Rheological properties of alumina injection feedstocks

Abstract

The rheological behavior of alumina moulding feedstocks containing polyethylene glycol (PEG), polyvinylbutyral (PVB) and stearic acid (EA) having different powder loading were analyzed using a capillary rheometer. Some feedstocks show pseudoplastic behavior with $n<0$, which could cause weld lines on molded parts, and shows a very high dependence of viscosity on shear rate. It was also observed the slip phenomena that could cause unsteady front flow. The results indicate that the feedstock containing lower powder loading show the best rheological behavior. The 55 vol. % powder loading feedstock presents the best rheological behavior and seems to be the most suitable, instead of formulation containing vol. 59% powder loading which attains viscosities higher than $10^3$ Pa.s for low shear rates, and it is not indicated for injection molding.

Keywords: alumina, rheological behavior, ceramic injection moulding
Rheological properties of alumina injection feedstocks

Krauss, VA*; Pires, EN; Klein, AN; Fredel, MC

Campus Universitário, Trindade, Florianópolis/SC, CEP: 88040-360
vkrauss@floripa.com.br

Universidade Federal de Santa Catarina – Departamento de Engenharia Mecânica
Programa de Pós-Graduação em Engenharia Mecânica - POSMEC
Laboratório de Materiais

Abstract

The rheological behavior of alumina moulding feedstocks containing polyethylene glycol (PEG), polyvinylbutyral (PVB) and stearic acid (EA) having different powder loading were analyzed using a capillary rheometer. Some feedstocks show pseudoplastic behavior with $n<0$, which could cause weld lines on molded parts, and shows a very high dependence of viscosity on shear rate. It was also observed the slip phenomena that could cause unsteady front flow. The results indicate that the feedstock containing lower powder loading show the best rheological behavior. The 55 vol. % powder loading feedstock presents the best rheological behavior and seems to be the most suitable, instead of formulation containing vol. 59% powder loading which attains viscosities higher than $10^3$ Pa.s for low shear rates, and it is not indicated for injection molding.

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1 Introduction
Powder injection molding (PIM) is cost effective for producing small, complex, precision parts in high volume. The PIM process developed from the traditional shape-making capability of plastic injection molding and the materials flexibility of powder metallurgy. The process involves several steps, from mixing to sintering, but the production of reliable shapes requires correct injection moulding conditions. The powder is blended with an organic vehicle in order to take advantage of the injection molding fabrication route. The binder system usually has three components – a backbone polymer that provides strength, a filler phase that is easily extracted in the first phase of debinding, and a surfactant to bridge between the binder and powder.

In a study of a variety of thermoplastic binder system (ceramic powder-polymer suspensions), it was concluded that such systems should possess three flow characteristics: a flow index smaller than one (power law), fluidity greater than 10 Pa.s at shear rate of about 100 s⁻¹, and a relatively low dependence of the viscosity on temperature at the same shear rate. Furthermore, shrinkages in the binder system due to phase changes or thermal contraction should be kept to a minimum.

The rheological properties are important for the injection molding step as it concerns the flow of the feedstock during injection molding. Rheological analysis can be used to quantify the stability of the feedstock during the molding process.

The aim of the present work was to characterize the flow properties of formulations based on a polymer and a component of lower molecular weight plus a surfactant to select a suitable feedstock for use in injection molding.

2 Experimental
2.1 Materials

Commercial purity alumina powder (Alcoa, A1000SG) was used in this study. The particle morphology and a typical size distribution are shown in Figures 1 and 2. Specific surface area was $9.3 \times 10^3 \text{ m}^2/\text{kg}$ according to supplier.

A multi-component binder system was used to prepare the alumina feedstock. The binders used in the experiments are listed in Table 1.

2.2 Compounding

Formulations containing 55 to 59% by volume of powder were prepared to understand the effect of solid loading on rheological behavior of alumina injection molding feedstocks.

The remaining volume consisted of the aforementioned binders with a volume ratio of PEG:PVB 2:1 and Al$_2$O$_3$:AE 25:1.

Table 2 illustrates the composition of the feedstocks used in this study. Alumina powder was dried before mixing in an oven at 110°C for 1h. Five feedstocks were prepared by using a sigma type blade mixer (Haake Polylab System) having a rotation frequency of 90 rpm. All the components of the feedstock were added at the same time at 180 °C for 30 min. Granules were obtained and mixed a second time at 160 °C for 30 minutes to achieve a homogenized feedstock.
2.3 Rheology

Viscosity of formulations was measured using a capillary rheometer (Haake 3000p) after each mixing experiment. The pressure drop across the length of the die (L/D = 30) was measured using a pressure transducer situated adjacent to the die entrance.

The piston velocity of the rheometer was varied in order to obtain different shear rates and the corresponding pressure drops were measured to calculate the shear stress. Shear stress divided by shear rate gives the apparent viscosity.

