Journal of the European Ceramic Society 21 (2001) 483–491

www.elsevier.com/locate/jeurceramsoc

Evaluation of slip in capillary extrusion of ceramic pastes

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Received 16 March 2000; received in revised form 11 July 2000; accepted 15 July 2000

Abstract

In this study, the capillary extrusion behaviour of an alumina paste material, made using submicron alumina powder, hydroxy ethyl cellulose (HEC), a polyelectrolyte dispersant, poly (methacrylate), and water is described. It confirms that the computed shear stress, obtained using estabilished analytical procedures, depends upon both the diameter and the length of the capillary tube. Additionally, for a given nominal shear rate, the shear stress so calculated is less for the smaller diameter capillaries than for the corresponding larger diameter capillaries. These trends are rationalised, along established lines, in terms of the preponderance of a material process slip at the wall of the capillary as opposed to cohesive or fully developed uniform flow. Moreover, for a given diameter of the capillary tubes the calculated shear stress is greater for the smaller length capillary tubes than the corresponding longer capillary tubes. It is concluded that these results are not amenable to meaningful analysis using classical capillary rheometery analytical procedures based upon the presumption of a fully developed flow. The extensive slip which inevitably occurs at the interface between the capillary and the extrudate negates the sensible application of these type of procedures. Instead, an attempt is made, using the same data, to interpret the slip characteristics of the paste-wall interface in terms of a quantity defined as the ''reference slip thickness'', which is seen to depend upon the extrudate velocity (or the apparent shear rate) but is independent of the dimensions of the capillary tube.

Keywords: Al_2O_3; Extrusion; Paste; Rheology; Suspension

1. Introduction

The term ''paste'' is not precisely defined and there are a many definitions in common use most of which focus upon the perceived mechanical response. For example, one of the definitions is 'any composition and mixture containing just enough moisture to render itself soft and plastic'. The rheological characteristics of a paste changes depending upon the composition and formulation. For example, a paste made from wheat flour and water will naturally have somewhat different rheological character to a ceramic paste made of a ceramic powder and other ingredients. Similarly, different ceramic pastes are likely to show different rheological (both bulk as well as interfacial) behaviour, depending upon the composition of the paste. A typical ceramic paste comprises of ceramic particles (of different size ranges), dispersing agents, binders, plasticisers and liquid(s) phases. The need to include these ingredients arises from the fact that ceramic powders cannot always be effectively extruded in their dry (powder form), as they offer a very high friction at the interface of the bulk material and the processing engine (e.g. the extruder). Also, the submicron powders usually form agglomerates of a non-homogeneous nature and do not produce a coherent dispersed mass which is suitable for useful processing. Therefore, a liquid, which functions as a continuous medium, is a necessary component and provides both a vehicle to homogenise the particles and also the medium to incorporate the necessary processing aids such as the binders and dispersants. In this way, a processable paste may be formed which is capable of providing a useful manufacturing base. In aqueous based alumina pastes, the addition of water alone is not sufficient to produce an extrudable paste. A paste produced which contains alumina powder and water alone will have two significant practical problems. Firstly, the particles will not be homogenised as van der Waals attractive forces will cause the aggregation of the particles,

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0955-2219/01/$ - see front matter
PII: S0955-2219(00)00213-2

Nomenclature

D	diameter of the barrel or ram
D_o	diameter of the capillary
L	length of the capillary
N	A characteristic number associated with end correction
P	extrusion pressure through capillary
P_o	extrusion pressure through orifice
Q	volumetric flow rate
Q_{obs}	observed volumetric flow rate
Q_{slip}	volumetric flow rate due to slip
Q_{true}	true volumetric flow rate
s	thickness of the slip layer
s_r	reference slip layer
V	reference slip layer
V_{slip}	extrudate velocity
V_{slip}	slip velocity
α	slip coefficient (Mooney's method)
β	modified slip coefficient (Jastrezebski's method)
$\dot{\gamma}_w = \dot{\gamma}_{ap}$	wall shear rate = apparent shear rate
$\dot{\gamma}_s$	shear rate in the slip layer
η_s	viscosity of the paste in the slip layer
τ_{ap}	apparent shear stress
τ_B	Bagley corrected shear stress
σ_d	deformation stress

and secondly, such a paste will normally "dewater" or phase-separate during many extrusion processes. This latter effect arises because the liquid phase (water) may migrate significantly more rapidly than the dispersed phase (powder) under the application of a pressure gradient. The result is that the paste becomes drier and as a consequence the extrusion pressure rises and eventually the paste becomes non-extrudable. In order to overcome the dewatering problem, the rheology of the liquid medium is modified by adding some "thickening" agents to the liquid medium. The thickening agent also functions as a binder in the finally formed ceramic body once the liquid phase has evaporated.

