Journal of the European Ceramic Society 21 (2001) 2843–2853

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Rheological study of waste porcelain feedstocks for injection moulding

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Received 9 August 2000; received in revised form 11 December 2000; accepted 16 December 2000

Abstract

Five types of hard porcelain powders for injection moulding have been studied, using the same commercial binder in all cases. These powders contained different amounts of recycled porcelain, since one of the principal aims of this work is to reuse waste porcelain in the injection moulding process. The evaluation of the flowability of different feedstocks was carried out using rheological parameters, like critical powder volume concentration (CPVC), melt viscosity, activation energy, yield stress, powder law index and rheological index. The correlation of these parameters with injection behaviour was established, in order to confirm the possibility of using this moulding process with recycled porcelain powders. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Injection moulding; Porcelain; Rheology; Waste materials

1. Introduction

At a time when market demands are extremely competitive, it is of great importance to obtain a cost-effective way of manufacturing a body without reducing the quality of the product. The ceramic injection moulding (CIM) process represents an excellent alternative for manufacturing porcelain products for the tableware industry in a faster and more automatic way. Furthermore the use of waste porcelain has a remarkable economical and environmental benefit.

The tableware industry in the EU is passing through very difficult times because of the strong competition from low wage paying countries in particular from the Republic of China. Although companies have been modernizing their equipment, the currently used technology is still old, especially in the productions of cups, saucers and complex shaped products. Ceramic injection moulding has a significant commercial potential and has progressed in the last years to have a certain advantage over conventional moulding technologies, particularly in obtaining complex shaped parts. This is very interesting for the tableware industry to produce porcelains requiring handles in a single step, whereas other conventional processes are dated, requiring the separate fabrication of the handle and container and then joining the two pieces. The advantages of using porcelain injection moulding (PIM) are: low cost machinery, good dimensional accuracy and consistent product quality. This technology also enables a fully automatic production of parts in a one step process, as has been proved for powder metal injection moulding.[1]

However, this practical application depends on finding cheaper raw materials to produce good quality parts, trying to flexibilize, increasing the production and reducing the undesirable environmental aspects. Recycled porcelains are particularly suited to the injection moulding process because they contain all the porcelain components in each grain as a result of their previous formation instead of being individual grains of each component.

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PII: S0955-2219(01)00210-2

Until now, this type of study in the tableware industry has not been thoroughly performed. The main technological achievements that promote innovations in this sector are related to raw materials, new technology, automation and environmental concern.

In the CIM process, in which the injection stage represents a critical step, the role of the feedstock is of primary importance. The flow properties of the feedstock (rheology) should permit good rheological behaviour and good filling of the die.[2] Feedstocks are prepared using minimum binder content that is compatible with flow properties. This allows the obtaining of high green densities and little shrinkage during sintering.[3]

This paper attempts to prove the possibility of using porcelain rejects for the manufacturing of components through the injection-moulding process. In order to evaluate the behaviour of the porcelain rejects, it is intended to establish a relation between powder characteristics and the rheological behaviour of the feedstock and to predict the behaviour of the feedstock in the injection machine by using rheological data.

2. Experimental procedure

Five types of hard porcelain (using waste porcelain) with the same binder, but different content were rheologically studied. The critical powder volume concentration (CPVC) was previously calculated using rheological mathematical models.

One of the key parameters of the flow properties of an injection moulding feedstock is its powder characteristics. After evaluating the physical properties of powders, they were correlated with rheology.

The relationship between the rheological data obtained in the plastometer equipment, which gives the fundamental rheological data of a viscous fluid, the injection moulding behaviour, was also studied.

2.1. Materials

2.1.1. Porcelain powder

Hard porcelain has been studied in this work. The most relevant characteristics of hard porcelain are the following: it is composed of kaolin, quartz and feldspar. Compared with other porcelains it is very hard and the firing temperature is higher: around 1350°C.[4,5]

Two types of powders have been used:

(a) Virgin porcelain.
(b) Recycled porcelain:

Two sources have been used to obtain recycled porcelain:

- From biscuit porcelain: this is waste porcelain that has been burnt at 900°C. This porcelain is easy to crush due to the fact that the thermal process of firing the porcelain has not been totally completed.
- From calcined porcelain: this porcelain has been burnt at 1350°C. This is the final stage of porcelain, the firing process is completed. This porcelain is more difficult to crush (harder).

Mineralogical composition of the porcelain powders used is shown in Table 1.

Five formulations were selected in the experiments to test the influence of the recycled porcelain in the rheology of feedstocks. The characteristics of these formulations are shown in Table 2. Formulations 1, 3 and 5 were selected to study the influence of calcined porcelain mixed with virgin porcelain. Formulation 5 contains the largest amount of calcined porcelain: 80 wt.%. Formulation 2 studies the influence of biscuit porcelain mixed with virgin porcelain. Formulation 4 was chosen as a reference, containing only virgin porcelain.

