Přednáška

THE RHEOLOGY OF CERAMIC PASTES

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INTRODUCTION

In the field of ceramics, forming is the technological operation during which bodies of required shapes and dimensions are formed from ceramic mixes. On using the content of binder (i.e. water, pressing oil, plastifiers, deflocculators, etc.) as a criterion for the classification of forming operations, three basic groups can be distinguished. The first group includes those operations during which the binder content in the mix varies over an interval necessary for the preparation of powdered mixes. The mixes are then formed by techniques based on the pressing of powder systems. The second group of forming operations consists of mixes whose binder content is sufficient for forming a plastic paste. This group of mixes is processed by plastic forming auch as hand throwing, jiggering and jolleying, overflow pressing and extrusion of plastic mixes on augers or piston presses. The third type of forming operations is represented by slip casting into gypsum moulds. For the latter operation, the binder content in the mix attains the values required for the creation of ceramic suspensions. All of the forming operations have the aim to achieve homogrneous compaction of the entire body, as this is the decisive factor influencing the final properties of ware. This is why the study of forming operations is paid considerable attention not only in the field of classical ceramics, bud also in that of progressive ceramic materials. Extrusion of plastic pastes using augers or piston presses is one of the commonest forming operations. The final shape of the body is created by flow of the paste through the auger steel die.

The present study had the purpose to survey the processes and methods employed in resolving the problems of forming ceramic pastes on augers or piston presses.

THE THEORY OF FLOW OF CERAMIC PASTES

To be able to control and optimize the forming of plastic paste on augers or piston presses one has to be familiar with the behaviour of the paste during flow, i.e. under the effect of a strength field.

The existing knowl dge of the flow behaviour of ceramic pastes is of diverse character and mostly aimed at obtaing data on the rheological state of the paste. This state is most frequently evaluated by methods of empirical nature, such as the plasticity number determined by Pfefferkorn's method [1], plastic strength and optimum forming moisture content established by Rebinder's method [2] or by plastometers of other designs [3]. The results obtained are related to empırical experience with the behaviour of pastes in the course of forming. Empirical rules

for the design of augers or its dies [4] are also a result of such studies. However, such results are not sufficient for controlling and optimizing the forming process, as the empirical methods employed are uncapable of characterizing quantitatively the flow behaviour of the paste.

Study of the deformation behaviour of ceramic pastes under the conditions of simple shear flow showed them to form coagulation structures and to exhibit a yield stress [5, 6]. The effect of a constant shear stress exceeding the yield stress results in plastic deformation bringing about stationary flow. The degree of structural disarrangement attained is determined by the excess shear stress above the yield stress. Study of the flow behaviour of ceramic pastes on Volatovich's viscometer [5] indicated that in the region of completely disarranged structure the plastic viscosity of the paste can be considered to be constant. This finding has led to the idea that the ceramic paste can be described by the linear constitutive equation of ideal viscoplastic liquid, having the form

$$\tau = \tau_{01} + \tau_{PL}\, dv_x/dy, \tag{1}$$

where τ_{01} is the yield stress, $\eta_{PL} = $ const. is the plastic viscosity and dv_x/dy is the rate gradient of shear deformation. Analogy of constitutive equation (1) with Newton's constitutive equation for purely viscous incompressible liquids ($\tau_0 = 0$) [7] lead to the description of steady-state laminar flow of ceramic paste under isothermal conditions, using the following dynamic equation:

$$\varrho \mathbf{v}\, \text{grad}\, \mathbf{v} = \varrho\, \mathbf{g} - \text{grad}\, p + \eta_{PL}\, \text{div grad}\, \mathbf{v}, \tag{2}$$

where ϱ is density, $\mathbf{v}$ is velocity, $\mathbf{g}$ is gravity acceleration, and the weight balance has the form:

$$\text{div}\, \mathbf{v} = 0. \tag{3}$$

Treatment of equations (2) and (3) in the form of criterial relationships was utilized for resolving the flow of ceramic pastes through the extruder mouth and in its designing [4, 8, 9, 10, 11]. Linearization of the constitutive paste equation, plotted in Fig. 1, leads to the calculation of incorrect velocity profiles, as demonstrated by Fig. 2. This is due to the assumption that $\eta_{PL} = $ const. over the entire interval $\tau \in \langle \tau_0; \tau_S \rangle$, which is in fact actually complied with only in the region of completely disarranged structure of the paste, i.e. over the interval $\tau \in \langle \tau_{01}; \tau_S \rangle$, where
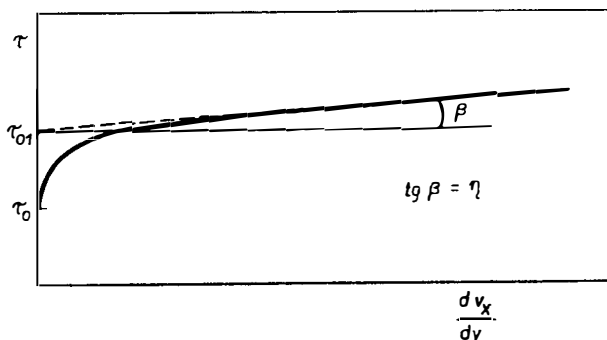

Fig. 1. Plot of the constitutive equation of a viscoplastic paste.

