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PIM of non-conventional particles

F.M. Barreiros [a,b], M.T. Vieira [b,*]

[a] Departamento de Engenharia Mecânica, ESTG, IPLeiria, Morro do Lena, Alto Vieiro, Apartado 4163, 2411-901 Leiria, Portugal
[b] ICEMS (Grupo de Materiais, DEM/FCTUC), Pinhal de Marrocos, Polo II, 3030-201 Coimbra, Portugal

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Abstract

The use of particles with shape, mean particle size, particle size distribution and stability traditionally considered inappropriate for powder injection moulding (PIM) requires the use of feedstocks with high quality. A method that leads to an accurate value of critical powder volume concentration (CPVC) was developed. The present study, based on torque rheometry, led to the evaluation of optimal feedstock from selecting a raw material powder with non-conventional characteristics for PIM (lamellar morphology, $d_{50} = 10.5$ μm, and $0.1 \leq d \leq 174.8$ μm). The optimal value of solids loading was calculated as the highest value resulted from the intersections of the adjustment of linear functions of the mixing torque versus powder content curves. The final products of this feedstock presented, after sintering, high density and flexural strength values.

Keywords: A. Mixing; A. Injection moulding; Non-conventional powder; Feedstock

1. Introduction

In the ceramic injection moulding process (CIM) a ceramic powder is mixed with a binder to obtain a homogeneous feedstock with characteristics that allow the injection of a product with a predefined form. After the removal of the binder, the powders are consolidated by sintering [1–3]. The optimal ceramic content in the ceramic/binder feedstock and a suitable mixing technique are the key to achieve a homogeneous feedstock with the best properties after injection, debinding and sintering steps [1–5].

The use of powder injection moulding (PIM) has been almost entirely limited to the production of technical components for applications that require high performance and dimensional precision, resorting to synthetic raw materials with controlled morphological and particle sizing characteristics. In fact, the manufacturing using natural raw materials or even wastes is almost non-existent, and only recently their utilisation has been researched [6–8].

This study analysed the efficiency of conventional processes used for powder content optimisation in feedstocks, resorting to particles with characteristics unsuitable for PIM technology. In addition, a more accurate analysis of torque rheometry tests was proposed. An inorganic natural powder resulting from cutting and polishing operations of dimensional stones was selected, since its characteristics obey to the referred requirements: lamellar morphology, large particle size, wide particle size distribution and, inherently, low packing rate.

Notwithstanding, this powder when conformed by uniaxial pressing followed by sintering produced a ceramic with good structural properties [9]. In addition, a previous morphological, chemical and mineralogical identification of different powder disposal batches guaranteed its reproducibility. Hence, all the inappropriate characteristics occurring simultaneously may be the basis of studies that might put in evidence the possibility to use the PIM technology for an enlarged range of raw materials [10–12].

As referred, the main objective of this study consisted in demonstrating the possibility to use powders with non-conventional characteristics in the manufacturing of ceramics components by PIM. The use of these powders

* Corresponding author. Tel.: +351 239790700; fax: +351 239790701.
E-mail address: teresa.vieira@dem.uc.pt (M.T. Vieira).

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is a challenge due to their almost completely different characteristics from those considered suitable for PIM [1,2]. However, the use of powders with non-conventional characteristics requires the use of techniques and methodologies more appropriate for powder content and mixing process optimisation.

2. Experimental

2.1. Materials

In this study, an inorganic natural powder with a chemical composition of SiO_2 = 54%, Al_2O_3 = 24%, and other oxides ≈20% was selected. This powder has all the ''deviations'' that would seem to be prohibitive for a PIM process. The powder surface area was measured by the BET technique (*Micromeritics* ASAP 2000) and the true density was measured by helium picnometry (*Micromeritics* Accupyc 1330). The tap density was also measured by a manual vibration method. The mineralogical composition was evaluated by X-ray diffraction (*Philips* model Xpert), at room and sintering temperatures. The shape and the particle size distribution of that powder were evaluated by scanning electron microscopy (*JEOL*, JSM-5310) and by laser diffraction spectrometry (*Coulter* LS 130), respectively.

