

RHEOLOGY OF CERAMIC INJECTION-MOLDING FEEDSTOCKS

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The flow behavior of ceramic alumina pastes with high solid loading designed for injection molding was studied in the relevant temperature range. In order to enable an adequate and experimentally sound rheological characterization the measurements were carried out with a laboratory capillary viscometer which had been specially adapted for measurements under conditions that could to a sufficient degree of accuracy be considered as isothermal. Detailed results including experimentally measured flow curves are shown for an alumina paste containing 66 vol.% (88.9 wt.%) of a commercial α - Al_2O_3 powder and 34 vol.% (11.1 wt.%) of a newly developed prototype binder mixture. The material parameters yield stress, consistency coefficient and flow index as well as apparent viscosities are compared for different temperatures (from 65 to 80 °C) and solid loadings (61, 63.4 and 66 vol.%). Motivated by the experimental results, the role of rheology for ceramic injection molding is discussed in general.

INTRODUCTION

Rheology is an important factor for the controlled performance of the forming step in ceramic injection molding. From a practical point of view rheology enables process control and allows calculations or estimates of the pressures needed for successful mold cavity filling, furthermore it serves for a general characterization of the respective materials used and is one of the main criteria for the selection of new perspective binder compositions. Apart from that, with regard to the expanding range of applications and the increasing demands concerning the properties of ceramic parts, an efficient microstructure control is of ever growing importance in all ceramic forming processes, including injection molding. There is no doubt that - beside powder preparation, mixing and compounding of the paste - forming is a critical step for microstructure formation during injection molding. It can even be expected that some features, e. g. orientation textures with anisometric particles, are almost exclusively due to the forming step. Defects originating from the forming (molding) step will persist in the final product, because usually there is no possibility to correct them in subsequent process steps. Debinding¹ and firing, when carefully performed, conserve most microstructural features of the as-molded green state while minimizing porosity, but they can never be expected to correct microstructural defects originating from earlier process stages.

From all these viewpoints it would seem desirable - apart from using the general rheological characterization of a material (based e. g. on the comparison of apparent viscosities) for direct process control - to predict to a certain degree the microstructure of a formed ceramic body on the basis of reliable calculations of the velocity

profile which the paste undergoes during flow, i.e. during mold cavity filling. Preliminary results concerning this problem have been presented earlier [3, 4] and a complete account will be given in a forthcoming paper [5].

It is clear that, when such a complex application is possibly intended, it cannot be sufficient to characterize the rheology of a ceramic paste by a single (conventional) parameter, such as the apparent viscosity (at a certain shear rate), the "melt flow index" or the so-called "spiral flow length", which are extensively used as empirical criteria for binder selection [1, 6, 7, 18].

Instead, a complete flow curve has to be measured in the temperature and shear rate range of interest and, if possible, its course has to be fitted by an appropriate analytical expression, e. g. the Herschel-Bulkley model proposed in [8, 9, 10]. According to literature references [11, 12, 13, 14] and practical experiences with traditional ceramic mixes [15] a piston-driven capillary viscometer appears to be a suitable device for the measurement of flow curves (i. e. the dependence of the shear stress on the shear rate) of pastes with a high apparent viscosity (of order, say, $10 \cdot 10^4$ Pa s at 100 s^{-1}). Although non-isothermal flow is common to injection molding, a

¹ It is well known that debinding, i.e. binder removal and the transformation of the as-molded green part to a binder-free powder compact of corresponding shape, is the most critical and size-limiting process step in ceramic injection molding practice [1, 2], because defects (e.g. cracks, flaws and internal stresses due microstructural nonuniformities) can develop, which may eventually destroy the ceramic part during further processing or under mechanical loading in the final applications.

reasonable rheological characterization of thermoplastic injection molding pastes requires a well-defined temperature for each flow curve and therefore an experimental arrangement to ensure to a sufficient degree isothermal flow conditions. In a recent paper [9] a heatable capillary viscometer has been described, which is capable of performing such nearly isothermal measurements of highly viscous pastes at arbitrarily chosen temperatures. In this paper, we present detailed results for selected thermoplastic alumina pastes at different temperatures. A systematic comparison is made for three pastes with different solid phase contents.

EXPERIMENTAL PART

The material: Thermoplastic alumina pastes

The ceramic injection-molding feedstocks used for this study are alumina pastes plasticized by an organic (paraffine-wax based) binder mix of prototype composition with a softening range between approx. 60 and 70 °C. The starting powder is a commercial high-purity (99.99 wt.%), agglomerate-free submicron α - Al_2O_3 powder prepared by hydrolysis of alumina isopropanolate (AKP 15 by Sumitomo Chemical Co. Ltd.; particle size 0.6-0.8 μm , specific surface 3 $\text{m}^2 \text{g}^{-1}$, particle aspect nearly isometric, particle shape nearly ellipsoidal-spherical, well rounded, see figure 1). The particle size distribution measured in aqueous suspension by low angle laser light scattering (LALLS) on the Fritsch Particle Sizer "Analysette 22" (and evaluated by Fraunhofer theory) is shown on figure 2. Mixing and

compounding of all mixes was performed according to a standard schedule (described in [9]) at temperatures of about 90-100 °C. In order to achieve appropriate homogenization, the last stage of the mixing process consisted in extruding the hot paste twice through the die land of the capillary viscometer before performing rheological measurements. The minimum binder content for which a homogeneous extrudable mix could be successfully prepared in this way, was 11.1 wt.% (34 vol.%), so that a paste resulted with the extremely high solid loading of 66 vol.% and a bulk density of approx. 2.7 g cm^{-3} . Further pastes with solid loading of 63.4 vol.% and 61 vol.%, respectively, were prepared for reasons of comparison.