The flow of paste-like materials invariably involves interactions at the interface between the material and the processing engine walls. The material flow response is highly dependent upon the interfacial characteristics of the boundary; therefore, the nature of the boundary is very important in the paste processing operation. Alternatively, the experimental results cannot be interpreted, to a reasonable degree of accuracy, without some knowledge of the interfacial rheology. The interface boundary characteristics dictate the extent of the mechanical work transfer between the material (paste) and the walls of the processing equipment. During the paste flow process the interfacial resistance naturally induces inhomogenities within the flow. These inhomogenities in the flow produce complex stress and strain (or shear) rate fields within the bulk of the flowing paste material. Therefore, the reaction or processing forces involved during the deformation are also greatly influenced by these induced inhomogenities flow conditions. An accurate knowledge of the boundary conditions provides, in principal, a means to obtain a true estimation of the intrinsic bulk rheological response.

In summary, the processing of these soft material involves four features of significance: the deformation geometry, the prevailing operating condition, the bulk intrinsic rheology and the boundary conditions. The geometry and the operating conditions are usually predetermined on the basis of the starting material and the end use of the product. The bulk intrinsic rheology determines the formation process of the product in the die/mould as well as in the processing equipment. However, the boundary conditions are very critical in all these operations. For example, if the interfacial conditions are not appropriate and slip occurs at interface of the material and the equipment, the material may not homogenise and satisfactorily mix, and as a consequence the final properties of the product may not be acceptable. A key practical requirement has thus been to find means of characterising both the bulk and interface rheologies.

Capillary extrusion flow has been very often utilised for a wide variety of paste-like materials in an attempt to characterise their bulk intrinsic rheology as well as their wall interface boundary conditions. The analytical procedures for treating the experimental data are now well established[1] (see also Theory section), including the end correction effects by Bagley[2] and subsequent treatment of wall slip phenomena by Mooney[3]. However, there may be many practical difficulties and limitations when applying these procedures. A number of papers have described these difficulties. The main problem is a deviation from the expected (based upon the common analysis) linear interrelationship between the applied extrusion pressure and the length/diameter (L/D) ratios of the capillaries is often encountered (some of the possible origins of these deviations are given elsewhere[4,5]).

In this study the capillary extrusion behaviour of an aqueous based alumina paste prepared using submicron alumina particles, a dispersing agent and a binder is described and discussed in the context of the potential for sensible data interpretation.

2. A theory of capillary flow

The apparent or nominal values of the shear rate, $\dot{\gamma}_{ap}$, and the wall shear stress, τ_{ap}, during the extrusion of a sample material through a capillary, are given by Eqs. (1) and (2), respectively

$$\dot{\gamma}_{ap} = \frac{8V}{D} \quad (1)$$

$$\tau_{ap} = \frac{PD}{4L} \quad (2)$$

where V is the mean extrudate velocity, D is the diameter of the capillary of length L and P is the extrusion pressure.

In deriving Eq. 2, it was presumed that the flow of the material is fully developed throughout the capillary and that the pressure gradient is linear in the capillary extrusion axis. However, in practice this may not be the case. At and near the entrance to the capillary tube, the axial velocity is obviously in a transitional state from the flow regime within the reservoir to the flow regime within the capillary tube. Furthermore, the pressure gradient within these regions may not be constant. Generally, the feed barrel has a significantly larger diameter than the capillary tube. This is necessary to produce high flow velocities in the capillary tubes. Consequently, the material passes through the barrel at a relatively low velocity until it approaches the die entrance region where it rapidly accelerates to achieve the final capillary velocity. This change in flow can result in an increased pressure gradient over this region. The length of this inlet region is relatively short and easily defined for Newtonian fluids. For non-Newtonian materials, however, the length of this region is a complex function of the viscous, elastic and plastic properties of the material under investigation. By using capillary tubes of extreme lengths the errors induced will become insignificant as the pressure drop due to the transition/end effect will be an insignificant fraction of the total pressure drop. The use of these extreme lengths of the capillary tubes are however impractical for many laboratories; an alternative method to calculate the effective length of the capillary tube (to a first order) was derived by Bagley.[2] Using Bagley's correction method, the wall shear stress, τ_B, is given by:

$$\tau_B = \frac{PD}{4(L + ND)} \quad (3)$$

where N is a characteristic number associated with the end correction. N may be found by extrapolating the plot for extrusion pressure versus capillary length; (see, e.g. Figs. 1–3). The line intercepts the length axis (X-axis) at ND. After accommodating the end corrections, the shear stress versus the apparent shear rate curve should be independent of the diameter of the capillary tube diameter. However, a detectable dependence upon the diameter of the capillary tube has still been identified by many researchers.[3,6–8] A lower magnitude of the shear stress is observed in smaller diameter of capillary tubes for a given apparent shear rate; N is a function of D. This effect has been associated with the presence of wall slip; this is discussed later.