The binder system was a commercial polymeric mixture (Hostamont TP EK 583 manufactured by *Höechst*) based on polyolefin waxes with a density of 1100 kg m^{-3}, a Vicat point at ≈115 °C and a viscosity of 6 Pa s (150 °C) with a high solubility in water (≈50%).

2.2. Powder content and mixing process optimisation

The critical powder volume concentration (CPVC) values of the powder were estimated by torque rheometry by monitoring the torque variation during their mixing with the commercial binder using the *Brabender* Plastograph mixer. The measuring principle of this technique is based on the resistance that material opposes to the rotation of the blades. In the methodology suggested in this work, after the temperature stabilisation, the speed rotation of the measuring heads was selected and the system was switched on. The speed rotation adopted was 60 rpm, which was based on previous tests and on the observation that this value corresponded to the best commitment between the time to stabilise the mixing torque and the effort to obtain an efficient mixture. The inorganic powders were entered into the mixing chamber to achieve a homogeneous temperature distribution. Then, the binder was added in the desired proportion, i.e., to have a powder content in the mixture differing only 1% between several tests. Each fraction of binder was pressed down manually using a piston and a load of 50 N. This load was removed after approximately 5 min. In every case the mixing time was 20 min. Tests with powder concentrations varying from 50 to 64% at pre-programmed temperatures of 140 °C (corresponding to critical alterations in the binder, but inferior to its degradation temperature) were performed.

Two feedstocks (**A** and **B**) were prepared using a continuous process technique of mixing (*Farrel* Continuous Mixer CP 23). The powder and the binder previously weighed (±0.1 g) and mechanically premixed (*T. K. Fielder* Limited mixer, model HMA 65) were entered in the feeding zone of the continuous mixer. Then, the pre-mixture was transported into a double screw mixer, where it was melted. Finally, the mixture was extruded in a single screw extruder. The double screw mixer temperature was 140 °C and the double screw rotation speed 1000 rpm. The barrel temperatures profile in the extrusion was constant, 150 ± 10 °C, and the screw rotation speed was 60 rpm. After the extrusion, the feedstocks were granulated.

2.3. Rheological characterisation of the mixtures

In this study, the method developed for evaluating the mixture viscosity was similar to that implemented in the capillary rheometer. However, instead of having a piston that forced the mixture to pass through a capillary tube by the action of an external pressure, it was the extruder screw that forced the mixture to cross the capillary tube. The mixture was extruded at a constant rotation speed and the pressure drop was measured before and after its passage in the capillary tube.

The tests of capillary rheometry were performed in a laboratorial single screw extruder (*Brabender* Stand Alone Extruder E 19/25 D) to which an extruder head was adapted. Capillary dies and a pressure transducer (*Dynisco*, model Dyna-4-70-15) located adjacently to the entrance of the capillary dies were inserted in the extruder head, allowing the measurement of the pressure drop along each one of the capillaries set. A set of three dies with constant diameter (2 mm) and lengths of 20, 30 and 40 mm was used to enable the Bagley correction [13]. The extruder nozzle temperature and the dies entrance temperature were fixed at 140 °C. Each mixture was tested using the set of three dies and for each mixture tests using at least four screw rotation speeds (30, 40, 50 and 60 rpm) were performed to produce four different flows. Several tests were done for each set die/rotation speed to obtain similar weight values of the extruded material (at least six tests).

2.4. Processing of the mixtures

Parallelepiped bars (92.40 mm × 5.80 mm × 3.80 mm) were conformed by injection moulding (*Arburg* model All Rounder 220/150 E) using both feedstocks prepared. The nozzle temperature was 140 °C and the mould temperature 40 °C.

The debinding was performed in dynamic air using the debinding cycle as follows: 0.4 °C min^{-1} up to 150 °C, followed by 0.2 °C min^{-1} up to 190 °C and, finally,

0.3 °C min^{-1} up to 600 °C, and cooling in the furnace to room temperature.