The method: Capillary viscometer measurements

A piston-driven capillary viscometer originally constructed for the measurement of conventional ceramic extrusion mixes at ambient temperature [15] has been adapted for measurements at elevated temperatures by adding external heating equipment coating the material chamber and the capillary. Details of the construction have been published elsewhere [9]. In order to guarantee fast and thorough heating of the bulk material, the whole viscometer is preheated before measurement up to a constant temperature (e.g. 83 °C) in a laboratory drier. Temperature measurements are performed by two Cu-Konstantan-Cu thermocouples, one at the capillary entry, the other at the exit. A steady flow situation was considered as isothermal from the practical point of view in those cases where the temperature gradients along the

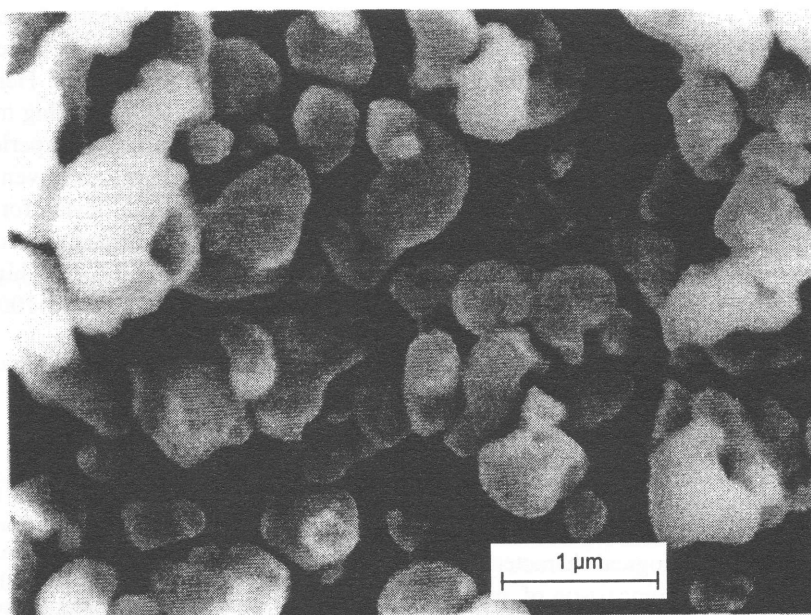


Figure 1. Alumina powder AKP 15 (Sumitomo), SEM micrograph.

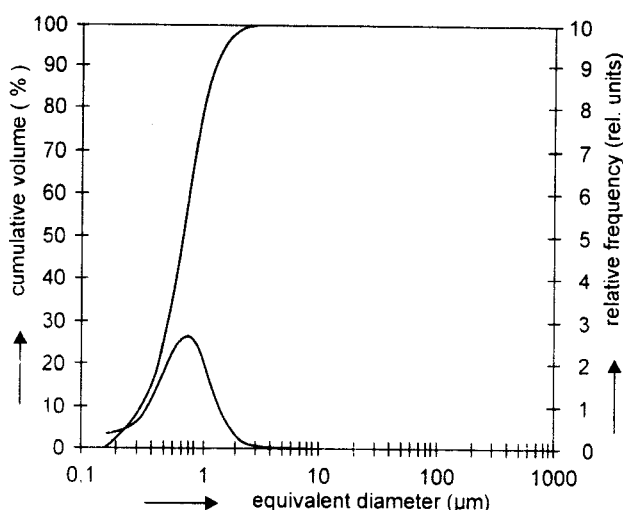


Figure 2. Particle size distribution of the alumina powder AKP 15 (Sumitomo) measured by LALLS (Fritsch Analysette 22, evaluation by Fraunhofer theory): a narrow-range monomodal size distribution with a median size of $0.71 \pm 0.02 \mu\text{m}$.

capillary (the die land) were not larger than the assumed precision of the thermocouples, i.e. about 1°C . The capillary viscometer is positioned in a universal testing machine with a force display, and the measurement principle consists in the registration of the force (pressure) necessary to sustain steady flow in the capillary when the piston of the material chamber is driven down with constant (preselected) velocity. This is done for two capillaries of different length (die land length 80 and 50 mm) and equal diameter (4 mm for the measurement of the flow curves) and the force differences (pressure differences) are then related to the difference length (hypothetical die land length or "effective capillary length" $80 \text{ mm} - 50 \text{ mm} = 30 \text{ mm}$). Using this difference procedure and verifying that the velocity profile is fully developed within a length which is small compared to the length of the shorter capillary (i.e. verifying that the entry length is well below 50 mm), measurements can be made without necessity of applying an additional Bagley-correction for entry and exit effects, as e.g. in [12]. For routine measurements, which should not be too time- and material-consuming, it turned out to be feasible to measure a whole temperature range with one viscometer filling, when the temperature is decreasing after the force has reached its steady state [9].¹

The evaluation procedure revisited

The evaluation procedure for both measuring modes (CT- and DT-mode) is described in the aforementioned paper [9] in great detail, and only a short summary is given here: Once the forces necessary to drive the piston

with constant velocity are measured in the desired temperature range, the force acting on the piston of the viscometer can be transformed into the pressure necessary to overcome the friction of the whole system (piston and material chamber wall, internal friction of the paste in the shear flow region near the capillary wall, entry and exit effects). This is done for each temperature in question. Taking the difference of the forces corresponding to the same temperature but measured for two capillaries of different length (80 and 50 mm) we obtain a pressure difference Δp that refers solely to the internal friction of the paste in the shear flow region near the capillary wall for an effective capillary length $\Delta L = 80 \text{ mm} - 50 \text{ mm} = 30 \text{ mm}$.² The wall shear stress τ_w is then calculated by the equation

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

where D is the capillary diameter. The preselected mean velocity is easily transformed into an apparent or mean shear rate γ_a according to the equation

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

where $\bar{v}$ is the mean velocity in flow direction. The graph τ_w vs. γ_a (called "apparent flow curve" in [9]) gives preliminary information about the flow behavior of the material. In order to obtain the flow curve proper it is necessary to relate the shear stress at the wall to the true shear rate at the wall γ_w . The necessary correction is made by the Mooney-Rabinowitsch equation:

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

where n' can be called "apparent flow index" [9]. While standard for pseudoplastic liquids, the Mooney-Rabinowitsch correction is useful also for materials exhibiting

¹ The corresponding measuring modes have been called "constant-temperature mode" (CT-mode) and "decreasing-temperature mode" (DT-mode), respectively, in [9].