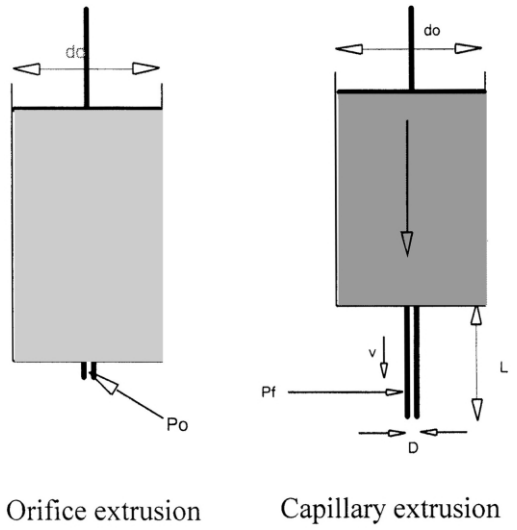

Fig. 1. Schematic representation of ram extrusion apparatus, (a) orifice (left) and (b) capillary (right).

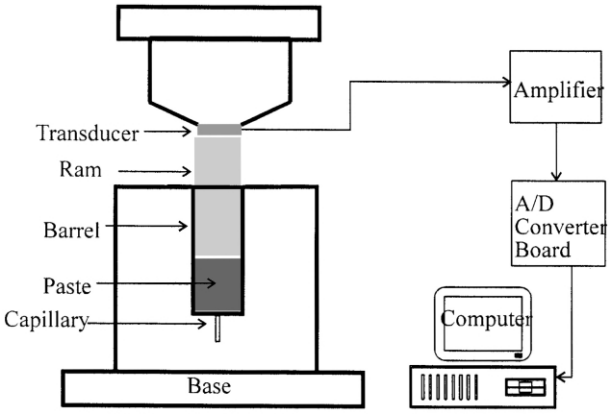

Fig. 2. A configuration of data logging system with Instron 6022 machine.

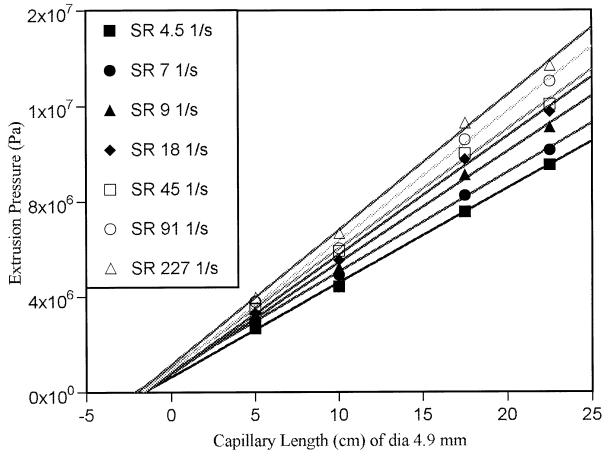

Fig. 3. Extrusion pressure against capillary length of 4.9 mm diameter at different apparent shear rates.

The experimentally observed flow rate, Q_{obs}, may be intuitively considered to be composed of two nominally separate flow contributions:

$$Q_{obs} = Q_{true} + Q_{slip} \tag{4}$$

The first term on the right hand side is the intrinsic internal (developed) shear flow rate, Q_{true}, and the second term is the separate contribution provided entirely by the slip at the wall. Eq. (4) may be converted to Eq. (5)(a,b):

$$\left(\frac{8V_o}{D}\right)_{obs} = \left(\frac{8V_T}{D}\right)_{true} + \left(\frac{8V_{slip}}{D}\right) \tag{5a}$$

or

$$V_o = V_T + V_{slip} \tag{5b}$$

where V_o, V_T and V_{slip} are the (mean) observed, true (internally derived) and wall slip velocities, respectively. The first terms on the R.H.S. of the equation describes the part of the nominal Newtonian shear rate that depends only upon the shear stress at the wall, as oppose to the capillary tube diameter. The parameter V_{slip} in Eq. (5) may be expressed as:

$$V_{slip} = f(\tau_B) \tag{6}$$

where $f(\tau_B)$ is a function of the (mean) Bagley Corrected (see later) wall shear stress (τ_B).

