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Production of alumina parts by powder injection molding with a binder system based on high density polyethylene

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Abstract

In this experimental work, injection molding of alumina parts was performed with a developed binder system based on high density polyethylene (HDPE), paraffin wax (PW) and stearic acid. Firstly, the optimum binder composition was determined by torque measurements and rheology. Alumina feedstocks with powder loadings between 50 and 60% in volume were prepared with the developed binder system. A suitable formulation for powder injection molding was chosen based on torque measurements, rheological behaviour and homogeneity of feedstocks. All the feedstocks studied exhibited a pseudoplastic behaviour with flow behaviour index $n < 1$. Feedstock with 58 vol.% solid loading exhibited the most suitable behaviour for ceramic injection molding and was chosen to perform the complete process. Debinding cycle was designed based on thermogravimetrical analysis and differential scanning calorimetry. The best results were found using solvent debinding followed by thermal debinding. Final parts had densities close to 99% after sintering at 1600 °C during 2 h.

Keywords: Injection molding; Al_2O_3; Polyethylene; Binders

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1. Introduction

Powder injection molding (PIM) is a cost effective technique in high volume production of small, complex, precision parts.[1] The process is a combination of conventional powder technology and plastic injection molding. The technology is commonly termed as metal injection molding (MIM) or ceramic injection molding (CIM), depending on whether metal or ceramic powder is used.

The process includes basically four steps: mixing, molding, debinding and sintering. These steps are dependent upon the types of binder used.[2] Successful production of parts by PIM is closely related to the binder system utilized. The role of the binder is to serve as a temporary or transient phase to impart flowability and moldability to the powder mixture. This will enable the shaping of the feedstock to the desired shape during injection molding.[3] An ideal binder system for CIM must have superior attributes: flow characteristics, interaction with powder, debinding and manufacturing. For example, the binder must have low viscosity at the molding temperature and rapid viscosity change during cooling, it must also have low contact angle and adhere to the powder during molding. During debinding shape of pieces must be hold and the binder has to be full decomposed before sintering with low ash content. For manufacturing the binder must be inexpensive and environmental friendly.[4]

The binder is usually designed as multi-component system. There is a backbone component, usually a thermoplastic that supports and maintains the shape of the part during all phases prior to the later stages of debinding. The second component, being commonly a wax that improves the flowability of the mixture and can be removed in early stages of debinding leaving open pores that allow the gaseous products of the remaining polymer to diffuse out of the structure.[3] Also additives as surfactant serving as a bridge between binder and polymer can be added.

Binder system for injection molding of alumina can be grouped according to the major component used: paraffin wax (PW),[5] polyethylene glycol (PEG),[6] ethylene-vinyl acetate copolymer (EVA),[7] polystyrene (PS),[8] polypropylene

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(PP),[9] low density polyethylene (LDPE),[10] polyoxymethylene (POM)[11] and agarose.[12] Systems based on waxes often exhibit binder–powder separation, agglomeration, poor green strength and there is higher risk for distortion during debinding.[13]

High density polyethylene (HDPE) is a polymer commonly used for plastic and powder injection molding. In particular we have used binder based on HDPE and paraffin wax as a second component for the manufacturing of M2 high speed steels[14] and bronze parts.[15] The main advantages we have found using this binder system were good homogeneity of blends, suitable rheological features allowing easy moldability, and finally, and due to the different melting temperature of both binder component ensure that when one component has melted, the remaining component act as backbone retaining the shape of the parts. Despite these advantages, in the reviewed literature this polymer has not been previously reported for alumina injection molding. There are some studies focused on low density and linear low density polyethylene based binders.[10,16,17] These studies are concentrated on the rheological behaviour of the mixtures, but the full process using these binders has not been reported.

In this paper we have studied the complete process of alumina injection molding with a developed binder system based on high density polyethylene (HDPE), paraffin wax (PW) and stearic acid (SA). The evolution of the torque during kneading, the homogeneity and flow properties of the mixtures were studied. The debinding conditions were optimized and finally sintering process was studied. The final goal was to determine the suitability of developed feedstock for use in injection molding process.

2. Experimental procedure

2.1. Materials

Alumina powder of commercial purity Alcoa, CT 3000 SG with a particle size/D50 Cilas of 0.8 μm and D90 of 2.5 μm according to supplier, was used in this study. Morphology of the powder was irregular in shape as shown in Fig. 1. This powder has a high tendency to agglomerate due to the small particle size.

A multi-component binder system was selected for this work. The binder consisted of a mixture of high density polyethylene (HDPE), paraffin wax (PW) and stearic acid (SA). The HDPE used in this study is a low molecular weight polymer with a melt flow index of 25, this assure low viscosity of binder but good green strength of pieces due to the crystalline feature of HDPE that confers good mechanical strength. Differential scanning calorimetry (DSC) analyses were conducted to determine the melting point of binder components. These experiments were performed on a Perkin–Elmer Diamond DSC at a heating rate of 10 °C/min and nitrogen as purge gas. Thermogravimetric analysis (TGA) was also performed, on a Perkin–Elmer TGA Pyrys 1, to determine decomposition temperatures of polymer and additives. Some characteristics of binder components are shown in Table 1.