After debinding, all the samples were sintered in static air: heating to 600 °C at 10 °C min^{-1} and to 1170 °C at 1 °C min^{-1}; the holding time at maximum temperature was 30 min, followed by cooling in the furnace to room temperature.

2.5. Physical and mechanical properties

The true densities of some sintered samples were measured in a helium picnometer (*Micromeritics* Accupyc 1330) and the apparent densities were measured by water immersion using a sealant (Archimedes method).

The sintered parallelepiped bars were used for mechanical tests (flexural strength). A *Gabbrieli* CRAB 424 testing machine was used to test the sintered bars, in order to estimate the quality of PIM products processed with both feedstocks prepared. Finally, the dimensional variations of parallelepiped bars before and after sintering were also measured, in order to estimate the shrinkage value.

3. Results and discussion

3.1. Powder characterisation

The surface area, the true density and the tap density related to theoretical density of the powder were 7.3×10^3 m^2 kg^{-1}, 2890 kg m^{-3} and 34.5%, respectively. The main constituents of the inorganic powder at room temperature were chlorite, mica and quartz. At sintering temperature (1170 °C) the main constituents were mullite, quartz, hematite, hercynite and glassy phase. The shape and the particle size distribution of that powder are shown in Figs. 1 and 2, respectively. The powder has lamellar particles, shows a wide particle size distribution (0.1–174.8 μm) and a mean particle diameter (d_{50}) of 10.5 μm.

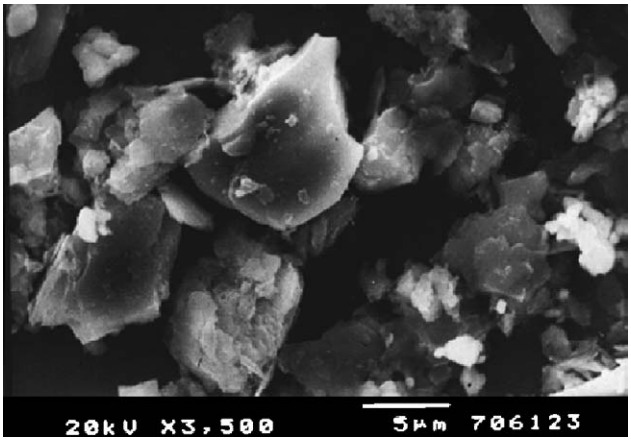

Fig. 1. Particle morphology of inorganic powder (SEM).

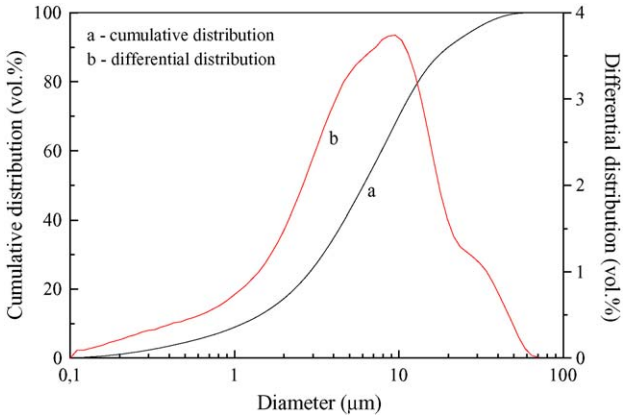

Fig. 2. Particle size distribution of inorganic powder.

3.2. Preparation and characterisation of the feedstocks

3.2.1. Optimisation of the powder content

Concerning the mixing torque as a function of mixing time (Fig. 3(a)), two different behaviours function of the powder concentration in the feedstock can be reported:

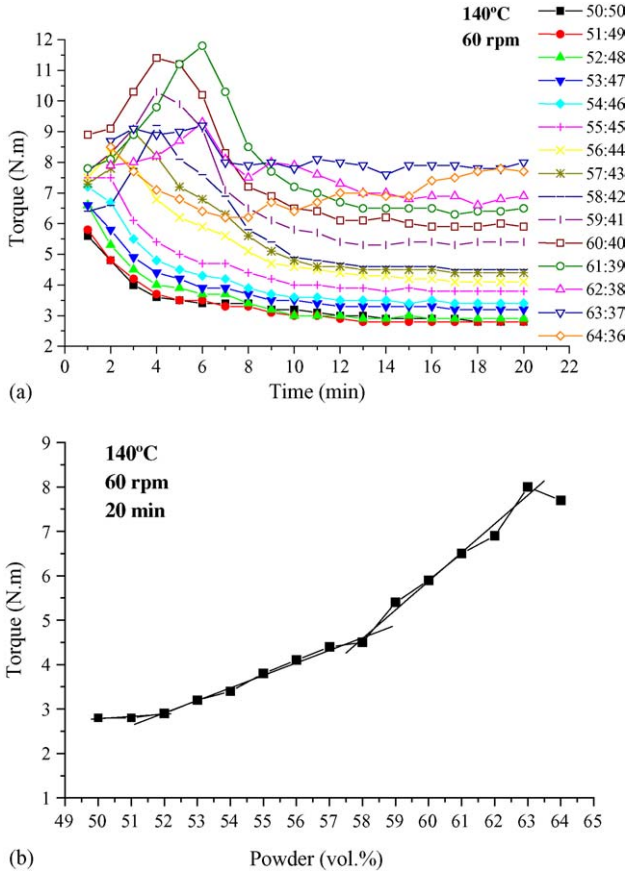

Fig. 3. (a) Mixing torque as a function of mixing time at 60 rpm and 140 °C, where **A**:**B** ratio means: **A**, powder (vol.%) and **B**, binder (vol.%); (b) Mixing torque as a function of powder concentration.

I. Fast decrease of the mixing torque (6–10 min) followed by the establishment of a steady state;
II. Maintenance or increase of the mixing torque, followed by a decrease in the first minutes of the test, reaching the steady state with a constant value after approximately 12–13 min.

The maximum powder concentration in the mixture may be related to the transition between the above two types of rheological behaviours. In fact, there is a significant difference in the shape of the curves. Therefore, a simple analysis of the mixing torque as a function of mixing time curves may allow an evaluation of the critical powder concentration in the mixture as well as of the optimal powder content. Thus, the analysis of the results permits to conclude that the most appropriate powder concentration in the mixtures is 53% (maximum value at which there is a continuous decrease of the mixing torque as a function of mixing time).

However, the method suggested is based, essentially, on the higher or smaller difficulty of mixing the inorganic powder with the binder before reaching a steady state. It is after reaching a steady state that the rheological characteristics of the feedstock to be processed should be compared. Thus, a curve representing the variation of the applied torque with the solids concentration after the establishment of the steady state ($t \cong 20$ min) is defined in this study. The relationship between the mixing torque applied to the different feedstocks is shown in Fig. 3(b).

According to Fig. 3 (b), concerning the mixing torque variation with the powder concentration, four regimes can be considered. In the range from 50 to 52% of solids loading the torque value is practically constant, after which it gradually increases up to 57–58%. For higher values, there is a significant increase of the mixing torque with each successive increase in the powder concentration, reaching a maximum value at 63% of solids. When the solids loading reaches 64% there is a decrease of the torque value, reflecting an excessive content of solids. Thus, both concentration values where there are disruptions in the curve of torque versus solids loading (52 and 58%) can be considered as CPVC values. However, it is worth noting that the torque variation observed for solids loading higher than 58% is almost three times that observed for 52%. In fact, at the end of the first regime, the torque increased from 2.9 to 3.2 N m, i.e., 0.3 N m, whereas from 58 to 59% the increase is 0.9 N m. In addition, even for concentrations higher than 58% the mixing torque is stable and a steady state is reached relatively fast (see Fig. 3(a)). Therefore, the feedstock with 58% of solids seems to be the best value for the CPVC. Nevertheless, as the best indicator of the optimal concentration is the feedstock behaviour after sintering, concentration values near the disruption points of rheological curves were selected for preparing two feedstocks to be processed by PIM (**A** and **B**).

