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Spray Drying Technique as a method for improving Rheology of Alumina Feedstocks for Powder Injection Moulding

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In this experimental work the effect of agglomeration in the starting powder of alumina feedstocks was analysed. Two pre-treated powders: one pre-coated with SA and a spray dried powder were used for comparison with the as received powder. Alumina feedstock was prepared with 58 vol. %. of powder and a binder system based on high density polyethylene (HDPE), paraffin wax (PW) and stearic acid (SA). The mixing process was optimized by means of mixing torque measurement. Rheological behaviour of three feedstocks was analysed using capillary rheometry. All the feedstocks exhibited a pseudoplastic behaviour with $n < 1$ according to the Herschel-Buckley model. Feedstocks with spray dried powder showed the lowest viscosity and this could allow to incorporate higher ceramic loading decreasing shrinkage and increasing densities of sintered parts.

1. Introduction

Powder Injection Moulding (PIM) has come out as a cost effective near-net shape processing technique that permits manufacturing ceramic (Ceramic Injection Moulding, CIM) or metals (Metal Injection Moulding, MIM) parts, fundamentally. This technology offers a large number of advantages involving capabilities to produce successfully complex, small and thin parts with high production capacity and relatively high dimensional precision [1].

This technology has associated a series of stages. The good knowledge of each of them should permit to obtain free-defect moulding. Selections of suitable powder-binder systems and mixing phase have to fulfil different requirements. In this sense, feedstocks of PIM technology have to show good flowability, while higher solid loading to reduce shrinkage and to reach higher densities after sintering process, is necessary [2].

It is clear that binder system is one the most important key that provides rheological properties and determine moulding capabilities of feedstocks. Although raw powder also plays a deciding role in this sense [1,2,3], it has been less investigated the influence of powder morphology and particle size distribution. In theory, a nonspherical particle shape is detrimental to the viscosity of powder-binder mixtures. On the other hand, the use of wetting agents, which form thin coatings on the powder, improves rheological characteristics [1].

The aim of this work was to determine the influence of two pre-treatments of alumina powders. Spray drying method was developed to agglomerate small and irregular alumina particles obtaining batches of spherical shape particles. Likewise, SA coating was also used to improve dispersion of the powder in binder system and to reduce the natural reagglomeration tendency regarding to the powder untreated.

According with a previous work, the solid content considered was 58%, which is the highest loading in alumina mixtures containing multicomponent binders based on HDPE, PW and SA [3].

2. Experimental procedure

2.1. Materials

A commercially available Alumina powder, Alcoa CT 3000 SG, with an average particle size of 0.8 µm according to the supplier and a reported surface area of 7.5 5 m^2/g was used in this study as a raw material. The binder used was developed in a previous work and it was based on high density polyethylene (HDPE), paraffin wax (PW) and stearic acid (SA) [3]. Some physical properties of the binder components are provided in table 1. Densities were measured in a He Picnometer (Micromeritics Accupyc 1330, Norcross, GA). Thermal characterization was performed by differential scanning calorimetry (DSC) and thermogravimetrical analyses (TGA). DSC was performed in a Perkin-Elmer Pyris Diamond DSC at a heating rate of 10ºC/min. Thermogravimetrical analyses was carried out in a Perkin-Elmer TGA Pyris1, also at a heating rate of 10ºC/min.

Table 1. Characteristics of binder components.

Binder component	Density(g/cm^3)	Tm* (°C)	ΔH_m** (J/g)
HDPE	*0,96*	*129,1*	*100.5*
PW	*0,91*	*56,9*	*145.0*
SA	*1,01*	*73,7*	*169.5*

*Melting temperature.
**Melting enthalpy.

2.2. Processing

Powder treatment

Alumina powder was pre-treated in two different ways. The first one, labelled as SDP (spray drying powder), was performed in an installation Büchi Mini Spray Dryer B-191. An initial dispersion consisting in 150-200 g of demineralised water, 2 g of polyethylenglycol (PEG 9000) as a binder and 150-200 g of Al_2O_3 were used. Flow of compresed air was 600 l/h and entrance and exit temperatures were 215 and 135 °C respectively. The second was prepared by a previous surface treatment of the powder whit 4% SA, labelled as PCP (pre-coated powder). To coat the powder a high-performance dispersing instrument (Miccra, Müllheim, KT D-9) at 20,000 min^{-1} for 10 min was used. Particle size distribution was analysed with a Malvern Mastersizer 2000 analyser while powder morphology was observed in a LEO 1525 scanning electron microscope.

Mixing and rheological behaviour

Three feedstock formulations were prepared with a solid loading of 58 vol.%, which is the highest level of solid loading reported for Al_2O_3 mixtures [3,4]. The binder formulation was prepared by mixing HDPE and PW in a volume ratio of 50:46 respectively. The amount of SA was selected to be 4% according to different studies which establish that optimal amount of SA vary between 3 and 5 wt. % [3,4,5].

