FORMING CERAMIC TILES FROM GELS

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ABSTRACT

The forming of materials from gels has undergone remarkable development in recent years, as a result of the great advantages that this procedure affords as opposed to other forming methods, such as slip casting or injection. The reason for this rapid advance is largely due to the use of the properties of compounds derived from agar, a polysaccharide that gels at low temperature, giving rise to gels with excellent mechanical strength.

In the present work, the feasibility has been studied of using gel casting as a ceramic tile forming method. For this, a standard ceramic composition has been used, based on a mixture of clay, feldspar and quartz, to which agar and other additives have been added in different proportions. Furthermore, two prototypes for the performance of the experiments have been designed: a water-cooled metallic die with relief for casting the gellable suspension and a dryer that enables uniform drying through both faces of the ceramic tile. The experiments were conducted in a low-pressure injector.

Using the foregoing composition and equipment, a study has been conducted of the different manufacturing process stages with a view to optimising these. The following stages were studied: preparation of the gellable suspension, gelling, drying, machining and sintering. Using the operating conditions established, 5x10 cm ceramic tiles were fabricated.

1. INTRODUCTION

Recent years have witnessed growing interest in the scientific community for the so-called direct consolidation techniques (DCT) for the forming of all types of ceramics[1][2]. What these techniques have in common is that the fluid suspensions involved can be transformed into rigid pieces without needing to remove the suspending liquid. The conservation of the structure of the starting suspension in the green piece is one of the main advantages. In addition, any type of shape can be obtained, no matter how complex, without the disadvantages of traditional techniques, such as slip casting, which is limited to objects of great thickness, or high-pressure injection, a method in which large quantities of organic additives are used that are subsequently eliminated by long heat treatments.

Numerous forming methods are available, which can be grouped under the term DCT. These can generally be classified in three large groups: methods that use gel casting for consolidation, methods based on the colloidal character of the suspension, and methods that use evaporation for the total or partial elimination of solvents[3] .

Of all these techniques, those belonging to the first category have probably been developed furthest. Gel casting basically consists of encouraging a polymer to develop a three-dimensional structure or network that bonds the suspension particles, thus avoiding particle agglomeration when the piece dries. The suspension is transferred to a mould where gelling occurs. The solid product is then demoulded, followed by the remaining process steps, such as drying, machining and sintering.

The original process patented in 1992[4] was based on chemically induced gelling of acrylamide monomers. However, the neurotoxic effect of acrylamide is the main disadvantage for its industrial application. Numerous alternatives have since been developed, including polymerisation by metallic complexes[5], or thermally induced gelling in which suspensions that contain biopolymers, such as agarose[6] or carrageenan[7], gel on cooling, or such as methylcellulose, which gel on heating. What all these processes have in common is that they use water as a solvent and a low concentration of gellable organic component, thus providing a rapid sintering process.

Although different gellable binders and gums (gelatin, chitosan, starch, etc.) have been used[8-10], agar derivatives produce gels with by far the greatest mechanical strength[6], and have therefore been the focus of special attention[11][12]. Their greater efficiency enables using smaller quantities, which facilitates processing of the gellable suspension and castings.

The present paper studies the feasibility of using agar as a gelling agent for the forming of ceramic tiles by casting. The ultimate objective is to determine whether this forming method could be used as an alternative to the various methods that are currently employed for the manufacture of ceramic trims, such as slip casting, plastic pressing or extrusion.

2. AGAR GELLING

Agar is a complex water-soluble polysaccharide, obtained from red algae of the Rhodophyceae family by extraction and leaching[13]. Agar is made up of two main fractions: agarose and agaropectin. Agarose is a neutral polysaccharide that contains non-sulphated groups and is the component responsible for the gelling power of agar. Its molecular formula consists of alternate chains of D - galactose - 3.6 - anhydrous – L - galactose. Agaropectin has a similar structure, but contains between 5-10% sulphate esters and other residues. It is a sulphated polymer, with ionic groups and very little gelling power. It is responsible for viscosity, which varies depending on the species of alga, production method and sulphate content. The proportion of these two polymers varies widely and the agarose percentage in agar producing algae ranges from 50 to 90%. Figure 1 shows the typical structures of agarose and agaropectin.

