

Gel-Extrusion: A New Continuous Forming Technique**

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In recent years a variety of direct shaping methods has been developed for the near-net shaping of ceramic powders.^[1,2] The main aim in developing these methods is to provide a simple route for manufacturing bulk complex-shaped bodies with increased green resistance in order to reduce or avoid final machining, which is the most expensive step in the fabrication process. In direct shaping methods, concentrated suspensions (typically above 50 vol.-%) are used and the liquid is not removed during consolidation. The methods using aqueous suspensions have the most promise for industrial transfer. Such is the case of gelcasting or low-pressure injection molding (LPIM) in water using thermogelling binders.

In particular, polysaccharides that gelate on cooling have been shown to be suitable for gelcasting and injection in molds, the most recognized in ceramic processing being agar derivatives.^[3-5] Their ability to form a strong, rigid gel in a very short time is a very attractive feature in powder shape forming. Important advantages are also that the use of biopolymers in water allows environmentally friendly production and safety conditions. Furthermore, the small amount of binder (≤ 1 wt.-%) means that no burn-out is required, with a subsequent energy saving. Finally, the high green strength facilitates machining before sintering, reducing the number of rejected pieces.

Up to now, these procedures have been used for individual bulk parts. We have described recently the possibility of applying the chemical gelation of alginates in the presence of Ca^{2+} ions to produce ceramic sheets by tape casting.^[6] A further improvement would be the development of an adequate gelcasting procedure for manufacturing continuous bodies with constant cross section (such as tubes and rods) like those obtained by extrusion.

The thermal gelation of methylcellulose solutions for extrusion of catalyst supports has been described,^[7] but this procedure fails because of the high viscosity of the methylcellulose solutions at room temperature. The gelling properties of this polysaccharide are not good enough to allow adequate mixing and a sufficient gel strength. The use of agaroids and carrageenans may solve these limitations. Their solutions have low viscosity at temperatures above the T_g and a sharp increase in viscosity occurs on cooling, up to one order of magnitude, thus suggesting that a strong gel is formed. The fast gelation on cooling would make it possible to convert a well-dispersed, low-viscosity slurry into a consolidated, continuous body if the column were forced to pass through a long-enough refrigerated die.

This communication reports a novel processing route for the continuous manufacture of ceramic and/or metal hollow or solid bodies based on the extrusion of aqueous suspensions that contain a small amount (< 1 wt.-%) of a gelling additive that gelates on passing through a refrigerated die.

Since this method makes use of an aqueous suspension, the interparticle potentials may be manipulated in order to provide the desired stability and to avoid agglomerates. A first step is to assure the optimum dispersing conditions, which can be controlled by rheological measurements.

Previous work regarding aqueous gelcasting on closed molds has demonstrated that higher homogeneity and density may be obtained when the gelling additive is first dissolved at temperatures higher than 90°C and then added to the powder suspension at $60\text{--}65^\circ\text{C}$.^[5] This temperature range is low enough to prevent much water evaporation and polymeric bridging, and is higher than the T_g of the polysaccharide, so no gelation takes place before cooling. It is important to control the rheological behavior of the slurry in the temperature range from mixing conditions ($\leq 65^\circ\text{C}$) to room conditions (below the T_g).

In this work, three powders of very different nature – alumina, a sanitaryware porcelain, and a nickel powder – have been selected to demonstrate the versatility of the proposed manufacturing method in the fields of technical ceramics, traditional ceramics, and powder metallurgy.

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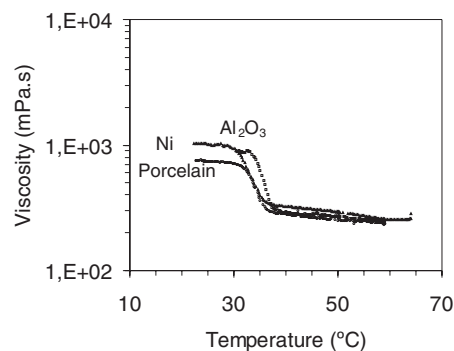


Fig. 1. Evolution of viscosity on cooling of aqueous suspensions of: a) 50 vol.-% alumina with 0.5 wt.-% agarose; b) 50 vol.-% sanitary porcelain with 0.5 wt.-% of agarose; c) 34 vol.-% nickel with 0.5 wt.-% of agar. Measurements were performed at a constant shear rate of 100 s^{-1} .