Subsequently, the mixtures powder-binder were processed in Haake Rheocord 252p mixer machine with a pair of roller rotor blades. The maximum capacity of the chamber is 69 cm^3. The equipment allows recording torque evolution with mixing time as a useful tool to evaluate feedstock homogeneity. According to thermal characterization, mixing temperature was chosen to be higher than melting point of HDPE and lower than decomposition temperature of low molecular weight components (PW and SA). In this sense, temperature control was set to be 155°C at 40 r.p.m. When the required mixing temperature was reached organic components were added. High molecular weight component were first added followed by low molecular specimens to avoid thermal degradation. Once the mixture was homogenized and temperature stabilized, alumina powder was loaded gradually. A maximum mixing time of 40 minutes was required for total homogenization in all the cases. Feedstocks were labelled according to alumina powder used as FARP (feedstock prepared with as received powder, FSDP (feedstock prepared with spray dried powder) and FPCP (feedstock prepared with SA precoated powder).

Feedstock rheology was studied using a ThermoHaake Rheocap S20 capillary rheometer at 155 °C with temperature control of ±1ºC over a range of shear stress rates from 100 to 10000 s^{-1}. A 1 mm diameter and 30 mm length die was used. In all the cases ten minutes were allowed to reach thermal equilibrium after charging the barrel.

3. Results and discussion

Morphology of spray dried and untreated particles are shown in figure 1. For as received alumina powder an irregular flatted particle shape is appreciated and a large number of agglomerates. In general, two kinds of sizes are observed: one corresponding to the real particle size according to the supplier and another, which can be associated to agglomerates that form as a consequence of the high surface energy of small alumina particles. In spray dried powder, scanning electron micrographs showed the presence of spherical morphology and a main type of particle size.

This fact can be confirmed by particle size distribution measurement of both powders (figure 2). In as received powder a bimodal distribution can be observed where 15% of primary particles are smaller than 1 µm while agglomerates of particles up to 100 µm represent about 85%. In contrast, spray dried powder exhibit a monomodal particle size distribution where 50% of particles are <5 µm in size.

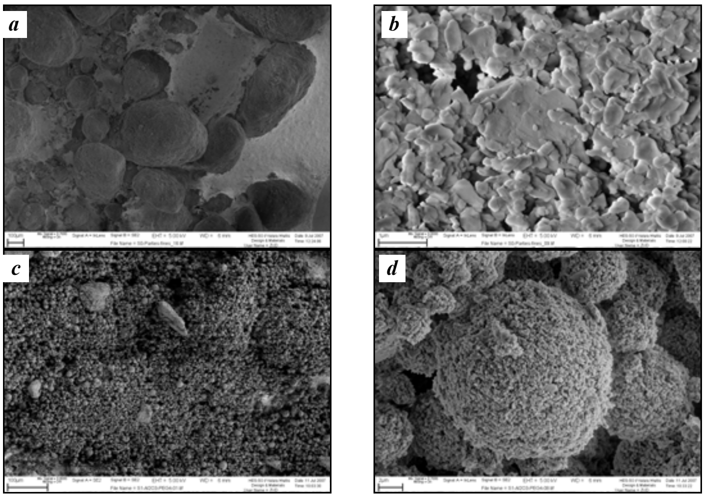

Figure 1. Scanning electron micrographs of (a), (b) untreated and (c), (d) spray dried alumina powder.

With regard to coated powder morphology of particles, this basically has not been modified in relation whit untreated powder. In this case, a bimodal distribution is also observed where some large agglomerates were broken into primary particles during dispersion process. Moreover several hard agglomerates were slightly reduced, in particular, primary particles <1 µm in size represent around 20% and agglomerates up to 60 represent about 85 %.

Two important stages in CIM process are sintering and debinding. In this sense the value of the slope of the cumulative frequency curve (S_w) is related to the amplitude of size distribution and helps to predict moulding, debinding and sintering behaviour.

$$S_w = \frac{2.56}{\log_{10}\left(D90/D10\right)} \tag{3.1}$$

Regarding this value, powders with high S_w have narrow particle size distribution and are not recommended for CIM process. In contrast, powders with wide particle size distribution improve moulding and sintering, but binder removal is slower. In this sense, the three kinds of powders that were prepared are suitable for the process since it is held that powders with S_w close to 2 are easy to mould [1,2].