3 Results and discussion

Figures 3 and 4 show the plots of time versus torque and density of processed feedstocks.

(insert here Figures 3 and 4)

Torque is a measure of the resistance on the rotor blades. By observing the mixing torque values, the homogeneity of a feedstock can be predicted: the lower the value, the better the mix\(^3\). The friction is created with higher powder loading; therefore, the resistance on the rotor blades was higher\(^4\).

Typically, it was observed that higher powder loadings resulted in higher torque level in the end of mixing process. The 55% solid loading presents the lowest torque as it was expected. Other feedstocks presented the same torque level.

Figure 4 shows that feedstock density is directly dependent on the powder loading volume, higher the powder loading, higher the density of the feedstock.
Figures 5 (a), (b) and (c) show the viscosity versus shear rate curve for three different temperatures for three of the five analyzed feedstocks.

Feedstocks exhibited pseudoplastic flow behavior and the viscosity decreased with increasing the shear rate for all working temperatures. F55 shown a critical value of shear rate, from that point a dramatic fall of viscosity can be seen. It will be discussed later. The decrease in viscosity with increasing shear rate indicates particle (or binder molecule) orientation with flow and may reflect and improve homogeneity. In addition, for ceramic injection molding, the shear rates can vary from 100 to 1000 s\(^{-1}\) and the flow rate during injection molding requires a viscosity lower than 1000 Pa.s\(^{1}\).

Because of this F59 is not recommended for use in injection molding process. As temperature went up, there was a slight drop in the feedstock viscosity in the tested temperature range.

The phenomenon is mainly due to (a) a fall in the powder volume caused by larger expansion of the binder when heat is introduced, and (b) disentanglement of the molecular chain when more heat is distributed to fluctuate the random molecular structure\(^{1}\).

Figure 6 shows the rheological behavior of feedstocks at the temperature of 175 °C.

Figure 6 shown that at low shear rate there is a difference among the viscosity curve for five powder volume formulations. Viscosity values of F57, F58 and F59 began to be more unstable from 500 s\(^{-1}\) because of an oscillating flow that was verified during the experiment.
Table 3 lists the flow behavior index $n$ assessed from the viscosity against shear rate plot at the nozzle temperature. Data obtained at shear rates higher than 900s$^{-1}$ was neglected for $n$ evaluation.

Table 3 shows that the increase in the powder loading leads to a dramatic fall in $n$ value. If the data higher than 900s$^{-1}$ were considered all $n$ values were negative.

Even that the difference was small in the amount of solid loading among the compositions, it arisen an anomalous behavior between 55 and the other feedstocks. It might be explained due to the approximation of the critical value of solids loading.

The critical solids loading corresponds to the particles rubbing on one another, so the mixture is free of voids, but has a very high viscosity. The critical loading is the composition where the particles are packed as tightly as possible without external pressure and all space between the particles asfilled with binder. Departures from ideal behavior show deficiencies in the binder content and formation of voids. Capillary forces resist void formation by pulling the particles together, increasing the friction to the point where the viscosity is unacceptably high.

As the powder to binder ratio increases the viscosity becomes essentially infinite at the critical solids loading. Small errors in formulating a feedstock cause moulding sensitivities because of rapid viscosity change in solids loading. Since the viscosity of a mixture changes most rapidly with composition near the critical loading, small errors are amplified into large viscosity shifts$^1$.

The exponent $n$ of the powder law index indicates the shear sensitivity. Smaller $n$ of the feedstock indicates a higher shear sensitivity and more pseudoplastic behavior of the feedstocks. Some molding defects such as jetting, are associated with small $n$, i. e., higher
shear sensitivity. Jetting occurs when the melt does not adhere to the walls as it emerges from the gate and enters the mold. Instead, the melt moves in a narrow ‘stream’ having approximately the width of the gate. Jetting is undesirable since it is the source of severe defects including weld lines and other imperfections in the final molded part. When $n = 0$, the no-slip condition at the wall is not valid and the material flows as a solid. Solid-phase jetting occurs when wall-slip takes place. Therefore, the value of $n$ can be used to predict the liquid-solid phase transition\(^{5}\). That considered, F55 had the best rheological behavior, and among the formulations is the one that should be processed. The other formulations do not have the necessary characteristics to injection moulding.

There were presented similar results of apparent viscosity versus shear stress in a former work\(^{6}\). It was verified three clear behavior regions in the graph. The behavior was typical of slip flow. The first portion of the apparent viscosity versus shear stress curve represented flow due to shear at lower shear stress. The apparent viscosity fall with increasing shear stress represented the behavior where a thin layer of liquid forms and the paste flowed as a plug. There was a clearly defined transitional region in the graph defined by a critical wall shear stress that can be exceeded during the extrusion or injection moulding of ceramic pastes, leading to a condition of slip flow.

It is essential that feedstocks present a steady front flow.