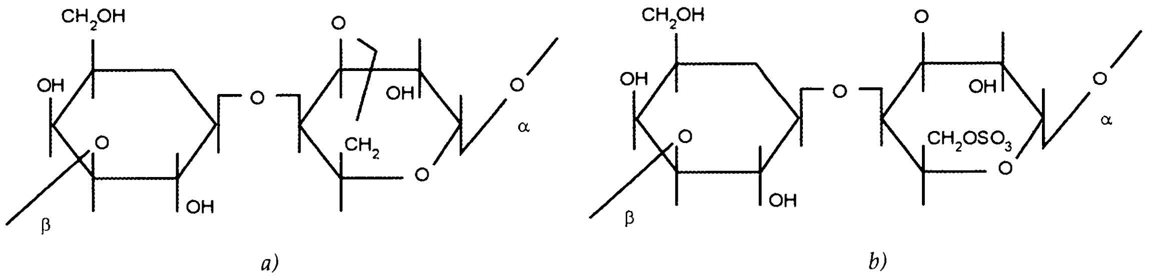


Figure 1. Molecular formula of a) agarose and b) agaropectin (source: www.agar.com)

Agar colour ranges from white to pale yellow. It is normally odourless, although it has a characteristic light smell. It is non-toxic, inflammable and requires no special safety precautions. One characteristic of this polysaccharide is its capacity to form resistant gels at very low concentrations, typically around 1% by weight. Gelling temperature is located around 37-39°C. The process depends exclusively on hydrogen bridging between its constituent polysaccharides. When solution temperature decreases, the disordered spirals that make up the material group in helices, producing aggregates, finally developing the macromolecules that form the gel. Figure 2 schematically illustrates the process. The agar gelling process is fully reversible; this means that it has the capacity to form gels simply by cooling hot solutions without needing to react with other products.

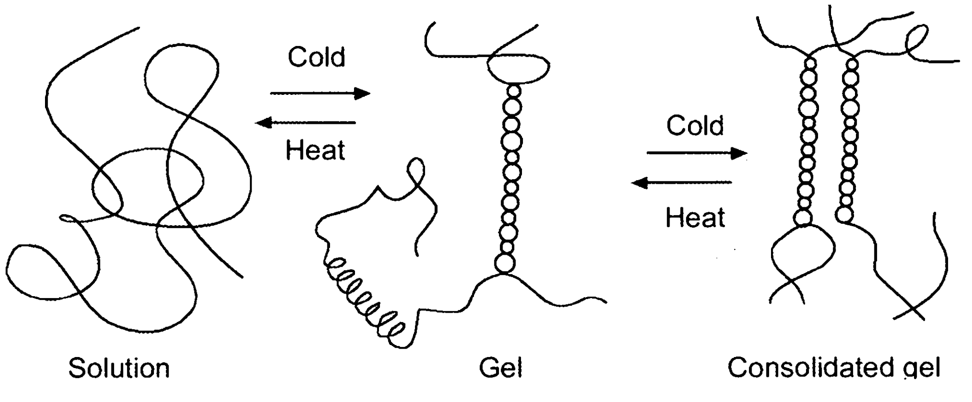


Figure 2. Schematic illustration of thermoreversible agar gelling (source: www.uct.ac.za)

Agar is insoluble in cold water, but dissolves completely at temperatures above 87°C. After it has dissolved, when the temperature of the solution is lowered, viscosity suddenly increases when the temperature drops below 36°C. This phenomenon is known as gel hysteresis, because there is a difference between gelling temperature and dissolution temperature.

3. EXPERIMENTAL

3.1. MATERIALS

The different compositions were prepared using the typical raw materials employed in porcelain tile manufacture: white clay, sodium feldspar and feldspathic sand. Table 1 details the chemical composition of these raw materials. The agar sample, reference Pronagar H-1417/01, was supplied by Hispanagar.

Oxides (%)	**White clay**	**Feldspathic sand**	**Sodium feldspar**
SiO_2	59.6	88.5	70.6
Al_2O_3	26.7	7.0	17.6
Fe_2O_3	0.85	0.1	0.09
TiO_2	1.29	0.08	0.12
K_2O	2.22	2.0	0.32
MgO	0.61	0.01	-
Na_2O	0.41	0.1	10.0
CaO	0.32	0.1	-
LOI	8.0	2.1	0.3

Table 1. Chemical composition of the raw materials used (% by weight)

3.2. EQUIPMENT

Casting of the gellable suspensions was carried out in a Peltsman Model MIGL-28 low-pressure injection machine. Figure 3 provides a general view of the machine and its parts. The machine basically consists of a stainless steel tank, a lid (1) connected to blades by means of a belt (2), a tank discharge pipe that feeds into the die (3), and three temperature controllers located in the tank, feeder pipe and die inlet, which are displayed on the instrument panel (4). In addition, the apparatus has two manual air valves: the first (5) controls the cylinder that clamps the die (6), and the second supplies pressurised air to the tank to enable filling the die (7).

