A Review on Aqueous Gelcasting: a versatile and low-toxic technique to shape ceramics

Laura Montanaro *, Bartolomeo Coppola, Paola Palmero, Jean-Marc Tulliani

Dept. Applied Science and Technology Politecnico di Torino, INSTM – R.U. PoliTO-LINCE Laboratory, Corso Duca degli Abruzzi 24 – 10129 Torino (Italy)

* Corresponding Author: Laura Montanaro, Dept. Applied Science and Technology Politecnico di Torino, Corso Duca degli Abruzzi 24 – 10129 Torino (Italy); e-mail address: laura.montanaro@polito.it; tel +39 011 090 3408; fax +39 011 090 4699

Abstract

This review aims to provide a comprehensive survey of recent low-toxic approaches used in the gelcasting process. In recent years, several natural gelling agents have been developed as possible alternatives to acrylamide systems, which were previously used extensively but are now rarely employed owing to their neurotoxicity.

This work collects some successful case studies on aqueous gelcasting based on low-toxic or non-toxic gel-formers that have been applied to produce both dense and porous ceramics. Major innovations in the development of nanocomposite materials, transparent ceramics and microstructurally graded materials are discussed as well.

Keywords (max 4):

Gelcasting; B. Porosity; A. Drying; A. Suspensions

1. Introduction

Gelcasting is a near-net-shape shaping method, initially set up in organic media and shortly thereafter transferred in water [1-3]. It combines casting into a non-porous mould and the subsequent formation of a tri-dimensional network promoted by a gel former. In this manner, the ceramic particles are entrapped and the homogeneity and quality of the liquid dispersion is preserved [1-7]. Gelcasting, was first developed at Oak Ridge National Laboratory (ORNL), USA, during the 1990s [8], and over the years, it has been the subject of increasing interest owing to its many advantages [9-11], such as:

- Versatility: it was first designed for the production of green bodies to be sintered in highly dense components, but was then progressively used for developing porous components;
- Capable of producing complex parts: if care is taken over die filling and demoulding, part complexity is mostly limited by the ability to design and fabricate complex-shaped moulds [12-15];
- Ease of implementation: similar to other well-established processes such as slip casting, it can be used for mass-production [16,17];
- High green strength: tensile strengths over 3 MPa can be easily achieved, assuring very good green machinability [11,18,19];
- Low organic content and easy binder removal performed during firing without the need for a dedicated burnout step;
- Highly homogeneous material properties.

The effectiveness of this shaping technique for yielding highly dense, fine and homogeneous green bodies is also borne out by recent papers in which it was exploited to develop transparent, polycrystalline ceramic components [20-23]. In addition, very recently, this method was successfully coupled to stereo-lithography for the production of complex-shaped components, opening up interesting new developments in mould-free shaping [24].

Many classification criteria have been proposed in the literature based on the nature of the gel former, the dispersion liquid (aqueous or non-aqueous medium) and the mechanism of gelation, which can be chemically- or thermally-induced [6].

The first gelcasting system was based on acrylamide (AM)–*N,N*-methylenebisacrylamide (MBAM), the former used as a main monomer, the latter as a cross-linking monomer. The *in-situ* polymerisation of this polymer system leads to a 3D gel that entraps the ceramic particles. The use of AM was progressively reduced owing to its neurotoxicity and research has been oriented to finding alternative low-toxic or nontoxic gel formers for a variety of ceramic materials [25-32] to reduce operative risks and environmental pollution.

Many synthetic monomers have therefore been proposed and tested, as well as many biopolymers and natural polymers [33,34]. The latter group includes globular proteins, such as bovine serum albumin, albumen (e.g. egg white), agar and agarose, gelatine, carrageenan, chitosan and sodium alginate [35-41].