$\tau_{01} \gg \tau_0$. The non-linearity of the $\tau = f(\mathrm{d}v_x/xy)$ relationship was experimentally proved even for other real liquids, such as solutions and melts of polymers, suspensions of foodstuff raw materials and paints [12, 13, 14, 15]. In view of their differences from the linear constitutive equation of a purely viscous Newtonian liquid. the liquids are called generalized Newtonian liquids [16] or non-Newtonian liquids. They are characterized by variable apparent viscosity η obtained experimentally from measurements of plain shear flow.
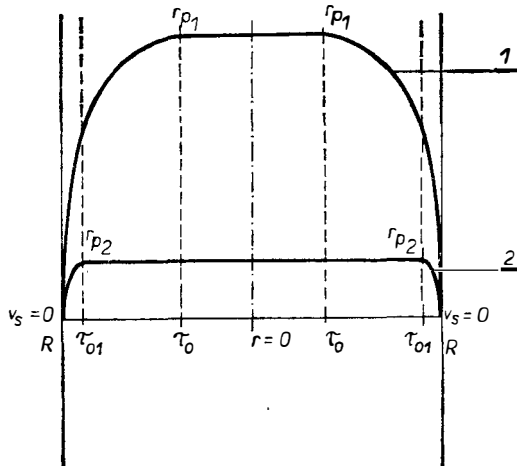

Fig. 2. Velocity profile during paste flow through a pipe 1 — actual, 2 — after linearization.

On introducing the assumption that stress at a certain point and time is explicitely determined by the deformation rate at the same point and time and not affected by deformations in the neighbourhood, the constitutive equation attains the following form [7, 16]

$$\tau = g\,(\mathbf{d}), \tag{4}$$

where $\mathbf{d}$ is the stretching tensor. If the function g is isotropic and symmetrical, equation (4) can be expressed in the form

$$g\,(\mathbf{d}) = \varphi_0 \boldsymbol{\delta} + \varphi_1\,\mathbf{d} + \varphi_2\,\mathbf{d}^2, \tag{5}$$

where φ_i is a scalar function of the three principal invariants of tensor $\mathbf{d}$. For an incompressible liquid, i.e. $\varrho = \mathrm{const.}$, it follows from equations (4) and (5) that

$$\tau = \varphi_1(\mathrm{II_d},\,\mathrm{III_d})\,\mathbf{d} + \varphi_2\,(\mathrm{II_d},\,\mathrm{III_d})\,\mathbf{d}^2, \tag{6}$$

where $\mathrm{II_d}$ and $\mathrm{III_d}$ are the second and third invariants of tensor $\mathbf{d}$. Functions φ_1 and φ_2 in equation (6) represent material relationships used to describe a particular liquid conforming to equation (6).

In the case of simple shear flow the following holds for the components of tensor $\mathbf{d}$:

$$[\mathbf{d}]_{12} = [\mathbf{d}]_{21} = \gamma/2, \tag{7}$$

and

$$[\mathbf{d}^2]_{11} = [\mathbf{d}^2]_{22} = \gamma^2/4, \tag{8}$$

where γ is the shear rate,

while the other components, **[d]** and **[d²]**, are zero. Joining of equations (6), (7) and (8) provides expressions for the stress tensor components:

$$\tau_{12} = \tau_{21} = \varphi_1\, \gamma/2, \tag{9}$$

$$\tau_{13} = \tau_{31} = \tau_{23} = \tau_{32} = 0, \tag{10}$$

$$\tau_{11} - \tau_{22} = 0, \tag{11}$$

$$\tau_{22} - \tau_{33} = \varphi_2\, \gamma^2/4, \tag{12}$$

while the functions φ_1 and φ_2 are calculated for $\mathrm{II_d} = -\gamma^2/4$ and $\mathrm{III_d} = 0$. Equation (9) conforms to any arbitrary dependence of apparent viscosity η and indicates that η is equal to one half of function φ_1. Equation (10) holds for simple shear flow of an arbitrary isotropic liquid. In contrast to the constitutive equation for a Newtonian liquid, equation (12) is indicative of unequality of normal stress components. This unequality was in fact established experimentally on a number of liquids during viscosimetric flow. However, the situation when $\tau_{11} = \tau_{22}$ according to equation (11) has not so far been experimentally proved for any real liquid having a non-zero difference $\tau_{22} - \tau_{33}$. This means that the behaviour of real liquids exhibiting $\tau_{11} - \tau_{22} = 0$ during viscometric flow can be described by the stretching tensor, i.e. $\varphi_2 = 0$, on the condition that the stress tensor has been explicitly determined.

