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Aqueous injection moulding of porcelains

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Abstract

This work studies the different processing parameters involved in the manufacturing of porcelains by injection moulding of an aqueous ceramic suspension. The industrial slip (68 wt.% solids) was optimised for the injection process (through evaluation of the homogenisation procedure) by increasing the solid loading to 72 wt.% (49.5 vol.%) and the dispersants concentration. Agar solutions with concentrations of 3 and 4 wt.% were prepared by heating at 92 °C, but a new procedure for increasing the agar concentration up to 10 wt.% by means of a pressure cooker was applied, also. The evolution of viscosity on cooling was studied for the different agar solutions and porcelain suspensions containing different quantities of agar. The best gel casting performance was reached by adding 0.5 wt.% agar prepared as a 6 wt.% solution. Using this suspension, the injection conditions were optimised for shaping in only one step a cup with handle, through development of a mould prototype and by studying the effects of pressure, residence time, suspension temperature in the tank and in the mould, etc. By controlling these parameters injection moulded cups with handle were obtained with a green density of 60% of theoretical and a weight variation in the dried products within ±2%.

Keywords: Injection moulding; Porcelain; Shaping; Suspensions

1. Introduction

Porcelains are vitrified and fine-grained whitewares usually produced from natural raw materials like clays (mostly of the kaolinite group), quartz and feldspar. In the wet state clay particles slip during flow as a consequence of the laminar structure of the more common clay minerals, in which the crystal structure has well-defined layers interlinked by weak bonds. This provides the characteristic plasticity of clay-based materials. For this reason tableware articles are mostly produced by plastic forming methods, the most widely used being jiggering.[1] The use of shaping machines based on the roller system has reached an important technological development for producing flat and axially symmetrical products, such as plates and bowls.[2]

However, asymmetrical articles cannot be produced by the conventional plastic methods. The manufacture of complex-shapes and hollowware requires the use of slip forming methods, where the low viscosity slip can fill thin sections of the mould, edges, etc. The main advantage of suspension processing techniques like slip casting is that the control of the slip stability allows to maintain particles apart each other even during forming, so that more homogeneous and denser bodies are obtained. The problem of slip casting is that it is intensive labour thus making more difficult a large scale, cost-effective production. A further development was pressure casting, which is similar to slip casting, but the casting rate is increased by applying an external pressure. Automatic pressure casting plants have allowed the manufacture of oval dishes and asymmetrical hollowware thanks to the development of resin moulds with controlled porosity and high strength.[3,4]

One of the most diffused articles in the tableware industry is the cup with handle. This is a low value added article which presents intrinsic technical difficulties, since

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the cup body and the handle are usually produced separately and then assembled together manually. This requires a constant production of plaster moulds, and facing problems arising from fettling and cutting, and the low precision in the shape and in the positioning of the handle on the cup. For these reasons the challenge for an improved industrial production would be the manufacturing of the cup with the handle in a single forming step. Some attempts have been reported to produce porcelain cups by conventional injection moulding,[5] but this technique is too expensive and complex to allow a competitive production, due to the high costs of the additives and the long debinding times resulting in a high consumption of energy and large number of rejected bodies. It has been recently developed a machine which produces the handle by pressure casting and attaches to it automatically, in presence of vibrations, a cup body produced by plastic forming.[6] Other machines have been recently produced by different companies (i.e. Elmeceram in France and Dorst in Germany).[7] This allows an improved quality control but the possible limitations refer to the high cost of the high pressure casting machine and the very expensive resin moulds. Nevertheless, nowadays industrial production is mainly still performed by forming independently the cup body and the handle and further attachment of the handle to the body.