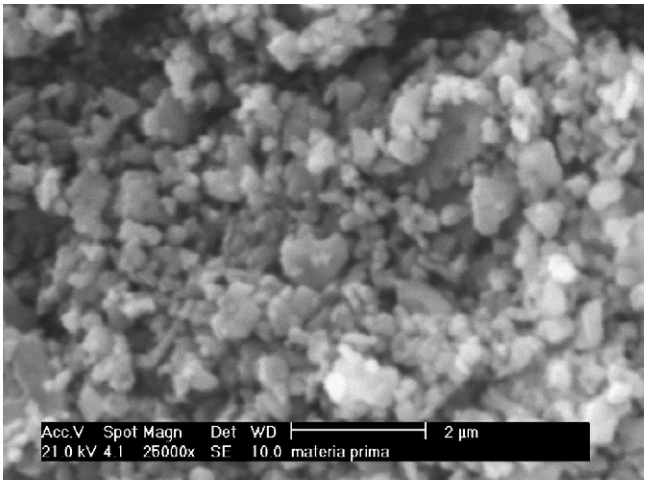

Fig. 1. Morphology of alumina powder observed by scanning electron microscopy (SEM).

2.2. Mixing

Mixing experiments of binders and feedstocks were conducted in a Haake Rheocord 252p mixer with a pair of roller rotor blades. The maximum capacity of the mixing chamber was 69 cm^3. The torque value is a measure of the resistance on the rotor blades. The homogeneity of the mixture can be predicted, through mixing torque curves.[1,18] Uniform mixing is achieved when torque reaches a steady state value.[19]

At first stage, HDPE/PW blends with different proportions were prepared by mixing at 140 °C and 40 r.p.m. during 10 min. The use of HDPE in the binder system allowed to work at low mixing temperatures avoiding the risk of decomposition of PW during processing. The effect of partial substitution of PW by SA (4 vol.%) was studied.

Four feedstock formulations containing between 50 and 60 vol.% of powder loading (Table 2) were mixed at 140 °C and 40 r.p.m. during 30 min. These feedstocks were labelled as A50, A55, A58 and A60 and the number indicates the powder loading in vol.%.

In order to produce larger batches for the injection molding step compounding of powder and binder was carried out in a twin screw extruder Haake Rheomex CTW100p. According to the thermal properties of the binder components the extru-

Table 1
Characteristics of binders components used in this study

Binder component	Supplier	Density (g/cc)	T_m (°C)	Decomposition temperature (°C)
SA	Panreac	0.94	71.05	200–400
HDPE	Dow Plastics	0.96	129.78	470–550
PW	Panreac	0.91	56.97	200–400

Table 2
Composition of feedstocks (vol.%)

Alumina	HDPE	PW	SA	Feedstock tag
50	25.0	23.0	2.0	A50
55	22.5	20.7	1.8	A55
58	21.0	19.3	1.7	A58
60	20	18.4	1.6	A60

sion temperature was set at 155 °C. This temperature is higher than the highest melting point of the mixture but lower than the lowest degradation temperature of the binder components. All the feedstocks were extruded twice to get homogeneous mixtures. After compounding, feedstocks were properly granulated.

2.3. Rheology

A Davenport capillary rheometer with temperature control of ±1 °C was used to measure the viscosities of the binders. Ten minutes were allowed to reach thermal equilibrium after charging the barrel. A 1.5 mm diameter, 45 mm length die was used. The piston velocity was varied to obtain shear rates ranging from 10 to 2500 s^{-1} and the corresponding pressure drop measurements across the length of the die were used to calculate the shear stresses. A pressure transducer situated adjacent to the die entrance was used to measure pressure drop. The paraffin wax viscosity was measured in a cone-plate Haake Rheostress RH150 rheometer. Feedstocks rheology was studied using a Haake Rheocap S20 capillary rheometer with temperature control of ±1 °C. A 1 mm diameter, 30 mm length die was used. Shear rates were varied from 10 to 10,000 s^{-1}.

2.4. Homogeneity

Feedstocks homogeneity was determined by pycnometer density measurements and capillary pressure. In the former feedstock density of three different portions of the same batch was obtained using a Micromeritics AccuPyc 1330 helium pycnometer. The deviation from the mean value reveals the homogeneity of the feedstocks, a large deviation from the mean value often indicates inhomogeneous feedstock.[19] The homogeneity of the feedstock can be also estimated with the capillary rheometer by studying the pressure fluctuation through a small capillary at a constant shear rate (1000 s^{-1}). Small variation of capillary pressure versus testing time indicates homogeneous feedstock,[20] while high fluctuations indicate heterogeneous distributions of powders in the binder where minimum and maximum pressure represent binder rich and solid-rich feedstock portions, respectively.[5,21]

2.5. Injection molding

Injection step was carried out in an Arburg Allrounder 220-s, 250-60 injection molding machine. Three-point bending samples were produced (62.7 mm × 12 mm × 3 mm). The injection molding parameters were optimized. Mold and injection temperature were 50 and 150 °C, respectively, and injection pressure was 1100 bar.