Very recently, a patented water-soluble alternating co-polymer consisting of isobutylene and maleic anhydride, ISOBAM®, has been receiving attention. In fact, it can produce dense green bodies with homogenous microstructures at high solid loading (up to 80 vol%) and low organic content (<1 wt% with respect to the ceramic powder component), showing low shrinkage and no cracking [42,43]. Gelcasting using ISOBAM has also been demonstrated to be effective for producing transparent ceramics [22,44,45].

To better understand the toxicological risks and hazards related to conventional gelcasting, **Table 1** presents health and safety information (according to European regulation n° 1272/2008) as well as oral, dermal and inhalation exposure limits (LD50 oral, LD50 dermal and LC50, respectively) for the most common gelcasting components (including monomers, cross linkers, gelling agents and commonly used additives). LD50 is defined as the dose that results in the death of 50% of tested animals (generally rats) in milligrams of chemical per kilogram of animal weight (mg/kg). As a reference, LD50 oral for water is > 90000 mg/kg. We can easily observe that acrylamide (AM) has the lowest LD50 oral value compared to all other monomers and cross-linkers, yet it is classified as a carcinogen and a germ cell mutagen. For this reason, a number of gelcasting systems characterised by lower toxicity have been progressively developed, from those based on methacrylamide (MAM), showing acute toxicity or 2-hydroxyethyl methacrylate (HEMA), a skin and eye irritant, to ISOBAM, which is classified as non-hazardous. It is worth observing that natural gelling agents (gelatine, collagen, agarose, agar, etc.) are classified as non-hazardous substances, with almost no available data concerning their LD50 values.

This paper reviews many experimental activities dealing with aqueous gelcasting of dense and porous materials made of single-phase or composite powders using low-toxic and natural gelling agents. It discusses the advantages in terms of versatility and effectiveness of this shaping process, but also underlines some limits and drawbacks and suggests strategies to minimise them.

2. Dense materials

As mentioned in the Introduction, gelcasting was developed to overcome some of the limitations of other complex-shaping techniques of ceramics, such as injection moulding and slip casting. As shown in the flow chart of **Figure 1**, the gelcasting process can be summarised by some key steps, which are listed as follows:

1) preparation of the aqueous slurry of a ceramic powder (additives such as dispersant and/or a pH modifier can be added to achieve a high-solid loading and stable suspension);

2) addition of the gel-former aqueous solution at a fixed temperature (extra-additives can be added to achieve proper rheological properties and thus improve flow ability and castability);
3) degassing and die filling (vacuum casting is preferred to further promote degassing) and *in-situ* polymerisation to form a green body having the shape of the mould;
4) Demoulding of the gelled part (chemical- or temperature-activated gelation);
5) Drying under controlled conditions (temperature and humidity controlled conditions)
6) Debinding (if required) and sintering

In order to produce highly dense, defect-free ceramic parts, ~~many~~ all processing steps have to be carefully controlled, and specifically some key parameters (e.g. choice of the gelling agent, control of suspension rheology, die filling, drying, demoulding, etc.), as discussed in the following paragraphs.

2.1. Natural gelling agents and their characteristics

With reference to **Figure 1**, gelcasting implies the preparation of the gelling agent solution, consisting of a solvent (which determines the nature of the process, *i.e.* aqueous or non-aqueous) and the solubilised gel-former. As mentioned in the Introduction, previous systems based on AM-MBAM have a certain degree of toxicity [46], leading the research towards the development of more environmentally friendly approaches.

Recently, the use of different low-toxicity variants on AM systems have been proposed, such as those based on 2-hydroxyethyl methacrylate (HEMA) [47] and HEMA with polyvinyl pyrrolidone [48]. As a drawback, HEMA only forms water-compatible gels at very high concentrations (8–40 vol%), increasing the processing cost and time and limiting its industrial use [49].

