions and Methods of Verification

Viewed theoretically, steady flow can only develop in materials with a memory short compared to the duration of the flow process [12] (for "fluids without memory" [1], of course, steady flow is easily achieved). From an experimental point of view the flow of real materials can be considered as steady after a certain initial phase, discarding the starting region with the force maximum in the force-time plot. Time-independence of non-memory fluids can in principle be verified experimentally by measuring flow curves (or at least some of their points, i.e. apparent viscosities at certain shear rates) increasing first from a state of rest or low velocity to a medium velocity and then decreasing the velocity from high to medium. If the points do not coincide within statistical errors of measurement there is measurable hysteresis, i.e. time-dependence.<sup>3</sup>

The absence of wall slip can be verified by measuring flow curves with capillaries of different diameter, where non-coincidence (within statistical errors of measurement) is indicative of wall slip [6]. In order to confirm laminarity of flow and to control whether the velocity profile can be considered as fully developed or not in the relevant flow region, values of the Reynolds number (generalized to non-Newtonian liquids) and the entry length have to be calculated. For the generalized Reynolds number we use the equation [6, 11]:

<sup>1</sup> It has to be kept in mind that, generally,  $n'$  need not be a constant over the whole range of shear rates. Deviations of the  $\log \tau_w - \log \gamma_a$  - plot from linearity are always indicative of non-power-law behaviour, which means that the final flow curves of these materials cannot be evaluated by the Ostwald-DeWaele or the Herschel-Bulkley model. It is not uninteresting to note, however, that the Mooney-Rabinowitsch equation (3) remains unaffected by all this holds even for such cases, since for its deduction [6,11] no reference has been made to a special model.

<sup>2</sup> Incompressibility of the fluid has to be ensured a priori by careful material preparation (mixing and compounding) during which all voids and gas inclusions have to be removed, e.g. by evacuation.

<sup>3</sup> In practice such measurements are highly nontrivial and with the method used here it seems unlikely that hysteresis effects could be detected within the measurement errors due to temperature and force uncertainties. Furthermore it is by no means evident how to distinguish hysteresis effects of inelastic, i.e. purely viscous fluids (in sense of thixotropy or rheopexy) from memory effects in viscoelastic fluids.

$$Re_{gen} = \frac{\rho D^n \bar{v}_z^{2-n'}}{K' 8^{n'-1}} \quad (7)$$

where  $n'$  can be determined from the tangent slope of the  $\log \tau_w - \log \dot{\gamma}_a$  - plot (see above; if nonlinear, for each shear rate value) or together with  $K'$  directly by nonlinear regression of the  $\tau_w - \dot{\gamma}_a$  - plot. The critical value of the Reynolds number denoting the transition from laminar to turbulent flow in tubes ("capillaries") is between 2100 and 2320 depending on the literature reference used [6, 15, 16]. For the hydrodynamic entry length, which separates the entry region of the tube ("capillary") from the so-called viscometric region [13], where the velocity profile is fully developed<sup>1</sup>, the following equation is frequently used [6]:

$$L_c = 0.0575D Re_{gen} \quad (8)$$

This equation (originally deduced with the classical Reynolds number for Newtonian liquids) applies very well to many non-Newtonian liquids for Reynolds numbers between 100 and 2000, although the numerical factor ranges from 0.04 to 0.06 depending on the literature reference used [15, 16]. With regard to the extremely low Reynolds numbers occurring in our experiments with ceramic pastes (see next section), we prefer for a more realistic estimation of the entry length an equation proposed for particulate materials by Atkinson et al. [14]:

$$L_c = 0.59D + 0.056D Re_{gen} \quad (9)$$

Material composition  
and preparation

The thermoplastic ceramic paste studied in this work is an alumina paste plasticized by an organic (paraffine-wax based) binder mix of prototype composition<sup>2</sup> with a softening range between approx. 60 and 70 °C. The starting powder used is a commercial high-purity (99.99 wt.%) submicron (0.6-0.8 μm) alumina ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub> labelled *AKP 15* by *Sumitomo Chemical Co. Ltd.*) and its content in the paste is unusually high (66.0 vol.%). The preparation of the paste was performed according to a standard schedule including preheating of the powder, melting of the binder mix, distributive mixing in a mechanical high-speed stirrer with stepwise powder addition (assisted by manual stirring in the last phase) and dispersive mixing by extruding the paste through a small-diameter capillary. Before measurement the whole viscometer (without peripheral devices) is placed into a convection drying box in order to achieve thorough heating of the whole material volume.