An interesting approach for the production of asymmetrical hollowware is injection moulding of aqueous ceramic suspensions through gelling of polysaccharides.[8] Such injection moulding enables the elimination of costly equipment for controlling noxious emissions of presently used synthetic binders used in traditional injection moulding. Furthermore, the moulding machine operates at very low pressure and temperature conditions (normally below 0.4 MPa and 90 °C), which strongly reduce the costs and enable the construction of moulds by using lower cost metals, like aluminium, thus allowing a self-production. An additional advantage is the use of naturally occurring binders, like those used in the food industry, thus improving safety and working environment. The amount of polysaccharide necessary to consolidate a rigid body is very low, typically below 1 wt.% with regard to dry solids.[9] The most widely used group of thermogelling polysaccharides is the family of agaroids.[10] Agar is a polygalactoside constituted by two major components: agarose and agaropectine. Agarose is the gelling fraction of agar and consists on repeating units (agarobiose) of alternating β-D-galactopyranosil and 3,6-anhydro-α-L-galactopyranosil groups. Agaropectine has a similar structure but contains 5–10% sulphate esters and other residues. Since agarose is the purified fraction it has a higher gelling power, but agar can also provide very rigid gels and has a much lower price. This fact linked to the simplicity of the process and the low machine requirements makes it interesting to explore the possibility of producing porcelain bodies with complex shapes, sharp edges or other geometry (difficult or impossible to obtain with a porous mould) by injection of aqueous slips with agar at reasonable costs.

The aim of the work is to optimise the rheological behaviour of a conventional porcelain slip to enable processing by injection moulding of aqueous slips. The injection parameters for obtaining a complex-shaped article, like the cup with handle, are selected as a case study in order to evaluate the technological aspects involved in the industrial application of this process for complex shaped porcelain bodies.

2. Experimental

A standard porcelain formulation supplied by a tableware producer was used in this work. The starting ceramic powder consists of soft granules that are easily broken by mechanical mixing. This powder is being used for industrial production of bodies by slip casting or plastic forming. The main characteristics are summarised in Table 1. The density of the powder was measured by He pycnometer (Multipycnometer, Quantachrome, USA), the specific surface area was measured by single point BET method (Monosorb MS-13, Quantachrome, USA), and the particle size distribution was determined using a laser analyser (Mastersizer S, Malvern, UK).

The morphology of the starting powder was observed by scanning electron microscope (SEM). At low magnification, the powder appears as spherical granules with typical diameters of 200 μm. Fig. 1a shows a low-magnification SEM picture of the as-received granulated powder. The observation of the microstructure of these granules reveals the existence of platelet-like particles, typical for clays, as can be seen in the high magnification SEM picture of Fig. 1b.

The industrial slip is prepared in the factory by mixing the powder and fixed amounts of deflocculant in water until the density of the slip is about 1.74 g/cm^3. For a typical porcelain composition the weight per cent of solids in a slip can be calculated from the measured slip density.[11] According to the measured density of the slip and that of the starting powder, the solid loading was calculated to be 68 wt.% (44.5 vol.%). The industrial slip

Table 1
Characteristics of the starting powder

Composition	(wt.%)	Density 2.65 g/cm^3
SiO_2	68.6	Surface area 9.5 m^2/g
Al_2O_3	26.4	Average diameter, 7 μm
Fe_2O_3	0.5	
Na_2O	0.15	
K_2O	3.9	