2.6. Debinding and sintering

The organic part was removed through thermal and a combination of solvent and thermal debinding. The solvent debinding was performed by immersion of samples in *n*-heptane at different temperatures from 25 to 60 °C. Thermal debinding was performed in air in a Goceram GC-DC-50 furnace. The thermal cycle was designed on the basis of thermogravimetrical analysis of the binder and feedstock. Pieces were sintered during 2 h at different temperatures (1500, 1550, 1600 and 1650 °C) in a high temperature furnace. Microstructure sintered parts were evaluated in a Philips XL 30 Scanning Electron Microscope equipped with a SE and BSE detectors. Density of sintered samples was determined using a water replacement method (Archimedes method).

3. Results and discussion

3.1. Mixing

Mixing of HDPE and PW at 140 °C was really easy and for all the prepared blends the steady state was achieved before 5 min. Mixing of blend with PW content higher than 70% was impossible due to the low viscosity of this component at this temperature. Fig. 2 shows a typical torque versus time curve obtained for a HDPE/PW blend. In the inset of this curve torque values at the steady state of blends versus paraffin wax content can be displayed. It can be seen that torque decreases as PW content increases indicating a reduction in viscosity. Rheological behaviour of HDPE, PW and HDPE/PW mixtures are displayed in Fig. 3. Viscosity of paraffin wax remains constant as shear rate increases according to a Newtonian behaviour while the viscosity of polyethylene decreases as the shear rate increases according to a pseudoplastic behaviour. HDPE-PW blends also displayed the same flow characteristics. This behaviour is the most suitable for injection molding process because viscosity of the mixture decreases when it is approached to the nozzle and when the mold is filled the viscosity increases.[2] On the other hand, and as expected, viscosity of these blends decreases as wax content increases in accordance with torque measurements. This

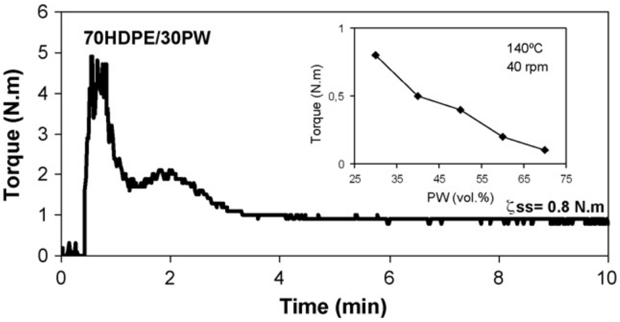

Fig. 2. Torque values at the steady state for blends with different content of paraffin wax.

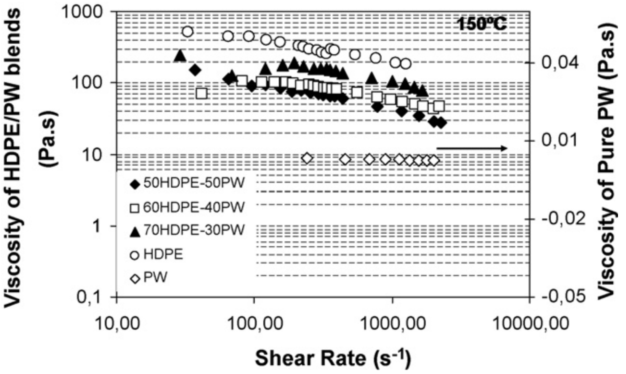

Fig. 3. Rheological behavior for the different HDPE/PW blends and pure components.

is a consequence of the low molecular weight and the low melting point of the paraffin wax which provide to the binder high flowability. In fact, waxes have been reported in some studies as processing aids (lubricants) in polyethylene processing.[22,23] However, blends with high PW contents are not suitable for PIM process because did not retain the shape during the polymer extraction and sintered parts are highly defective. In this sense the blend with 50/50 HDPE/PW exhibited the most convenient behaviour for injection molding step.

The addition of small quantities of SA to binder systems used in PIM is beneficial because substantially reduces the abrasion of the powder/binder mixture against the machine/die walls. Stearic acid reduces the contact angle by lowering the surface energy of the binder–powder interface minimizing the separation of binder from the powder–binder mixtures during injection molding, allowing increase the solid loading and giving a better homogeneity.[2,24,25] Lin et al. added 4 vol.% of SA to binder system for alumina feedstock and studied the interaction between binder and powder obtaining a reduction of the apparent viscosity by a factor of 20.[24]

In this sense a small amount of PW was replaced by SA (4 vol.%). As shown in viscosity curve (Fig. 4), the presence of this organic acid slightly reduces the viscosity of the mixture and the pseudoplastic behaviour is maintained as expected since surface active agents lower the mixture viscosity but do not alter the basic shape of the viscosity versus shear rate curve.[2] At this point, the mixture 50/46/4 (HDPE/PW/SA) was believed to be the most suitable for alumina injection molding.