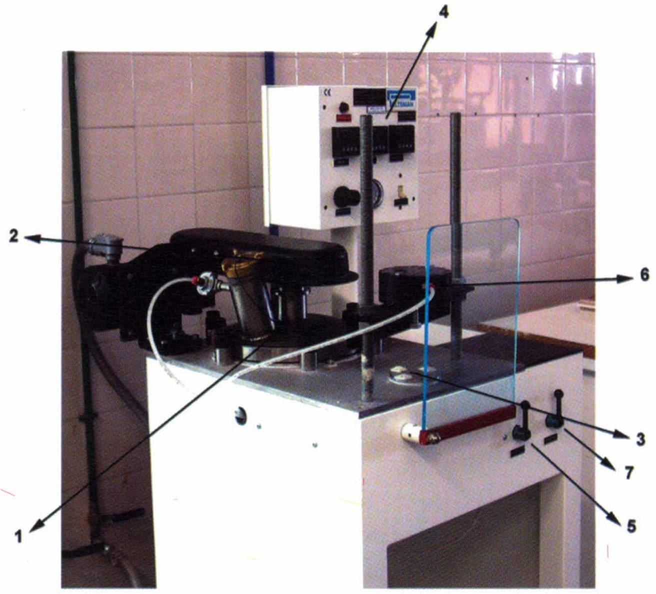


Figure 3 Low-pressure injection equipment used for gel casting

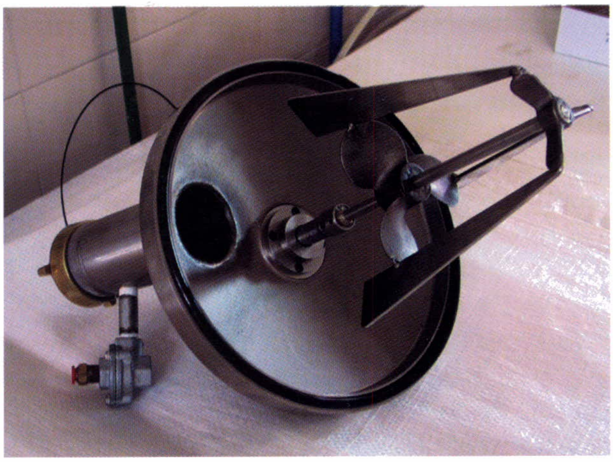
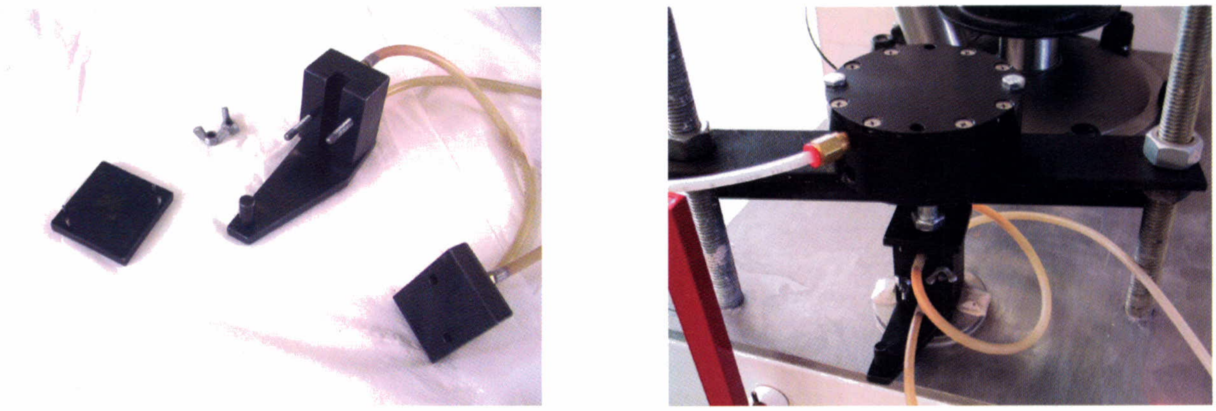


Figure 4. Detail of the tank lid and mixing blades

Finally, the machine has a metal die, with a parallelepiped cavity (Figure 5) measuring 1x1x5 cm. This die has a water-cooled jacket for accelerating gelling.



a) die parts

b) die fixed to the machine

Figure 5. Detail of the die used in the low-pressure injection machine

3.3. EXPERIMENTAL PROCEDURE

3.3.1. Preparation of the gellable suspension

The literature indicates that for the best exploitation of the gelling properties of agar, particular attention is to be paid to the way in which agar is incorporated into the ceramic suspension[7]. It has been verified with alumina suspensions that the best results are obtained when the agar is fully dissolved before incorporating it into the ceramic suspension, performing this addition at temperatures of at least 60°C, to avoid flocculation of the suspension.

Based on this information and the results of some preliminary experiments, a gellable suspension preparation method has been designed. First, the agar is added to the water at a temperature of 90°C, holding this temperature until achieving total dissolution of the solid. The solution is cooled to 60°C and the mixture of ceramic raw materials (milled beforehand to a reject of less than 1% by weight at 60 mm) is then slowly added, together with the deflocculant mixture. This is done while controlling temperature to ensure these additions do not lower temperature excessively. After all the solids have been added, the mixture is stirred at 60°C until achieving thorough dispersion. This takes around one hour.