As a second approach, the low-toxic and water-soluble ISOBAM® previously mentioned in the Introduction has been developed [42-45,50-54]. Interestingly, this product acts as both binder and dispersant (up to a maximum solid loading in the ceramic slurry [54]) at very low concentrations (< 1 wt% with respect to the ceramic powder) and at room temperature [52]. While the exact gelling phenomenon is still unknown, two mechanisms have been proposed. The first is based on ionic interaction/hydrogen bonding amongst functional groups of ISOBAM and the ceramic surface particles; the second on a bridging mechanism, which occurs when some of the ISOBAM molecules from one particle are absorbed onto the uncovered surfaces of adjacent particles [54].

As a further approach, a variety of food-grade biopolymers have also been investigated, including polysaccharides (such as agaroids, starches, curdlan and carrageenan [33,34,36-38,41,55] and proteins (such as gelatine [35,56,57] and albumin [39]).

Polysaccharides are thermoreversible systems; in fact, upon cooling, hydrated polysaccharides will gel through the formation of ordered, double helixes, which revert to disordered, coiled chains upon reheating, as schematically shown in **Figure 2a**. The gelling behaviour of such polysaccharides can be evaluated by rheological measurements during the heating/cooling cycles, as depicted in **Figure 3** in the case of agar. When heated, there is an initial viscosity increase, giving rise to a peak corresponding to the hydration of the gelling powder. With further heating, dissolution of the hydrated molecules occurs, which is accompanied by a certain reduction in viscosity. During cooling, a moderate increase of viscosity occurs, followed – near T_g — by a final steeper increase upon gelation [34,55]. Gelation hysteresis is calculated as the difference between the melting and the gelation temperatures. Agarose and carrageenan show a similar behaviour to agar, even though carrageenan reaches complete dissolution at around 70 °C, which is approximately 20 °C lower than the temperature required to dissolve agaroids [55]. At the same time, the maximum viscosity when heating carrageen is several times higher than the corresponding maxima observed for agaroids [55]. Curdlan is an extracellular bacterial polysaccharide composed entirely of (1,3) –b-D-glucosidic linkages. It is insoluble in water and allows gels to form via heating of the suspension (from 55 °C to 80 °C) and subsequent cooling to room temperature. However, it is soluble in alkali and gels can alternatively be formed in the absence of heating simply by the neutralisation of this solution [41].

Other systems, such as those based on gellans, form gels in the presence of divalent ions. An example is provided by sodium alginate gels, which exploit an ion exchange mechanism whereby a mono-valent cation is replaced by a di-valent one (such as calcium), resulting in a cross-linking process [55-59]. Thus, gelation results from specific and strong interactions between calcium ions and blocks of guluronic acid, where the gel strength is related to the level of polyguluronate present [60]. Concerning the structural features involved in the gelation process, it has been shown that calcium ions induce chain-chain associations, which constitute the junction zones responsible for gel formation [61]. A model for the junction zone has been derived, popularly known as the "egg box model" [61], depicted in **Figure 2b**, showing pairs of 21 helical chains packed with the calcium ions located between them.

As with polysaccharides, several protein-based systems exhibit proper gelling behaviour. Amongst them, the most commonly used systems are gelatine [34,35] and albumin [39]. Gelatine, consisting of denatured collagen, is extracted from the skin or bones of animals, and is widely used as a food stabiliser. Two types of gels can be obtained. The first, named "physical gel", is thermo-reversible and is obtained upon cooling the solution due to the conformational transition of the gelatine chains from coil to triple helix. The second is named "chemical gel" and results from crosslinking of the chains induced by specific reagents added to the aqueous solution [56]. With reference to physical gels, gelatine shows an important advantage with respect to agaroids, as it can be dissolved quickly at a significantly lower temperature (approximately 40 °C) [62]. Gelatine gels tend to be relatively elastic in their mechanical response, and show behaviours broadly similar to natural rubbers [57]. In the case of albumin, when heated at the gelation temperature (80 °C), individual molecules from egg-white proteins are denatured and then form a typical thermo-irreversible gel, which is held together by covalent bonds [63]. Below this gelation temperature, the attractive hydrogen bond favours junction-zone formation [64]. The use of both gelatine and albumin systems allows the processing of water-based suspensions, typically prepared under neutral or slightly basic pH. However, a serious drawback of both gelling systems is their tendency to foam, which requires the use of a careful de-airing step or application of anti-foaming agents, as described in § 2.3. Owing to this drawback, the use of protein-based additives for the gelcasting of dense samples has received less attention than polysaccharide systems.