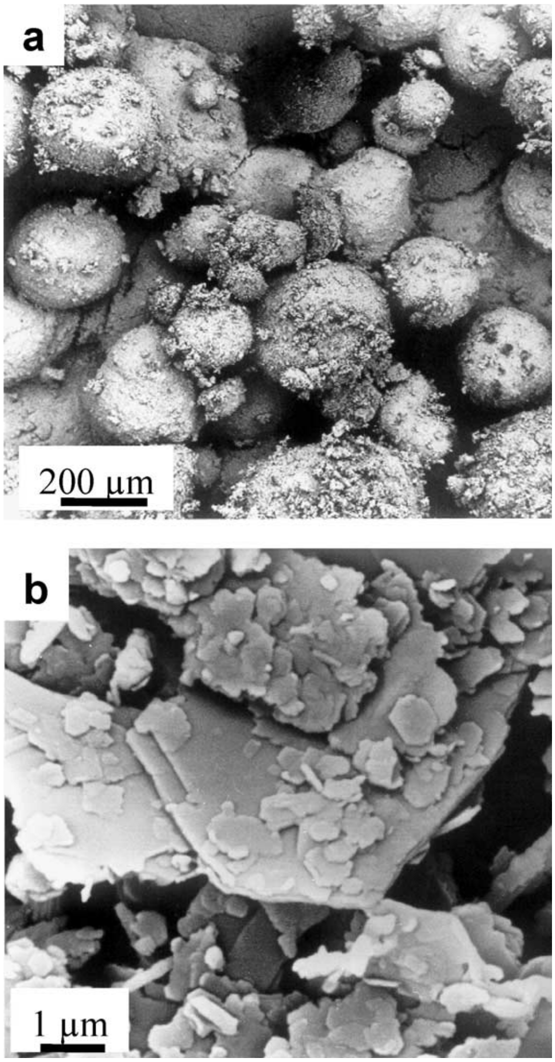

Fig. 1. SEM microstructure of the as-received granulated powder (a) and a detail of the microstructure at high magnification (b).

is prepared by adding two different silicate-based deflocculants, Giessfix W 162/10 and Formsil D (Zschimmer & Schwarz, Germany) in concentrations of 0.11 and 0.035 wt.%, respectively, referred to dry solids. This formulation was used to prepare different laboratory batches by strong mechanical agitation using a high shear mixer (Silverson L2R, UK, 6000 rpm).

The solid content seems excessively low for injection moulding, which usually requires more than 50 vol.% solids. So, the first objective was to increase the density of the slip. Solid loading was increased up to 72 wt.% (49.5 vol.%) maintaining the same relative proportions of dispersants. This slip was prepared following three different homogenisation procedures:

(1) Strong mechanical agitation with a high shear mixing for 3 min.
(2) Ball milling (18 h).
(3) Slow mechanical agitation with helices (35 min).

The effect of the concentration of dispersants on the viscosity was studied for the optimised slip but the relative ratio of each dispersant was maintained constant.

A commercially available agar (Grand Agar, Hispanagar S.A., Burgos, Spain) was used as gelling agent. It is supplied in the form of powder with a mean particle size of 150 μm, but gelling efficiency increases when it is added as a solution.[9] Solutions of agar were prepared following two different procedures, depending on the concentration: (1) solutions with concentration $\leqslant 4$ wt.% were prepared by mixing with water and heating up to 92 °C to dissolve the agar, and (2) higher concentrations of agar (6, 8, and 10 wt.%) cannot be obtained by simple heating due to the high viscosity of the mixture prior to dissolution. Thus, concentrated solutions were prepared using a pressure cooker, where relatively low pressures and temperatures around 110 °C allowed to obtain a clear solution.

All the solutions, with concentrations ranging from 3 to 10 wt.%, were characterised and added to the porcelain slips in such a quantity that the final concentration of agar in the slips ranged between 0.5 and 1.0 wt.%, on a dry solids basis. The gel casting or injection slips were always prepared by mixing the dispersed porcelain slip and the required amounts of agar solution at 60–65 °C.

The rheological behaviour of the agar solutions and the porcelain slips was studied using a rheometer (Haake RS50, Germany) with a double-cone and plate measuring system, equipped with a solvent trap to reduce evaporation. Rheological characterisation included flow curves determination, by controlled rate measurements at room conditions. The evolution of viscosity with temperature of the solutions of 3 and 4 wt.% agar were measured on heating up to 92 °C followed by cooling, while concentrated solutions were measured only on cooling. Measurements were performed at shear rates of 100 and 5 s^{-1}. Slips without agar were measured at a shear rate of 100 s^{-1} by heating from 25 to 65 °C and further cooling down to 20 °C, and those containing agar were measured only on cooling. In all cases, the heating rate was 2.1 °C/min and the cooling rate was 1.2 °C/min.

Test bars were obtained by gel casting the differently prepared slips in stainless steel moulds with dimensions $81.5 \times 10 \times 10$ mm^3. The moulds were cooled by flowing water for times below 30 s and then opened for demoulding. After 48 h drying at room conditions, green samples were characterised by measuring the density by Hg immersion, the drying shrinkage and the weight loss.

Injection moulding was carried out with the formulation that provided the best performance in gel casting using a semiautomatic low-pressure injection machine (Peltsman, MIGL-33, USA) applying a pressure $\leqslant 0.2$ MPa. The tank was maintained at 65 °C and the mould at room conditions. Different models were designed to fabricate the mould for injection of a cup with a simple shaped handle focusing the attention on the gate shape and location, the optimal curvature radii to allow filling, the minimisation of demoulding constrains exerted by the handle and easy demoulding. Moulds were opened 3 min after injection. The cup was left inside the mould for drying at 40 °C in oven for 30 min.