Mooney[3] proposed an expression for $f(\tau_B)$ which depends upon the wall shear stress only:

$$V_{slip} = \alpha\tau_B \tag{7}$$

where α is the slip coefficient and hence;

$$\left(\frac{8V_o}{D}\right)_{obs} = \left(\frac{8V_T}{D}\right)_{true} + (8\alpha\tau_B).\frac{1}{D} \tag{8}$$

Consequently, a plot of nominal Newtonian shear rate ($8V_o/D$) versus the reciprocal of the capillary tube diameter at a given wall shear stress, τ_B, should produce a straight line. However, in many cases the Mooney method may not be applicable.[9] This is especially the case when the flow curves (shear stress versus shear rate) are rather "flat" or when the difference in the slopes of the different curves is very large. In an investigation by Jastrzebski,[6] it was found empirically that the apparent slip velocity also appears to be affected by the diameter of the capillary tube in addition to the wall shear stress, such that:

$$f(\tau_B) = \frac{\beta}{D}\tau_B \tag{9}$$

where β ($=\alpha/D$) is the corrected/modified slip coefficient. Eq. (5a) may again be rewritten as:

$$\left(\frac{8V_o}{D}\right)_{obs} = \left(\frac{8V_T}{D}\right)_{true} + (8\beta\tau_B).\frac{1}{D^2} \tag{10}$$

Thus, a plot of the apparent shear rate against $1/D^2$ should produce a straight line for a given wall stress, τ_B, and from the slope ($8\beta\tau_B$) the wall slip velocity can be calculated.

When extruding some types of material, coloured markings (flow visualisation) can be applied to the material, allowing the relative contributions of the internal shear deformation and the wall slip to be estimated directly.[10] The direct visualisation technique has also been used to evaluate the slip contribution in the current study using torisonally induced flows (parallel plate rotational rheometer) by marking a line on the outer surface of the material.[11] In some extrusion experiments on ceramic pastes, it was found that the computed slip velocity is actually equal to the extrudate velocity;[9] the total transfer was accommodated by wall slip or "plug flow". In that case the second term on the R.H.S. of Eq. (5a) is equal to the observed apparent shear rate and the "true" shear rate (internal flow) is $[(8V/D)_{true} = 0]$ is effectively zero. Naturally, if this is the case, the classical capillary rheometeric analysis in not applicable.

In order to characterise such paste materials, where the wall slip process predominates, the following parameters, which are a function of the extrudate velocity, can be defined[9,12]

Deformation stress, σ_d

$$\sigma_d = \frac{P_o}{2\ln(D_o/D)} = f_d(V) \tag{11}$$

$$\tau_B = f_s(V) \tag{12}$$

where P_o is the extrusion pressure through an orifice, D_o and D are the diameters of the barrel and capillary, respectively, and σ_d is a function of extrusion velocity $[f_d(V)]$. The term $f_d(V)$ describes the shear and extensional deformation and the corresponding phenomenon that occur at the transit region between the barrel and the capillary tube entrance. In a study by Zheng,[12] it was concluded that, at the capillary entrance, the material displays stick (non-slip) behaviour. Consequently, if the behaviour of σ_d versus V is compared with the corresponding plot for τ_B versus V useful information about the slip component of the material in the extruder can be gathered. If slip is occurring within the capillary tube and the deformation stress is due to the stick boundary condition the slope of the σ_d versus V curve should be steeper than that in the corresponding σ_B versus V curve.[12] Computer simulation shows that the slope of the σ_d versus V curves is a material property that is independent of the D_o/D ratio.

Graczyk and Gleissl[9] found, for their paste systems, that although paste flow through capillary tubes was solely due to plug flow, a dependency of the wall shear stress upon diameter capillary was still observed. The variation in shear stress was related to the "thickness" of a slip layer, s, between the bulk material and the wall of the capillary tubes. If the thickness of the slip layer, s, is very small compared to the diameter of the capillary tube, i.e. $D >> s$, then the curvature at the capillary wall is comparatively negligible, and the following equation applies:

$$\frac{V}{s} \approx \dot{\gamma}_s \tag{13}$$

where γ_s is the interfacial shear rate in the slip layer, and

$$\frac{\tau_B}{\dot{\gamma}_s} = \eta_s \tag{14}$$

where η_s is the apparent viscosity of the paste interface in the slip layer of thickness, s.