## RESULTS AND DISCUSSION

Concerning heat loss the capillary is the weak link in viscometer measurements because its exit is in direct contact with the surrounding atmosphere and due to its smaller dimensions (compared to the viscometer material chamber) its heat capacity is relatively low. The already small heat content can thus be easily reduced even more by convective heat transfer. For this reason the temperature drop in the capillary is the critical criterion for establishing whether the flow situation for the viscometric measurements can be considered as isothermal or not. Figure 3 shows measurements of the temperature difference between capillary entry and exit. It is evident that for an unheated material chamber and unheated capillaries the temperature drop can for low volumetric flow rates achieve values up to 14.6 K for the longer ( $L_1 = 80$  mm) and 8.5 K for the shorter ( $L_2 = 50$  mm) capillary. These values are certainly unacceptable, since the transition from complete fluidity to total solidification of the paste occurs in a temperature range of just the

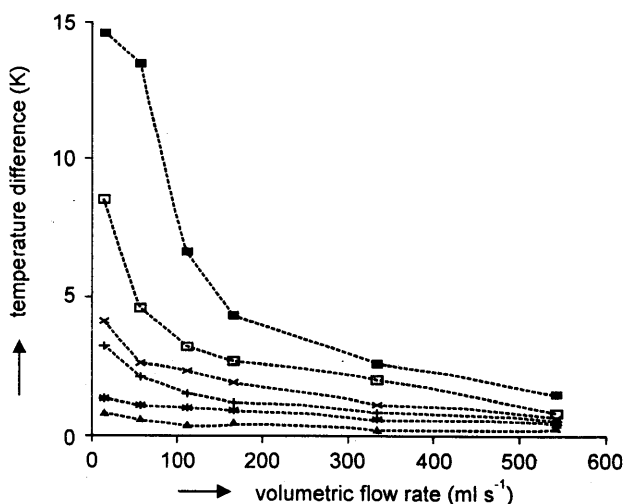


Figure 3. Temperature drop from capillary entry to capillary exit (longer capillary with  $L_1 = 80$  mm and shorter capillary with  $L_2 = 50$  mm) in dependence of the volumetric flow rate: (1) material chamber and capillary without heating, (2) material chamber with, capillary without heating, (3) material chamber and capillary with heating.

■ - (1)  $L = 80$  mm, □ - (1)  $L = 50$  mm, × - (2)  $L = 80$  mm, + - (2)  $L = 50$  mm, \* - (3)  $L = 80$  mm, ▲ - (3)  $L = 50$  mm

<sup>1</sup> A velocity profile is fully developed when the local axial velocity on the symmetry axis of the tube, i.e. the maximum velocity in the profile is 98 or 99 % (depending on the literature reference used [6, 15, 16]) of the final value for an infinite length (which is attained only asymptotically of course).

<sup>2</sup> The composition of the binder mix proper has been developed by Ing. V.Trdlička, CSc. and is part of the know-how of a Czech ceramic factory.

same order of magnitude (between 70 and 60 °C). As can be seen on figure 3, the situation could be effectively improved by using the thermostatic heating coil around the material chamber and the electroresistant heating wire around the capillaries: the temperature drop could be reduced to maximum values between 1.3 and 0.8 K for the respective capillaries even in the most critical case of low volumetric flow rates. For higher flow rates the temperature drop is totally negligible in comparison with the accuracy of the thermocouples and other errors of measurement.

Table 1 and figure 4 present force values  $F_1$  and  $F_2$  measured in the constant-temperature mode (CT) for extrusion with a constant mean velocity of  $26.6 \text{ mm s}^{-1}$  using long ( $L_1 = 80 \text{ mm}$ ) and short ( $L_2 = 50 \text{ mm}$ ) capillaries of diameter  $D = 4 \text{ mm}$ . For reasons of comparison figure 5 shows analogous results using the decreasing-temperature measuring mode (DT), where the material chamber has been preheated to ca.  $85 \text{ °C}$ , the temperature of the thermostatic heater has been chosen ca.  $70 \text{ °C}$  for the material chamber and  $65 \pm 1 \text{ °C}$  for the capillary. The agreement in this case is satisfactory and the same is true for higher mean velocities. Since measurements in the constant-temperature measuring mode (CT) are extremely time- and material-consuming the decreasing-temperature measuring mode (DT) is preferred whenever possible. However, in the case of lower mean velocities (when the change of rheological properties in the capillary is too large) the decreasing-temperature measuring mode (DT) can lead to unreproducible results and has to be discarded.