3.2.2. Feedstocks preparation

Using the continuous mixing technique, and according to the results obtained in the powder content optimisation experiments, two feedstocks were prepared (**A** and **B**). These feedstocks were evaluated as to their homogeneity and powder content by monitoring their weight loss after debinding at a temperature of 400 °C during 3 h. The temperature of 400 °C was selected accordingly to the weight loss of inorganic powder during the heat treatments at higher temperatures. The results of the binder loss (vol.%) as well as the corresponding standard deviations and their respective solids loading are summarised in Table 1.

Table 1
Binder loss fraction average and solids fraction average (vol.%)

Feedstock	Binder loss $\pm \sigma$ (vol.%)	Solids loading $\pm \sigma$ (vol.%)
A	47.24 ± 0.10	52.76 ± 0.10
B	40.68 ± 0.12	59.32 ± 0.11

A low value of the standard deviation associated with the calculation of the average weight loss tests indicates a high homogeneity for the feedstocks studied [14]. The results of the weight loss tests are representative of homogeneous feedstocks, however, the feedstocks are not exactly formulated since they present powder concentrations differing from the theoretical ones. This was due to the industrial mixing method adopted. According the results of weight loss, the powder content of mixtures **A** and **B** are approximately 53 and 59 vol.%.

The feedstock homogeneity was also evaluated by torque rheometry; after 8 min of mixing the feedstocks reached the steady state. This behaviour reflects the existence of a significant degree of homogeneity in the feedstocks [1].

3.2.3. Rheological behaviour

During powder injection moulding the shear rate usually varies between 10^2 and $10^4/10^5$ s^{-1} and, in this range, the maximum value of viscosity suitable to feedstocks at the moulding temperature is 1000 Pa s [2,3,15]. Moreover, almost all the PIM feedstocks exhibit a pseudoplastic behaviour, i.e., their viscosity decreases with the increase of shear rate [15].

To estimate the Bagley end-correction (e), the pressure drop (ΔP) function of die length/die diameter (l/d) for each extruder speed was plotted. For a fixed l/d the values of ΔP were obtained and the corrected shear stress values at the capillary wall for each throughput computed [$\tau_w = \Delta P/2(l/r + e)$]. The apparent shear rate for each throughput was also computed ($\dot{\gamma}_{app} = 4Q/\pi r^3 \rho$, where Q is the gravimetric throughput rate and ρ the melt density). The non-Newtonian flow behaviour index (n), which is the slope of the straight line plotting log shear stress function of log apparent shear rate, was also computed. By application of the Rabinowitsch

Table 2
Rheological characteristics of feedstocks

Feedstock	n (Pa s)	$n-1$ (Pa s^2)	η ($\dot{\gamma}_w = 100\,s^{-1}$) (Pa s)	$1/\eta$ ($\dot{\gamma}_w = 100\,s^{-1}$) ($Pa^{-1}\,s^{-1}$)
A	0.43	−0.57	364.3	2.7×10^{-3}
B	0.30	−0.70	1033.5	9.7×10^{-4}

Table 3
Apparent and true densities, and close porosity of bars after sintering

Feedstock	ρ_{apps} (kg m^{-3})	ρ_s (kg m^{-3})	P_{total} * (%)
A	2400	2570	7.7
B	2550	2570	1.9
Conventional [17]	2560	2600	1.5

* Theoretical density of sintered powder = 2600 kg m^{-3}.

correction, the true shear rates at the capillary wall were calculated [$\dot{\gamma}_w = \dot{\gamma}_{app}(3n + 1/4n)$]. Finally, the viscosity values for each throughput were computed ($\eta = \tau_w/\dot{\gamma}_w$) [13].