3. Results and discussion

3.1. Rheological behaviour

Porcelain slips were prepared in the laboratory at the same conditions of the industrial slip (solids content, 68 wt.%, deflocculants content, 0.145 wt.%) by high shear mixing and further agitation with helices, as a reference. The preparation of the slip was optimised by increasing the solids loading, by improving the homogenisation procedure and by increasing the concentration of dispersing aids. Good slips were obtained when increasing the solid content to 72 wt.% maintaining the same contents of dispersants. This slip was prepared by the three mixing techniques reported in the experimental section.

The flow curves of the three concentrated slips are shown in Fig. 2. The viscosity curve of the reference slip is also included for comparison purposes. This slip has a low viscosity, below 200 mPa.s at a shear rate of 100 s^{-1}, which strongly increases with solid loading. For 68 wt.% slips, the lowest viscosity and thixotropy are obtained when the high shear mixer is used. However, this mixer is not suitable for further increments of powder concentration, and many bubbles appear. Ball milling promotes the reduction in particle size and both dilatancy and thixotropy increase. The pH of the mechanically stirred slips is ~8.3, lower than the ball milled one (9.1). Ball milling reduces the mean particle diameter with respect to that obtained by mechanical mixing procedures (5.3 and 5.8 μm, respectively), also. With these considerations, mechanical stirring with helices seems to be the more adequate procedure for the slip homogenisation.

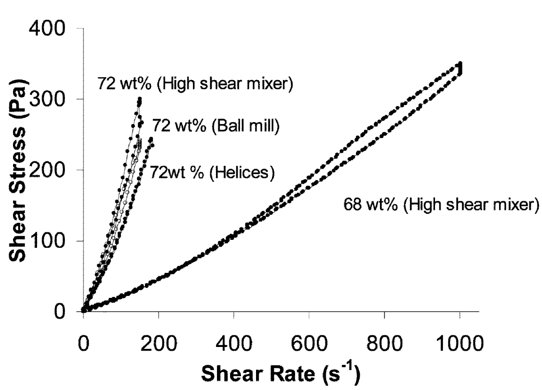

Fig. 2. Flow curves of the industrial formulation (68 wt.% solids) and of slips with 72 wt.% solids prepared by different mixing procedures.

The effect of heating and cooling on viscosity was studied for these slips. Fig. 3 shows the corresponding curves. The worse results were obtained for the high shear mixing, where a broad, open thixotropic cycle is obtained. In addition, above 60 °C the slip becomes non homogeneous and stability is not recovered. The ball milled slip has a lower thixotropy, the stability is not irreversibly lost, but the viscosities in the heating ramp are the highest ones. The lower viscosity in the whole temperature range is obtained for the slip stirred with helices, both in the heating and the cooling ramps. According to this study, further work was performed by mechanically stirring the slips with helices. The reference slip with 68 wt.% solids shows a much lower viscosity but, also, large differences between the cooling and the heating behaviour, thus suggesting a lack of stability that makes it necessary to increase the dispersants content.

A further step was to optimise the concentration of dispersants to improve the rheological behaviour of slips prepared to a solid loading of 72 wt.%. Fig. 4 shows the flow curves for the different dispersant concentrations. Both the viscosity and the thixotropy have a minimum for the slip dispersed with a total content of deflocculants of 0.25 wt.%. The evolution of viscosity with temperature for these slips is plotted in Fig. 5, where no significant differences in the cooling viscosity are found.

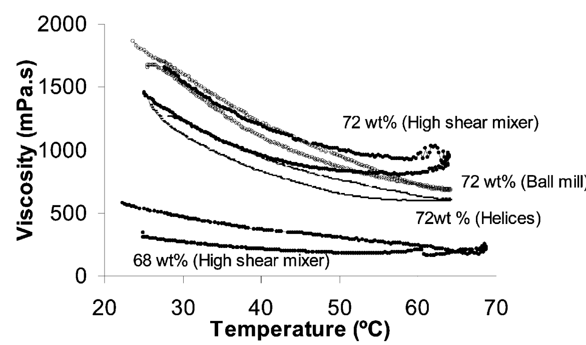

Fig. 3. Evolution of viscosity with temperature of the industrial formulation and 72 wt.% slips prepared by different mixing methods.