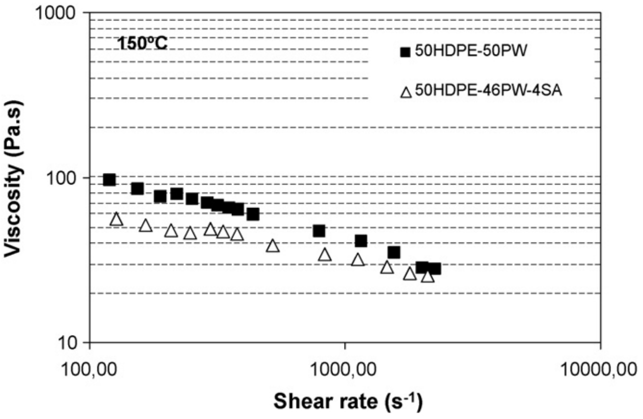

Fig. 4. Effect of substitution of PW by SA on viscosity curves of 50/50 HDPE/PW blend.

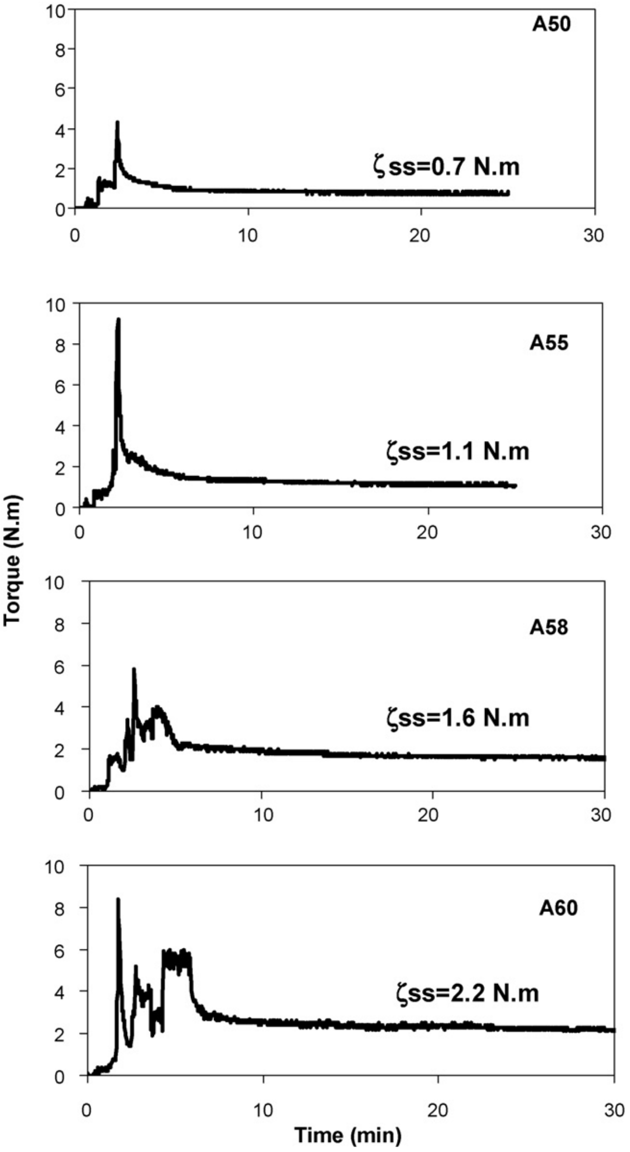

Fig. 5. Torque curves for different volumetric powder loading.

Fig. 5 shows torque curves of feedstocks with different powder loadings. Higher powder loading produced higher steady state torque level, indicating differences in viscosity of the mixture. The homogenization time for the mixture slightly increased with the powder loading as a consequence of higher resistance on the rotor blades. However all the feedstock reached the steady state in a mixing time below 30 min. In the case of sample with 60 vol.% of powder, although torque value at steady state is not much higher than the others mixtures, the external aspect was slightly different from the rest of the feedstocks prepared, the homogeneity had to be evaluated. In order to determine the suitability of the formulations for CIM, homogeneity was evaluated through feedstock density measurements of different portions of the same batch and capillary rheometry.

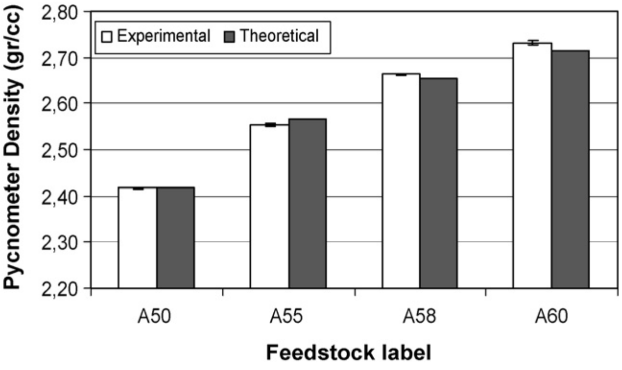

Fig. 6. Pycnometer density of different feedstocks composition and theoretical value calculated through the rule of mixtures.