Table 2 shows some rheological characteristics of the prepared feedstocks. The viscosity and the fluidity values were extrapolated to a shear rate of 100 s^{-1}, since one of the conditions imposed to the feedstocks to be used in the PIM process is that they must have a viscosity lower than 1000 Pa s at a shear rate of that order of magnitude [2,3,15]. The non-Newtonian flow behaviour index values reveal that all the formulations have a pseudoplastic behaviour ($n < 1$), which means that viscosity decreases when shear rate increases. This behaviour is very well expressed in Fig. 4 that represents the variation of log η as a function of log $\dot{\gamma}_w$, with correlation coefficients higher than 0.999 for the tested feedstocks. From Fig. 4, it is also possible to conclude that the feedstocks present identical rheological behaviour in different ranges of viscosity. As expected, feedstock **B**, which contains the highest powder content, presents the highest value of viscosity. This feedstock is on the threshold to be used in the PIM process, since it has a viscosity of 1033.5 Pa s at a shear rate of 100 s^{-1}. This is quite interesting having in mind that this feedstock has a powder content slightly superior to that predicted for CPVC. In contrast, the mixture **A** has a low viscosity for the same shear rate (364.3 Pa s). Thus, the feedstock **A** has an excessive amount of binder, which may explain the appearance of some defects after sintering. However, both formulations satisfy the pseudoplasticity criterion, thus they are both potentially appropriate to injection moulding [15].

3.3. Properties of final product

3.3.1. Density and porosity

Table 3 summarises the values of apparent (ρ_{apps}) and true (ρ_s) densities and the porosity content (P_{total}, relationship between apparent density and theoretical density of sintered powder). The feedstock **B** originated products with higher apparent density and lower porosity value than feedstock **A**. The densification of the products resulting from the feedstock **B** was 98.1%, revealing a good performance for PIM. In fact, the bars moulded with this feedstock only presented an irregular surface finishing that could be imputed to the phase transformations of powder with temperature [16]. On the contrary, the bars resulting from the injection of feedstock **A** had visible defects after debinding and sintering. The density and porosity values were compared with that of conventional shape-forming process, uniaxial pressing and sintering (Table 3) [17]. As it can be observed, both processes give rise to final products with high densification (>98%).

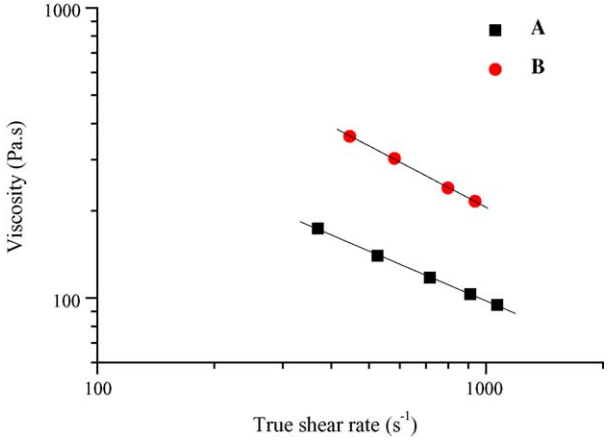

Fig. 4. Viscosity of the feedstocks.

3.3.2. Flexural strength and shrinkage

To evaluate the performance of the PIM feedstocks, the flexural strength (σ_0) and the Weibull modulus (m) of the sintered bars was also performed (Table 4). In addition, the dimensional variations were also evaluated to estimate the shrinkage in length (l), width (w) and thickness (t) (Table 4). These characteristics were also compared with that of conventional shape-forming process (Table 4) [17].

The increase of the powder content originated an increase of the mechanical properties (σ_0 = 93 MPa), which are similar to conventional shape-forming process (σ_0 = 92 MPa).

Concerning the dimensional variations, the increase of the powder content induced a sharper decrease in shrinkage of width and thickness. The shrinkage along these dimensions is identical and higher than the shrinkage measured for length, especially for feedstock with high binder content. Comparing the results with those observed for conventional shape-forming process, the dimensional anisotropy is less pronounced. In spite of orientation of particles along the flow direction during the moulding process could contribute for an anisotropic shrinkage in sintering [17].