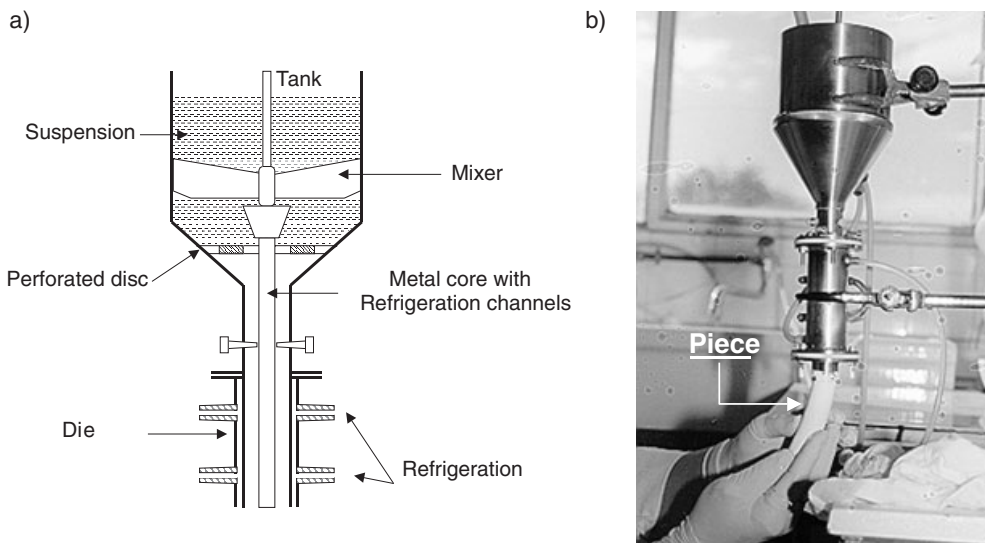


Fig. 2. a) Schematic drawing of the designed gelextrusion apparatus; b) the apparatus during forming.

Suspensions of each powder were first studied and optimized to achieve maximal solid loading (50 vol.-% for both ceramic powders and 34 vol.-% for the nickel one) while maintaining high flowability. The selected dispersing conditions are described in the experimental section. Figure 1 shows the evolution of viscosity on cooling at a shear rate of 100 s^{-1} for the aqueous suspensions of the three powders containing the gelling agent. In all cases, viscosity follows a similar trend with a sharp increase at the glass transition temperature, independently of the powder characteristics (metal or ceramic). Gelation occurs through the formation of aggregates of double helices of the gelling additive by means of H-bonds, so that a network of the polymer is formed that encapsulates the particles.^[8] The viscosity values at each temperature, the jump in viscosity at T_g , and T_g itself, depend on the solid loading of the suspension and on the type and concentration of gelling binder. It must be noted that all the suspensions were prepared with a total content of gelling additive of 0.5 wt.-% on the basis of dry solids by adding the required amount of a 3 wt.-% solution of the corresponding additive, but the additive concentration must be substantially increased to enhance the green strength. The viscosity increases at least five times at T_g , when viscosity is measured at a shear rate as high as 100 s^{-1} where the gel formation is retarded by the high shear forces. Obviously, when the suspension is poured or injected into a mold, shearing tends to zero and the jump in viscosity increases by orders of magnitude.