In the selected physical properties of the formulations, mean particle size and particle size distribution are particularly important in the injection moulding process. The particle size distribution has been determined by means of the compaction rate and the slope parameter, S_w.

Besides the amount of recycled porcelain there are other differences in the physical characteristics of the formulations:

- Formulations 1 and 3 have the same amount of recycled porcelain, but different milling times that causes them to have a different mean particle size.
- Formulations 1 and 2 have the same mean particle size, but different particle size distribution (S_w or compaction rate). The same comparison can be made with formulations 3 and 4.
- Formulations 4 and 5 have the same compaction rate but different mean particle size.

In Fig. 1 SEM photographs of all the powders are shown. The different particle sizes of each powder and their particle geometry can be seen.

As can be observed, powder 4 is the least irregular and is more spherical than the other powders. Although it cannot be clearly appreciated in the photograph, it should be pointed out that powder 5 is the most angular powder.

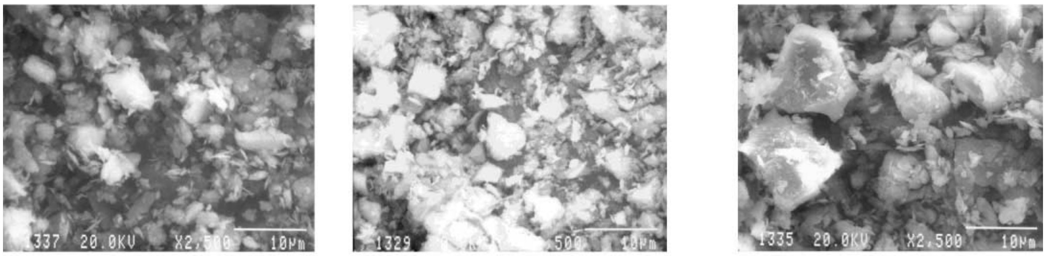
Table 1
Composition of the hard porcelain

Raw materials	Percentage (%)
Kaolin	50
Feldspar	25
Quartz	25

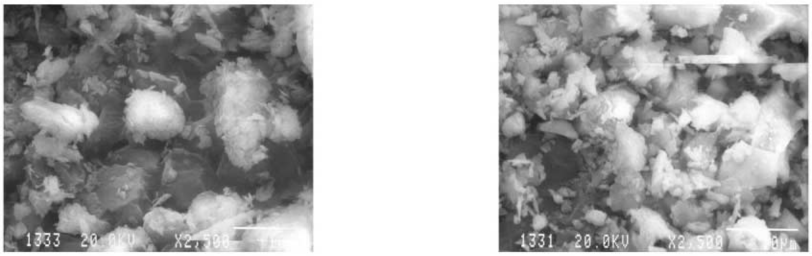
Table 2
Porcelain powders characteristics

Porcelain formulations		1	2	3	4	5
Virgin porcelain (%)		50.00	50.00	50.00	100.0	20.00
Recycled porcelain (%)	Biscuit	–	50.00	–	–	–
	Calcined	50.00	–	50.00	–	80.00
Milling time (h)		16	8	11	Dry mixing	9
D_{90} (μm)		12.50	12.68	21.69	29.99	24.59
D_{10} (μm)		1.08	1.05	1.33	1.31	1.33
Mean diameter, D_{50} (μm)		4.12	4.00	6.51	6.56	7.02
Specific surface (m^2/g)		2.3948	2.4708	1.8108	1.8301	1.7709
Slope parameter (s_w)[a]		2.41	2.11	2.37	1.88	2.02
Compaction rate (%)		60	66	60	69	69

[a] Slope parameter (s_w): parameter to measure particle size distribution. Large values of the distribution slope s_w correspond to narrow particle size distribution.[6]



Powder 1 Powder 2 Powder 3



Powder 4 Powder 5

Fig. 1. SEM micrographs of the five porcelain powders. Magnification: 2500.

2.1.2. Binder

The same commercial binder was used in all cases. This one was found to be the most suitable for preparing porcelain feedstocks for injection moulding. Its characteristics can be seen in Table 3.

2.1.3. Feedstocks

The binder and the powders were premixed in a Sigma blade mixer at 140°C for 2 h. This mixture was then mixed and pelletized in an APV twin-screw extruder at the same temperature.

