Rheological Characterization of Powder Injection Moulding using Feedstock Based on Aluminium Oxide and Multicomponent Water-Soluble Polymer Binder

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Abstract: - Rheological analysis of powder injection moulding of feedstock based on aluminium oxide powder and multicomponent partly water-soluble polymeric binder is carried out with the aim to produce the defect-free and non-porous parts. As this process is characterized by the flow of highly filled (60 vol.%) compound into a mould cavity, rheological properties supplemented by thermal and pressure-volume-temperature characteristics are measured and described. Structural changes of the feedstock caused by shear deformation are quantified in terms of yield stresses obtained using the Herschel-Bulkley and Casson models. For a description of non-monotonous flow behaviour of the feedstock, the rheological model valid in the whole shear rate range measured is developed.

Key-Words: - Powder injection moulding, Viscosity, Aluminium oxide, Polymer binder

1 Introduction

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: 1) compounding metal or ceramic powder with polymers mixture (called binder) to obtain homogeneous highly filled feedstock, 2) injection moulding of prepared feedstock into a mould with required design resulting in a green part, 3) thermal and/or solvent removal of a polymer binder creating brown part, and 4) sintering remaining powder structure to a high density component [1].

The process phase still requiring clarification and optimization is flow of highly filled feedstock into a mould cavity during injection moulding since the defects in the final parts (after sintering) are created during moulding and cannot be reduced or eliminated during the following steps as debinding and sintering [2].

While rheology of suspensions of non-interacting spheres seems to be well established, understanding of rheological behaviour of multiphase systems as those intended for PIM is necessarily a difficult task. For the cavity filling with minimized jetting a pseudoplastic flow that relieves processability is required [1]. Although, it is common cause for unfilled polymers, PIM compounds show rather complicated sensitivity to variations with shear rate, even if binder behaves in a Newtonian fashion. Upon powder loading the Newtonian plateau becomes reduced or disappears. It has been widely accepted that the change into non-Newtonian flow arises from the disruption of agglomerates formed by particles [3]. The two mechanisms affecting viscosity can be discerned: agglomerates' destruction during shearing causes decrease of the amount of suspending fluid entrapped among particles, and thus viscosity decreases due to the drop of an effective volume fraction of powder [4], or the change in viscosity is related to the dissipation energy rising from rotation and distortion of particle agglomerates (e.g. [5]).

A yield point often appears at low shear rates as an indication of temporary particle network structure within melt (e.g. [6,7]). The Casson model [5] based on energy dissipation mechanism or the empirical Herschel-Bulkley model [8] are widely accepted ways of yield stresses evaluation.

Upon further increase of shear rates the particle structure is destroyed, particles and polymer orientate and order in the flow direction to allow interparticle motion, and the viscosity is dominated

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by hydrodynamic interactions [9] resulting in shear thinning.

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 [10,11]. The mechanism of these flow instabilities is however different as investigated and reported in [12-14].

Because PIM is a high-pressure moulding process, flow behaviour and compressibility of powder and polymer-based binder in a pressurized melt-stage are key indicators for assessment of processing conditions. The pressure-volume-temperature (PVT) characteristic provides the information of feedstock's specific volume at moulding temperature and pressure necessary for production of the defect-free injection moulded parts. Although the shrinkage of a green body is needed to be incorporated into the mould design, PVT studies on PIM materials are reported scarcely [15-18]. Further, Greene and Heaney [17] proved that holding pressure could be effectively used to control the dimensional stability of the final sintered parts. An overholding pressure may cause relaxation problems and higher shrinkage as reported also by Laddha et al. [15] for aluminium oxide (56 vol.%) feedstock resulting in a suggestion of choosing the holding pressure level after appropriately referring to PVT-diagram so that the residual pressure in a cavity before mould opening is near to the atmospheric.

In this paper we optimize the PIM process of aluminium oxide (alumina) feedstocks. Although metals as stainless steels (316L, 17-4PH) are nowadays prevailing powder injection moulding material, aluminium oxide parts (thread guides) represent the earliest PIM application dated back to the 1930's [19]. The advantage of alumina powder as the most widely used PIM ceramic [20] in comparison to metals is that it combines good mechanical properties with low specific weight. The PIM alumina products find their application in areas where extreme conditions such as high temperatures, corrosive atmosphere, abrasive conditions or high loads at extreme temperatures are applied [21].

The aim is to produce non-defect parts via careful control of the flow properties of the feedstock. As already pointed out, the problems created during flow into a mould appear during/after debinding and/or sintering, and therefore, their solution consists in rheology.

2 Experimental

2.1 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^2/g, bulk density ~0.90 g/cm^3, green density 2.20−2.40 g/cm^3 and fired density (1,600 °C, 2h) 3.80−3.92 g/cm^3 was used, see Fig.1.

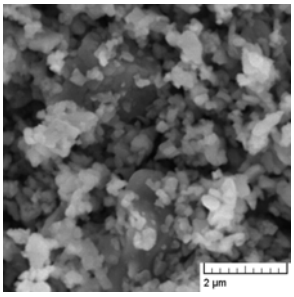

Fig.1 Scanning electron micrograph of alumina powder.

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^3, 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.

2.2 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.

Pressure-volume-temperature (PVT) character-istics were obtained with PVT-100 (SWO, Germany) apparatus. The specific volumes were examined at pressures and temperatures in the range 30–200 MPa and 50−250 °C, respectively, in a measurement mode of isobaric heating with a heating rate of 5 °C/min.

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3 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 Fig.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 [22].