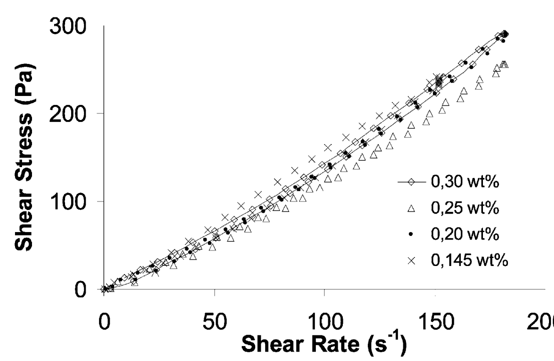

Fig. 4. Flow curves of 72 wt.% slips containing different concentrations of dispersant.

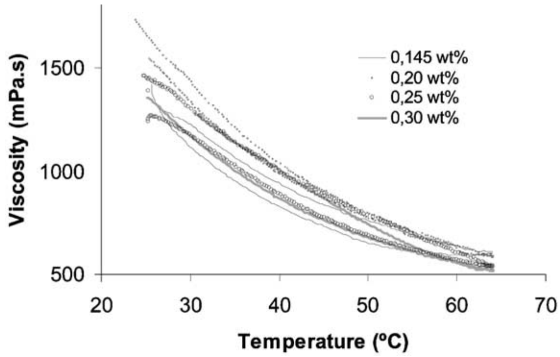

Fig. 5. Evolution of viscosity with temperature of 72 wt.% slips containing different concentrations of dispersant.

3.2. Gel casting

The effect of agar additions on the viscosity of porcelain slips was studied for the industrial 68 wt.% slip, and for slips prepared to reach a solid content of 72 wt.% with 0.25 wt.% dispersant.

First, the rheological behaviour was studied for agar solutions prepared to concentrations of 3 and 4 wt.% by simple heating at 92 °C, and 6, 8 and 10 wt.% prepared in the pressure cooker. The evolution of viscosity on cooling was first measured at a shear rate of 100 s^{-1} (Fig. 6a). It must be noted that the solution with 6 wt.% agar prepared in pressure cooker has lower viscosity than that with 4 wt.% prepared by simple heating at 92 °C. This suggests that at 92 °C most agar is dissolved, but full dissolution has not been reached, as it was believed and reported in previous work. The high viscosity of the concentrated solutions provokes overloading of the torque in the rheometer before gelation. In order to reduce the sticking effect of these solutions, the evolution of viscosity on cooling was measured at a lower shear rate (5 s^{-1}) and the obtained results are plotted in Fig. 6b. In all cases the T_g can be evaluated, but the increment of viscosity due to gelation cannot be fully registered for solutions with concentration >6 wt.% as the torque of the rheometer is exceeded.

The gel casting slips were prepared by adding the required amounts of agar solution to provide a final content of gelling matter of 0.5 wt.% (from solutions with 3, 4, and 6 wt.% agar), 0.75 wt.% using a 3 wt.% agar solution, and 1 wt.% from the 6 wt.% solution. The corresponding flow curves, obtained at a temperature of 60 °C, are shown in Fig. 7. The curve for the 68 wt.% industrial slip with 0.5 wt.% agar (3 wt.% solution) is also shown as reference. The addition of the agar solution promotes a decrease in the final solid content, as it can be seen in Table 2. In order to reduce the amount of water added with the agar it is necessary either to increase the concentration of the solution or to increase the initial solid loading of the slip. A slip with 74 wt.% solids was prepared but it was not worthy for