Table 1. Forces and pressures corresponding to the long ( $L_1 = 80 \text{ mm}$ ) and the short ( $L_2 = 50 \text{ mm}$ ) capillary, pressure differences corresponding to the difference length ( $\Delta L = L_1 - L_2 = 30 \text{ mm}$ ) and wall shear stresses (mean velocity  $26.6 \text{ mm s}^{-1}$ , capillary diameter  $4 \text{ mm}$ , CT-mode).

$T \text{ (°C)}$	$F_1 \text{ (N)}$	$F_2 \text{ (N)}$	$p_1 \text{ (kPa)}$	$p_2 \text{ (kPa)}$	$\Delta p \text{ (kPa)}$	$\tau_w \text{ (kPa)}$
69	4600	2700	2341	1374	967	32.2
72	2500	1250	1273	636	637	21.2
75	1625	700	827	356	471	15.7
78	1250	550	636	280	356	11.9
80	1100	500	560	255	305	10.2

Once the forces are measured for the temperatures of interest (either at selected temperatures - CT - or in a whole temperature range - DT) the subsequent evaluation procedure is the same in both cases (CT and DT) and is as follows: Forces (acting on the piston of the viscometer, cross-section area  $19.64 \text{ cm}^2$ ) are transformed into pressures according to the equation  $p(\text{kPa}) = 0.509 F \text{ (N)}$  (see table 1) and pressure differences are obtained (see figure 6), which can directly be transformed into shear

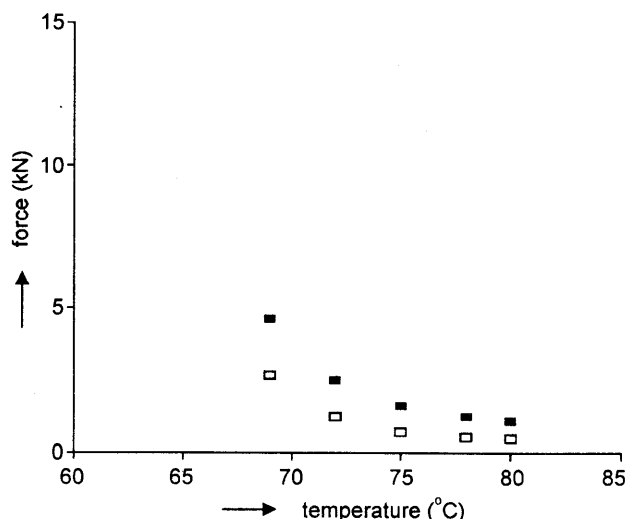


Figure 4. Forces registered for five different temperatures for extrusion with a mean velocity of  $26.6 \text{ mm s}^{-1}$  in a 4 mm-diameter capillary (CT-mode).

□ -  $L = 50 \text{ mm}$ , ■ -  $L = 80 \text{ mm}$

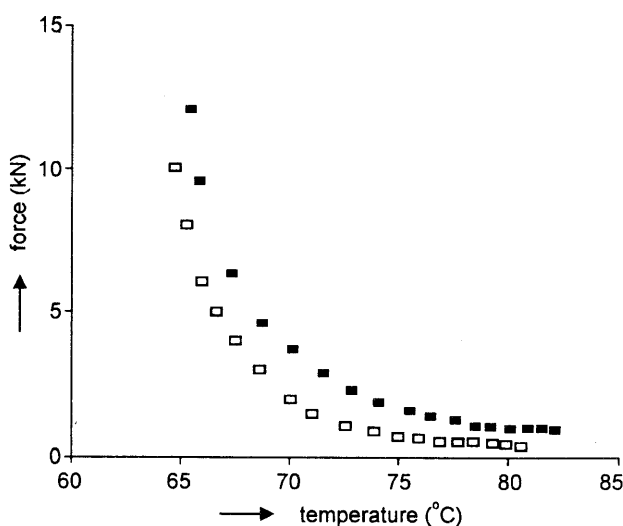


Figure 5. Force-temperature plot for extrusion with a mean velocity of  $26.6 \text{ mm s}^{-1}$  in a 4mm-diameter capillary (DT-mode).