For the proposed gelextrusion process, a specific apparatus was designed and constructed. Figure 2a shows a schematic view of the equipment. It has two different sections: the reservoir and the die. The reservoir containing the slip is closed to prevent temperature gradients and evaporation. The homogeneity of the slip is maintained by stirring. The base of the reservoir is conical to allow a free flow of the slurry towards the die. The die length is a function of the production rate, the pressure, the shape and the dimensions of the

extrudate, and the gelling power of the additive. Some pressure is necessary to facilitate the flow of the slurry and to allow the continuous body to leave the die. The hydrostatic pressure acting on the body must be higher than the friction forces between the body and the die walls. Thermogelation of agaroids and carrageenan is accompanied by a water exclusion process, referred to as syneresis. The gel exudes a water film that acts as a lubricant and contributes to demolding. In general the slurry itself provides the pressure required for shaping, but external pressure may be necessary for viscous slurries. The hydrostatic pressure can be increased by increasing the reservoir height and/or the agitation speed. In addition, the cover plate is directly supported on the slurry, thus providing an additional pressure.

Figure 2b shows the gelextrusion apparatus during forming. The die is refrigerated with tap water, thus allowing the slurry to gelate. A longer die allows a longer time for cooling, which reduces flow gradients and fronts. The body obtained has a gel consistency and is easily deformable at the low additive content, so careful handling is required. It is convenient to form a long extrudate and to help consolidation with cold

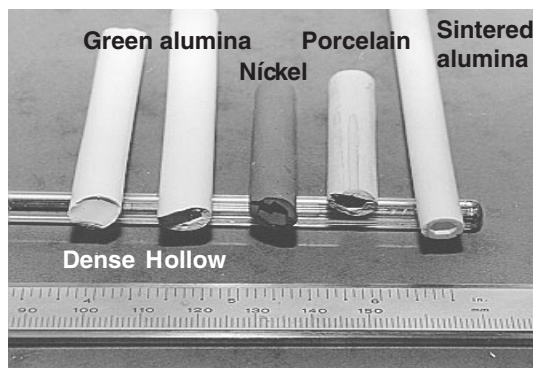


Fig. 3. The gelextruded green tubes obtained from the different powders and a sintered alumina tube.

Table 1. Characteristics of the gelextuded tubes.

Formulation	Green density [g/cm ³]	Relative density [%TD]	Weight loss [%]	Drying shrinkage [%]
Ni/agar	3.5	40	29	18.0
Al ₂ O ₃ /agarose	2.1	53	27	10.7
Porcelain/agarose	1.7	66	31	12.4

air. It must be noted that the large quantity of water in the slurry is constant during consolidation and is only eliminated on drying. As a consequence, the linear shrinkage after drying is also large, as in the case of gelcasting of bulk pieces. The addition of gelling binder used herein is very low, as well as the concentration of the precursor solutions. Obviously, an increase of both the precursor concentration and the final content of gelling matter will provide a more rigid extrudate, which facilitates the manipulation of the wet body and enhances the green strength after drying.

The wet bodies obtained were cut into 10 cm lengths and left in air to dry for 48 h. Figure 3 shows a view of the resulting tubes of the three materials studied. The characteristics of the green bodies are summarized in Table 1. Both hollow and solid bodies were obtained, the shape of the cavity depending on the geometry of the core rod coupled to the die, as for conventional extrusion. After sintering at 1600 °C/2 h in air, alumina bodies show a final density of 97 % of theoretical. The nickel compacts reach a relative density of 95 % of theoretical with treatments at 900 °C in argon, while higher temperatures lead to increasing grain growth without significantly increased density. The porcelain exhibits near to zero porosity, since a glassy phase is formed on sintering at 1230 °C/1 h in air.

In summary, a novel shape forming process is described for the continuous manufacture of ceramic and/or metal parts by a colloidal route. This process involves the preparation of stable suspensions in water to which a small concentration of gelling polysaccharide is added at a temperature of 60–65 °C. These suspensions are led to pass through a refrigerated die, thus allowing the suspension to gel. This work has shown the versatility of the process for a variety of materials, including traditional and advanced ceramics, and powder metallurgy. It is thought that the same procedure can be applied to metal/metal, ceramic/ceramic, and metal/ceramic composites, which are increasingly used in new technologies, such as tubular designs for solid oxide fuel cells, honeycombs, or microhollowed piezoelectrics.