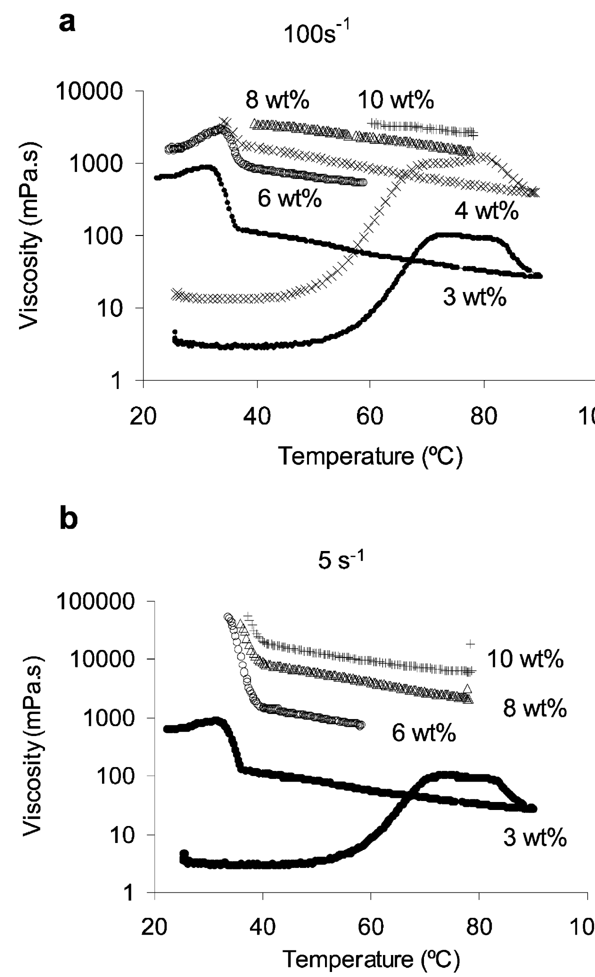

Fig. 6. Evolution of viscosity of agar solutions on cooling at shear rate values of 100 s^{-1} (a) and 5 s^{-1} (b).

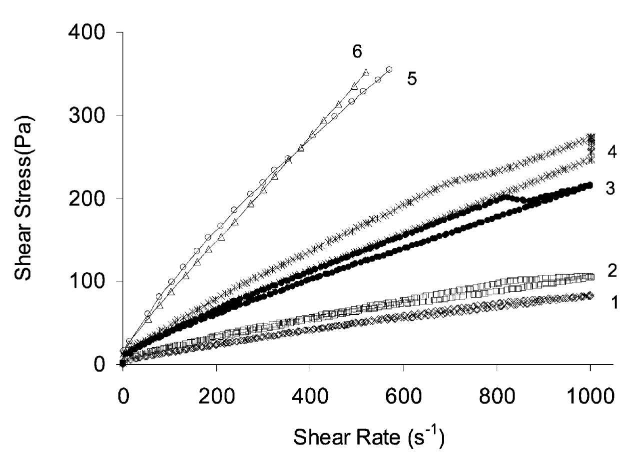

Fig. 7. Flow curves of porcelain slips with agar measured at a temperature of 60 °C: (1) industrial slip with 0.5 wt.% agar (3 wt.% solution); (2) slip with 0.75 wt.% agar (3 wt.% solution); (3) slip with 0.5 wt.% agar (3 wt.% solution), (4) slip with 0.5 wt.% agar (4 wt.% solution), (5) slip with 1.0 wt.% agar (6 wt.% solution), and (6) slip with 0.5 wt.% agar (6 wt.% solution).

Table 2
Characteristics of the green porcelain bodies obtained by gelcasting with agar

Slip	Total agar (wt.%)	Wt.% agar (solution)	Final solid loading (wt.%)	Weight loss (%)	Shrinkage (%)	Density (% TD)
1	0.5	3	61	38	16	60
2	0.75	3	61	31	10	62
3	0.5	3	64	30	9	63
4	0.5	4	66	32	10	63
5	1.0	6	65	33	12	63
6	0.5	6	68	28	8.5	64

further processing, probably due to the fast evaporation. The addition of a 4 wt.% solution of agar to the slip with 72 wt.% solids slightly decreases the amount of water in the injection slip. Although the control of the rheological properties as a function of temperature is more difficult, the preparation of this mixture does not present special problems, so it can be expected that it is useful for shaping. The slips with agar added as a 6 wt.% solution have still low viscosity to be manipulated and provided increased gel strength and maintain a higher solid loading, thus reducing shrinkage.