² This holds provided there is no additional slip of the paste as a whole at the capillary wall. This highly non-trivial problem has been the subject of many studies (for references see [8,10]), and it is evident that generalizations for wider classes of materials cannot be made. Experimental evidence, whether wall-slip is present or not in a certain situation, can be obtained by repeating measurements with capillaries of identical length but different diameters. In the case of wall-slip being absent the measured flow curves must coincide [15,16]. In our case wall-slip could be successfully avoided by using capillaries with an internal thread [9].

yield stress, e.g. for Herschel-Bulkley fluids with a constitutive equation of the form:

$$\tau = \tau_0 + K\dot{\gamma}^n \quad (4)$$

where $\tau \equiv \tau_{rz}(r)$ is the shear stress, $\dot{\gamma} \equiv \left(\frac{dv_z(r)}{dr}\right)$ the shear rate (or in cylindrical coordinates the radial gradient of the axial velocity component), K the coefficient of consistency and n the flow index. In this case, it is advantageous to determine the "apparent flow index" n' directly from the $\tau_w - \dot{\gamma}_a$ plot by non-linear regression [9].

The Mooney-Rabinowitsch equation has been deduced for general incompressible time-independent fluids under the assumption of fully developed, steady laminary flow with the boundary condition of no wall slip. All these assumptions have been discussed in [9]. The generalized Reynolds numbers reported in [9] for alumina pastes with 66 vol.% solids content (generalized Reynolds numbers between $0.9 \cdot 10^{-3}$ and $2.6 \cdot 10^{-3}$) show clear laminarity and guarantee a fully developed velocity profile in the viscometric region. For the more dilute pastes (61 and 63.4 vol.%) the values are slightly higher (Reynolds number between $2.1 \cdot 10^{-3}$ and $7.2 \cdot 10^{-3}$ for the highest mean velocity used, i.e. 35.6 mm s^{-1} in a 4-mm-diameter capillary, see table 2 below), but nevertheless still many orders of magnitude below the critical value for turbulent flow.

Table 1. Measuring table for paste Alumina-1-a presenting forces, pressures, pressure differences and wall shear stresses for a selected mean velocity (26.6 mm s^{-1}) in a 4-mm-diameter capillary (corresponding to a mean shear rate of 53.2 s^{-1})

T (°C)	F_1 (N)	F_2 (N)	p_1 (kPa)	p_2 (kPa)	Δp (kPa)	τ_w (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

Table 2. Generalized Reynolds numbers for all three pastes at minimum and maximum velocity and temperature.

	T (°C)	$\nu_{\min} = 1.3 \text{ mm s}^{-1}$	$\nu_{\max} = 35.6 \text{ mm s}^{-1}$
Alumina-1-a	69	$1.9 \cdot 10^{-5}$	$0.9 \cdot 10^{-3}$
	80	$2.9 \cdot 10^{-5}$	$2.6 \cdot 10^{-3}$
Alumina-1-b	65	$3.7 \cdot 10^{-5}$	$2.1 \cdot 10^{-3}$
	80	$5.8 \cdot 10^{-5}$	$5.8 \cdot 10^{-3}$
Alumina-1-c	65	$6.1 \cdot 10^{-5}$	$4.7 \cdot 10^{-3}$
	80	$10.1 \cdot 10^{-5}$	$7.2 \cdot 10^{-3}$

RESULTS AND DISCUSSION

Flow curves and rheological data

Table 1 shows for one selected mean velocity¹ and five temperatures ranging from 69 to 80 °C measured values of forces acting on the piston, from which forces per unit area, i.e. pressures, and the pressure differences Δp corresponding to the effective capillary length of $\Delta L = 30 \text{ mm}$ were calculated.² The example shown refers to the alumina paste Alumina-1-a with a solid loading of 66 vol.%. Similar measurement tables have been set up for all other mean velocities and the same has been done for the remaining two pastes Alumina-1-b and Alumina-1-c in the temperature range from 65 to 80 °C (solid loadings 63.4 and 61 vol.%, respectively). Since the evaluation procedure is totally identical for all three pastes we confine the following detailed step-by-step presentation of results to the paste with the highest powder content, and for the two other pastes we only add the final results.

After calculation of the wall shear stress and the mean shear rate according to equations (1) and (2) a non-linear regression analysis of the graphical representation of τ_w vs. $\dot{\gamma}_a$ (cf. the apparent flow curves in figures 3 and 4) is used to extract in a first step the parameters K' and n' necessary to perform the Mooney-Rabinowitsch (MR) correction (equation (3)) and to calculate the generalized Reynolds numbers. The values of K' and n' obtained from the apparent flow curve of the paste Alumina-1-a at 78 °C e.g. are $0.76 \text{ kPa s}^{0.68}$ and 0.68, respectively. Values of the generalized Reynolds number (calculated using K' and n' as obtained from the apparent flow curves) are shown in table 2 for the minimum and maximum mean velocity used and the minimum and maximum temperature measured. It is evident that for all three pastes the generalized Reynolds number is between 6 and 8 orders of magnitude (!) lower than its critical value for tube flow (2100). Any deviation from laminary flow can therefore be excluded with certainty. Moreover, even in the most critical case (lowest solid phase content, highest temperature, highest mean velocity) the second term in the entry length equation (equation (9) of our previous paper [9]) affects only a correction of approximately 00004 D to the value of the entry length and is therefore

¹ The mean velocity selected for this example is 26.6 mm s^{-1} , which in the 4-mm-diameter capillary used corresponds to a mean shear rate of $\dot{\gamma}_a = 53.2 \text{ s}^{-1}$.

² Subscripts indicate the length of the capillary used, F_1 , p_1 and F_2 , p_2 referring to the 80 mm and the 50 mm capillary, respectively.