□ -  $L = 50 \text{ mm}$ , ■ -  $L = 80 \text{ mm}$

stresses at the wall according to equation (1), see figure 7. The mean shear rate is calculated from the mean velocity according to equation (2) and when the same is done for all mean velocities measured, an apparent (i.e. uncorrected) flow curve are determined for each temperature. Examples are shown on figures 8 and 9 for 69 and 80 °C, respectively.

The apparent flow curves serve now first to determine the parameters  $K'$  and  $n'$ , the latter of which is necessary to perform the Mooney-Rabinowitsch correction according to equation (3). With the resulting "true" (MR corrected) shear rate values flow curves can

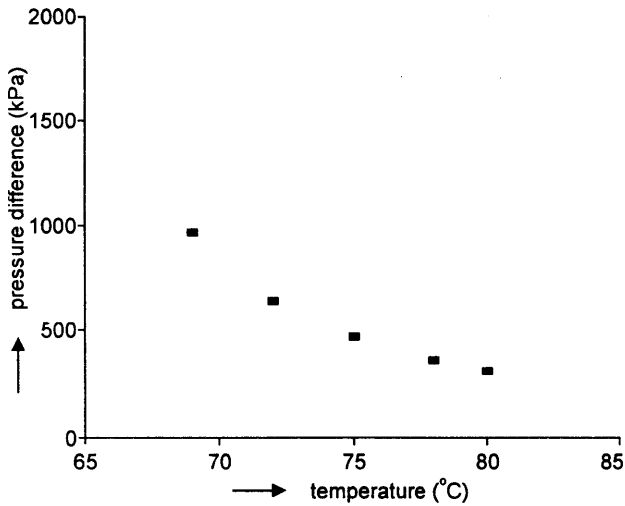


Figure 6. Pressure differences corresponding to a capillary difference length of  $L_1 - L_2 = \Delta L = 30$  mm (mean velocity  $26.6 \text{ mm s}^{-1}$ , 4 mm - diameter capillary, CT-mode).

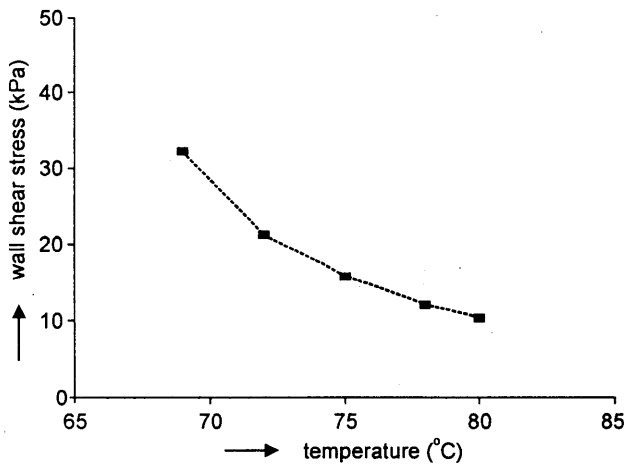


Figure 7. Wall shear stresses versus temperature (mean velocity  $26.6 \text{ mm s}^{-1}$ , 4 mm - diameter capillary, CT-mode).

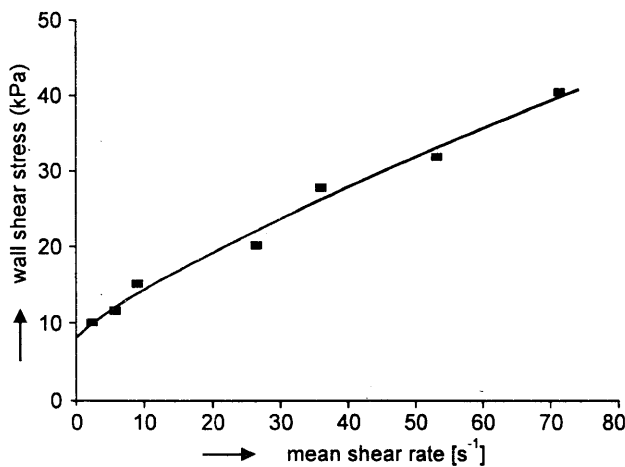


Figure 8. Apparent flow curve ( $\tau_w - \gamma_a$  plot) for a temperature of  $69 \text{ }^\circ\text{C}$  (measured points, uncorrected).