Fig. 8 shows the evolution of viscosity on cooling for the slips shown in Fig. 7. The viscosity at 60 °C and a shear rate of 100 s^{-1} is similar for slips 3 and 4, both with a total agar content of 0.5 wt.%. Slip 2 shows a lower viscosity at any temperature because the higher amount of agar implies a higher addition of water. Although all the slips show a sharp increase of viscosity on cooling below 35–37 °C due to the formation of a gel network, those containing agar prepared as a 6 wt.% solution exhibit a sharper viscosity gap, thus leading to a more rigid wet body, as expected from the higher solids loading.

All these compositions were cast into a steel mould to obtain test bars. Table 2 shows the main characteristics of the gel cast porcelain bodies in the green state in relation with the preparation conditions (total content of agar in the green and concentration of the precursor solution of agar added to the slurry). The weight loss (Δm) during drying was about 38, and 30%, for slips prepared with solid loading of 68 and 72 wt.%, respectively. Green densities are about 60% of theoretical for the industrial slip, and increases to 64% for a solid loading of 72 wt.%.

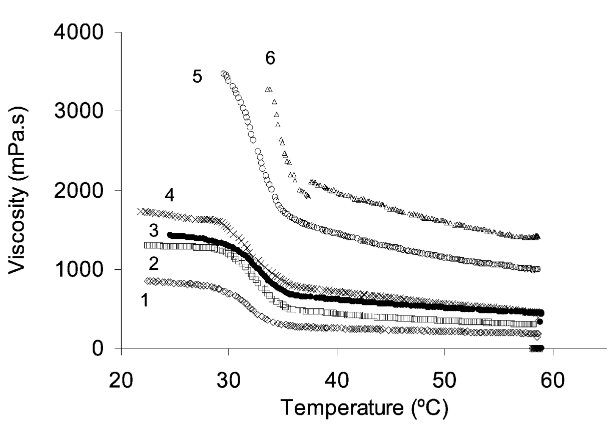

Fig. 8. Evolution of viscosity of porcelain slips with agar on cooling. Numbers correspond to the same formulations plotted in Fig. 7.

From these results it can be said that the addition of agar as an aqueous solution significantly reduces the final solid loading of the injection slip, so that the amount of water in the shaped body is very high. Hence, high linear shrinkage and lower green densities are obtained.

3.3. Injection moulding of aqueous suspensions

Porcelain injection slips were prepared by adding the required amount of 6 wt.% agar solution to give a final concentration of 0.5 wt.% using the optimised porcelain slip.

Using an own expert system, BC started to simulate moulding systems and moulding for simple geometry specimens. These experiments aimed to gather the processing parameters and to forecast possible moulding problems in order to minimise their negative effects. Particular attention was paid to the following parameters:

- shape of the cup bottom;
- shape of the cup handle;
- air evacuation path in the junction line of the two moulds halves;
- air evacuation path, through introducing a movable mould piece which shapes the handle.

The sequential disassembling of the mould permitted us to obtain good quality greens of "cup with handle".

The "cup with handle" model is shown in Fig. 9, which is a simple prototype with a full handle. The possible defects in the injected body would be related to the contact zone with the cup and no additional problems are expected for a hollow handle in comparison, for example, with slip casting, where the contact points between hollow handle and cup body produce a differential shrinkage. Furthermore, the injection moulded body is dried out of the mould, so allowing a more controllable drying. Finally, a further design with a hollow handle is now being developed by suitably designed mould which can be disassembled in different parts.

Different combinations of mould temperature, pressure and time were studied in order to reach the most appropriate injection moulding parameters. A lot of tests were carried out to overcame different problems. The most important ones were: irregular filling of the mould; macro-defects formation (bubbles, cavities or shape irregularities) either during shaping, or during de-moulding