An inhomogeneous feedstock produces density gradients within the molded part and cause distortion.[19] In Fig. 6 picnometric density values of feedstocks are displayed These values are also compared with the theoretical density, determined by the rule of mixtures. The good agreement between experimental and theoretical values and the small deviations of the measurements indicates a very good homogeneity of the mixtures.

Finally, feedstock homogeneity was also evaluated by measuring pressure fluctuation through a small capillary at 1000 s^{-1}. Fig. 7 shows pressure–time curves for the different feedstocks at 150 °C. It can be noticed that pressure value increase with solid loading as expected. In the case of feedstocks A50, A55 and A58 small pressure fluctuations can be observed indicating good homogeneity of the mixtures while feedstock A60 exhibited higher pressure fluctuations indicating lower homogeneity.

3.2. Feedstock rheology

The rheological properties of feedstock are very important in order to know if the mixture can be injected. The shear rates encountered in the gates and the mold range from 100 to 1000 s^{-1} for this reason most of rheological studies are made in this interval. However shear rates during injection molding can occasionally reach 10,000 s^{-1}, which is still considered suitable for injection molding. In accordance to this our rheological study was developed in this range of shear rates.[26] Fig. 8 shows the variation of the viscosity with the shear rate at 150 °C for the four prepared feedstocks. Viscosity of the powder–binder mixture is very sensitive to solid content. In this sense, in the analysed shear rate range, viscosity increases as the powder loading increases as expected. In all the cases the viscosity decreases as the shear rate increases according to a pseudoplastic behaviour. Pseudoplastic flow is often sought in the molding process to ease mold filling, minimize jetting, and help to hold component shape.[2] However, some molding defects such as jetting are also associated with high pseudoplastic character or low value of the exponent *n* of the power law index. The power law index indicates shear sensibility and a low index indicates higher shear sensibility. The power law indexes obtained for each feedstock are 0.56, 0.54, 0.50 and 0.53 for feedstocks A50, A55, A58 and A60, respectively. These values are higher than others encountered in literature for others binders systems.[27] It assures that this kind of defects will be avoided. From this point of view, all the feedstock studied exhibited suitable flow behaviour for CIM.

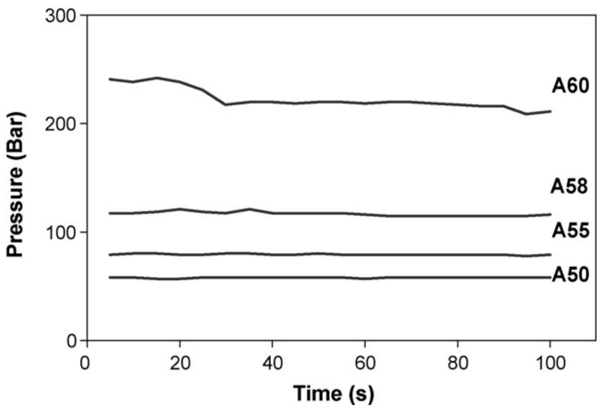

Fig. 7. Pressure evolution with time for feedstocks at 1000 s^{-1}.

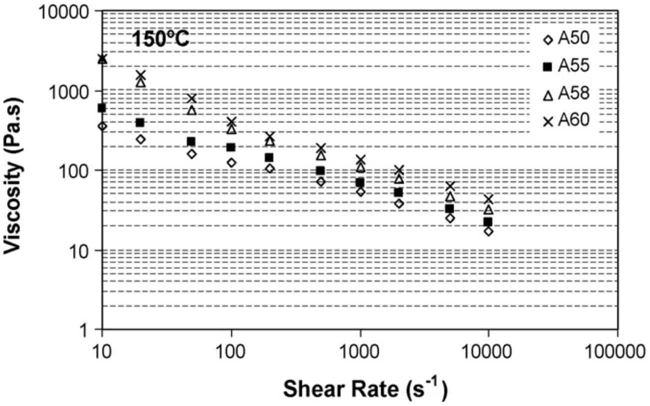

Fig. 8. Viscosity curves of feedstocks with different powder loadings.

There are different rheological models that predict the critical powder volume concentration (CPVC).[28–32] Most of them are not suitable for PIM purpose because do not consider suspensions with high solid loadings. For PIM purpose a good model for describing the behaviour of feedstock against solid loading is the proposed by Janardhana-Reddy et al.[32] According to this model, critical solid loading can be calculated by the following equation:

$$\eta_{\mathrm{m}}\Phi_{\mathrm{L}} = \eta_{\mathrm{m}}(\Phi_{\mathrm{L}})_{\mathrm{c}} + \eta_{\mathrm{L}}(1-(\Phi_{\mathrm{L}})_{\mathrm{c}})$$

where η_{m} is the feedstock viscosity, Φ_{L} the binder volume fraction, $(\Phi_{\mathrm{L}})_{\mathrm{c}}$ the critical binder volume fraction, η_{L} the binder viscosity and Φ_{c} is the critical volume solid loading, $\Phi_{\mathrm{c}} = 1-(\Phi_{\mathrm{L}})_{\mathrm{c}}$.