Initially, the "viscosity" in the slip layer is unknown because it depends not only upon the shear rate (i.e. on the unknown slip layer thickness), but also upon the binder/plasticizer (HEC) concentration. The concentration at the wall is probably different from that in the bulk, as was described earlier. By comparing Eqs. (13) and (14), a new quantity termed the reference slip layer thickness, s_r, is defined:

$$s_r = \frac{s}{\eta_s} = \frac{V}{\tau_B} \tag{15}$$

s_r is readily calculated as V and τ_B are known (or calculable) quantities. Naturally, extensive plug flow of the material within the capillary tube is a necessary condition for employing Eq. (15). The parameter, s_r, maybe interpreted as a measure of the extent of the wall depletion; basically the larger the values of s_r will reflect a greater wall depletion through an increase in s and a decrease in η. The lower bound will be zero.

3. Experimental

3.1. Material

The alumina AES-11 (Mandoval Ltd., Surrey, UK) used in this study was 99.8% pure, and had a BET surface area of 8.14 m^2/g with a mean particle size of 0.4 μm. The commercial dispersant used was "Darvan C", an ammonium salt of poly(methacrylate) (R. T. Vanderbilt Company, Inc., USA). Hydroxy-ethyl-cellulose (HEC) (Hercules chemical Co., UK), 250 M grade, Mw 700,000, was employed as a thickener or viscosity enhancer.

The water used in all the experiments, to make different suspensions/samples, was taken from a Purite (Purite Ltd., Oxon, UK) water-purifying unit, which uses a combination of deionisation and reverse osmosis processes.

3.2. Paste preparation

The paste was prepared from the alumina AES-11 powder, the hydroxy-ethyl-cellulose (HEC), "Darvan C" and water. First, 500 g of alumina AES-11 powder, 5 g "Darvan C" and 103 ml of water were charged in a double sigma blade high shear mixer (Winkworth Machinary Ltd., Staines, England). The contents were allowed to mix for about 10 min so that some of the agglomerates were broken down. Hydroxy-ethyl-cellulose (HEC) molecular weight 250, 000, M grade, was then added, and all the ingredients were mixed for about 30 min. At various intervals during the mixing, the process was stopped and paste was detached from the blades of the mixture (if it was stuck to the blades) using a spatula. The prepared paste was stored in sealed containers for approximately 48 h at room temperature (25°C) before the rheological characterisation was undertaken.

3.3. Ram extrusion rheometer

The ram extrusion experiments were carried out using a ram extruder which composed of a rigid barrel with a smooth surface and a rigid cylindrical ram. On the surface, close to the bottom of the ram, there were two circular grooves that were fitted with synthetic rubber O-rings to minimise the interface friction between the barrel and the ram and also to prevent the leaking of the material out of the extrusion cavity. Fig. 1(a) and (b) shows schematically the apparatus with the orifice and capillary attachments, respectively.

The internal diameter and length of the barrel were 20 and 130 mm, respectively. The dimensions of the ram were 20×132 mm. The barrel could be fitted with different orifices and capillaries (or dies) of different diameters; an orifice is a capillary of negligible length. The arrangement used consisted of orifices and capillaries of diameters ranging from 1 to 5 mm. The lengths of the capillaries were either 10 or 30 mm. Table 1 shows the dimensions of the extrusion system used. During the extrusion, the ram of the extruder was displaced downward with fixed predetermined velocity by a universal testing machine [Instron Machine (6022), UK] in which a load cell (force transducer) was mounted.

The barrel of the extruder was clamped on a stand specially constructed for this purpose; (see Fig. 2). The stand itself was bolted to the static bottom foundation of the Instron Machine. The ram was attached to the load cell situated at the lower part of the moving cross

Table 1
Dimensions of the different extruder components

Components	Diameter (mm)	Length (mm)
Barrel	inner 20	130
Ram	20	132
Capillaries	2.94	50, 75, 125
Capillaries	4.1	50, 150, 200
Capillaries	4.9	100, 175, 225

head. The barrel of the extruder was completely filled with the paste before every experiment. Capillaries of different sizes were attached to the bottom of the barrel and the ram was moved downward by moving the top cross head of the Instron Machine. The interfacial friction generated between the ram and the cylinder walls was, negligible compared to the extrusion load/pressure.

4. Results and discussion

Figs. 3–5 show the extrusion pressure, P, as a linear function of the capillary length for three tube diameters at various nominal shear rates ($8V/D$). All three Figures show a negative intercept on the capillary length axis (abscissa). The value of this intercept, equal to ND [Eq. (3)], depends both upon the apparent shear rate and the diameter of the capillary tube. The figures also show that slopes of the extrusion pressure versus capillary length increase as the apparent shear rate is increased. However, this increase of the slope with the increasing of apparent shear rate is greater for larger diameter capillary tubes (Figs. 3 and 4) than for the smaller diameter capillaries (Fig. 5).