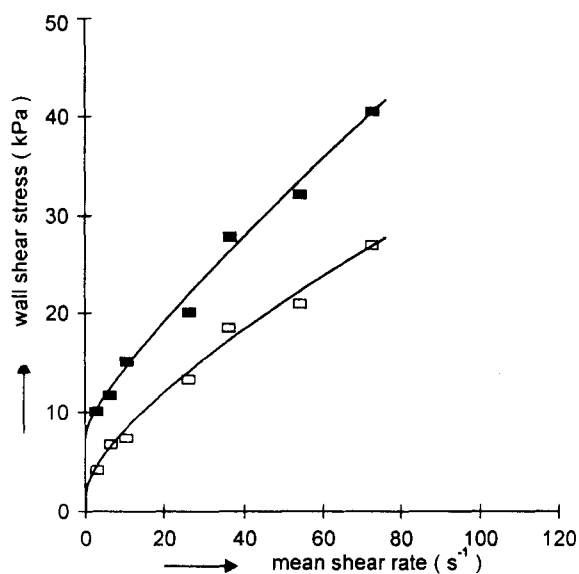


Figure 3. Apparent flow curves for the paste Alumina-1-a (66 vol.% solids content).

■ - 69 °C, □ - 72 °C

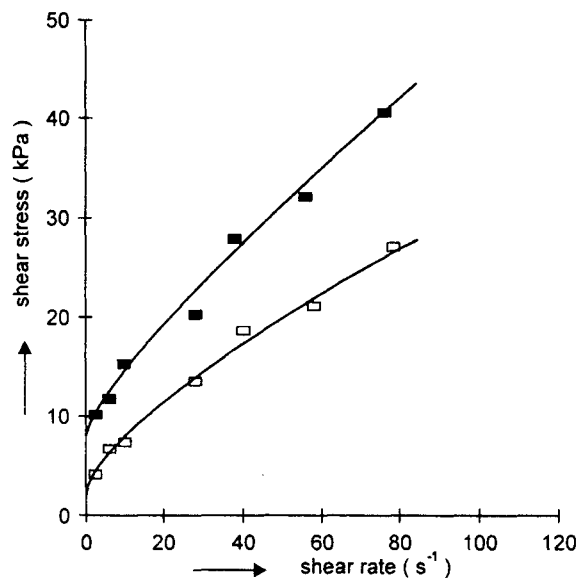


Figure 5. Flow curves (MR-corrected) for the paste Alumina-1-a (66 vol.% solids content).

■ - 69 °C, □ - 72 °C

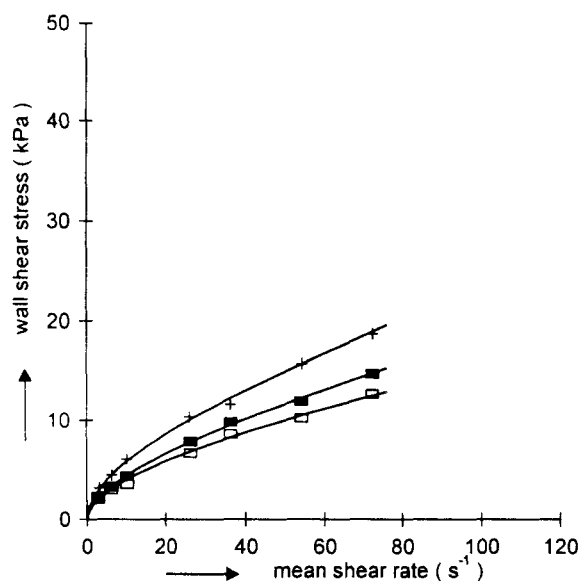


Figure 4. Apparent flow curves for the paste Alumina-1-a (66 vol.% solids content).

+ - 75 °C, ■ - 78 °C, □ - 80 °C

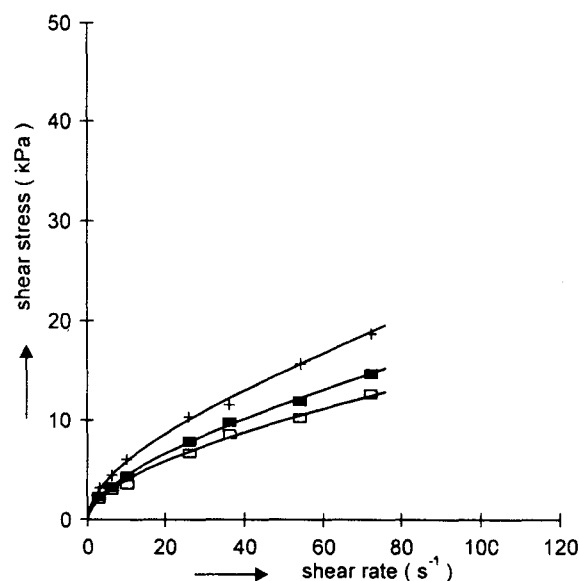


Figure 6. Flow curves (MR-corrected) for the paste Alumina-1-a (66 vol.% solids content).

+ - 75 °C, ■ - 78 °C, □ - 80 °C

negligible in comparison with the first term. Consequently the velocity profile in all measurements can be assumed fully developed after an entry length of $L_e \approx 0.59 \cdot D = 2.36$ mm, cf. [9]. As the length of the shortest capillary is 50 mm, measurements referring to the capillary difference length of 30 mm (downstream off the entry region) are unaffected by entry effects. The values n' are further used to perform the Mooney-

-Rabinowitsch (MR) correction according to equation (3), transforming mean shear rates $\dot{\gamma}_a$ into (true) wall shear rates $\dot{\gamma}_w$. For n' values ranging from 0.65 to 0.81 e.g. the MR correction changes the shear rate values for about 6 to 13 %. Using the MR-corrected shear rates we obtain the flow curves which are presented on figures 5 and 6 for the paste Alumina-1-a. Fitting these flow curves according to equation (4) we are able to determine all

three parameters¹ relevant for the rheological characterization of the paste. Tables 3 through 5 present the values of yield stress, coefficient of consistency and flow index for all three pastes in the temperature range measured and figures 7 to 9 show their temperature dependence. Two main conclusions can be drawn from these results:

- The paste with the highest powder content (Alumina-1-a) shows rather high yield stress values at all temperatures of interest, while for the others (Alumina-1-b and Alumina-1-c) the yield stresses are significantly lower. There seems to be a considerable increase in yield stress and consistency coefficient as soon as a certain concentration limit is exceeded.
- All three parameters show a temperature dependence. In all cases the trend is towards higher values of yield stress, coefficient of consistency and flow index with decreasing temperature. Extremely high is the temperature dependence of the yield stress for the paste with the highest powder content (Alumina-1-a).