Table 3 shows critical solid loading calculated at three different shear rates. In all the cases the regression coefficient is higher than 0.99 indicating the goodness of fitness. In order to avoid any wear in the mixing and molding equipment, in general a solid loading between 5 and 10% below the theoretical value is advisable. In this sense, feedstocks labelled as A58 and A60 seemed to be most suitable. In general, during the CIM process, the shear rates can vary from 100 to 1000 s^{-1} and the flow

Table 3
Critical solid loading

Shear rate (s^{-1})	Φ_c (%)	R^2
100	64	0.9989
500	65	0.9987
1000	66	0.9985

rate during injection molding requires a viscosity of less than 1000 Pa s.[33] All prepared feedstocks could be injected, however feedstock A60 is in the limit recommended for this process. Besides its homogeneity is not as good as feedstock A58 as it was explained before.

According to torque measurements, rheology analysis and homogeneity feedstock labelled as A58 was chosen as the most suitable for the process since it has high solid loading and exhibited low torque value, good rheological behaviour and good homogeneity. In general, sintered parts are better if their feedstocks are produced homogeneously. Besides the quality of the mechanical strength of ceramic injection molded parts is relevant to the solid loading (55–60 vol.%) of feedstocks,[5] for this reason is believed that sintered parts produced with feedstock A58 will have good mechanical properties. In fact the green strength of the pieces were higher (20 ± 1 MPa) in comparison with others encountered in literature.[5]

3.3. Debinding

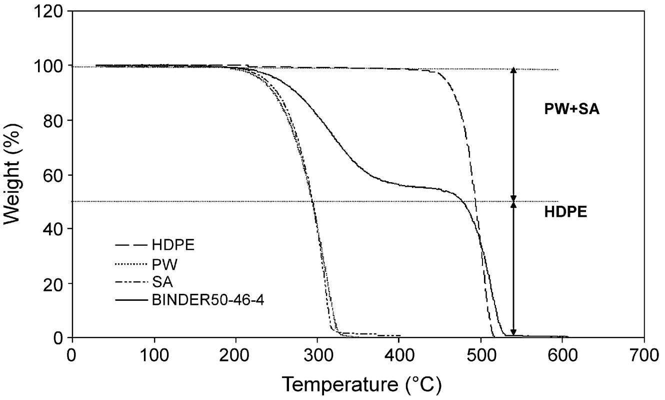

Fig. 9. Thermogravimetric analysis of binder 50/46/4 HDPE/PW/SA vol.%. Heating rate was 10 °C/min.

Table 4
Debinding schedule

Stage	Heating rate (°C/min)	Debinding temperature (°C)	Debinding (hold) time (min)
Thermal cycle			
1	1	200	60
2	0.5	470	60
3	1	550	60
4	5	30	0
Total time			17.9 h
Thermal cycle after solvent debinding			
1	2	470	60
2	1	550	60
3	5	30	0
Total time (thermal + solvent debinding)			13.7 h

Binder removal was carried out by two different processes, thermal and a combination of solvent–thermal debinding. The thermal elimination of binder was optimized by means of thermogravimetric analysis of the binder, which provides information on the degradation temperature range of the binder components. Fig. 9 shows weight loss with temperature of binder and pure components heated at 10 °C/min in air. Pure components decompose in one step. PW and SA start to decompose at 200 °C and total evaporation occurs at approximately 400 °C. HDPE decomposition starts around 470 °C and finish at 550 °C. On the other hand, binder decomposition occurs in two steps. The first weight loss takes place between 200 and 400 °C and it corresponds to PW and SA elimination. In the second step degradation is faster than in the first step and it occurs from 470 to 550 °C. This gradual and wide decomposition temperature range is beneficial from a technological point of view at least for two reasons: (i) in the initial stage the remaining binder component will serve to retain the shape of the part and (ii) allows a smooth way out of decomposition products. Moreover the fact of the first main component, PW, decompose in a wider temperature range avoids the formation of cracks during the process because at the beginning of the process no pores or free space are present, while when the decomposition of HDPE takes place there will be a interconnected pore channels that serve as escape paths for decomposition gases.