2.2. Powder suspensions

One of the crucial steps in gelcasting is the preparation of a suitable powder suspension in terms of its rheological properties, solid loading, homogeneity and stability. High solid loading and low viscosity are important to avoid casting issues that are correlated to green body physical and mechanical properties [65-67].

The rheological properties of the suspensions are mainly influenced by solid loading and gelling agent content and generally show a pseudo-plastic behaviour (**Figure 4a**) [35,51,54,68-71]. However, a critical value of solid loading can be defined, which determines the shift from a shear-thinning behaviour to a shear-thickening one (**Figure 4b**) [65-67]. Several authors consider the value of 1 Pa.s, determined for shear rates between 10 s^{-1} and 100 s^{-1}, to be the limit of apparent viscosity that allows good de-airing and casting processes to take place [35,51,65,71].

Recently, a method to prepare alumina suspensions with high solid loading (up to 62 vol%) and low viscosity (0.29 Pa.s) by using irregular particles was proposed [15]. In particular, the authors investigated the effects of particle gradation on suspension viscosity and observed that all suspensions first showed a shear-thickening behaviour at low shear rates due to the internal friction amongst particles, and then a shear-thinning behaviour due to cluster disaggregation. Moreover, particle gradation reduced the viscosity of the slurries owing to the high packing density of the particles.

Generally, as natural gelling agent content increases, an increase of viscosity occurs as well [41,55,70]. As reported in [70], the rheology of zirconia, determined at 60 °C and 33 vol% solid loading, was generally constant within the shear rates. Upon agarose addition, even small amounts (0.25–1 wt%), a sharp increase of viscosity (from 0.1 to 10 Pa.s) was observed, while a shear-thinning behaviour was noted as shear rates increased. By increasing the solid loading (from 20 to 35 vol%) viscosity increased as well (from 1 to 60 Pa.s). An opposite behaviour was observed with ISOBAM; with increasing monomer content, viscosity decreased until it reached a certain threshold [43,51,54]. For example, in 50 vol% mullite slurries with different monomer contents (i.e. ISOBAM110, in the range 1.5 – 4.5 vol%), the lowest viscosity was achieved in the system with 3 vol% monomer [51].

Ceramic suspension viscosity is also influenced by dispersants. The use of ISOBAM as the gelling agent with ammonium citrate tribasic (TAC) as the dispersant has been investigated [54]. A small amount of TAC (< 0.5 wt%) was effective in reducing the viscosity of the system and increasing the gelation time. However, when an excess of ISOBAM or TAC was present, the opposite behaviour was observed, attributable to ceramic particle surface saturation. This behaviour has also been observed in yttria-stabilised zirconia using ammonium polyacrylate (PAA-NH_4) as a dispersant [71].

Gelation time is an important parameter in colloidal suspensions; high gelation rates lead to casting difficulties, while low gelation rates produce ceramic powder sedimentation in the slurry [51]. To modify gelation time, several parameters can be considered: monomer-gelling agent content, monomer/cross-linker ratio and temperature. It has been found that gelation rate decreased with increasing ISOBAM content owing to different saturation rates of the ceramic particles, which enabled the occurrence of flocculation [43].

As stated in § 2.1, gelation using natural gelling agents takes place upon temperature changes. This makes it possible to evaluate the gel stability upon heating/cooling and by considering the storage modulus in a time interval. For instance, the effect of zirconia solid loading (in the range 20–35 vol%) on the suspension storage modulus (G’) was studied [70]. G’ increased by increasing the solid loading up to 27 vol%, followed by a decrease at 30 vol% due to closed solid particles hindering the formation of a well-structured network of the agarose gel. By further increasing the solid loading up to 35 vol%, segregation occurred, resulting in areas with higher agarose concentration, and the storage modulus increased again.