Table 3. Material parameters of the paste Alumina-1-a (66 vol.% solids content)

T (°C)	τ_0 (kPa)	K (kPas ^{<i>n</i>})	n
69	8.1	0.98	0.81
72	2.5	1.00	0.73
75	1.1	0.90	0.68
78	0.8	0.69	0.68
80	0.6	0.68	0.65

Table 4. Material parameters of the paste Alumina-1-b (63.4 vol.% solids content).

T (°C)	τ_0 (kPa)	K (kPas ^{<i>n</i>})	n
65	1.3	0.48	0.78
69	0.9	0.33	0.74
72	0.6	0.37	0.68
75	0.4	0.36	0.65
78	0.2	0.35	0.64
80	0.2	0.34	0.61

Table 5. Material parameters of the paste Alumina-1-c (61 vol.% solids content)

T (°C)	τ_0 (kPa)	K (kPas ^{<i>n</i>})	n
65	0.5	0.30	0.69
69	0.3	0.24	0.64
72	0.3	0.23	0.60
75	0.2	0.24	0.55
78	0.1	0.25	0.52
80	0.1	0.20	0.52

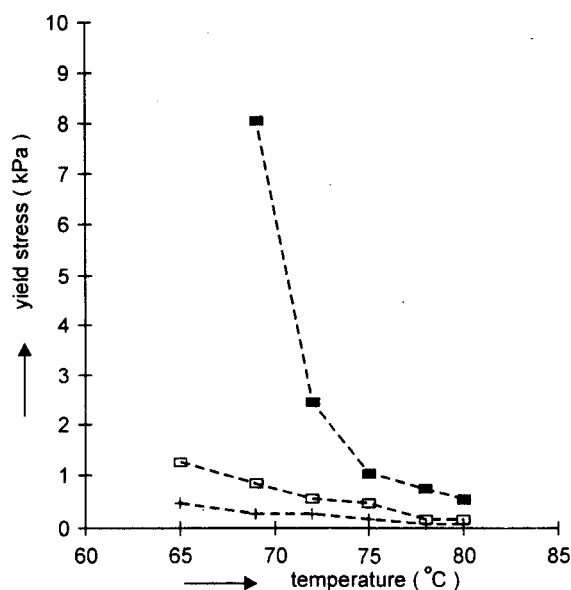


Figure 7. Temperature dependence of the yield stress for all three pastes.

■ - Alumina-1-a, □ - Alumina-1-b, + - Alumina-1-c

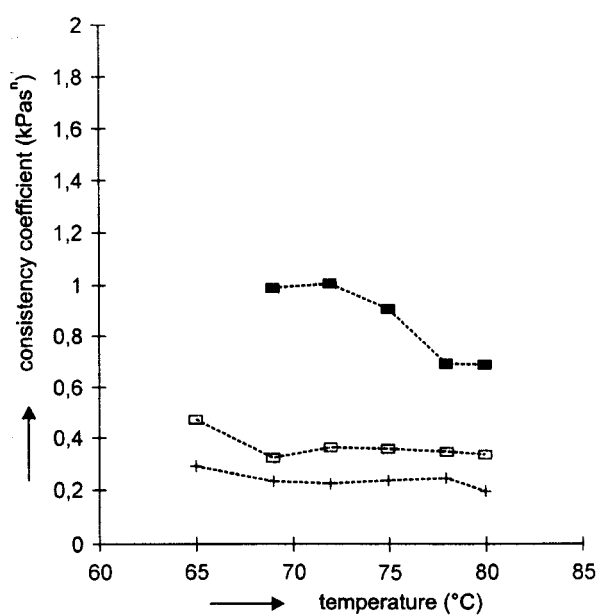


Figure 8. Temperature dependence of the consistency coefficient for all three pastes.

■ - Alumina-1-a, □ - Alumina-1-b, + - Alumina-1-c

¹ The yield stress values determined in the non-linear regression fit of the apparent flow curve remain unchanged. This is reasonable because - irrespective of the prefactor in equation (3) - the MR correction is infinitely small for shear rates approaching zero.

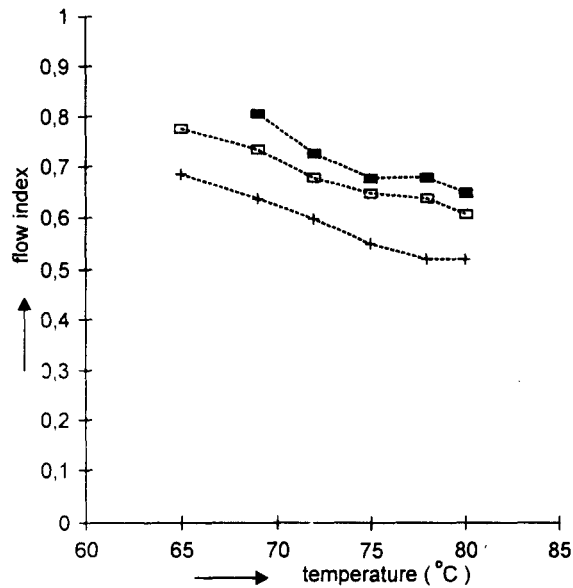


Figure 9. Temperature dependence of the flow index for all three pastes.

■ - Alumina-1-a, □ - Alumina-1-b, + - Alumina-1-c

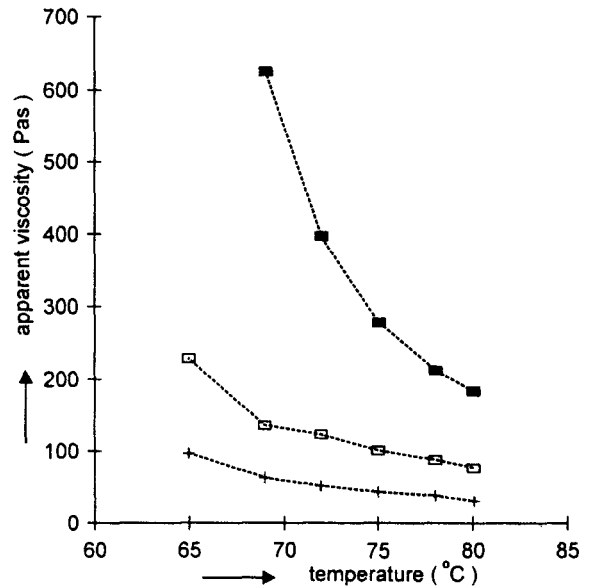


Figure 10. Temperature dependence of the apparent viscosity at a shear rate of 50 s^{-1} for all three pastes.