In Fig. 6, the values of the computed wall shear stress, τ_{ap} [Eq. (2)], are plotted as a function of the apparent shear rate [Eq. (1)] for various capillary tube lengths and diameters without considering end corrections. The smaller length capillary tubes show a higher wall shear stress at a given shear rate and a given diameter indicating that end corrections should be usefully made in order to ensure that a shear stress independence of the capillary length is obtained. Fig. 7 is a plot of the shear stress against the apparent shear rate after having made an appropriate allowance for such end corrections [Eq. (3)]. The Figure indicates that the shear stress, as calculated for the smaller diameter capillary tubes, is less than the shear stress for the larger diameter capillary tubes. The difference in the shear stress versus shear rate behaviour for the two diameters of capillary tubes

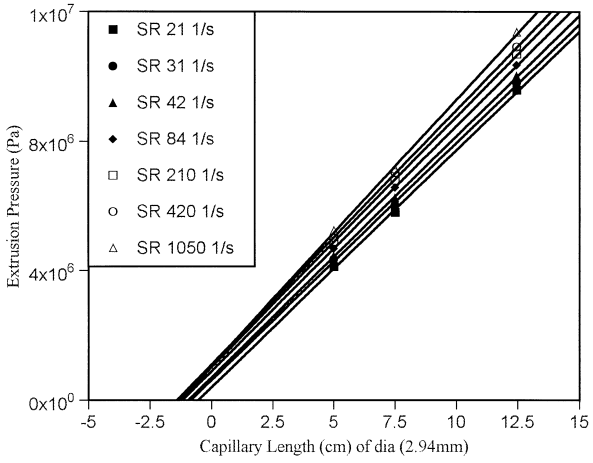

Fig. 5. Extrusion pressure against capillary length of 2.94 mm diameter at different apparent shear rates.

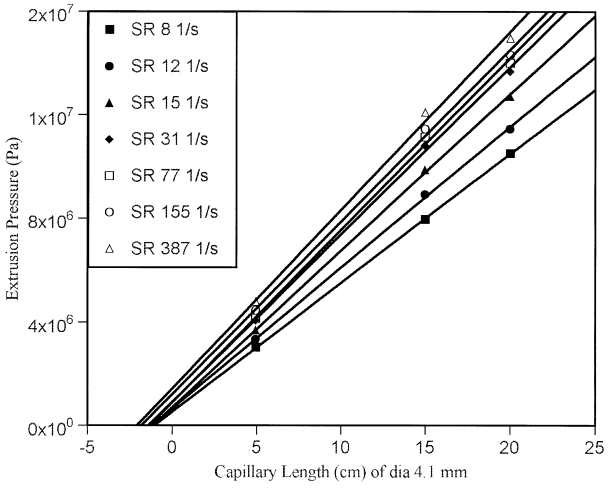

Fig. 4. Extrusion pressure against capillary length of 4.1 mm diameter at different apparent shear rates.

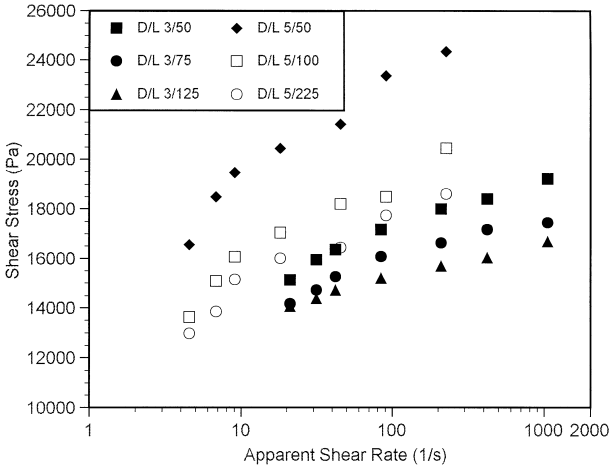

Fig. 6. Shear stress without end corrections against apparent shear rates for different diameter to length (D/L) ratios of capillaries of different diameters.