A special form of constitutive equation (6) holds for the Newtonian liquid for which $\varphi_1 = 2\eta = $ const. and $\varphi_2 = 0$. Another consequence of equation (6) is provided by the case when $\varphi_2 = 0$ and $\varphi_1 = f\,(\mathrm{II_d})$ and the constitutive equation has the form

$$\boldsymbol{\tau} = 2\eta\,(S)\,\mathbf{d}, \tag{13}$$

where parameter S is given by the equation

$$S = -4\,\mathrm{II_d} - 2\mathrm{tr}\,(\mathbf{d^2}) = 2\mathbf{d}:\mathbf{d}, \tag{14}$$

where $\mathrm{tr}\,(\mathbf{d^2})$ is the trace of the stretching tensor. For unidirectional shear flow it thus holds that

$$S = \gamma^2. \tag{15}$$

Equation (3) holds at the same time for incompressible liquids. In the case of liquids the stress tensor **P** [7] is given by the equation

$$\mathbf{P} = -\boldsymbol{\delta}p + \boldsymbol{\tau}, \tag{16}$$

where $-\boldsymbol{\delta}p$ is the reversible part of the stress tensor, p is isotropic pressure, $\boldsymbol{\delta}$ is the unit tensor and $\boldsymbol{\gamma}$ is the dynamic stress tensor. On the assumption that the heat liberated by energy dissipation during liquid flow is sufficiently removed by transmission into the environment, the ensuing temperature gradients are negligible and do not affect the properties of the liquid; this means that for an isothermic situation one obtains the generalized dynamic Navier—Stokes equation for an isotropic, incompresible non-Newtonian liquid in the form

$$\varrho D\mathbf{v}/Dt = \varrho\mathbf{g} - \mathrm{grad}\ p + 2\eta\,(S)\,\mathrm{div}\ \mathrm{grad}\ \mathbf{v} + 2\mathbf{d}\ \mathrm{grad}\ \eta\,(S). \tag{17}$$

The system of equations (3), (13), (17) forms a general mathematical model for the flow of a defined non-Newtonian liquid. Solution of the model for suitably selected initial and boundary conditions and the known concrete form of constituti-

ve equation (13) allows the velocity field during laminar flow of a non-Newtonian liquid, or the relationship between volumetric rate of flow and the pressure gradient, to be calculated.

Knowledge of the form of constitutive equation (13) is a prerequisite for resolving the model. The literature [16, 17, 18, 19] gives a number of forms for the function $\eta = f(S)$ contained in equation (17). Extensive use in the resolving of unidirectional flow of polymers and foodstuff raw materials has been made of the $\eta(S)$ relationship having the form

$$\eta(S) = KS^{(n-1)/2}, \tag{18}$$

where K is the consistence factor and n is the law index. The following type of function $\eta(S)$ has also found wide application:

$$\eta(S) = [\eta_0 \operatorname{arsh} (\sqrt{S\lambda})]/\sqrt{S\lambda}, \tag{19}$$

where η_0 and λ are constants, while η_0 is virtually equal to the bottom limit of apparent viscosity:

$$S \rightarrow 0, \qquad \eta \rightarrow \eta_0. \tag{20}$$

The behaviour of ceramic pastes and other liquids exhibiting yield stress τ_0 is described by the constitutive equation having the following form:

$$\tau = \tau_0 + \eta(S)\,\gamma, \tag{21}$$

where the functional dependence $\eta(S)$ is expressed by equation (18).

With most pastes encountered in ceramic technology, the deformation behaviour is considerably affected by the history of previous processing. This finding necessitated additional expansion of the theory of constitutive equations which would provide adequate description of the flow behaviour of real liquids. Astarita [16] has given this concept the name "hydrodynamics of non-linear liquids with memory". Description of the behaviour of real liquids is based on the general assumption that the stress is determined by the complete history of previous deformations. As such a complete history cannot be described, attention is paid to material models describing the memory in finite time, e.g. materials with a differential memory [20], or those with a fading memory [16]. The term fading memory is based on the idea that the effect of earlier deformations on those taking place at a certain moment decreases in terms of time. The mathematical expression of the fading memory is associated with the application of functionals, as the history itself is a functional relationship representing the functional argument. The constitutive equation of a material with fading memory has then the form

$$\tau = \prod_{s=0}^{s=\infty} [G^t(s^t)], \tag{22}$$

where the functions $G^t(s^t)$ describe the history of deformation, $s^t = t - t^+$, where t is the time of measurement, and it holds that $t^+ \leq t$. Expression of constitutive equation (22) requires all the functions determining the respective functional to be established experimentally. The basic problem of the experiment is that the spatial arrangement is unknown and the experiment is difficult to formulate over a certain interval of the space, if it is not described by a finite number of scalar parameters. The solutions have so far been simplified through restriction to a cer-

tain type of flow with a defined deformation history, where each term is determined by a finite number of parameters. Another type of simplification is based on limiting the solution by a material model described by a non-general already known constitutive equation which contains a finite number of parameters or experimentally determinable functions.