3.3.2. Moulding

The suspension prepared according to the foregoing procedure was poured into the tank where it was kept under constant stirring at a temperature above 55°C. After the forming conditions (injection pressure and temperatures of the pumping channel and feed inlet into the die) had been set, the die feed valve was actuated to fill the die, which was cooled by water from a bath thermostatted at 5°C. The injection pressure used ranged from 0.3 to 0.5 MPa. After moulding time (which varied depending on the experiment), suspension feed was halted by closing the corresponding valve and the piece was manually demoulded. The process was repeated for each piece.

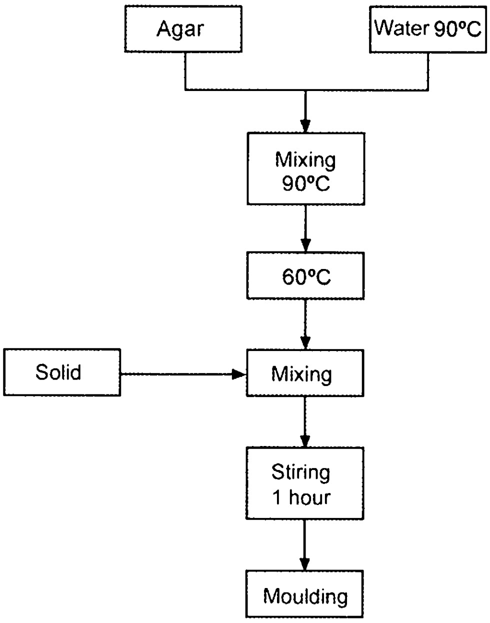


Figure 6. Description of the usual route for gellable suspension preparation

3.3.3. Drying and firing of the pieces

The castings were initially dried at ambient temperature for 24 hours. They were then placed in a laboratory oven at 110°C where they remained for at least 2 hours to fully remove the moisture. When necessary, the dry pieces were polished with abrasive paper to level and smooth their faces. They were then set in an electric laboratory kiln where they were fired according to a fast cycle (60 min) with a 6-min dwell time at peak temperature.

3.3.4. Characterisation of the resulting pieces

The consistency of the castings was measured with the plasticimeter used in the determination of the Atterberg plasticity index by indentation[14]. The apparatus uses a conical indenter that penetrates into the test specimen at a constant displacement rate. In this case, the conical shape was replaced by a flat indenter to avoid breaking the test specimen. The force-displacement curve was recorded and used to obtain the maximum force, termed consistency (C), which corresponded to the maximum indenter penetration into the test specimen.

Some of the dry pieces were examined in the scanning electron microscope (SEM) to observe their microstructure. Mechanical strength was also determined in some of these pieces by three-point bending, using a universal testing machine. Finally, fired bulk density and firing shrinkage of the sintered pieces were evaluated.