2.2. Equipment and test conditions

2.2.1. Extrusion plastometer tests

The equipment used to obtain the rheological data was a Tinius-Olsen Melt-In MWLD MP 993 dead weight extrusion plastometer. The shear stress was fixed for each measurement by means of a dead weight. All measurements were carried out under the ASTM standard.[7] A capillary with a diameter, D, of 2.0955 mm and a length, L, of 8.000 mm was used, the L/D ratio being 3.82.

Table 3
Binder characteristics

Melting point	93–100°C
Viscosity (130°C)	4.7 Pa s
Density (g/cc)	0.96
Composition	PE + poliestheramide + polisiloxane

The feedstocks were studied in a temperature range of 130–160°C and a shear rate range of 5–2000 s^{-1}.

The information from the extrusion plastometer can be used, not only to determine viscosity, but also to reveal the stability and homogeneity of feedstocks and extent of powder binder separation.

Using the data obtained from the extrusion plastometer the flow properties of the five different powders were studied and related to the powder characteristics. The studied rheological parameters were as follows:

- CPVC: it is crucial to reduce the amount of binder in the injection feedstock. The binder is only a vehicle that will be burnt out in later steps, and, therefore, will not remain in the final product. A feedstock should contain the minimum amount of binder, not only because the binder is removed in the debinding stage, but also because of cost factors.
- Viscosity: the viscosity is the most important rheological parameter for powder injection moulding. The viscosity of the feedstock should be studied in the injection moulding temperature range and shear rate range.
- Powder law index (n): for injection moulding the feedstocks should have a pseudoplastic behaviour: the viscosity decreases with the shear rate. Using Ostwald and De Waele Power Law mathematical expression the degree of shear sensitivity can be calculated by means of "n".
- Yield stress (τ_y): yield stress is defined as the minimum stress that a molten material requires in order to start flowing. This is important in the injection moulding process due to the fact that the feedstock should continue flowing along the paths of the mould (runners, sprue, gate and die) and, because of the pressure drop, the feedstock must be able to continue flowing with minimum pressure (stress).
- Activation energy (E_a): The dependence of the viscosity on the temperature plays an important role in powder injection moulding. The value of E_a represents the influence of temperature on the viscosity of the feedstock. A high value of E_a gives a significant influence of temperature. It is desirable for temperature to have a low influence on the viscosity during the injection moulding, because the mould is cold and if the viscosity is very sensitive to temperature, the mixture could have very high viscosity and solidify before filling the die. This produces short shots or undue stress concentrations. On the other hand the influence of temperature on viscosity during cooling should be high, in order to be able to manipulate the part without breakage.
- General rheological index (α_{STV}): this is an attempt to have a general rheological index in order to evaluate feedstock flow properties. There are many factors that affect flow properties and mould filling: melt compressibility, melt elasticity, specific heat and thermal conductivity among others. It has been proved, measuring the thickness of the extrudates, that melt elasticity is not relevant in this case ($d_j/d = 0.96$, being d_J: diameter of the extrudate and d: diameter of the capillary). Therefore, for simplicity, only the parameters studied in previous sections have been taken into account. In general, a feedstock with low viscosity, low powder law index and low activation energy is preferable for injection moulding. There is usually a contradiction between these factors: one feedstock has good viscosity, while another is better from the shear sensitivity point of view.

2.2.2. *Injection moulding*

Bending bars, recommended by MPIF, were injection moulded using five kinds of porcelain feedstocks in an ARBURG 370C 800-225 injection-moulding machine. A diagram of the PIM standard bending bar is shown in Fig. 2. This mould geometry was selected due to its simplicity and in order to avoid any moulding. No bending trials were performed.

3. Results and discussion

In this section the results obtained from the analysis of the rheological parameters described in Section 2 are shown.

This section tries to relate the results with the powder and feedstock characteristics.

3.1. *Determination of CPVC*

The CPVC has been determined for five types of porcelain by means of rheological models for highly loaded mixtures. Six mathematical models have been studied:[8–13]

Maron–Pierce model:

$$\boxed{\eta_r = \left(1 - \frac{\Phi}{\Phi_c}\right)^{-2}}$$

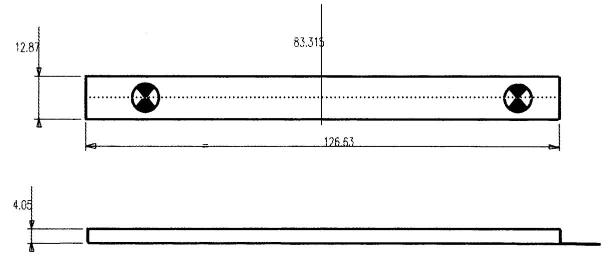


Fig. 2. Diagram of standard PIM bending bar.