be set up (see figure 10), which can be fitted by the Herschel-Bulkley equation (5) to yield definite values of the yield stress  $\tau_0$ , the consistency  $K$  and the flow index  $n$ . With the numerical values of these three parameters the 1D constitutive equations (Herschel-Bulkley model) for the alumina paste investigated (with a solid content of 66.0 vol.%) are explicitly determined as follows:

$$\tau = 8.1 + 0.98 \gamma^{0.81} \quad \text{for } T = 69 \text{ }^\circ\text{C}$$

$$\tau = 0.6 + 0.68 \gamma^{0.65} \quad \text{for } T = 80 \text{ }^\circ\text{C}.$$

In order to confirm the assumptions of laminarity of flow and a fully developed velocity profile in the lower part of the capillary a generalized Reynolds number and the entry length can be calculated by equations (7) and (9), respectively, using the parameters of the apparent flow curves ( $K' = 1.01$  and  $n' = 0.81$  for  $T = 69 \text{ }^\circ\text{C}$  and  $K' = 1.01$  and  $n' = 0.81$  for  $T = 80 \text{ }^\circ\text{C}$ ). For the two cases shown (flow curves for 69 and 80 °C) the generalized Reynolds numbers are maximally  $0.9 \times 10^{-3}$  (for the highest mean velocity at 69 °C) and  $2.6 \times 10^{-3}$  (for the highest mean velocity at 80 °C), which is several orders of magnitude lower than the critical value for tube flow. It is also clear that for all cases here the second term in equation (9) is negligible and thus the entry length can be calculated by

$$L_e = 0.59D + 0.0001D \approx 0.59D,$$

which yields for a 4mm-diameter capillary  $L_e = 2.36$  mm, i.e. after an initial zone of 2.36 mm at the capillary entry the velocity profile will be fully developed and remains so in the downstream part of the capillary, especially in the part which is relevant for measuring (viscometric region).

A very intricate problem which has not been given due attention in this paper and which seems not to be satisfactorily solved in literature so far is the wall-slip problem, i.e. the question whether pastes in general and the paste investigated here in special can slide along the wall without shear or not. While for ordinary one-phase liquids the question seems to be answered once and for all (Coleman, Markovitz and Noll [12] report that even liquid mercury does not exhibit wall slip during Poiseuille tube flow in a smooth glass capillary!) the question arised anew in connection with multiphase systems such as pastes and high-molecular organics (for some new research consult e.g. [17]) and has not yet been settled. In our case it seems that within errors of measurement wall slip has been effectively avoided by using capillaries with an internal thread (see above). Figure 11 shows the apparent flow curve for a temperature of  $69 \text{ }^\circ\text{C}$  measured with a 4 mm-diameter capillary (as presented on figure 8) and additional points

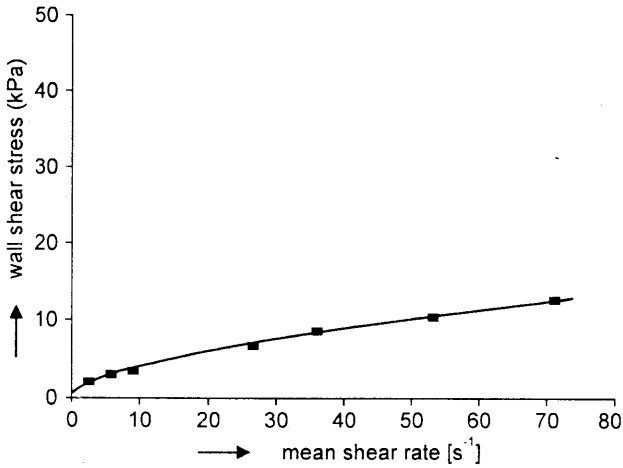


Figure 9. Apparent flow curve ( $\tau_w - \gamma_d$  plot) for a temperature of 80 °C (measured points, uncorrected).