4. RESULTS AND DISCUSSION

4.1. PRELIMINARY EXPERIMENTS TO ESTABLISH THE COMPOSITION AND DEFLOCCULANT MIXTURE TO BE USED

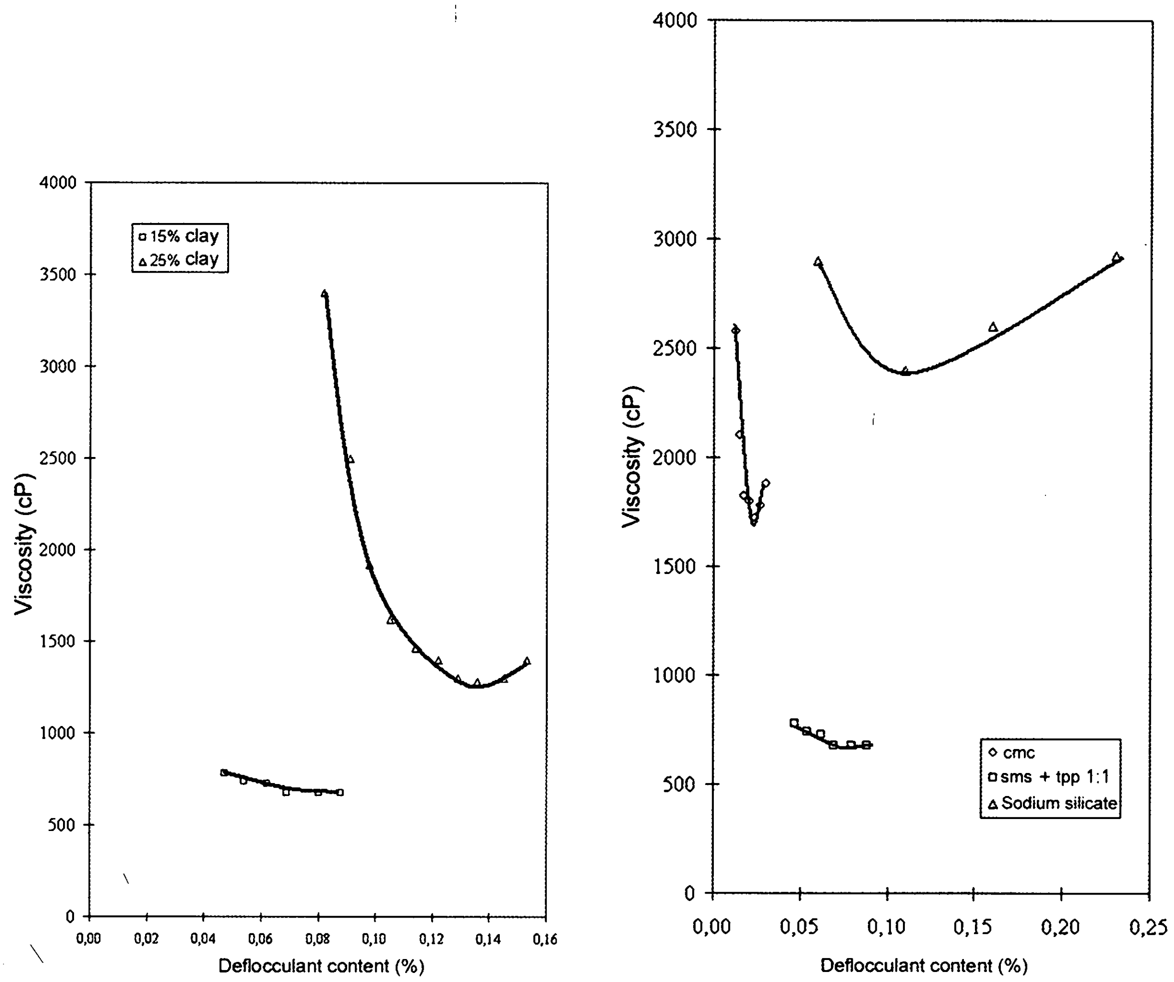
The addition of agar to the gellable suspension raises suspension viscosity in every case, since it is a powerful thickener. This effect needs to be minimised by appropriate design of the starting composition (raw materials). For this, a series of experiments was performed to optimise the starting composition and the deflocculant mixture. The solids content was kept constant in every case at 74% by weight. The standard composition (STD) used contained 15% clay by weight, while the rest was a mixture of sodium feldspar/feldspathic sand in a 3:1 ratio by weight. The deflocculants used were sodium silicate, a 1:1 mixture by weight of tripolyphosphate (TPP)-sodium metasilicate (SMS), and a carboxymethylcellulose (CMC) of low molecular weight. Table 2 details the conditions set in the experiments.

Experiment	Composition	Deflocculant mixture
1	STD	TPP-SMS
2	STD	sodium silicate
3	STD	CMC*
4	25% clay	TPP-SMS

**The solids content used was 73%*

Table 2. Conditions set in the experiments designed to optimise suspension rheological behaviour

Figure 7 compares the deflocculation curves obtained with the above experiments. The TPP-SMS mixture is clearly more effective, despite the composition's low clay content. The behaviour of the low molecular weight CMC was intermediate, although the solids content used in this case had to be brought down to 73%. With regard to clay content, this needed to be reduced because of its great repercussion on suspension viscosity. However, a minimum quantity is required to facilitate processing of the suspension and moulded piece. In order to verify this, a composition was prepared that contained 10% clay by weight. Its deflocculation curve could not be obtained due to the serious problems of dilatancy on stirring the composition.



a) deflocculant: SMS + TPP, 1:1

b) 15% clays

Figure 7. Optimisation of starting suspension rheological behaviour: a) influence of clay content, b) influence of the deflocculant used: sodium metasilicate-tripolyphosphate (SMS+TPP 1:1), sodium silicate and carboxymethylcellulose (CMC) of low molecular weight

4.2. ESTABLISHING LABORATORY-SCALE OPERATING CONDITIONS FOR GEL CASTING IN THE LOW-PRESSURE INJECTION MACHINE

Using the TPP-SMS deflocculant mixture and a composition with 15% clay by weight, a series of experiments was conducted in order to optimise the agar quantity and solids content of the suspension and establish suitable temperature conditions in the process to assure that the suspension remained stable prior to gelling, with subsequent gelling in the die as rapidly as possible.