The optimized thermal cycle (Table 4) was established on the basis of this thermogravimetric analysis, and taking into account that high heating rates produce the presence of cracks and blis-

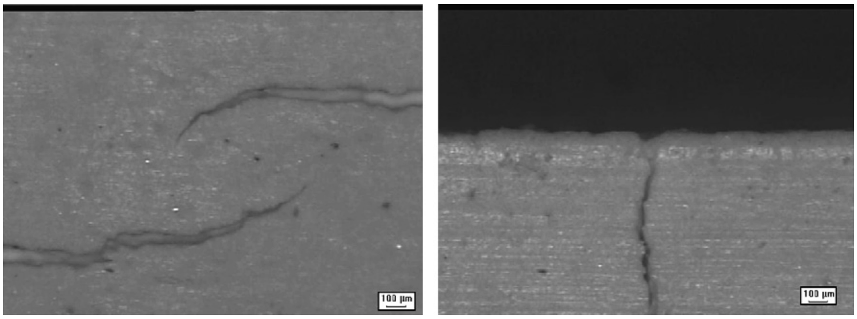

Fig. 10. Typical defects found after thermal debinding: (a) cracks, (b) transversal cracks.

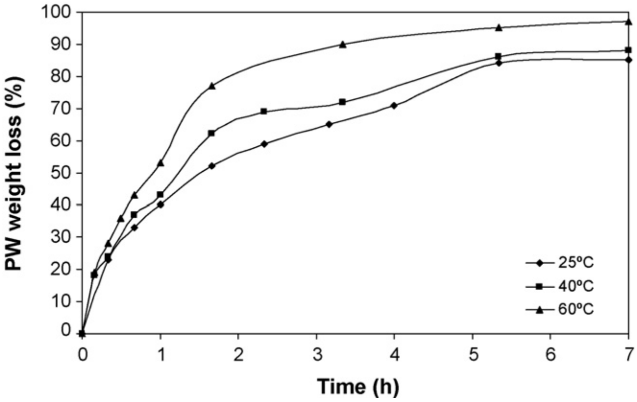

Fig. 11. Effect of debinding temperature on the weight loss of alumina compact immersed in heptane for various extractive times.

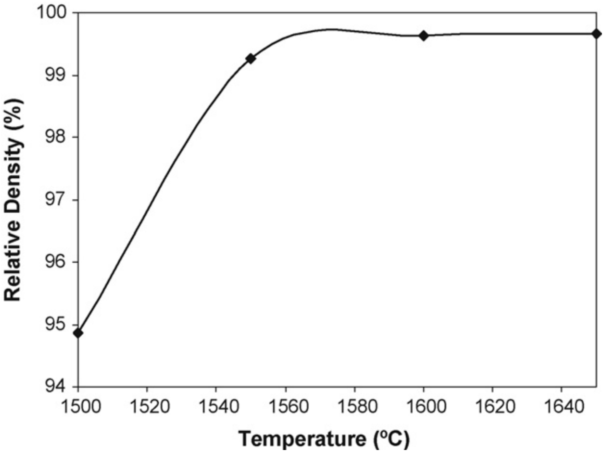

Fig. 12. Sintering curve.

ters into the sample. Up to 200 °C, since no decomposition takes place we chose a heating rate of 1 °C/min. From 200 to 470 °C the heating rate was critical and had to be slow to prevent blistering and bloating since the first binder component decompose and the pores are opened. Higher heating rates produced typical defects seen in Fig. 10, this cracks are caused by pressure build up and temperature gradients inside the compact. Best results were found using lower heating rates (0.5 °C/min). Finally, the last heating up to 550 °C takes place at 1 °C/min.

The optimized thermal cycle lasted 17.9 h. Unfortunately, the reduced particle size of the alumina is useful to improve sintering densification and shape retention but make more difficult the elimination of the binder.[2]

In order to reduce the total debinding time solvent debinding was conducted by immersing the parts in a bath with heptane. In this solvent PW and SA are soluble. Different bath temperatures were tested. Fig. 11 shows the effect of temperature on the extraction of PW and SA with the immersion time from 25 to 60 °C. A higher efficiency was achieved as bath temperature increased due to a larger solubility and diffusivity of the components on heptane with temperature. In addition, the debinding rate was reduced when the debinding time increased and also debinding rate was also faster at short times for higher temperatures.

From this analysis, solvent debinding was performed at 60 °C during 5 h. In general 95% (mass based) of the soluble ingredients could be extracted. Total cycle, including thermal debinding, lasted around 13.7 h and all the pieces were defect free for this reason solvent debound parts were chosen for the sintering. Defects such as cracking, slumping and sagging are frequently found in PIM parts. These defects are partly related to the swelling of the binder component during solvent debinding.[34] The absent of this kind of defect in tested pieces could be partially due to the crystallinity of the HDPE, since swelling is reduced for semicrystalline polymers.[35] Besides during thermal debinding the viscous flow can cause distortion due to thermal expansion of binder. This effect could be minimized due to the presence of HDPE because when PW is melted the