The synergic effect of different natural gelling agents on increasing the gel strength was demonstrated [72]. Mixtures of agar and galactomannan (*i.e.* locust bean gum) were added to concentrated aqueous alumina suspensions (from 40 to 60 vol%) to demonstrate the synergic effect of the two polysaccharides, which improved the strength of the gel. The authors also reported an increase of G’ when increasing alumina content and observed that the storage modulus was always higher than the loss modulus (G’’) at all investigated temperatures, indicating that the elastic characteristic of the suspensions dominated the viscous one. G’ sharply increased upon cooling in the range 50–40 °C, even for small polysaccharide solution content (0.50 – 1.50 wt%).

Finally, considering emulsified systems, several authors observed hysteresis in these slurries due to a modification of the suspension microstructure during shear-rate increases [73,74]. Alumina suspensions emulsified with soybean oil, and with gelatine added, exhibited shear–thinning behaviour well-fitted with the Herschel-Bulkley model for all the studied systems (35 to 50 vol% of alumina suspensions, 0.50 to 1.00 oil:suspension ratio, 5 wt% of gelatine) [73].

In conclusion, casting conditions depend mainly on suspension viscosity, which is ~~strictly~~ related to gelling agent content and solid loading. Green body strength should also be considered as a key parameter towards the fulfilment of a good gelcasting process. Therefore, all these parameters have to be considered for obtaining gelling agent/solid loading ranges that are suitable for casting. An example is provided in **Figure 5**, where these variables are considered together for defining the optimum range in which to obtain zirconia-agarose suspensions with suitable viscosity and high green body strength [70].

2.3 Shaping procedure: Moulding, degassing, drying

Because gelcasting is a low temperature process (from T_{room} to ~ 80°C), a variety of mould materials such as aluminium, stainless steel, plastic, glass and wax can be used. Properties of the mould materials coupled with the mould design play a significant role in producing complex shapes, as they must allow shrinkage to occur and minimise stresses in the cast part during drying. These problems can often be addressed by the use of soft mould materials, which can deform under the stresses developed during drying shrinkage. Fabrication of complex shapes may also pose problems during removal of the gelled part from the mould. The use of materials such as wax, which can be selectively dissolved away after gelation, as well as sacrificial polymers to be burned out during the sintering step [75], are preferable for casting pieces of complex shape [76].

Once the proper mould is selected, the ceramic suspension is submitted to a degassing procedure. Mixing the ceramic slurry with the premix solution involves the formation of air bubbles, which can be eliminated through a de-airing process normally performed before or after casting. In the first case, the suspension is degassed under vacuum until the bubbles disappear; in the second case, the mould containing the cast suspension is evacuated [75]. An original procedure was employed by the Authors in [77], in which the suspension is cast under vacuum with the twofold benefit of degassing both the suspension and the mould. Once again, the use of complex-shape moulds makes it more difficult to complete gas removal, thus requiring two de-airing steps, carried out before and after casting [75]. Moreover, as mentioned in §2.1, gelatine and albumin tend to foam during mixing, requiring the addition of specific anti-foaming agents. The Authors in [77] demonstrated that the addition of a small amount of poly(ethylene) glycol (PEG) as the anti-foaming agent is effective. As shown in **Figure 6** (gelcast zirconia with gelatine as the gel-former), large pores are visible in PEG-free samples, while fully dense and defect-free materials were successfully produced with PEG.