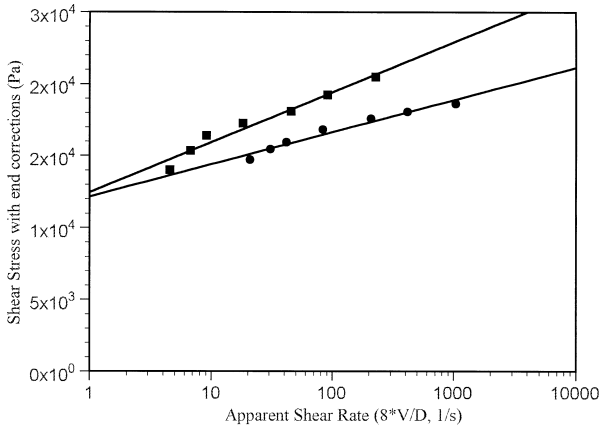

Fig. 7. Shear stress against apparent shear rate after end corrections for two diameter capillaries: ■ length 22.5 cm/diameter 4.9 mm; ● length 12.5 cm/diameter 2.94 mm.

increases as the apparent shear rate is increased. The lower values of the computed shear stress, for the smaller diameter capillary tubes, is probably due to the extensive occurrence of wall slip at the wall of the capillary tube; the extent of this slip increases as the imposed shear rate is increased.

In order to estimate the wall slip velocity, the application of Mooney's method [Eq. (8)] was attempted and it was found that slip velocity rose exponentially as the shear rate is increased. In addition, for apparent shear rates beyond 21 s^{-1} the slip velocity, the computed value of V_{slip}, was found to be greater than the extrudate velocity, V, which is clearly a non-physical situation. As a consequence, this analytical method was abandoned. When the Jasterzebski correction analysis [Eq. (10)] was used it was found that the extrudate velocity and the slip velocity were almost identical. Significant slip (almost total) was also directly observed at the interface of the material and the plates, using a parallel plate rotational rheometer, when the paste was sheared torsionally between the two plates. This extensive occurrence of wall slip was also noted using a direct visualisation method by marking a vertical line on the paste when it was deformed between the two parallel plates. The method was essentially the same as that used by other researchers.[11] The shear stresses for this method using a parallel plate rheometer could not be measured since it was beyond the range of the rheometer used (Bohlin VOR, Holland). However, wall slip was observed by switching off the shear stress measuring mechanism and applying a certain shear rate. The Jasterzebski analysis and results from the parallel plate rotational rheometer show that the current paste formulation in the capillary tubes is most probably conveyed primarily via a wall slip process near to the wall. Significant levels of slip were also observed for the pure continuous phase of water and HEC (binder used in this case) when the viscosity was measured using a Bohlin VOR rheometer with concentric cylinder C 25 measuring system, as a function of shear rate. Furthermore, the difference in the shear stress for different diameters of capillary tube may be due to the development of slip layers of different thickness. Naturally, where the slip velocity is equal to the observed extrudate velocity, V, the data cannot be usefully analysed using the conventional capillary rheometer procedure developed for Newtonian Fluids where wall slips are not developed.

Fig. 8 shows the calculated deformation stress, σ_d, and wall stress, τ_B, as a function of the measured extrudate velocity Eqs. (11) and (12). The slopes for the plots of the deformation stress, σ_d, as a function extrudate velocity are higher than the corresponding plots for the wall shear stress, τ_B, against the extrudate velocity. The deformation stresses were calculated using the data for the 5 cm length capillary tubes used in this study. Had there been orifice data available, it is presumed that the slopes of the τ_d versus V would have been much steeper than the corresponding τ_B versus V slopes, because the contribution from the capillary tube wall in deformation stress would have been absent. However, comparison of the σ_d and τ_B versus V plots shows that significant wall slip is occurring at the wall of the capillary tubes. Furthermore, the similarities in the slope values of the σ_d against V data for the two diameters of capillary tubes are consistent with the predictions of Zheng.[12]

Fig. 9 shows the computed reference slip velocity layer thickness, s_r, as a function of the extrudate velocity for different diameters of the capillary tubes. The sharp increase in the computed reference slip velocity layer thickness, s_r, [Eq. (15)] with the increasing of the slip velocity (~extrudate velocity) is probably mainly due to the pronounced decrease in the viscosity of the depleted (in particulates) wall zone. The reference slip layer thickness is thus a potentially valuable parameter

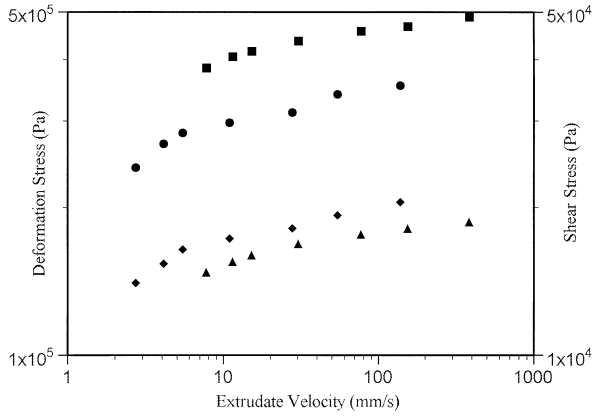

Fig. 8. Deformation stress (σ) and shear stress (τ) against extrudate velocity for two diameter capillaries: ■ σ for 2.94 mm; ● σ for 4.9 mm, ◆ τ for 2.94 mm; ▲ τ for 4.9 mm.