Mooney model:

$$\boxed{\eta_r = \exp\left(\frac{2.5\Phi\Phi_c}{\Phi_c\Phi}\right)}$$

Chong et al. model:

$$\boxed{\eta_r = \left(\frac{\Phi_c - 0.25\Phi}{\Phi_c - \Phi}\right)^2}$$

Eilers model:

$$\boxed{\eta_r = \left(1 + \frac{1.25\Phi\Phi_c}{\Phi_c - \Phi}\right)^2}$$

Zhang and Evans model:

$$\boxed{\eta_r = \left(\frac{\Phi_c - C\Phi}{\Phi_c - \Phi}\right)^2}$$

Janardhana et al. model:

$$\boxed{\eta\cdot\phi_b = \eta\cdot(\phi_b)_c + \eta_b\left(1 - (\phi_b)_c\right)}$$

where η_r: relative viscosity; ϕ: volume fraction; ϕ_b: binder volume fraction; ϕ_c: critical powder volume fraction; η: mixture viscosity; $(\phi_b)_c$: citical binder volume concentration.

The relative viscosity is defined as follows: η_m/η_b; η_m: mixture viscosity; η_b: binder viscosity.

Note that: $\phi_c = \left(1 - (\phi_b)_c\right)$.

According to the regression coefficients obtained from the different models (Table 4), the Janardhana et al. model best represents the behaviour of the five type of porcelain powders, with a regression coefficient higher than 0.99 in all cases. In previous studies, Maron–Pierce and Zhang and Evans model were found to be successful in the prediction of CPVC for other ceramic and metallic powders,[12,14–17] but this new model proposed by Janardhana et al. gives a better fitting with experimental data, moreover this model has been compared to other methods of determining the CPVC such us torque rheometry and the result match well in both cases.[13]

It should be pointed out that the powder granulometry (through mean particle size, particle size distribution and compaction rate) has a great influence on the CPVC value.

1. Compaction rate; 2. Mean particle size: D_{50}; 3. Particle size distribution: S_w.

Figs. 3–6 show this tendency in a general manner.

Observing the above graphs it can be said that: there is a clear dependence of the critical powder volume concentration on the granulometry of the powder: mean particle size and particle size distribution:

1. The bigger the particle size, the higher the CPVC.
2. The broader the particle size distribution, small values of S_w, the higher the CPVC. The powder size range should be either smaller than 2 or should be greater than 7 for a maximum flowability of mixtures.[18,19]
3. The higher the compaction rate, the higher the CPVC.

Due to the fact that the powder/binder mixture could contain some hetereogeneities and in order to avoid any wear in the mixing and moulding equipment, the usual powder content of a feedstock is around 5% lower than the CPVC (depending on the powder characteristics: particle shape). All the feedstocks except F2 contain 2% less of porcelain than the CPVC. In preliminary trials made with powder 2, some contamination (coming from the mixing equipment) was found, it was therefore decided to increase the binder content in this feedstock to 4% above the CPVC.

As a conclusion of this study and taking into account the CPVC obtained, the following feedstocks (Table 5) were prepared to be injection moulded.

According to previous tests made with Bone China porcelain, the usual solids content in the feedstock is around 81 wt.%.[20] It can be observed that these Hard porcelain feedstocks are in the same range: F1 and F2 are below 81% powder content, F3 and F4 contain just the same amount of powder and F5 is over the 81% solid content.

Table 4
Fitting of the six different models

Porcelain formulation	CPVC (regression)					
	Maron–Pierce	Mooney	Chong et al.	Eilers	Zhang and Evans	Janardhana et al.
1	**0.62** (0.97043)	**0.79** (0.9915)	**0.61** (0.8960)	**0.62** (0.94629)	**0.64** (0.9960)	**0.59** (0.9996)
2	**0.64** (0.8873)	**0.82** (0.94091)	**0.63** (0.6926)	**0.63** (0.8353)	**0.66** (0.9898)	**0.60** (0.9984)
3	**0.69** (0.98074)	**0.92** (0.99624)	**0.67** (0.97467)	**0.68** (0.96739)	**0.7238** (0.9963)	**0.65** (0.9992)
4	**0.68** (0.98032)	**0.89** (0.9900)	**0.67** (0.95651)	**0.67** (0.96757)	**0.70** (0.9906)	0.65 (0.9994)
5	**0.72** (0.95478)	**0.97** (0.99303)	**0.71** (0.90881)	**0.72** (0.93929)	**0.70** (0.9976)	**0.70** (0.9964)

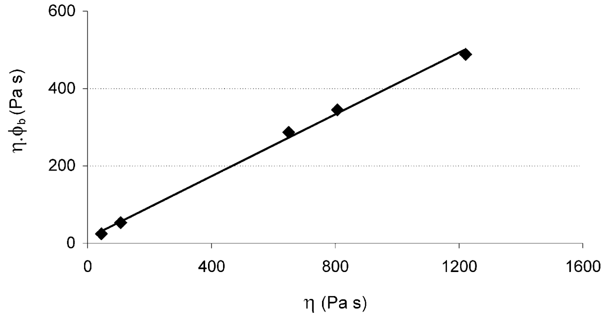


Fig. 3. Example of the Janardahna et al. model fitting to the experimental viscosity values.