Table 4
Flexural strength, Weibull modulus and dimensional variations of bars after sintering

Feedstock	σ_0 (MPa)	m	$\Delta l/l \pm \sigma$ (%)	$\Delta w/w \pm \sigma$ (%)	$\Delta t/t \pm \sigma$ (%)
A	68	6	12.88 ± 0.47	13.90 ± 0.76	13.84 ± 0.67
B	93	10	12.42 ± 0.35	13.27 ± 0.57	13.10 ± 0.27
Conventional [17]	92	25	10.2 ± 0.1	10.2 ± 0.2	15.8 ± 0.9

4. Conclusions

The present study demonstrated that it is possible to use PIM feedstocks from raw materials with particle characteristics dissimilar to the conventional ones. However, an accurate CPVC value needs to be calculated. Different methods have been developed, but they propose variable contents for the composition of the feedstocks. This study proposed the adjustment of the mixing torque versus powder content using three different linear functions to which correspond two different intersection points. The ambiguity between the minimum and the maximum powder content for optimised feedstocks was overcome by comparing the quality and mechanical properties of final products that were injected using both two limit feedstocks. The best quality was achieved with the highest value of powder content studied. This methodology should be used for raw materials that present non-conventional characteristics.

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References

[1] R.M. German, Powder Injection Molding, Metal Powder Industries Federation, Princeton, USA, 1990.
[2] R.M. German, A. Bose, Injection Molding of Metals and Ceramics, Metal Powder Industries Federation, Princeton, USA, 1997.
[3] B.C. Mutsuddy, R.G. Ford, Ceramic Injection Molding, Chapman and Hall, UK, 1995.
[4] S.T.P. Lin, R.M. German, The influence of powder loading and binder additive on the properties of alumina injection-moulding blends, J. Mater. Sci. 29 (1994) 5367–5373.
[5] R.E.F.Q. Nogueira, D.T. Gawne, M.J. Edirisinghe, Fabrication of engineering ceramics by injection moulding a suspension with optimum powder properties. Part I. Processing and microstructure, J. Mater. Sci. 28 (1993) 4167–4174.
[6] U. Haupt, Injection molding of porcelain, Ceram. Eng. Sci. Proc. 17 (1) (1996) 99–101.
[7] I. Agote, A. Odriozola, M. Gutierrez, A. Santamaría, J. Quintanilla, P. Coupelle, J. Soares, A rheological study of porcelain feedstock for injection moulding, Interceramics 49 (6) (2000) 428–436.
[8] I. Agote, A. Odriozola, M. Gutierrez, A. Santamaría, J. Quintanilla, P. Coupelle, J. Soares, Rheological study of waste porcelain feedstocks for injection moulding, J. Europ. Ceram. Soc. 21 (2001) 2843–2853.
[9] M.T. Vieira, L. Catarino, M. Oliveira, J. Sousa, J.M. Torralba, L.E.G. Cambronero, F.L. González-Mesones, A. Victoria, Optimization of the sintering process of raw material wastes, J. Mater. Proc. Tech. 92/93 (1999) 97–101.
[10] F.M. Barreiros, M.T. Vieira, R.A. Terpstra, Performing new techniques for optimise ceramic:binder mixtures for CIM, in: Proceedings of 1st International Conference on Advanced Materials Processing, 2000, pp. 113–119.
[11] F.M. Barreiros, M.T. Vieira, R.A. Terpstra, Optimising ceramic feedstock to injection moulding, Key Eng. Mater. 206–213 (2002) 281–284.
[12] F.M. Barreiros, M.T. Vieira, Powder injection moulding to recover slate wastes, Key Eng. Mater. 230–232 (2002) 247–250.
[13] E.A. Leach, H.G. Karian, Obtain viscosity data from laboratory extruder with capillary dies, Plastics Eng. 5 (1982) 69–71.
[14] R. Raman, W. Slike III, R.M. German, Experimental evaluation of the mixing process for the preparation of feedstock for powder injection molding, Ceram. Eng. Sci. Proc. 14 (11-12) (1993) 166–186.
[15] M.J. Edirisinghe, J.R.G. Evans, Properties of ceramic injection moulding formulations. Part 1. Melt Rheology, J. Mater. Sci. 22 (1987) 269–277.
[16] F.M. Barreiros, M.T. Vieira, Structural phase evolution with temperature of non-conventional particles in PIM, submitted for publication.
[17] M.T. Vieira, F.M. Barreiros, L. Catarino, Recovering inorganic wastes, J. Mater. Proc. Tech. 143 (2003) 454–457.