

## ON THE MODELLING OF NON-MONOTONOUS VISCOSITY DESCRIBING FEEDSTOCK BEHAVIOUR IN POWDER INJECTION MOULDING

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### ABSTRACT

Feedstocks used in the process of powder injection moulding characterized by the flow of highly filled (60 vol.%) compound into a mould cavity, sometimes exhibit non-monotonous flow behaviour of viscosity in dependence on shear rate. A new 7-parameter rheological model was proposed and applied to the feedstock based on aluminium oxide powder and multicomponent partly water-soluble polymeric binder. Structural changes of the feedstock caused by shear deformation were quantified in terms of yield stresses obtained using the classical monotonous Herschel-Bulkley and Casson models. Unlike these models the newly proposed 7-parameter rheological model is valid in the whole shear rate range measured.

### INTRODUCTION

Rheological approach represents an inevitable tool for characterization of behaviour of entry components in the process of powder injection moulding. Powder injection moulding (PIM) is an effective alternative to the traditional processes for production of complex-shaped small parts. It combines common processing route for plastics - injection moulding - with metallurgical sintering. PIM process might be generally divided into four consequential steps: compounding metal or ceramic powder with polymers mixture (called binder) to obtain homogeneous highly filled feedstock, injection moulding of prepared feedstock into a mould with required design, thermal and/or solvent removal of a polymer binder, and sintering remaining powder structure to a high density component [1]. Rheological description of a feedstock participates in an evaluation whether the final products of the PIM method will be defect-free and non-porous.

Highly concentrated compounds (about 50 vol.% solids and higher) may exhibit a radical change on their flow curves accompanied by distortions of the extrudate surface expressing themselves similarly to spurt flow of e.g. linear polyethylene [2,3]. The mechanism of these flow instabilities is however different as investigated and reported in [4-6].

In the case of aluminium oxide powder MARTOXID® MR70 compounded with a commercial multi-component binder Licomont EK 583-G (60 vol.%), the measured viscosity data of the feedstock cannot be modelled with the help of the classical empirical models as they exhibit strongly non-monotonous character in the dependence on shear rate. The goal of the present contribution is to propose and applied a suitable empirical model respecting non-monotonicity of flow behaviour of the feedstock used. An agreement between the empirical model and the data seems to be good in the whole shear rate range measured.

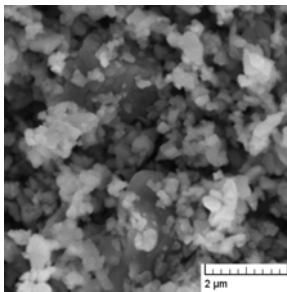
### EXPERIMENTAL

#### Materials

In this study, highly compressive superground aluminium oxide (alumina) powder MARTOXID® MR70 (Albemarle Corporation, USA) with a specific surface area (BET) 6–10 m<sup>2</sup>/g, bulk density ~0.90 g/cm<sup>3</sup>, green density 2.20–2.40 g/cm<sup>3</sup> and fired density (1,600 °C, 2h) 3.80–3.92 g/cm<sup>3</sup> was used, see Figure 1.

The powder was compounded with a commercial multi-component binder Licomont EK 583-G (Clariant, Switzerland) which is partially water-soluble with a density 1.05–1.15 g/cm<sup>3</sup>, viscosity (at 130 °C) 1,200–1,500 mPa·s and the softening point at 105–115 °C. During mixing in a blade kneader at 160 °C for 2h a surfactant (1 wt. % oleic acid) was added.

Subsequently, 60 vol.% feedstock in a form of pellets was acquired from single-screw extruder.