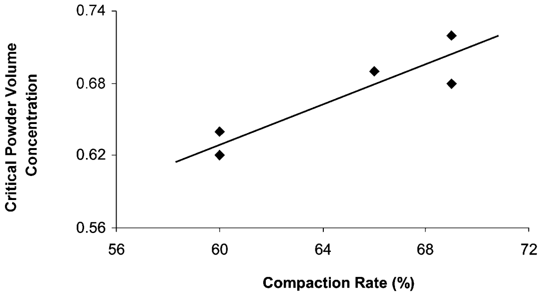


Fig. 4. Influence of compaction rate on critical powder volume concentration.

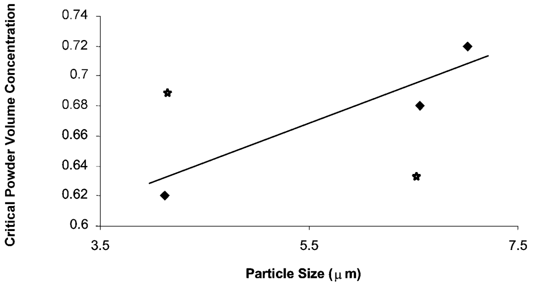


Fig. 5. Influence of mean particle size on critical powder volume concentration. It should be noted that the star shaped points are out of the tendency observed because having the same mean particle size than the points they have below and above, they have different compaction rate and, therefore, different CPVC.

3.2. Viscosity measurements

The rheological behaviour of five different feedstocks was studied using an extrusion plastometer. Under conditions of steady flow and from the measurements of the pressure drop or volumetric flow rate through the capillary, the shear stress and shear rate can be determined, from which viscosity can be calculated. For a Newtonian fluid, the shear stress and shear rate can be calculated as follows:

$$\sigma_{\mathrm{w}} = \frac{\Delta P}{2(R/L)}$$

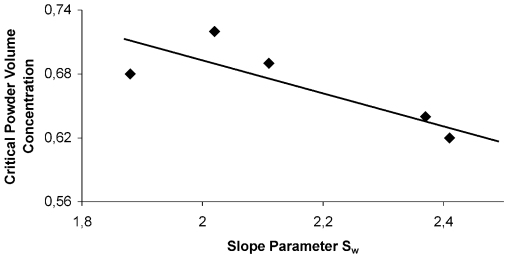


Fig. 6. Influence of particle size distribution on critical powder volume concentration.

Table 5
Composition of prepared feedstocks

Powder	Feedstock	Powder vol.% (wt.%)
1	F1	57 (77)
2	F2	56 (76)
3	F3	63 (81)
4	F4	63 (81)
5	F5	67 (84)

where σ_{w} is the shear stress at the capillary wall; ΔP is the pressure drop across the capillary; L is the length of the capillary; R is the radius of the capillary.

$$\dot{\gamma}_{\mathrm{a}} = \frac{4Q}{\pi R^3}$$

where γ_{a} is the apparent shear rate; Q is the volumetric flow rate; R is the radius of the capillary.

Although the binder behaves as a Newtonian fluid, these feedstocks, and in general all powder injection moulding feedstocks, are considered to be non-Newtonian fluids, and it is, therefore, necessary to correct the shear rate using the Rabinowisch correction:[21]

$$\dot{\gamma}_{\mathrm{w}} = \frac{\dot{\gamma}_{\mathrm{a}}}{4}\left(3 + \frac{\mathrm{dln}\dot{\gamma}_{\mathrm{a}}}{\mathrm{dln}\sigma_{\mathrm{w}}}\right)$$

where γ_{w} is the shear rate at the capillary wall. The viscosity can be calculated using the following mathematical expression:

$$\eta = \frac{\sigma}{\dot{\gamma}_{\mathrm{w}}}$$

The viscosities of each feedstock at different temperatures and different shear stresses were studied (see Table 6). The lower the value of the viscosity the easier the mixture flows, and the easier the die is filled. It can be observed that feedstock F2 gives the lowest viscosity at any shear stress (or shear rates) and temperature. It can also be observed (Table 6) that the viscosity of any feedstock decreases with the temperature and with the