■ - Alumina-1-a, □ - Alumina-1-b, + - Alumina-1-c

Table 6. Apparent viscosities of the paste Alumina-1-a (66 vol.% solids content)

T (°C)	η_{50} (Pas)	η_{100} (Pas)
69	628	490
72	398	313
75	279	217
78	213	166
80	185	142

Table 7. Apparent viscosities of the paste Alumina-1-b (63.4 vol.% solids content)

T (°C)	η_{50} (Pas)	η_{100} (Pas)
65	229	187
69	137	109
72	126	98
75	102	77
78	90	69
80	78	58

Table 8. Apparent viscosities of the paste Alumina-1-c (61 vol.% solids content)

T (°C)	η_{50} (Pas)	η_{100} (Pas)
65	99	77
69	65	49
72	54	39
75	45	32
78	40	28
80	33	23

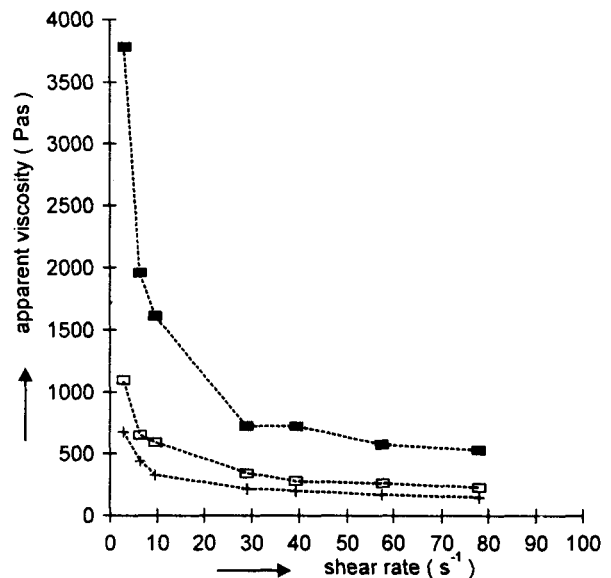


Figure 11. Dependence of the apparent viscosity on the shear rate for the paste Alumina-1-a.

■ - 69 °C, □ - 75 °C, + - 80 °C

Apart from the three-parameter description of the rheological behavior of the pastes given above it is of course possible to extract other types of useful information from the measured flow curves. For an orientational characterization of the material behavior during processing e.g. the knowledge of apparent viscosities might be a helpful guideline in some cases of practical interest. Tables 6 through 8 show apparent

viscosity values (interpolated for a shear rate of 50 s^{-1} and extrapolated for a shear rate of 100 s^{-1} , respectively) for the three pastes in the respective temperature ranges. An example illustrating the temperature dependence of the apparent viscosity for the paste Alumina-1-a is given on figure 10. This curve could be fitted by one of the many empirical relationships, e.g. of the Arrhenius or Vogel-Fulcher-Tamann type, but we will not do this here. Apparent viscosity values plotted against shear stress (see figure 11 for the paste Alumina-1-a at $T = 69, 75$ and $80 \text{ }^{\circ}\text{C}$) clearly show that asymptotically the apparent viscosity approaches infinity as the shear stress approaches its yield value.

Rheological characterization of injection-molding feedstocks

According to the well-known paper of Mutsuddy [17] pastes with apparent viscosities of less than 1000 Pas within the shear rate range 100 to 1000 s^{-1} can be regarded as usable formulations for ceramic injection molding, cf. also [18, 21]. Edirisinghe and coworkers emphasize the special importance of the low shear rate (apparent) viscosity as a criterion for material selection [19, 20]. Since the apparent viscosities of our pastes with the highest solids content (Alumina-1-a with 66 vol.% alumina powder) are between 142 and 490 Pas (depending on temperature) for a shear rate of 100 s^{-1} (and presumably even lower for higher shear rates) all pastes examined here can be considered as suitable injection-molding feedstocks from this point of view.

For micronsize silicon powders (particle size around $1 \text{ }\mu\text{m}$, specific surface area $5.7 \text{ m}^2 \text{ g}^{-1}$) compounded to pastes with a solids content of approx. 65 vol.% by polypropylene or polypropylene-wax based binders (containing stearic acid as a processing aid) Edirisinghe and Evans [18] report for their injection-molding feedstocks at temperatures of 195 and $225 \text{ }^{\circ}\text{C}$ apparent viscosities between 547 and 1576 Pas for a shear rate of 108 s^{-1} (depending on binder composition and temperature), which decrease down to the range 102 to 353 Pas at a shear rate of 1075 s^{-1} . For another (wax-based) formulation used with the same powder system they report an apparent viscosity of 126 Pas at a shear rate of 108 s^{-1} and a temperature of $90 \text{ }^{\circ}\text{C}$. For micronsize alumina powders compounded to pastes with a solids content of approx. 54.8 vol.% by polypropylene-stearic acid based binders Edirisinghe [20] reports apparent viscosity values of about 100-700 Pas, which decrease down to 45-150 Pas at a shear rate of 1075 s^{-1} (temperature $200 \text{ }^{\circ}\text{C}$). In all these cases, apart from the basically different binder composition, the higher apparent viscosities are obviously due to the high polydispersity of the powders used and the strongly irregular particle shape.