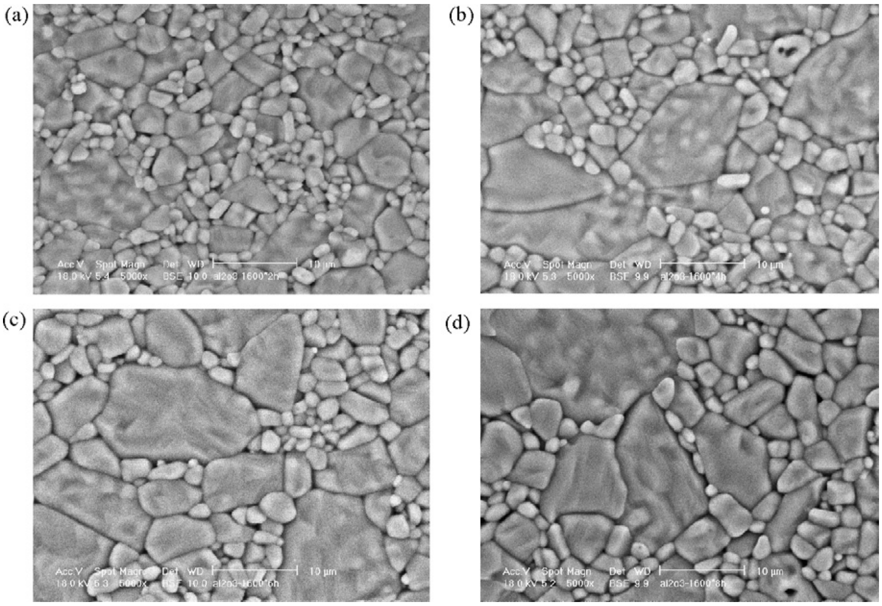

Fig. 13. SEM images of alumina parts sintered at 1600 °C during: (a) 2 h, (b) 4 h, (c) 6 h and (d) 8 h.

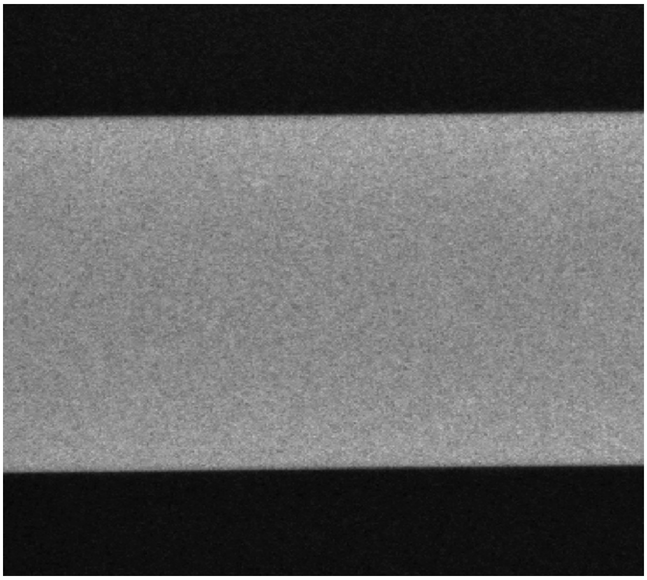

Fig. 14. Radiography of alumina parts sintered at 1600 °C during 2 h.

HDPE is solid and provides the required mechanical strength to minimized distortion during the flow of the wax. After melting of PW, due to their low molecular weight, it evaporates from surface and there is less risk of defects.

3.4. Sintering

Fig. 12 shows relative density to the theoretical of the injection molded alumina parts sintered in air at different temperatures. Full density was achieved over 1600 °C and from this temperature density values remain constant. This was considered a suitable temperature to sinter compacts at different times since relative density of the parts was near 99.6% slightly higher than those obtained by other authors.[36–38]

Fig. 13 shows SEM images of sintered parts at various times. It can be seen that longer sintering times made difficult to control grain growth. The abnormal grain growth observed in parts sintered at times above 4 h is undesirable for final properties. Microstructure obtained by sintering at 1600 °C during 2 h could be the most beneficial for the strength of the parts. Finally, a radiography of the sintered part can be seen in Fig. 14. The homogeneity of the image confirms that there are not density gradients along the part that could reveal the presence of defects such as holes, internal cracks, etc. This result is in accordance with the high densities obtained experimentally and evidence that parts are defect free.

4. Summary

A multi-component binder system suitable for use in feedstocks for shaping alumina powders by for powder injection molding has been formulated and tested. This binder has as main components HDPE and PW and small amount of stearic acid. The binder presents a pseudoplastic behaviour which remains with the addition of powder. The thermal characteristic of binder allowed to perform the injection molding at relatively low temperatures, as well as a easy thermal degradation favouring the debinding process. Moreover, the different solubility features in heptane of both main components permitted to use a two-step debinding process (solvent and thermal) reducing considerably the total debinding time and the formation of defects during debinding process. The PW can be removed from the molded part by solution in *n*-heptane and thermogravimetric analysis was used to develop a suitable thermal treatment for second stage of the binder elimination process.

By means of torque and rheological measurements of different feedstock formulations the optimum powder loading was established as 58 vol.%. This powder loading is one of the highest found for fine alumina powder in the reviewed literature, with the suitable characteristic to be injected. The injected green parts had high mechanical strength, which was conferred by the crystallinity of HDPE. The high powder loading allowed to obtain sintered parts with 99.6% of the theoretical densities. The density of the pieces are also one of the highest found in the literature.

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