Table 6
Viscosity of the feedstocks at different temperatures and shear stresses

		Shear stress (Pa)				
		45337	90673	135103	150518	194947
Feedstock	Temperature (°C)	Viscosity (Pa s)				
F1	130	2674.6	717	407.3	348.6	234.3
	140	1408	454.3	274	207.6	167
	150	802	319	176.1	166	121
	160	493	219	142	123	92
F2	130	769	346	228	200	145
	140	490	236	154	137	101
	150	337	173	112	97	93
	160	245	119	78	67	53
F3	130	865	369	252	207	157
	140	509	256	175	153	112
	150	369	181	120	103	76
	160	238	131	86	80	58
F4	130	2087	689	383	329	222
	140	1409	483	267	226	158
	150	937	347	189	164	117
	160	666	234	143	125	91
F5	130	2919	1225	758	662	389
	140	1578	707	474	396	298
	150	841	510	316	282	227
	160	605	313	223	182	98

shear rate. From the flowability point of view this is the best feedstock of those studied. In general, during ceramic injection moulding shear rate typically varies between 100 and 1000 s^{-1}. It is accepted that flow into the mould cavity requires viscosity of less than 1000 Pa s.[22,23] However, this arbitrary value must depend on machine pressure and sprue, gate and mould design, making it possible for higher viscosities to be tolerated. It should be pointed out that all the feedstocks studied in this work give lower viscosity than 1000 Pa s at 100 s^{-1} (F1: 650 Pa s; F2: 435 Pa s; F3: 476 Pa s; F4: 693 Pa s and F5: 724 Pa s). According to these figures the five feedstocks could be injectable from this point of view.

3.3. *Influence of shear rate on viscosity: powder law index:* n

In general PIM feedstocks are considered to be shear thinning or pseudoplastic fluids: the case of porcelain is not an exception. The main characteristic of a pseudoplastic fluid is that viscosity decreases with the increase of the shear rate. This kind of fluids fits very well to the Ostwald and De Waele power law:[24,25]

$$\dot{\gamma}_{\mathrm{a}} = K\sigma^{n}$$

where γ_a is the apparent shear rate; τ is the shear stress; K is a constant; n is the power law index $n < 1$.

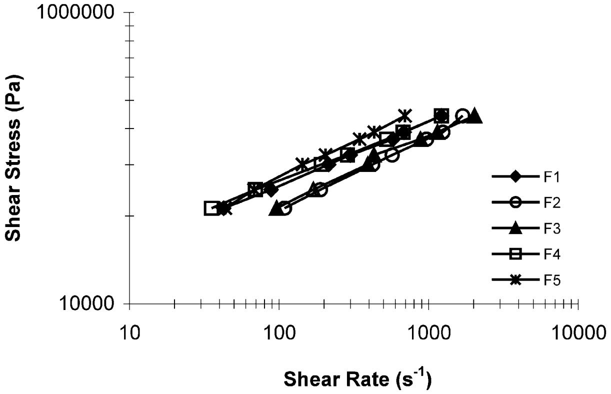


Fig. 7. Log shear stress vs. log shear rate at 150°C.

The value of n indicates the degree of sensitivity of viscosity against shear rate. The lower the value of n the more sensitive is the viscosity against shear rate. During the injection moulding process pseudoplastic behaviour is desirable and, therefore, a decrease in viscosity with an increase in the shear rate. This dependent behaviour of the viscosity against the shear rate is especially important when producing complex and delicate parts, which are important products in the CIM industry. In Fig. 7 a comparison of the five feedstocks is shown.

The values of n (taken in the shear rate range of 50–1700 s^{-1}) are calculated from the slope of the Fig. 7 curves. The lower the value of n, the more quickly the viscosity of the feedstock changes with the shear rate. It can be seen that feedstock F4 is the most sensitive to shear rate while feedstock F2 the least sensitive, this lower sensitivity could be due to the high binder content in this feedstock (the binder itself has a Newtonian behaviour). From a shear rate sensitivity point of view, F4 is the best feedstock (Table 7).

3.4. *Determination of yield stress*

In order to calculate yield stress, the model of Casson[26] has been used. This model was successfully applied to many suspension systems and as a result it has been found that this model also describes the behaviour of porcelain feedstocks.[27–30]

$$\sigma^{1/2} = \sigma_{y}^{1/2} + C\gamma^{1/2}$$

where σ is the shear stress; σ_y is the yield stress; C is a constant; γ is the shear rate.

The yield stress was calculated from the graph $\tau^{1/2}$ vs $\gamma^{1/2}$ at 150°C. The yield stress corresponds to the value of shear stress when the shear rate is zero (Table 8).

F2 gives the lowest yield stress; nevertheless, all the feedstocks show very similar values of yield stress. Furthermore, this is a low value of yield stress and all of them should be considered good from the yield stress point of view.