Table 3 summarises some of the experiments conducted. Based on descriptions in the literature of other ceramic compositions[7][15], three agar contents were tested: 0.25%, 0.5% and 1% by weight, relative to the suspension solids content (experiments 5 to 7). On the other hand, with a view to maximising the suspension solids content and thus facilitating subsequent processing, solids contents exceeding 74% (experiments 8 and 9) were tested. With regard to process temperature, taking into account information in the literature for avoiding suspension flocculation in the tank and gelling prior to die entrance, the following constraints were set:

- Tank temperature: >55°C
- Temperature of the suspension feeder pipe to the die: >45°C
- Temperature of the die inlet: >40°C

Based on these constraints, standard conditions were then set to assure appropriate suspension processing and subsequent gelling. These conditions involved temperatures of 60°C, 50°C and 45°C respectively for the tank, feeder pipe and die inlet (experiments 5 to 9). Based on these standard conditions, two experiments were then performed in which these three temperatures were reduced (experiment 10) and raised (experiment 11).

			Temperature (°C)		
Experiment	% agar	% solids	Tank	Pipe	Inlet
5	0.25	74	60	50	45
6	0.5	74	60	50	45
7	1.0	74	60	50	45
8	0.5	76	60	50	45
9	0.5	78	60	50	45
10	0.5	74	55	47	42
11	0.5	74	75	65	60

Table 3. Experiments conducted to establish laboratory-scale operating conditions

In order to evaluate the processibility of the suspension and the characteristics of the moulded piece, the following determinations were made:

- Relative viscosity of the suspension (μ_R). Given the high temperature of the suspension, this determination was made in qualitative form, comparing the viscosity of a suspension containing agar stirred at 60°C, with that of the STD suspension (74% solids content) without agar at ambient temperature.
- Gelling time (t_G)
- Consistency of the moulded piece (C)

Table 4 summarises the results obtained, in addition to some observations concerning the processing of the materials.

Experiment	μ_R *	t_G (min)	C (N)	Observation
5	1	>20	2.1	Excessive deformability of the moulded piece
6	2	8	3.9	
7	5	3	7.8	
8	3	5	6.3	
9	5	3	9.1	Excessive viscosity. Difficulty in moulding
10	4	6	3.5	
11	2	7	4.0	Loss of liquid by evaporation

**Evaluated qualitatively as increasing viscosity rated from 1 to 5: 1, slightly higher and 5, much higher than the composition without agar, with 74% solids content, at ambient temperature*

Table 4. Results of experiments 5 to 11

As was to be expected, raising agar content (experiments 5 to 7) led to an almost proportional increase, in terms of the added amount, in consistency, and a much more pronounced reduction in gelling time. On the other hand, as a negative feature, suspension viscosity underwent exponential growth. As a result of the balance of requirements to be met, i.e., minimisation of gelling time, but particularly of viscosity, and maximisation of moulded piece consistency, the optimum agar content chosen was 0.5%. Smaller quantities produced excessively deformable castings.

On the other hand, raising solids content (experiments 6, 8 and 9) had important positive repercussions: it reduced gelling time, notably increased consistency of the moulded piece and facilitated subsequent drying by reducing the amount of water to be removed. However, it also adversely affected suspension viscosity, hampering the moulding process. As a compromise, a solids content of 76% was selected.

It was furthermore verified that although raising process temperature (experiment 11 compared with 6) favoured greater suspension solids content owing to the reduction in suspension viscosity, this could lead to important losses by evaporation, particularly when the suspension was fed too hot into the die. Although eliminating the solvent could also accelerate the moulding stage, this hampered control of suspension solids content. On the other hand, lowering the temperature of the suspension feed into the die (experiment 10 compared with 6) hardly improved gelling time.

Finally, no defects were observed in the pieces after drying, which was performed according to the conditions set out in point 3.3.3 (24 hours at ambient temperature and 2 hours in an oven). As an example, Figure 8 shows a micrograph of a dry test specimen corresponding to experiment 8. The microstructure is observed to be quite homogeneous, with not very dense particle packing, however with no segregations or accumulations of agar in any part of the test specimen.

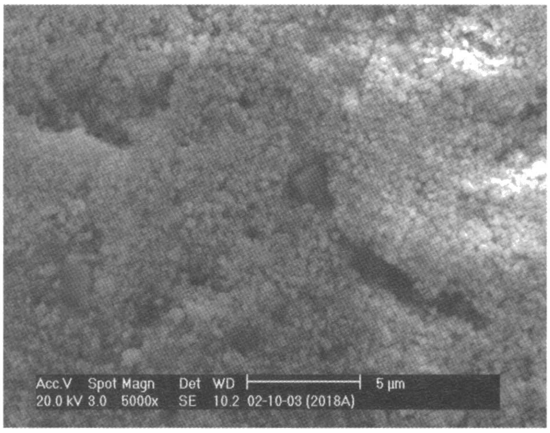


Figure 8. Micrograph of a dry piece from experiment 8

4.3. PILOT-SCALE FABRICATION OF CERAMIC TILES BY GEL CASTING IN THE LOW-PRESSURE INJECTION MACHINE

In the previous sections the characteristics of the gellable suspension and the operating conditions in the low-pressure injection machine have been optimised. Based on this information, experiments were then conducted on a pilot scale, with the following objectives:

- Verifying the feasibility of making small size tiles (5x10 cm) that contain pronounced reliefs in their design. For this, a special die was made that featured these characteristics (dimensions and relief).
- Designing a drying facility that enables drying the pieces in an accelerated way, avoiding the appearance of defects usually associated with gel drying, such as cracks and deformations.
- Estimating the capacity of the moulded material to withstand green machining.
- Determining certain fired product characteristics (linear shrinkage and density).

Figure 9 shows the parts of the die, made of aluminium, to facilitate heat transfer by the liquid heat exchanger during moulding. The relief consists of 15 half-spheres, with a very small curvature radius (3 mm). These were intended to verify the reliability of the method for obtaining more or less complex geometries, one of the advantages of the method, a priori. The die also displays an opening to which the suspension feeder pipe of the injector is fitted, as well as a jacket for water cooling or heating.

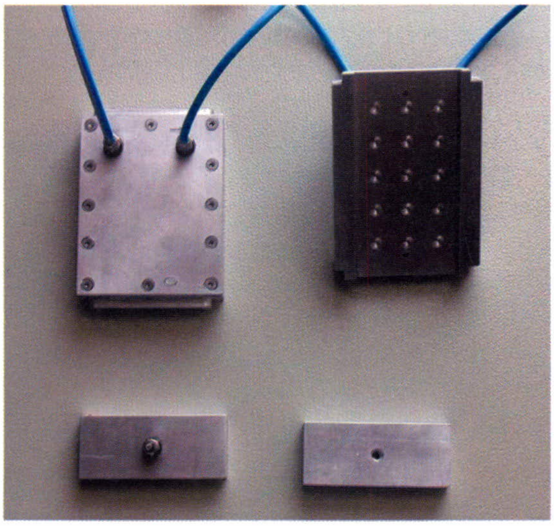


Figure 9. Parts of the die for making 5x10 cm tiles with relief

The operating conditions were the same as those set on a laboratory scale in the previous section for experiment 4: 0.5% agar, 76% solids content and operating temperatures of 60°C in the tank, 50°C in the feeder pipe and 45°C at the die inlet.

According to the literature[16][17], gel drying presents great difficulties as a result of the high shrinkage (stresses) that occurs during solvent elimination and because of the high deformability of the material (low modulus of elasticity). If it is intended to accelerate the drying cycles in larger-size pieces, it is therefore essential to have facilities in which there are minimal differences in heat contribution to the different regions of the piece in the operation. A pilot dryer was therefore designed that enabled controlling the temperature to which the tile top and bottom face was subjected during drying, and which by means of the temperature enabled simultaneously counteracting the different heat contributions undergone by both faces. Figure 10 shows two photographs corresponding to a plan and profile view of the designed facility. Heating takes place by electric heating elements, so that the heat is fundamentally transmitted to the piece by radiation, minimising the convective currents that propitiate the appearance of thermal gradients.

a) Profile *b) Plan*

Figure 10. View of the designed drying facility

After judiciously operating with the installation, a standard drying cycle was designed similar to the one shown in Figure 11. The pieces remained inside the chamber for 6 hours while the thermal gradient reflected in the figure was held, with a view to eliminating most of the shrinkage water. The temperature was then raised to 110°C, in order to remove the moisture fully, holding this temperature for a minimum period of 1 hour. This yielded pieces without deformations in relatively short drying times (7-8 hours).