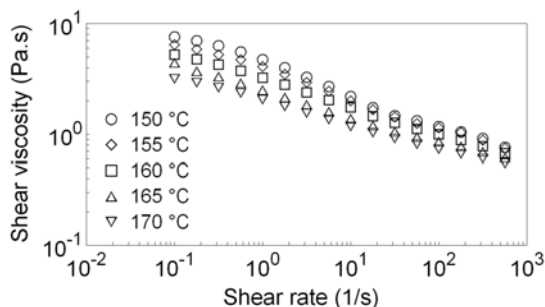
**Figure 1** Scanning electron micrograph of alumina powder

### Methods

Rheological properties of the alumina feedstock were measured on a capillary rheometer Rheograph 2001 (Göttfert, Germany) at shear rates from 10 to 1,000  $s^{-1}$  at temperatures 150, 160, and 170 °C. The length-to-diameter ( $L/D$ ) ratio of capillary was 30. The apparent viscosity values are presented since the data measured with orifice capillary ( $L/D=0.12/1$ ) were rather scattered. The rheological behaviour of the binder was determined using a rotational viscosimeter Physica MCR501 (Anton Paar, Austria). The shear viscosities were examined at shear rates in the range from 0.1 to 600  $s^{-1}$  and at temperatures from 150 to 170 °C in steps of 5 °C.

### RESULTS AND DISCUSSION

From FTIR analysis (not included) it is supposed that the binder contains polyolefines, paraffin waxes and polyethyleneglycols. Its rheological characteristic was acquired at five different temperatures in the range 150–170 °C in 5 °C steps on the rotational rheometer MCR501. The effect of temperature, especially at shear rates higher than 10  $s^{-1}$ , becomes negligible with increasing temperature above 160 °C, see Figure 2. Overall level of binder viscosity lies in the range proposed for PIM technology, i.e. less than 0.1 Pa.s at the processing shear rate in order to provide PIM mixtures with viscosity below 1,000 Pa.s [7].

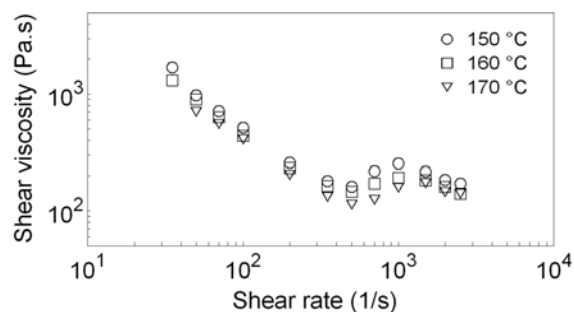


**Figure 2** Temperature-dependent viscosity versus shear rate of multicomponent binder

Filling the binder with 60 vol. % alumina powder resulted in the feedstock with flow properties far from required above.

Fine alumina powder is relatively hydroscopic and binder is rather sensitive to destabilization in water resulting in enhanced viscosity. This problem can be solved via improving the flowability of the system with dispersants and lubricating agents. Reduction of viscosity about one order of magnitude has been reported by Lin and German [8] for 56 vol.% alumina powder in a paraffin wax added with 4 wt.% of stearic acid (SA). In case of Chan and Lin [9] SA molecules adsorption on alumina powder surface changed the flow course from dilatant to pseudoplastic.

The rheological data obtained for 60 vol.% alumina feedstock modified with 1 wt.% oleic acid are depicted in Figure 3. Oleic acid has been chosen with regard to investigation of Tseng [10] comparing the effect of stearic acid, oleic acid and 12-hydroxystearic acid (2 wt.%) on the flow behaviour of 60 vol.% alumina feedstock. Their measurements at high shear rates region (1,000–15,000  $s^{-1}$ ) showed similar effect of SA and oleic acid on mixture viscosity at 150 °C. In addition Persson et al. [11] demonstrated that 1 % of SA added to the iron-based feedstock has the same effect as 2 % of SA - decreasing viscosity four times.