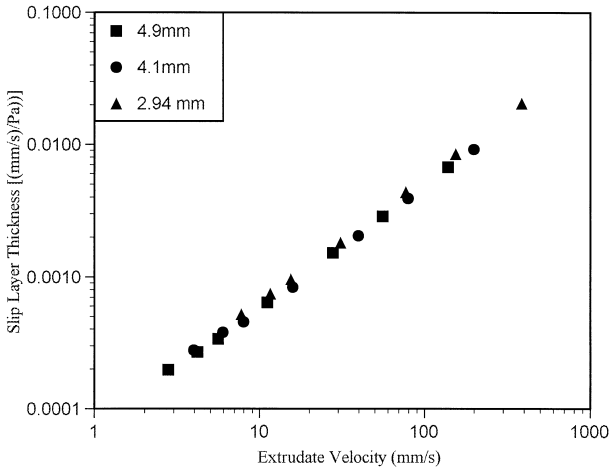

Fig. 9. Reference slip layer thickness against extrudate velocity for different diameter (D, mm) capillaries and their maximum length (L, cm); ■ $D/L = 3/22.5$, ● $D/L = 4.1/20$; ▲ $D/L = 2.94/12.5$.

for characterising the slip properties of these paste systems under defined extrusion conditions. It is also worth emphasising that this parameter can only be usefully employed where the plug flow regime predominates which is the case in the current study.

The existence of slip is well estabilished and has been discussed by several researchers.[3,6–8] A rationalisation of the slip process may be explained as follows: At static equilibrium (non-flow situation), the material (paste) is uniformly dispersed within the volume of the capillary tube. As a deformation force is applied, and the paste starts flowing, the region immediately adjacent to the wall will rapidly become relative free of the dispersed (alumina) material. It will be depleted in terms of the particle concentration. This is because the particulates in the paste begin to order along the direction of flow as the paste starts flowing; the greater the shear rate the greater the ordering. As a consequence of this ordering, a lower viscosity in this depleted zone results allowing, or promoting, slip to occur between the liquid and the wall of the capillary tube. This is in stark contrast to the rather homogeneous arrangement of the particles prior to the imposed deformation. This situation arises since the shear stresses must be greatest at the wall of the tube and zero along the centre axial line. Therefore, the difference in the shear stress provides a driving force for the migration of the particles towards the region of lower stresses at the centre. In addition to the migration of particles due to the action of the imposed shear stresses there may also be physicochemical interactions present between the particulates and the wall of the capillary tube causing depletion of the particle close to the wall. Other phenomena, for example, viscous wall heating may be present in the system especially at higher shear rates. However, the observation of a reasonable linear dependence of the shear stresses upon the capillary tube lengths at higher shear rates indicates that this may not be the case for the current material under the flow conditions encountered in this study.

5. Conclusion

The paste system used in the study was deduced to be flowing during capillary extrusion predominantly by a slip process at the walls of the capillary. This conclusion was established by observing the slip directly using a parallel plate rotational rheometer and also using the analysis given by Jastrzebski. The use of the Mooney method to calculate the slip velocity was found not to be suitable for interpreting the rheological behaviour of the paste under investigation, as the paste material flowed principally by a slip process at the walls of the capillary. The deformation stress is found to be independent of the ratio of the barrel diameter to capillary diameter, i.e. D_o/D. The slip component of the paste flow was analysed in terms of a quantity defined as the reference slip layer thickness as a function of extrudate velocity. The thickness of the depleted layer appears to increase with the increase of extrudate velocity. Also, the reference slip layer thickness is independent of the diameter of the capillary tube and depends only upon the extrudate velocity or the apparent shear rate. Considering these data and the associated analyses serves to emphasise the intrinsic difficulties of characterising the rheological properties of ceramic paste materials using conventional procedures. For most useful ceramic formulations the occurrence of wall slip will always be a major concern in the analysis of data or the application of a particular processing operation in practice.

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