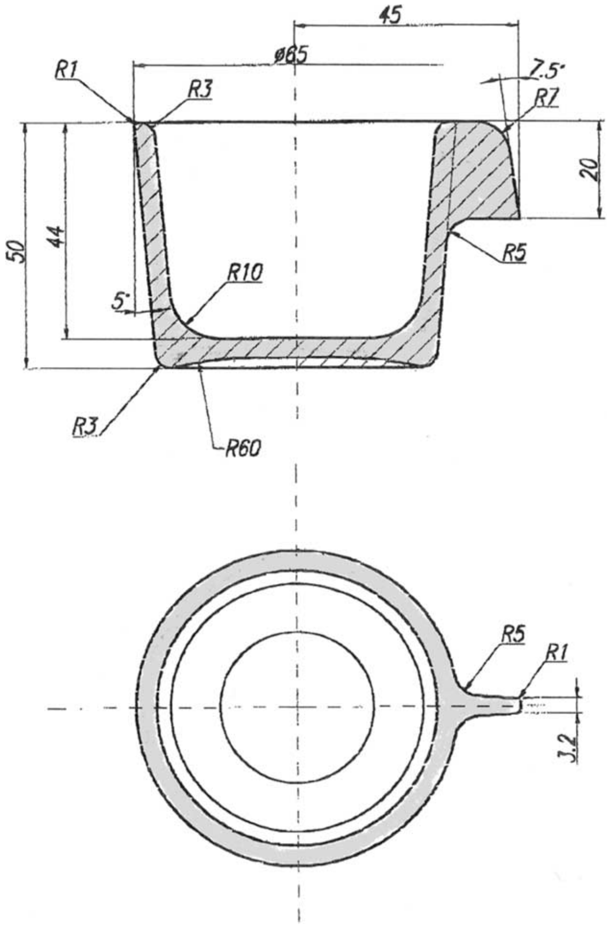

Fig. 9. Design of the cup with handle mould.

of the cup; cracks formation during drying of the cup. Finally, it was possible to produce injection moulded "cups with handle" having good geometrical shape and no forming defects. A sintered cup, made with the porcelain mix, is shown in Fig. 10. Repeated tests confirmed that the best shaping conditions (with the laboratory machine and modified prototype mould) were obtained by using the following injection moulding parameters: mix temperature: 65 °C; injection pressure: 0.2 MPa; injection time: 100 s; cooling of the mould, by tap water, after injection. The open moulds with the injected bodies were left to dry in oven for 30 min to avoid deformation during handling in the laboratory. By using these parameters a very high moulding constancy was obtained, which was reflected by the fact that the weight of the dried cups ranged within ±2%. The green density of the injected bodies was 1.73 g/cm^3 (~60% of theoretical).

All the above results were obtained at laboratory conditions. Obviously, for the process to be scaled-up to an industrial production higher versatility is required. In this sense, we are developing a carrousel line which allows the continuous motion of the body to a drying furnace. Previous tests demonstrate that it is possible to

Fig. 10. Picture of a sintered porcelain cup obtained by aqueous injection moulding.

transfer the as-injected body into a non metallic mould that acts as a receptacle for drying, so allowing a more efficient drying. In this way the continuous machine would require only two metallic moulds, so that when the first one is being filled the second is being opened to transfer the body to the receptacle.

4. Conclusions

An industrial porcelain slip with 68 wt.% solids was rheologically optimised for injection moulding by increasing the solid loading to 72 wt.% and the dispersant concentration. Agar was used as thermogelling polysaccharide in the form of aqueous solutions. For shaping, both the agar solution and the slip were mixed at a temperature of 60–65 °C. Gel casting was first studied by adding agar solutions with concentrations of 3–4 wt.%, to maintain a low viscosity suspension suitable for pouring. Concentrated agar solutions (from 6 to 10 wt.%) have been prepared by means of a pressure cooker. This new procedure allows to reduce the amount of water added with the gel-former, thus maintaining a higher solids loading and reducing shrinkage. Homogeneous green bodies with a relative density of 64% of theoretical have been obtained by gel casting the porcelain slip with 0.5 wt.% agar prepared as a 6 wt.% solution.

Injection parameters were studied by using a purposely designed and manufactured mould for shaping a cup with handle. The better results in terms of product homogeneity and process reliability were obtained by applying a pressure of 0.2 MPa, for an injection time of 100 s, by maintaining the tank at 65 °C and the mould at room temperature. After injection, the slip gelates in the mould by cooling with tap water and the open moulds with the injected bodies were left to dry in oven for 30 min. Green densities were 60% of theoretical and the variation in weight was within 2%. Further improvements are being investigated for scaling-up the process to industrial production.

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