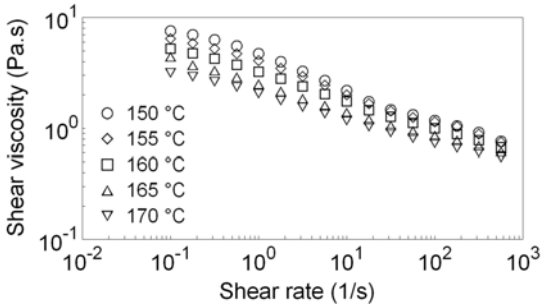

Fig.2 Temperature-dependent viscosity versus shear rate of multicomponent binder

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 [23] for 56 vol.% alumina powder in a paraffin wax added with 4 wt.% of stearic acid (SA). In case of Chan and Lin [24] SA molecules adsorption on alumina powder surface changed the flow cause from dilatant to pseudoplastic.

The rheological data obtained for 60 vol.% alumina feedstock modified with 1 wt.% oleic acid are depicted in Fig.3. Oleic acid has been chosen with regard to investigation of Tseng [25] 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. [16] demonstrated that 1 % of SA added to the iron-based feedstock has the same effect as 2 % of SA - decreasing viscosity four times.

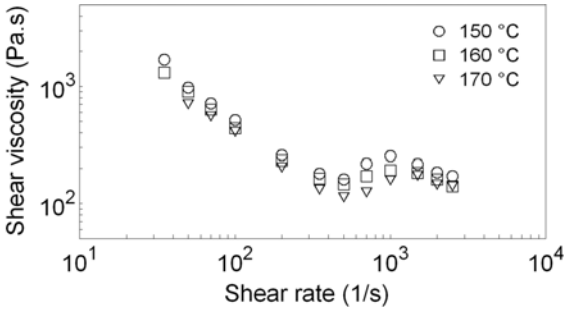

Fig.3 Temperature-dependent viscosity versus shear rate of alumina feedstock

The viscosity values (Fig.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 [26], 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 [27], 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 [28] 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 [8] and Casson [5] 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. [3] studying inorganic pigment/paraffin wax compounds, supporting Casson's idea of energy dissipation mechanism responsible for viscosity variation with shear rate.

The Herschel-Bulkley and Casson models allow describing the flow properties of alumina feedstock

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only up to 1,000 s^{-1}, therefore we apply the following empirical model (Filip et al. [29] extending the 6-parameter model in David and Filip [30]) covering the whole range of measured shear rates

$$\eta = \frac{a_1 \exp(-f_1)}{b_1 + \exp(f_1) + \exp(-f_1)} + \frac{a_2 \exp(f_2)}{b_2 + \exp(f_2) + \exp(-f_2)} \quad (1)$$

where

$$f_1 \equiv f(\dot{\gamma}; c_1, p_1) = \log(c_1 \dot{\gamma})^{p_1} \quad , \quad (2)$$

$$f_2 \equiv f(\dot{\gamma}; c_2, p_2) = \log(c_2 \dot{\gamma})^{p_2} \quad , \quad (3)$$

$$\tau = \eta \cdot \dot{\gamma} \quad . \quad (4)$$

The results of the fitting the experimental data with this model are shown in Fig.4, the parameters are depicted 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.

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

Table 2 Parameters of rheological model applied to viscosity data of alumina feedstock.

Temperature (°C)	Parameter (-)			
	a_1	b_1	c_1	p_1
150	148.8	-1.9	0.034	0.635
160	125.9			
170	107.8			
	a_2	b_2	c_2	p_2
150	0.025	-1.99986	0.00072	0.028
160	0.023			
170	0.020			

The PVT data of the alumina feedstock under isobaric heating regime is shown in Fig.5. As it can be seen the temperature transitions are imperceptible. In contrast, Persson et al. [16] reported (using the same device) for 420 stainless steel feedstock transition zones corresponding to the particular components of their commercial binder. Similarly, Wei et al. [18] when using PVT-100 device for 85 wt.% alumina with paraffin wax based binder system obtained the transition zones indicating clearly the binder components. The result obtained for alumina feedstock might be explained as the consequence of the multicomponent character of the binder whose particular components have overlapping melting zones.

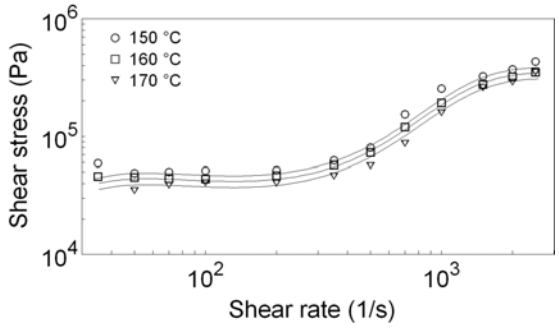

Fig.4 Temperature-dependent shear stress versus shear rate of alumina feedstock; solid lines represent data fitting by the rheological model

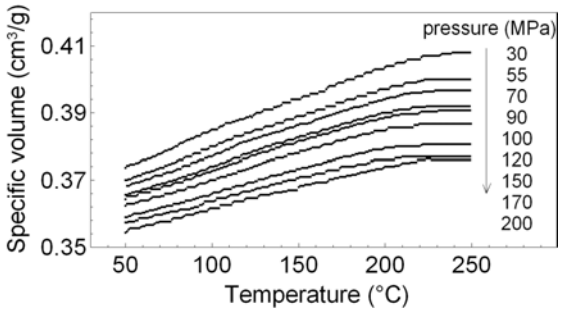

Fig.5 Pressure-volume-temperature characteristic of alumina feedstock under isobaric regime

4 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 was carried out with the aim to optimize the production of nonporous homogenous ceramic parts.

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