In our case the commercial powder used (AKP 15 produced by Sumitomo Chemical Co. Ltd.) is an advanced submicron powder, which - due to its narrow particle size distribution and its nearly ellipsoidal-spherical particle shape - allows the preparation of extrudable injection-molding feedstocks with comparably high solid loadings. It is clear, however, that a solid phase content of 66 vol.% is an upper limit which certainly cannot be significantly exceeded for these powders, since the packing density of a random-close packed (rcp) powder system¹ is 63.7 vol.% in the case of monodisperse spherical particles, cf. e.g. [22]. We attribute the excess solid loading above the rcp limit to the small degree of polydispersity and the deviations from the spherical particle shape and presume that the preparation of two-phase (i.e. gas-free) mixtures with higher solid loadings in our system would not be possible even with an optimized mixing and compounding procedure. According to an older paper [23], in ceramic injection molding 50-70 vol.% solid phase content is desired. More recent experience has shown, however, that for the powders routinely used the upper limit of 70 vol.% usually does not lead to moldable mixes. Edirisinghe and Evans [21] - although successful in the preparation of a 69 vol.% and a 74 vol.% paste of (highly polydisperse) silicon powder (with irregularly shaped particles) plasticized by a polypropylene-wax blend (with stearic acid as a processing aid) - report that the extrusion characteristics of those highly loaded pastes were not acceptable. Their highest acceptable powder loading [18, 21, 24] comes with 65 vol.% very close to the solid phase content achieved in the alumina paste with the highest solids loading studied in the present paper. Nogueira, Edirisinghe and Gawne [25] prefer slightly lower solid loadings (60-63 vol.%) for a micronsize alumina powder (A152.SG from Alcoa Industrial Chemicals, particle size around $1 \text{ }\mu\text{m}$, specific surface area $9.2 \text{ m}^2 \text{ g}^{-1}$).

Two characteristic features concerning the rheology of all these highly loaded pastes are intimately connected with the high solid phase content: the occurrence of a yield stress and the nonlinear flow curve (which cannot be described by the traditional Bingham model). For cases where the yield stress is low, it has been suggested to neglect it totally in the rheological characterization of the paste, and at the same time it has been fully recognized that measurement above approximately 100 s^{-1} cannot be used to deduce the yield stress [18]. On the other hand it is well known that the yield stress is quite

¹ The packing density for the rcp structure lies between the packing density of the primitive cubic (54.2 vol.%) and the cubic or hexagonal close-packed (74.1 vol.%) arrangement.

an important parameter in injection-molding: a too excessive yield stress can cause coiling during injection into the mold cavity (causing air entrapment and mechanical stresses) and, vice versa, the absence of yield stress could lead to deformation during binder removal [17, 26]. Seemingly the first quantitative assessment of the yield stress in ceramic injection-molding pastes is due to Edirisinghe, Shaw and Tomkins [26]. They measured the flow curves of ceramic pastes containing 48, 54, 58, 60 and 64 vol.% of a submicron alumina powder plasticized by a polypropylene-wax binder (with stearic acid as a processing aid) at a temperature of ca. 220 °C and obtain yield stress values of 4, 8, 9, 11 and 24 kPa, respectively, when evaluated by the Casson model:

$$\sqrt{\tau} = \sqrt{\tau_0} + \sqrt{\mu_\infty} \sqrt{\dot{\gamma}} \quad (5)$$

For the pure binder blend without powder they determine a yield stress of 0.4 kPa at the same temperature. In a second evaluation step the authors conclude (in our opinion without too much justification) that the yield stresses are negligible in comparison with the shear stresses measured (which range from about 42 up to about 138 kPa in the case of the 64 vol.% paste, i.e. are of the same order of magnitude as the yield stress itself, viz. 24 kPa !) and use the pseudoplastic model

$$\tau = K\dot{\gamma}^n \quad (6)$$

to evaluate the flow index n , for which they obtain values ranging from 0.43 to 0.54 for the powder-filled pastes and 0.70 for the pure binder blend. In the same work pastes containing basically different binder formulations (alcohol-oil and alcohol-water compositions) were observed to fit a straight line and could accordingly be evaluated using the Bingham model

$$\tau = \tau_0 + \mu_{pl} \dot{\gamma} \quad (7)$$

but flow curves were evidently measured only for shear rates higher than 500 s⁻¹, so that a nonlinear flow curve range in the low shear rate region might have remained undetected (the yield stresses determined for those pastes are 28 and 63 kPa and the plastic viscosities 29 and 24 Pas, respectively) [26].

The reason for such a non-unique and theoretically unsatisfactory hybrid approach is clear: in order to circumvent the practical problems of a nonlinear regression procedure, which is necessary in the case of the three-parametric Herschel-Bulkley model used in the present work, other authors try to classify their pastes into one of the two-parametric constitutive models mentioned above, where the parameters can be easily and uniquely determined by linear regression. Such an approach, although its certain degree of pragmatic

usefulness is to be admitted, can lead to the impression that certain classes of pastes (classified e.g. according to the binder system used) could be satisfactorily described by one or the other two-parametric model. This is evidently not the case. The approach becomes totally insufficient when a temperature dependence is to be registered in the region just above the softening (stiffening) point (interval) of the paste, where the changes in rheology can be considerable.

Although nonlinear regression has to be employed for the evaluation of the material parameters in the present work, the approach used here gives a unified description of all (time-independent) flow curves observed for thermoplastic pastes with high solid loadings and contains the pseudoplastic model (nonlinear flow curve without yield stress) and the Bingham model (linear flow curve with yield stress) as special cases. The three-parametric Herschel-Bulkley model chosen is the simplest model possible which is able to account for all experimentally observed physical facts (nonlinear flow curve with yield stress) and at the same time to reduce to the well-known two-parametric models. Furthermore it is possible to obtain an analytical solution for the velocity profile in unidirectional tube flow [5], which can be shown to reduce to the well-known special cases (power-law parabola and Buckingham-Reiner profile with central plug flow). It has to be emphasized that the Casson model (which is also able to describe nonlinearity and yield stress) has the disadvantage that it does not reduce to neither of these special cases.