Experimental

For this study three different materials were used: α -Al₂O₃ (Alcoa CT3000SG, Germany), consisting of near spherical particles with mean particle size of 0.5 μ m and surface area of 7.5 m²/g; a sanitaryware composition with 26 wt.-% clay, 30 wt.-% kaolin, 22 wt.-% quartz, and 22 wt.-% feldspar, the

mixture having a broad distribution of shape and size, with an average size of 10 μ m; and nickel, as metal powder (Inco TI 10, UK) with mean particle size of 2.5 μ m and surface area of 1.0 m²/g.

The gelling additives were agar (Grand Agar) and agarose (D1 LE), both supplied by Hispanagar, Burgos, Spain. These additives were received as coarse powders (100–150 μ m in average size), so they were first dissolved by mixing with water in a concentration of additive of 3 wt.-% and then heated up to > 90 °C to assure full dissolution. Afterwards, the solutions were maintained at 60–65 °C and added to the slurries at this temperature. In all cases, the required amount of solution to give a final gelling matter of 0.5 wt.-% referred to dry solids was added.

Aqueous suspensions were prepared as follows.

Slip 1: Alumina in water at a solid loading of 80 wt.-% (50 vol.-%), by adding 0.8 wt.-% of a commercial polyelectrolyte (Duramax D-3005, Rohm & Haas, USA). The mixture was ball milled for 6 h and further heated to about 60 °C. Then the necessary amount of agarose solution was added to the slurry at 60–65 °C with mechanical agitation for 15 min. This slip was gelextuded and left in air to dry for 48 h and then sintered at 1600 °C for 2 h at a heating and cooling rate of 10 °C/min.

Slip 2: A clay-based slip of conventional composition for sanitaryware was prepared in water to a solid loading of 72 wt.-% (50 vol.-%) by adding 0.4 wt.-% (with regard to solids) of a commercial dispersant (Dolapix PCN, Zschimmer-Schwarz, Germany). The mixture was prepared by mechanical agitation and further heated prior to the addition of agarose solution. Afterwards, it was processed similarly to alumina slips. Porcelain bodies were sintered at 1230 °C/1 h in air.

Slip 3: Nickel suspension was prepared to a solid loading of 82 wt.-% (34 vol.-%) by adding 0.8 wt.-% of the same polyelectrolyte used in slip 1. Homogenization was performed using an ultrasound probe for 2 min and further mechanical agitation for 1 h. Then agar solution was added at 60–65 °C. The gel-extruded bodies were sintered at 900 °C in argon atmosphere.

The gelextuded tubes were characterized by measuring the weight loss and the linear shrinkage on drying. Green densities were measured by Archimedes' method in mercury.

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- [1] L. Wang, F. Aldinger, *Adv. Eng. Mater.* **2000**, 2, 110.
- [2] W. M. Sigmund, N. S. Bell, L. Bergström, *J. Am. Ceram. Soc.* **2000**, 83, 1557.
- [3] A. J. Fanelli, R. D. Silvers, W. S. Frei, J. V. Burlew, G. B. Marsh, *J. Am. Ceram. Soc.* **1989**, 72, 1833.
- [4] T. Zhang, S. Blackburn, J. Bridgwater, *Br. Ceram. Trans.* **1994**, 96, 229.
- [5] A. J. Millán, R. Moreno, M. I. Nieto, *J. Eur. Ceram. Soc.* **2000**, 20, 2527.
- [6] I. Santacruz, C. A. Gutiérrez, M. I. Nieto, R. Moreno, *Adv. Eng. Mater.* **2001**, 3, 906.
- [7] N. Sarkar, G. K. Greminger, *Am. Ceram. Soc. Bull.* **1983**, 62, 1280.
- [8] R. Armisén, in *Thickening and Gelling Agents for Food*, 2nd ed. (Ed.: A. Imeson), Blackie, London, UK **1997**.