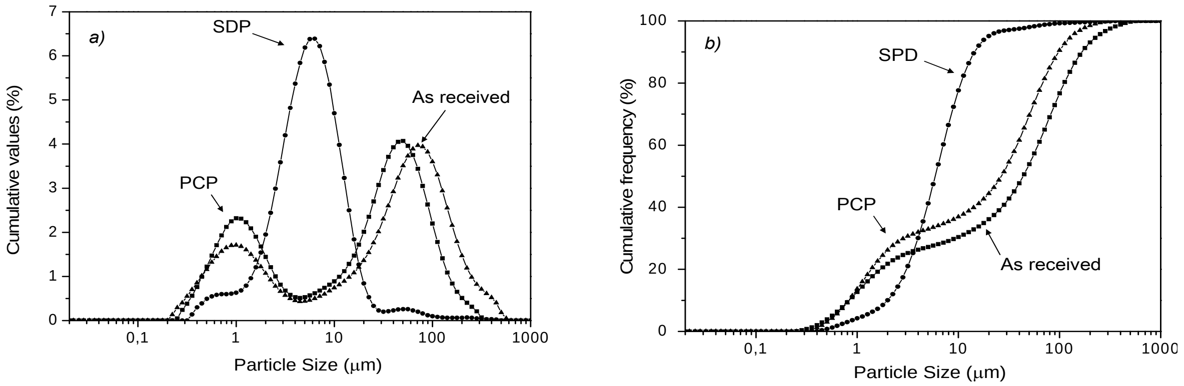

Figure 2. Particle size distribution of powder as-recived, spray dried (SDP) and treated whit 4% stearic acid (PCP).

Table 2. Particle size distribution parameters of powder as-recived, SDP and (PCP).

Powder	D10 (µm)	D50 (µm)	D90 (µm)	S_w
As received	0,8	43,7	166,1	1.1
SDP	2,0	5,9	14,4	3,0
PCP	0,8	26,6	97,9	1.2

Mixing and rheology

The progress of the mixing can be followed in the torque rheometer by monitoring torque evolution with mixing time. The mixing torque, which is proportional to the shear stress of the blend, is an indication of the work required to mix the components.

In Figure 3 torque evolution with mixing time has been plotted. Firstly torque values shows a rapid rise when the binder component are added followed by further increase corresponding to alumina powder additions. The irregular peaks indicate the melting and consolidation steps. Afterward, the torque reaches an almost constant value known as a steady state torque (τ_{ss}) which indicates that the mixture is homogeneous. For all the powder-binder system mixing time required to reach this steady state is not higher than 40 minutes.

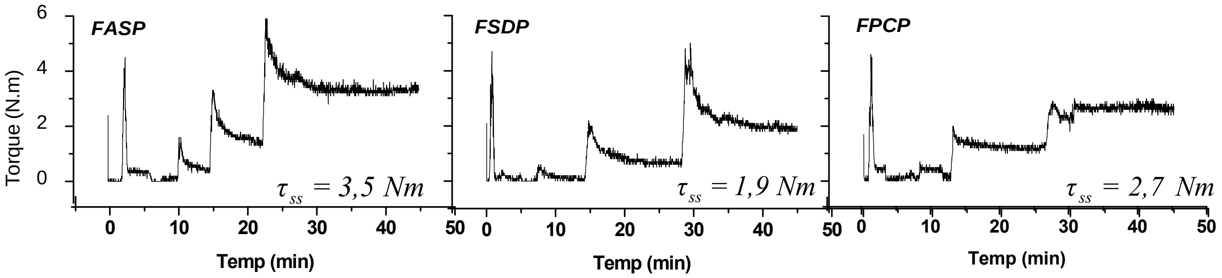

Figure 3. Mixing behaviour for feedstock prepared with as-received powder (FASP), spray dried powder (FSDP) and pre-coated powder (FPCP)

Varying powder treatment showed variation in steady state torque value indicating differences in viscosity of mixtures [1,3,6]. It was observed that FSDP exhibited the lowest τ_{ss} and the highest corresponded to FARP. Therefore, and in principle, it allows predicting rheological behaviour.

Figure 4 shows viscosity variation with shear rate at 150ºC for the three feedstocks. The suspensions exhibit a viscosity order of $\eta_{FSDP} < \eta_{FPCP} < \eta_{FARP}$. Viscosity is related with interparticle friction, this effect is highlighted by irregular shape and small particle size of alumina powder. As expected, in the FSDP spherical shape of particles improve the flow features showing the lowest viscosity [1,2]. On the other hand, the addition of a lubricant such as SA improves powder-binder interaction enhancing powder dispersion in the binder during mixing. A better adhesion between powder and binder causes a reduction of flow viscosity of the mixture. By comparing feedstocks FARP and FPCP it can be appreciated that

precoating the powder with SA reduce flow viscosity and this can be attributed to the better dispersion and powder-binder interaction before mentioned. Therefore, it is not only the SA coating but also the dispersion method which determines decrease in viscosities values.
During ceramic injection moulding (CIM) it is known that flow into the mould cavity requires viscosity values less than 1000 Pa.s between 100-1000 s^{-1} [2,7]. In this sense all the mixtures prepared are suitable for CIM process.