In the case of steady flow the pressure for a particular shear rate quickly reaches a steady value. The pressure-time of an unstable formulation shows the phenomenon of “oscillating flow” at high shear rates. Here the pressure oscillates widely during slip-stick flow through the die rather than showing a constant pressure trace. Similar observations have been made in unfilled polymers and attributed to slippage (non-zero velocity of the fluid at the solid-liquid interface\(^{7}\)) of the melt at the capillary wall\(^{8}\).
This phenomenon, which depends on both temperature and shear rate, is responsible for unsteady front flow observed during injection molding. In consequence, wall slip can be correlated with the presence of injection flaws. The fact that the extrudate emerged from the die at variable rates suggests that a similar effect would be in operation during injection molding. This kind of flow pattern could give rise to weld lines in the mouldings, which create planes of weakness.

Some of the results obtained in this work indicated the presence of wall slip at high shear rates. The pressure-time behavior of all tested formulation presented an oscillating flow at shear rates higher than 300 s\(^{-1}\), except F55. This behavior is one more reason that explains this one is the most suitable choice for injection molding.

These problems can be solved through some procedures. Firstly, there is the opportunity of a choice. In this case, F55 can be used among five formulations tested. Secondly, some changes in the components can be made to improve the characteristics of injection molding feedstocks like using powders with bimodal distribution or use another additives for injection molding.

5 Conclusions

The results of this work shown the pseudoplastic behavior of the feedstocks. It is clear that higher is the solid loading lower is the flow index behavior \(n\) value leading to slip flow phenomena that can cause molding defects. The temperature dependence of viscosity was not evidenced in the tested range. On this basis the formulation with 55% vol. powder loading showed the best rheological behavior.

Acknowledgements
Vivian A Krauss is grateful for the financial support provided by CNPq.
References


Table 1 – Characteristics of binders used in the present study

<table>
<thead>
<tr>
<th>Binder</th>
<th>Molecular Weight</th>
<th>Supplier</th>
<th>Pycnometer density (kg/m$^3$)</th>
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<tr>
<td>Stearic Acid (AE)</td>
<td>284</td>
<td>Vetec</td>
<td>940</td>
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<tr>
<td>Polyethylene glycol (PEG)</td>
<td>6000</td>
<td>Oxiteno</td>
<td>1220</td>
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<tr>
<td>Polyvinylbutyral (PVB)</td>
<td>50000 – 80000</td>
<td>Solutia Inc.</td>
<td>1120</td>
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<tr>
<td>Feedstocks</td>
<td>% by weight</td>
<td>Feedstock abbreviation</td>
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<tr>
<td>------------</td>
<td>-------------</td>
<td>------------------------</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Al₂O₃</td>
<td>PEG</td>
<td>PVB</td>
</tr>
<tr>
<td>Solids loading, vol. %</td>
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<tr>
<td>55</td>
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<td>59</td>
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Table 3 – Flow behavior index $n$

<table>
<thead>
<tr>
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<th>180 °C</th>
<th>185 °C</th>
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<tbody>
<tr>
<td>F55</td>
<td>0,37</td>
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<td>F56</td>
<td>0,27</td>
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<td>0,13</td>
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<td>F58</td>
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<td>*</td>
</tr>
<tr>
<td>F59</td>
<td>*</td>
<td>0,02</td>
<td>*</td>
</tr>
</tbody>
</table>

* $n$<0
Figure 1 – Scanning electron micrograph of alumina

Figure 2 – Particle size distribution of alumina

Figure 3 – Mixing behavior for different volumetric powder loadings

Figure 4 – Feedstocks densities

Figure 5 – Viscosity vs. shear rate graphs of different formulation: (a) F55; (b) F57 and (c) F59

Figure 6 – Feedstocks viscosity versus shear rate at 175 ºC
1 - Krauss, VA; Pires, EN; Klein, AN; Fredel, MC
2 - Krauss, VA; Pires, EN; Klein, AN; Fredel, MC
3 - Krauss, VA; Pires, EN; Klein, AN; Fredel, MC
4 - Krauss, VA; Pires, EN; Klein, AN; Fredel, MC
5 (a)- Krauss, VA; Pires, EN; Klein, AN; Fredel, MC
Viscosity (Pa.s) vs. Shear Rate (s$^{-1}$) at different temperatures:

- **175°C**
- **180°C**
- **185°C**

5 (b) - Krauss, VA; Pires, EN; Klein, AN; Fredel, MC
Viscosity (Pa.s) vs. Shear Rate (s\(^{-1}\))

- 175ºC
- 180ºC
- 185ºC

5 (c) - Krauss, VA; Pires, EN; Klein, AN; Fredel, MC
Viscosity (Pa.s) vs. Shear Rate (s$^{-1}$)

- F55
- F56
- F57
- F58
- F59

6 - Krauss, VA; Pires, EN; Klein, AN; Fredel, MC