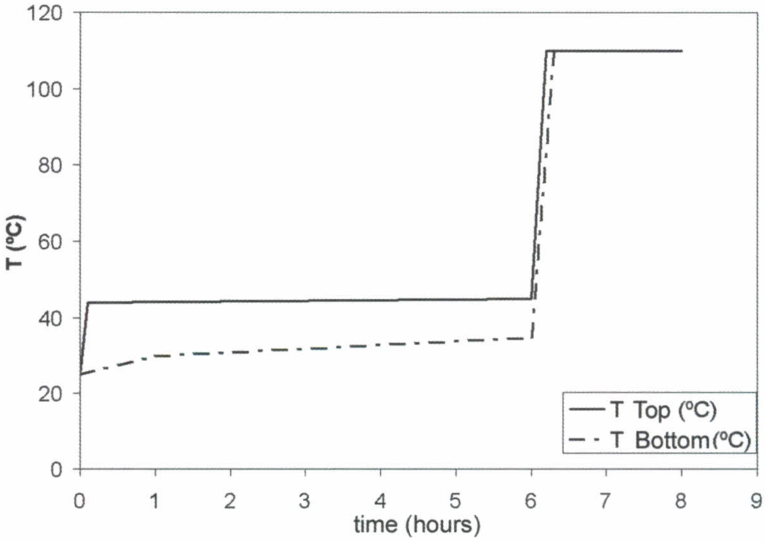


Figure 11. Standard cycle followed to dry the tiles produced on a pilot scale

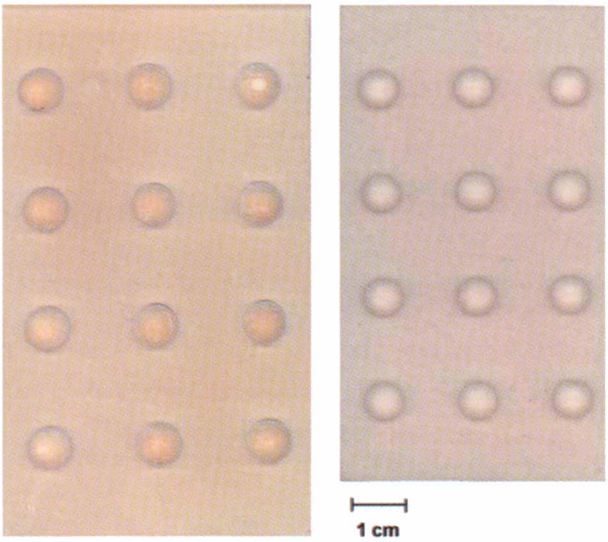
Ten tiles were made, following the set drying and firing conditions. The dry tiles were machined with abrasive paper to smooth their surface and rectify their sides. The machining operation presented no difficulties, as the mechanical strength of the dry pieces far exceeded the recommended minimum values for machining unfired pieces (around 2 MPa)[18].

Table 5 sets out the following physical properties of the pieces after drying and subsequent firing at maximum densification temperature (1220°C): dry relative density and mechanical strength, fired relative density and linear firing shrinkage. As the table shows, the dry piece has high mechanical strength, despite the low clay content (15%), due to the bonding effect of agar. With regard to the characteristics of the fired product, a material of high density is obtained (since the starting composition resembled that of porcelain tile), with high firing shrinkage as a result of the low relative casting density. All these features could be improved by appropriate composition design.

Characteristics	Value
Dry relative density (%)	60 ± 2
Dry mechanical strength (MPa)	3.5 ± 0.4
Relative density of the sintered piece (%)	92 ± 2
Linear shrinkage (%)	13.4 ± 0.1

Table 5. Characteristics of the dry and fired tiles made on a pilot scale

Finally, Figure 12 shows two photographs of a tile after drying and machining, and after firing. The good definition of the resulting reliefs can be clearly observed, as well as the high shrinkage that occurs in the sintered product.



a) Unfired piece *b) Fired piece*

Figure 12. Appearance of one of the tiles before firing and after firing at maximum densification temperature (1220°C)

5. CONCLUSIONS

- The feasibility has been verified of making ceramic tiles in a low-pressure injector (0.3-0.5 MPa) by gel casting, using gellable agar as a precursor and water at 5°C as a cooling liquid. The method could be a valid alternative to present procedures for manufacturing trims, which include slip casting, plastic pressing and extrusion, since it would allow obtaining any desired geometry.
- The key aspects of the manufacturing process by gel casting are: preliminary dissolution of agar in water at 90°C and subsequent mixing with the ceramic suspension, minimum viscosity of the gellable suspension (<1500 cP) to facilitate moulding and maximum solids content (at least 74% by weight) to increase the rigidity of the moulded pieces and facilitate deformation-free drying.
- Taking into account the foregoing aspects, the following operating conditions were set: 0.5% agar (by weight, relative to the dry solid), 76% solids content by weight, suspension temperature in the mixing tank of at least 60°C, moulding temperature of 45°C and gelling times of less than 5 minutes.
- To fabricate tiles on a pilot scale it has been necessary to design a die for moulding pieces measuring 5x10 cm with reliefs, fitted with a cooling jacket, and a dryer with electric heating elements that operate by radiation. After optimising the drying cycle in order to avoid deformations or cracks in the pieces, a drying time of 7-8 hours was achieved.
- The tiles made display low compactness, as a result of the small quantity of clay required in the process. However, they exhibit high mechanical strength, owing to the bonding effect of the gel, which enables easy machining of the material before firing. With regard to the characteristics of the fired material, this exhibits high density but also high firing shrinkage owing to the low compactness of the moulded material. However, this last aspect could be improved by appropriate design of the particle-size distribution in the starting composition.

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