3.5. Influence of temperature on rheological behaviour

Temperature plays an important role in injection moulding. The dependence of the feedstock on the temperature can be expressed by the Arrhenius type equation:

$$\eta(T) = \eta_0 \exp\left(\frac{E_a}{RT}\right)$$

where E_a is the flow activation energy; R is the gas constant; T is the temperature; η_0 is a reference viscosity.

Plotting viscosity (at a shear rate of 100 s^{-1}) against temperature inverse, the Activation energy is calculated from the slope of this curve (Table 9).

As can be seen in Table 9, the values for activation energy are very similar for all the feedstocks, at the same time, very similar to activation energy of the pure binder ($E_a = 31$ kJ/mol). The absence of effect of solid concentration on E_a is a typical result of filled-polymer systems.[31] Nevertheless, F4 gives slightly better values as regards temperature sensitivity. On the other hand, F5 is the most sensitive feedstock to the temperature.

Table 7
Power law index, n, for the five feedstocks

Feedstock	Powder law index: n
F1	0.44
F2	0.51
F3	0.48
F4	0.41
F5	0.49

Table 8
Yield stress values for the five feedstocks

Feedstock	Yield stress (Pa)
F1	30,000
F2	22,000
F3	28,000
F4	33,000
F5	23,000

Table 9
Activation energy values (taken as shear rate of 100 s^{-1})

Feedstock	E_a (kJ/mol)
F1	29
F2	26
F3	28
F4	22
F5	31

3.6. General rheological index

In order to establish a general moulding index, the model Weir proposed for polymers has been used including the main parameters as regards flow.[32]

$$\alpha_{STV} = \frac{1}{\eta_0} \frac{\left|\frac{\partial \log \eta}{\partial \log \dot{\gamma}}\right|}{\frac{\partial \log \eta}{\partial 1/T}}$$

where, η, is the viscosity η_0 is a reference viscosity T is the temperature γ is the shear rate and α_{STV} is the rheological index. Simplifying the above equation:

$$\alpha_{STV} = \frac{1}{\eta_0} \frac{|n-1|}{E/R}$$

where, η_0, is a reference viscosity, E is the activation energy, n is the power law index, and R is the universal gas constant.

The higher the value of α_{STV}, the better the rheological properties. In order to calculate this rheological index, a temperature of 150°C and a shear rate of 100 s^{-1} have been chosen. The results are as in Table 10. (these values have been multiplied by 10^6).

According to these figures, F4 feedstock gives the highest rheological index and, therefore, it would be the best from a rheological point of view. F1, F2 and F3 are very similar. On the other hand F5 givers the lowest value and it could be considered to be the worst candidate for injection moulding in terms of flowability.

3.7. Injection moulding

Injection moulding trials were carried out in order to:

1. Confirm the relation between the rheological properties and injection moulding behaviour.
2. Compare the feedstocks.
3. Confirm that these feedstock are injectable.

The feedstocks were injection moulded in a bending bar mould. After many trials for the optimisation the best injection parameters are as follows:

1. Injection temperature: 150°C
2. Injection Speed: 15×10^{-6} m^3/s
3. Holding Pressure: 60 MPa
4. Cooling time: 25 s.

All the samples had an excellent appearance after injection moulding: no sink marks nor weld lines were appreciated in any sample (Fig. 8).

However, feedstock F5 gave bad results in terms of mould integrity. Due to worse rheological properties and particle geometry, the mould was damaged (Fig. 9),

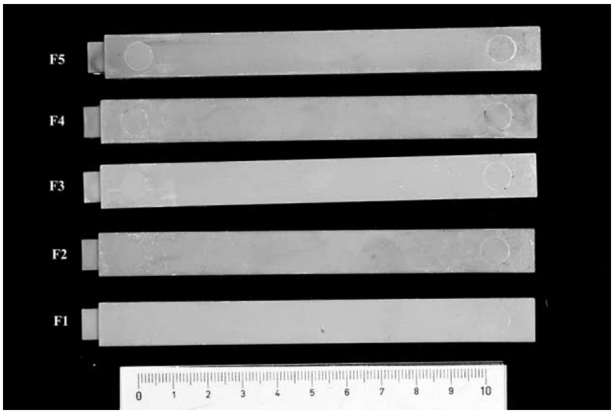


Fig. 8. Photograph of the injected feedstocks.