Once the ceramic is gelled, the liquid casting medium (e.g. water) and additives are removed through drying and firing, respectively. The rate of water removal must be controlled to avoid the generation of excessive stress within the sample due to differential drying. Differential drying can lead to non-uniform shrinkage, warpage and cracks [78]. A key to control this drawback is to reduce the water content in the ceramic slurry, which allows reduction of drying shrinkage and weight loss. For instance, for a zirconia/agarose system, it was observed that when the solid loading increased from 24 vol% to 39 vol%, the linear shrinkage during drying decreased from 23% to 6% and the green density increased from 46% to 52% [70].

To maximise both solid loading and agarose concentration in alumina slurries, agarose solutions have been prepared under overpressure conditions in a closed vessel at high temperature (110–115 °C), reaching a concentration of 5.6 wt% [38]. This procedure allowed the solid loading of the gelcasting suspension to increase from 80 to 84 wt%, resulting in lower shrinkage and higher green densities. Regardless of the suspension, the best drying process that avoids the appearance of cracking and shortens the drying period must be designed. For instance, the optimal drying process for $ZnAl_2O_4$ gelcast samples was set as follows: *i*) a preliminary drying step was carried out in a climatic chamber with the temperature and relative humidity ranging from (40 °C, 90%) to (70 °C, 60%). Temperature, relative humidity and the holding time increments for each step were set equal to 10 °C, 10% and 5 h, respectively; *ii*) a final drying step was carried out at 75 °C for 12 h [79]. However, from this example, it is clear that conventional methods such as air drying or temperature drying may be time-consuming, especially if the part is large. Liquid desiccant drying has been developed to address the above issues and shorten the drying period [78]. Following this method, gelled parts are immersed in a concentrated polymer solution. An osmotic pressure difference between the gelled part and the liquid desiccant solution causes water to transfer from the gelled parts into the solution. This method provides several benefits over conventional drying methods. For example, the water is uniformly removed from the gelled part, avoiding uneven shrinkage during the drying process. The liquid medium also provides a buoyant force that helps to prevent warpage [80]. Because the gelled ceramic sample is completely immersed in a liquid, capillary stresses do not arise within the sample, further reducing warpage and cracking [81]. Typically, the liquid desiccant is prepared by dissolution of polyethylene glycol (PEG) in deionised water. Several parameters affect the process, such as the ceramic solid loading, the PEG concentration, the related osmotic pressure, and the shape and thickness of the gelcast green body [80]. PEG at the highest molecular weight (80.000 g/mol) provided the most effective liquid desiccant effect [82], as shown in **Figure 7a**. In fact, the smaller molecules in lower-molecular weight PEG penetrated the pores in gelled bodies, reducing the total water removal and produced an inhomogeneous structure of the ceramic body. **Figure 7b** shows an example of successful use of optimised osmotic drying of alumina samples. Osmotic drying followed by air-drying enabled crack-free processing, in contrast to the one-step air-drying carried out at room temperature and humidity.

The nature of the gelling agent also affects drying behaviour. By comparing large gelcast pieces (400 × 50 × 10 mm^3 mould) obtained by using ISOBAM or epoxy-amine (EA) as gelling agents, clearly different behaviours were observed, particularly during the constant rate period (CRP), which characterises water transportation from inner channels to the surface [83]. CRP of a sample fabricated with ISOBAM was twice that of a sample fabricated with EA, but residual water after CRP and after final drying was significantly lower (less than a third) for the former material. This difference was imputed to the presence of smaller pores in the EA system, which impeded water transportation. A different microstructural evolution was observed as well. With ISOBAM, during drying the particles moved closer to each other, with a thin layer of gel enveloping the alumina particles, which easily collapsed and thus generated stress relaxation. On the other hand, EA formed a dense organic network generating large shrinkage and no collapse, thus developing large stresses. The clear differences in drying behaviour are depicted in **Figure 8**, showing the severe warpage characterising the EA system, while an un-deformed and crack-free ISOBAM-based green body was successfully produced.