**Figure 3** Temperature-dependent viscosity versus shear rate of alumina feedstock

The viscosity values (Figure 3) are about three to two orders of magnitude higher in comparison to binder viscosity at the corresponding shear rates. At lower shear rates (up to 500  $s^{-1}$ ) the viscosity of feedstock decreases with increasing shear rate suggesting particle or binder molecule orientation and ordering with flow. When the shear rate reaches 500  $s^{-1}$  particles cannot form layers and slide over each other as firstly reported by Hoffman [12], and shear thinning turns into a dilatant flow. Similar phenomenon was observed for all investigated temperatures. There is still considerable uncertainty about the source of such behaviour. Jansma and Qutubuddin [13], who studied this phenomenon using different viscometers, showed that it could not be an experimental artefact due to the slip at the wall. The mechanism proposed by Barnes [14] is that with increasing shear stress (rate) the layers formed in the pseudoplastic flow region becomes disrupted, and at a certain shear stress/rate are fully eliminated (flow turns into dilatant). It implies that every highly concentrated suspension exhibits dilatant flow if proper flow conditions (depending on filler concentration, particle size distribution as well as viscosity of a polymer component) are selected.

For the alumina feedstock investigated, this structure restructuralization appears repeatedly. The Herschel-Bulkley [15] and Casson [16] models applied to the rheological data resulted in similar values of yield stress as can be seen from Table 1, corresponding well to Kurzbeck et al. [17] studying inorganic pigment/paraffin wax compounds, supporting Casson's idea of energy dissipation mechanism responsible for viscosity variation with shear rate.

**Table 1** Yield stresses values calculated from the Herschel-Bulkley and Casson models

temperature (°C)	yield stress (kPa)	
	Herschel-Bulkley	Casson
150	50	47
160	45.5	44
170	40	37

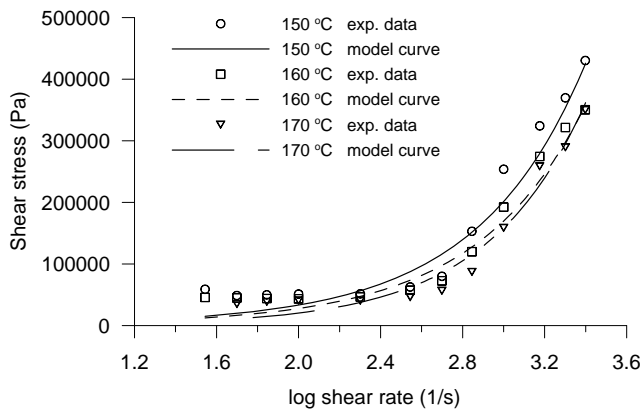
The Herschel-Bulkley and Casson models allow describing the flow properties of alumina feedstock only up to  $1,000 \text{ s}^{-1}$ , therefore we propose in the expression relating shear stress with shear rate

$$\tau = \eta \cdot \dot{\gamma} \quad (1)$$

the following 7-parameter empirical model for a determination of a non-monotonous course of viscosity

$$\eta = k \frac{[a^{1/r} + (k\dot{\gamma})^{p/r}]^r}{[b^{1/s} + (k\dot{\gamma})^{q/s}]^s} \quad (2)$$

The results of the fitting the experimental data with this model are shown in Figure 4, the parameters are summarized in Table 2. It is supposed that the empirical parameters can be further linked to the materials characteristics when the corresponding database will be created.



**Figure 4** Temperature-dependent shear stress versus shear rate of alumina feedstock

**Table 2** Parameters of the rheological model applied to shear rate vs. shear stress data of alumina feedstock

parameter	temperature		
	150°C	160°C	170°C
$k$	10,00	8,40	10,00
$a$	2,00	2,00	0,80
$b$	0,55	0,70	1,20
$p$	-0,90	-0,80	-0,26
$q$	-2,40	-1,70	-1,80
$r$	7,00	7,00	6,00
$s$	1,00	1,30	2,00

## CONCLUSION

Alumina powder grade for powder injection moulding technology was combined with a commercially available multi-component binder. An oleic acid was used as modifier to attain suitable viscosity level of 60 vol.% feedstock. Rheological analysis including a description of non-monotonous behaviour of viscosity by means of the 7-parameter empirical model was carried out with the aim to optimize the production of nonporous homogeneous ceramic parts. The number of parameters appearing in the empirical models should be always reduced as much as possible. However, the 6-parameter model introduced in [18] seems to be inadequate for a proper description of flow behaviour in this case and the 8-parameter model in [19] exhibits one more parameter in comparison with the model in rel.(2).

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