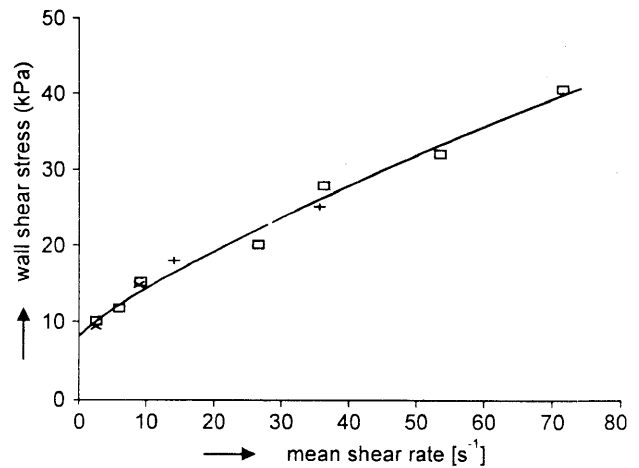


Figure 11. Points of an apparent flow curve for  $T = 69\text{ }^{\circ}\text{C}$  measured with capillaries of various diameters. —  $D = 4\text{ mm}$  (fit),  $\square$  -  $D = 4\text{ mm}$ , + -  $D = 6.9\text{ mm}$ ,  $\times$  -  $D = 11\text{ mm}$

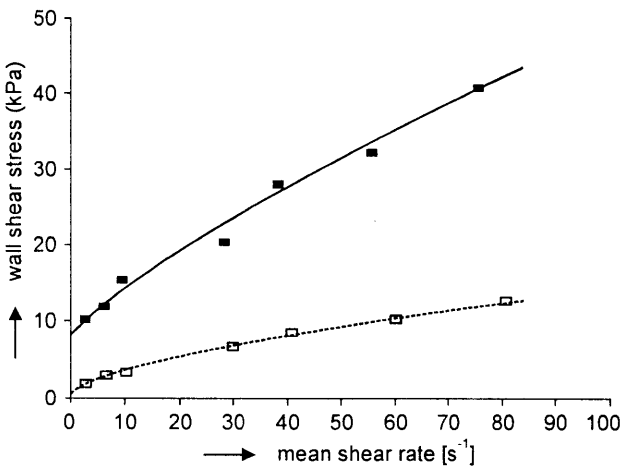


Figure 10. Flow curves (measured points Mooney-Rabinowitsch corrected) for temperatures of 69 and 80 °C (curves fitted by the Herschel-Bulkley model). —  $T = 69\text{ }^{\circ}\text{C}$  (fit),  $\blacksquare$  -  $T = 69\text{ }^{\circ}\text{C}$  (points),  $\cdots$  -  $T = 80\text{ }^{\circ}\text{C}$  (fit),  $\square$  -  $T = 80\text{ }^{\circ}\text{C}$  (points)

measured with capillaries of different diameter (6.9 and 11 mm), which are in good agreement with the former. It is known that coinciding flow curves, when measured with capillaries of different diameter, can be considered as indicative of the absence of wall slip [6, 11].

A coarse estimate of the statistical errors involved in the force and shear stress measurements can be made as follows: Admitting a possible error of  $\pm 50\text{ N}$  for force measurements at  $T = 69\text{ }^{\circ}\text{C}$  and  $\pm 25\text{ N}$  for force measurements at  $T = 80\text{ }^{\circ}\text{C}$  (where the force values are lower and consequently a smaller range can be chosen for force registration) the errors in the resultant wall shear stress will lie between  $\pm 5.3\text{ }%$  and  $\pm 8.3\text{ }%$ , respectively.

### CONCLUSIONS AND OUTLOOK

As was shown in the previous sections, the capillary viscometer method can be successfully applied for the rheological characterization of thermoplastic alumina pastes when the viscometer is adequately adapted to measurements at elevated temperatures (temperature control by thermocouples and the use of two independent heating systems - one for the material chamber, one for the capillary). As soon as the points of the apparent flow curve are determined, all information which is directly accessible from measurements (apparent viscosities for a certain range of shear rates) is in principle known and all subsequent steps consist only in an evaluation procedure including the Mooney-Rabinowitsch correction and curve fitting by nonlinear regression.