The measurements in this work were carried out in the low shear rate region (below 100 s⁻¹) in order to obtain realistic yield stress values. It has been established that for the pastes Alumina-1-b and Alumina-1-c (63.4 and 61.0 vol.%, respectively) the yield stress in the temperature range between 80 and 65 °C is relatively low (0.1 to 1.3 kPa), while for the paste Alumina-1-a (66.0 vol.%) significantly higher yield stresses are determined (0.6 to 8.1 kPa for temperatures from 80 down to 69 °C). In all cases the yield stress increases with decreasing temperature and it is evident that the temperature dependence is especially strong for the paste with the highest solid loading (approximately one order of magnitude for a temperature interval of 10 °C above the stiffening/softening region). The order of magnitude of the yield stresses correlates well with the above mentioned values determined by Edirisinghe, Shaw and Tomkins [26] with the Casson model. For all pastes studied in the present work the flow index is between 0.52 and 0.81, i.e. smaller than unity, and therefore all these pastes show shear-thinning behavior (i.e. a decrease of the differential viscosity with growing shear rate) without dilatancy in the range of shear rates measured. This is of course a basic requirement that injection-molding feedstocks should meet, cf. [17, 18].

CONCLUSIONS

It is one of the main goals of modern ceramics research to replace empirical knowledge (gained by trial-and-error methods) by rational approaches and theoretical predictions on a physically sound basis. A great challenge for ceramics engineering is the fabrication of ceramic parts with tailor-made properties, which can only be achieved by an efficient control of microstructure. As far as ceramic injection molding is concerned, it is well known, that the velocity profile during the molding step is the decisive factor for the formation of the green microstructure, but, up to now, no rational method has been applied in this field to make quantitative calculations of the velocity profile by using the rheological properties of the paste as an input information. This task will be attacked in a subsequent paper [5]. With regard to this future application, a unified description of the rheological behavior of ceramic pastes has been chosen here, based on the Herschel-Bulkley model (constitutive equation), which includes the frequently used "power law" (Ostwald-De Waele model) and the classical Bingham model as special cases. In contrast to the not very satisfying approach chosen by many other authors, which consists in neglecting sometimes yield stress, sometimes the nonlinearity of the flow curve for their special material considered, or in choosing a hybrid two-step fitting procedure, where in a first step the material is considered to be a Casson type material (to extract a yield stress value) and in a second step the same material is considered to be a power law fluid (to extract a flow index), our description is "unified" in the sense that only one fitting equation (the Herschel-Bulkley model) must be applied to cover the material behavior for all cases, i.e. in a wide range of temperatures and solid loadings. This ensures a direct comparison between the material parameters of different pastes and is a necessary precondition e.g. when it is intended to build up a reasonable data base for ceramic pastes. The reason for using a constitutive equation to fit an experimentally measured flow curve is clear: Instead of using rather arbitrary empirical measures of "fluidity" or "moldability", for which the flow situation is too complicated to be exactly defined in physical terms (spiral flow length, melt flow index) or for which just one value is chosen by convention (e.g. the apparent viscosity at 100 s^{-1}), the whole flow curve can be characterized for a wide class of nonlinear materials by a few material parameters (yield stress, consistency coefficient, flow index), which are (for viscometric flows) not less fundamental than the material parameter "viscosity" in the linear case, i.e. for Newtonian fluids. The main advantage of such an approach can of course be fully estimated only when this quantitative rheological characterization of ceramic pastes (i.e. the knowledge of

numerical values of the coefficients occurring in their constitutive equation) is exploited further for the solution of differential equations describing the forming process under appropriate boundary (evtl. also initial) conditions. This will be done in the subsequent paper mentioned [5]. Since it can be reasonably expected that the velocity profile (i.e. the solution of the corresponding boundary value problem) is responsible for the formation of the green microstructure, rheology need not remain a mere tool for the estimation of workability of ceramic pastes and the conditions of injection molding, but can play a main part in the understanding of microstructure formation in ceramic bodies and future developments will probably show that rheology is the key to quantitative microstructure control.

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REOLOGIE KERAMICKÝCH SMĚSÍ PRO INJEKČNÍ VSTŘIKOVÁNÍ

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Tokové chování keramických past oxidu hlinitého s vysokým obsahem pevné fáze je studováno v rozsahu teplot, který je relevantní pro injekční vstřikování těchto past. Měření byla prováděna pomocí kapilárního viskozimetru, který byl pro tento účel konstruován a který umožnil měření při podmínkách blízkých se izotermnímu stavu. Detailní výsledky jsou uvedeny pro pastu oxidu hlinitého s obsahem 66 obj.% (88.9 hm.%) komerčně vyráběného prášku oxidu hlinitého a 34 obj.% (11.1 hm.%) nově vyvinutého organického plastifikátoru. Pro tuto pastu jsou uvedeny experimentálně měřené (a pomocí Mooney-Rabinowitschovy rovnice korigované) tokové křivky. Materiálové parametry jsou porovnány pro různé teploty (od 65 do 80 °C) a pro různé obsahy pevné fáze (61, 63.4 a 66 obj.%). Výhody zvolené tříparametrové konstitutivní rovnice (Herschel-Bulkleyova modelu) k úplné reologické charakterizaci past jsou v práci podrobně diskutovány a její volba je zdůvodněna z principiálních hledisek. Pro pasty této práce bylo zjištěno, že všechny tři parametry Herschel-Bulkleyova modelu (tj. mez toku, koeficient konzistence a index toku) závisí na teplotě, a to tak, že jejich hodnoty stoupají s klesající teplotou. Zvlášť výrazná je teplotní závislost meze toku pro nejkonzentrovanejší pastu s obsahem 66 obj.% pevné fáze, kde mez toku roste od 0.6 kPa při 80 °C na 8.1 kPa při 69 °C. Index toku je vždy menší než 1, což svědčí o poklesu diferenciální viskozity s rostoucí rychlostí deformace jako u tzv. pseudoplastických kapalin. Je to jedna z požadovaných vlastností směsí pro úspěšné injekční vstřikování. Získané výsledky jsou v rámci možností porovnány s údaji v literatuře pro podobné systémy a na některých místech je námi zvolený metodologický přístup kriticky srovnán s pracemi jiných autorů. Je naznačeno, v jakém smyslu se reologie keramických past, která byla až donedávna často považována pouze za pomocný prostředek při výběru hmot, optimalizaci složení či k empirickému řízení procesů, může stát klíčem k řízení mikrostruktury výsledné keramiky.