CONCLUSION

The above survey of findings on the flow of ceramic and other pastes allows the conclusions concerning quantitative description and thus also the control of the forming process to be formulated into the following points:

1. Ceramic pastes constitute coagulation structures characterized by variable apparent viscosity and yield stress under the conditions of viscometric flow.

2. Study of the behaviour of ceramic pastes in an active force field on the basis of various empirical tests does not provide data for quantitative description of the flow behaviour of the paste.

3. Description of the behaviour of ceramic pastes by constitutive equations with a linear dependence of the stress tensor on the stretching tensor is satisfactory when using constant parameters of this stretching tensor. Utilization of this procedure is bound to the knowledge of the actual dependence $\tau = f(\gamma)$ of the given paste, where it is possible to evaluate the error of the solution due to linearization of the actual course of the dependence. In view of the limited number of literary data on these relationships for various types of ceramic pastes, there may even be pastes with which this idealization would not result in any major errors in the solution of engineering and technological problems.

4. The present state of development of the theory of constitutive equations for non-linear liquids with memory does not yet allow the behaviour of ceramic pastes in an external force field to be explicitly described; however, it represents a promising way towards exact solution of the flow of non-Newtonian liquids.

5. Description of the behaviour of ceramic pastes in a force field by constitutive equations using parameters of nonlinear dependence of the stress tensor on the stretching tensor, where flow of the paste is characterized by apparent viscosity which in turn depends on the deformation rate on the assumption of explicit determination of the stress tensor by means of the deformation rate tensor, is suitable for a well descriptive, but not generally valid solution of engineering and technological problems associated with the flow of ceramic pastes.

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KOMPOZITNÍ MATERIÁL GRAFIT — KEVLAR byl vyvinut firmou Hughes jako materiál nahrazující některé kovové součásti kosmických raket. U těchto materiálů nedochází, na rozdíl od kovů, k roztahování nebo smršťování vlivem extrémních tepelných podmínek ve vesmíru. Firma vyrábí z tohoto materiálu složité spojovací prstence s průměrem 2 m pro kosmické lodě náhradou za hliník.

(High Technol., *7*, 1987, č. 10, s. 2)

Fryntová

MATERIÁL NAHRAZUJÍCÍ AZBEST byl vyvinut firmou Pyrotek k nahrazení azbestu u různých zařízení přicházejících do styku s horkým sklem. Materiál s označením NAD-11 je vyroben na bázi skla, slídy, křemene a cementu. Vyznačuje se vysokou mechanickou pevností, nízkou tepelnou vodivostí a vynikající tepelnou stabilitou a odolností proti oděru. Je použitelný do teplot 650 °C.

(Glass Ind., *68*, 1987, č. 10, s. 8)

Fryntová

NOVÝ KOMPOZITNÍ MATERIÁL — skleněné vlákno ze skla S-2 s matrix z fenolové pryskyřice vyvinula firma Owens-Corning. Materiál je určený jako vyztužovací prostředek pro letecký a lodní průmysl. Tatáž firma vyvinula i další kompozitní materiály — na bázi skleněné příze kompatibilní s epoxidovou pryskyřicí — vhodné např. pro odpalovací zařízení kosmických raket a předtvarované rohože ze skleněných vláken určené pro automobilový průmysl.

(Glass Ind., 68, 1987, č. 10, s. 36)

Fryntová

BÓROVÁ A UHLÍKOVÁ VLÁKNA bez jádra je možné vyrábět pyrolytickým procesem vyvinutým v Midwest Research Institute. Tento proces, využívající laseru, umožňuje výrazné zlepšení vlastností vláken — snížení elektrického odporu, zvýšení pevnosti v tahu na 5,2 GPa a zvýšení rychlosti výroby.

Am. Cer. Soc. Bul., *66*, 1987, č. 3, s. 424)

Fryntová

CERMETOVÉ SUPRAVODIČE s transformačními teplotami nad 90 K vyrábí Gorham Advanced Materials Institute, Gorham, Maine. Firma hledá způsoby zvýšení hustoty proudu docílením požadované orientace krystalů v supravodivé keramice. Vyšší houževnatosti a pevnosti je dosaženo zpevněním whiskry a technologickým postupem přípravy plně zhutněných cermetů při teplotách pod 400 °C.

Cer. Ind., *129*, 1987, č. 7, s. 16.

Fryntová