For the material studied in this paper (an alumina paste with the extremely high solids loading of 66.0 vol.%) the three material parameters determined from the final flow curves are clearly dependent on temperature, which is especially pronounced for the yield stress (increasing from 0.6 kPa for 80 °C up to 8.1 kPa for 69 °C indicating a strong change in rheology). The flow index being lower than 1 corresponds to the fact that the pastes exhibit "shear-thinning" behavior (i.e. a decrease of apparent viscosity with increasing shear rate) similar to pseudoplastic fluids and is one of the main requirements for successful injection molding feedstocks [19]. The calculated values of the generalized Reynolds number and the entry length demonstrate that the a priori assumptions underlying the evaluation procedure (viz. laminarity and a fully developed velocity profile in the region relevant for viscometric measurements) are very well confirmed a posteriori. Furthermore within errors of measurement no experimental evidence could be found



for wall slip, which indicates that wall slip could be effectively avoided by using capillaries with an internal thread. Apart from systematic and statistical errors originating from uncertainties in the temperature (of order  $\pm 0.5$  K), statistical errors occurring in the force measurements can be expected to yield errors of about 5-10 % in the shear stresses.

The material model selected (the three-parameter Herschel-Bulkley model) is the simplest 1-D model that can account for both yield stress and the general nonlinearity of the flow curve and its place within the framework of more general 3-D theories was elucidated in a previous paper [1]. Although the practical difficulties of a nonlinear regression procedure should not be underestimated an advantage of this model consists in the fact that it reduces in a natural way to the two special cases of pseudoplastic and Bingham materials. Furthermore an analytical solution is known for the Poiseuille tube flow of Herschel-Bulkley fluids [18] and so it is possible to calculate the velocity profile in cylindrical tubes and similar flow geometries whenever the constitutive equation has been determined. Especially the temperature dependence of the yield stress has a fundamental significance for the velocity profile during the forming process and thus also for the microstructure of the resulting green bodies. These aspects will be dealt with in a subsequent paper.

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#### METODA KAPILÁRNÍHO VISKOZIMETRU PRO REOLOGICKOU CHARAKTERIZACI TERMOPLASTICKÝCH KERAMICKÝCH PAST

WILLI PABST, JIŘÍ HAVRDA, EVA GREGOROVÁ

Ústav skla a keramiky,  
Vysoká škola chemicko-technologická,  
Technická 5, 166 28 Praha 6

Je popsána praktická varianta známé metody měření reologických vlastností pomocí kapilárního viskozimetru, která umožňuje charakterizaci reologického chování termoplastických keramických past při zvýšených teplotách, popř. i určení teplotní závislosti jejich materiálových parametrů. Na rozdíl od standardní metody měření při pokojové teplotě, v tomto případě řada opatření je nutná k zajištění podmínek toku, který - v rámci přesnosti měření - může být považován za izotermní. K tomu patří mimo jiné použití dvou topných systémů a teplotní kontrola pomocí termočlánků. Poměrně dobrá reprodukovatelnost hodnot sil naměřených pro jednotlivé teploty dokladuje účinnost všech těchto opatření. Měřicí proces včetně kompletního postupu vyhodnocení jsou důkladně popsány na příkladě měření vysoce koncentrované pasty  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (AKP 15, 66.0 obj.% pevné fáze plastifikované organickou směsí na bázi vosků a parafinů, s teplotním intervalem měknutí mezi 60 a 70 °C) a zvláštní důraz je kladen na ověření všech předpokladů, které jsou obsaženy implicitně v proceduře vyhodnocení, speciálně v korekci rychlosti deformace na základě rovnice Mooneye-Rabinowitsche. Pokud možné, je uváděn odhad přesnosti měření a statistických chyb. Výpočet materiálových parametrů při aplikaci Herschel-Bulkleyova modelu ukazuje, že proměřená pasta - ačkoliv vysoce koncentrovaná - vykazuje v celém oboru teplot index toku  $n$  menší než 1, tj. pokles zdánlivé viskozity s rostoucí rychlostí deformace, což je jeden z důležitých předpokladů např. pro možnost tvarování past injekčním vstřikováním. Dále je vidět že mez toku  $\tau_0$  při poklesu teploty výrazně roste (od 0.6 při  $T = 69$  °C do 8.1 kPa při  $T = 69$  °C). Tento fakt má zásadní význam pro rychlostní profil toku během tvarovacího procesu a tím významně ovlivňuje i mikrostrukturu vytvářených těles, jak bude ukázáno v další publikaci na tuto navazující.