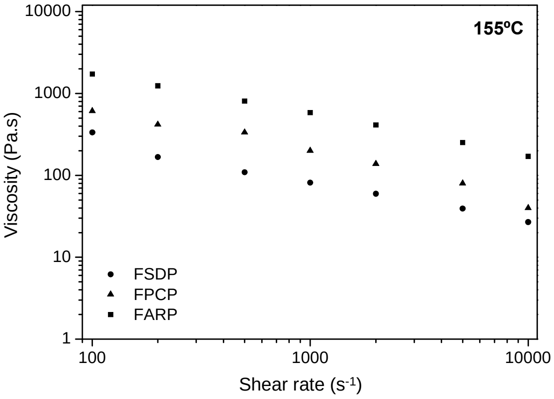

Figure 4. Rheological behaviour of feedstocks processed whit a solid loading of 58% using the different powders: as-received (FASP), spray dried (FSDP) and pre-coated (FPCP)

In figure 4 it can also be appreciated that in all the cases viscosity decreases as shear rate increase according to a pseudoplastic behaviour. This flow behaviour is desirable in order to make easy mould filling and avoid moulding defects. However, high pseudoplastic character can also produce anomalous mould filling like the phenomenon known as jetting [8]. A model commonly used for ceramic feedstock, named Herschel-Buckley model [9] was used to describe and fitting flow curves. This model shows the dependence of the shear stress on the shear rate:

$$\tau = \tau_0 + K \dot{\gamma}^n \qquad (3.2)$$

Where τ is the applied stress, $\dot{\gamma}$ is the shear rate, τ_0 is the yield stress, K is the consistency coefficient and n is the flow behaviour index. This index indicates the shear sensitivity. According whit this model, lower values of n correspond to a greater pseudoplastic character of feedstocks. Figure 5 shows the flow curves for each powder-binder system and its corresponding fitting based on this rheological model. The results indicate that τ versus $\dot{\gamma}$ plots, show a power relationship with correlation coefficients greater than 0.97 (table 3) for all the mixtures, indicating the goodness of fit.

Table 3. Yield stress, flow behaviour index and correlation coefficients accord whit Herschel-Buckley model.

Feedstock	τ_0 (10^{13} [KPa])	n	R
FARP	3.02	0.47	0.99
FSDP	3.29	0.51	0.99
FPCP	4.70	0.35	0.97

The yield stress can be considered as the minimum force required to induce a relative movement between particle assemblies. In this sense all powder-binder system exhibited a low value of τ_0, indicating the good flowability of feedstocks. In fact, other models like Ostwald de Wale [10, 11] power law have assumed that $\tau_0 << \tau$ and its simplifies equation 3.2 to obtain a single powder relation. With regard to n values all feedstocks prepared showed a pseidoplastic behaviour.

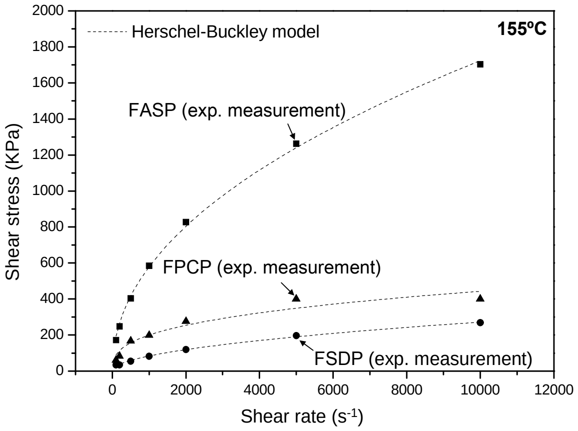

Figure 5. Flow curves of feedstocks whit as-received powder (FARP), spray dried powder (FSDP) and pre-coated powder (FPCP). Dash lines correspond to different fittings based on Herschel-Buckley model.

4. Conclusions

Rheological behaviour of three feedstocks formulations with different surface powder treatment was studied. Spray dried process was able to break all hard particle agglomerates conducting to a monomodal particle size distribution with spherical morphology. In contrast, coating alumina powder with SA did not produce important morphology changes. Bimodal particle size distribution of as received powder was also observed in coated powder. However, when the powder is previously treated with SA in a high-performance dispersing instrument, some big agglomerates are disintegrated into primary particles.

Feedstock prepared with these three kinds of powders exhibited a pseudoplastic behaviour with suitable viscosity values in the shear rate range recommended for CIM. Besides treating the powder is effective to improve flow behaviour of mixtures showing lower viscosities in comparison with untreated powder. This could allow to increase powder loading in alumina feedstocks permitting higher densities, lower shrinkages and therefore better properties of final parts.

Acknowledgements

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