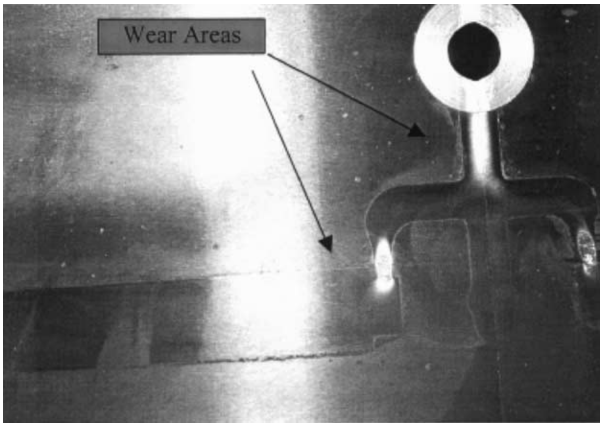


Fig. 9. Wear in the mould produced by feedstock F5.

Table 10
General rheological index

Feedstock	α_{stv}
F1	55
F2	53
F3	52
F4	74
F5	35

especially in the narrowest paths (gates). It can be said that F5 it is not a good candidate for injection moulding.

It has been confirmed that there is a relation between the rheological properties and the injection moulding behaviour.

All the feedstocks would be good candidates for injection moulding except F5 from a moulding point of view.

As this paper is being written, further investigations are being made with these feedstocks.[33] As a preliminary result of this investigation, which is out of the scope of this paper, it can be anticipated that F4 is not only the best feedstock in the injection moulding stage, but also, in the debinding and sintering stages. F1, F2 and F5 feedstocks show debinding problems such as cracks and blisters. F3 also has some debinding problems, nevertheless its behaviour is better than for F1, F2 and F5. Therefore, it seems that the rheological properties somehow influence the quality of the finished sample.

Table 11
Summary of most relevant properties of the porcelain powders formulations

Powder	D_{50} (μm)	S_w	CPVC
1	4.12	2.41	0.62
2	4.00	2.11	0.64
3	6.51	2.37	0.69
4	6.56	1.88	0.68
5	7.02	2.02	0.72

Table 12
Summary of the rheological characteristics of the powders

Feedstock	η^a (Pa s)	n	Yield stress (Pa)	Activation energy (kJ/mol)	Rheological index
F1	650	0.44	30,000	29	55
F2	435	0.51	22,000	26	53
F3	476	0.48	28,000	28	52
F4	693	0.41	33,000	22	74
F5	724	0.49	23,000	31	35

[a] Viscosity taken at $T = 150°C$ and shear rate of 100 s^{-1}.

4. Conclusions

Tables 11 and 12 summarise the main powder characteristics and the rheological properties of the studied feedstocks.

After the study carried out the following points can be concluded:

1. It has been successfully proved that it is possible to use recycled porcelain in the ceramic injection moulding process. Nevertheless, the powder characteristics are of great importance because using the same binder the characteristics of the powder change the rheological behaviour of the feedstock.
2. Concerning the CPVC concentration, the best model for describing the behaviour of the porcelain feedstocks against the different solids content is the model proposed by J.Janardahna et al., being the most updated model among the others studied.
3. Critical solid loading is strongly influenced by the powder granulometry: the CPVC is inversely proportional to powder particle size. As powder size increases, critical solid loading decreases. But critical

solid loading is also dependent on particle size distribution and compaction rate: the broader the particle size distribution, the higher the solid loading, and the higher the compaction rate the higher the solid loading. Confirming this reasoning, powder 5 gives the highest critical powder concentration.

4. From the standpoint of shear sensitivity, F4 has the lowest powder law index and is, therefore, considered to be the best feedstock in terms of pseudoplasticity. On the other hand, F2 and F5 give the lowest yield stress value. These two feedstocks should be considered as the best feedstocks from that point of view.
5. In terms of influence of temperature on rheological properties, all the feedstocks are very similar, because they all have the same binder, and the binder is the main influence on the activation energy. Nevertheless, feedstock F4 shows slightly better behaviour.
6. At a reference temperature of 150°C and shear rate of 100 s^{-1}, F4 has the best rheological general index and, therefore, shows the best flow properties.
7. F5 gives the lowest rheological index and, therefore, it is considered to be the worst candidate for injection moulding. On the other hand it has been proved that, when using the same binder, the characteristics of the powder change the rheological behaviour of the feedstock.
8. The rheological properties of a feedstock will somehow determine whether a feedstock is good for moulding or not. The rheological index appears as a good parameter for simple evaluation of feedstock for injection moulding. It has been proved that the feedstock with the worst general rheological index (F5) also gave the worst results for injection moulding.

Acknowledgements

The authors would like to thank the European Community for supporting this Brite Euram project with the reference BE95-1465, KPCL, Soarmoldes and Porcelanas del Bidasoa for giving their insights on porcelain powders manufacturing. The University of the Basque Country (project UPV 203.215-605/199) is also acknowledged

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