2.4 Green and fired bodies: microstructural features and properties

Homogeneous and highly compact green bodies are the first requirement to achieve high density in fired bodies. Therefore, maximising solid loading is one key to achieve high density in both green and sintered materials. To this aim, a concentrated agarose solution was used in an alumina slurry, with the aim of increasing solid loading (> 80 wt%) and achieving full density [38].

Natural gelling agents have been demonstrated to provide high green strength, similar to traditional acrylamide systems. As an example, the green strength of gelcast ZrB_2-SiC obtained with Na-alginate was even higher (> 60 MPa) than that of a material fabricated with AM-MBAM (48.5 MPa) [84].

However, in most cases, to achieve high green and sintered strength, the use of the gelling agent has to be carefully controlled. For instance, gelation and strength of gellan gum should be tailored through proper use of a cation [85,86]. In particular, di-valent ions have been demonstrated to be more effective in enhancing gel strength compared to mono-valent ions [87]. Alumina suspensions, with added optimised amounts of gellan gum (to 0.5 wt% of gellan gum and 13 mmol/L of magnesium chloride), achieved high density in green and sintered bodies, as well as a high bending strength of approximately 330 MPa [40].

Curdlan has also been demonstrated to be an affective gelling agent [41]; by properly adjusting alumina suspension solid loading as well as curdlan concentration (see values in **Table 2**) it was possible to realise complex-shape green bodies, as depicted in **Figure 9**. Sintered samples achieved a high fired density (> 98%), with a flexural strength of approximately 350 MPa.

When egg white proteins (EWP) are used as the gelling agent, a pre-heating process is needed to improve the properties of green and sintered bodies [39]. In fact, in the case of alumina suspension with added EWP, a pre-heating step at 80 °C/1h was necessary before cooling to room temperature, followed by drying for 24 h to initiate gelation. The authors demonstrated that the alumina ceramics produced by this process exhibited improved uniformity and higher strength in both green and sintered states compared to samples that were simply air-dried. In addition, the green and sintered densities as well as the mechanical properties were dependent on the EWP concentration, with 6 wt% being the optimal value. Under this condition, the green and sintered strengths were 7.3 MPa and 314 MPa, respectively. Finally, the alumina ceramics were green machined, verifying that the green bodies were strong enough to be submitted to such process.

When gelatine is used, its content has to be carefully controlled to tune the slurry viscosity to allow casting. For alumina suspension at 53 vol% solid loading, a gelatine maximum value of 4.5 wt% (referred to water) was determined necessary to maintain the slurry viscosity lower than 1 Pa.s. For gelatine content > 6 wt%, the apparent viscosity was higher than 3 Pa.s; the slurry did not flow easily into the mould, agglomerates or flocculation occurred, and the homogeneous microstructure of the ceramic body was destroyed [35]. The authors used gelatine to produce both alumina and zirconia gel cast samples [88]. For both slurries, gelatine content had to be kept < 4 wt% to maintain the apparent viscosity lower than 1 Pa·s at 20 s^{-1} to allow proper casting. Under this condition, homogeneous alumina and zirconia green bodies were successfully produced. As shown in **Figure 10a** for alumina, the green microstructure was highly homogeneous and characterised by a well-packed and defect-free microstructure (green density of 55%), which gave rise to highly dense (> 96%) fine and homogeneous sintered bodies. In [77,89,90] the authors prepared dense zirconia ceramics by exploiting both gelatine and agar as gel-formers. After careful optimisation of the sintering schedule, it was possible to achieve highly dense (97-98%) ceramics characterised by an ultrafine microstructure, as shown in **Figure 10b**. From nano-indentation test results, the material achieved an average hardness and elastic modulus of approximately 14 GPa and 226 GPa, respectively. In addition, samples were submitted to room- and high-temperature (1500°C/30 min) bending tests, exhibiting an evident plastic-like behaviour mainly imputable to the grain boundary sliding phenomena promoted by the ultrafine Y-TZP microstructure [89]. In [70], agarose was used as the gelling agent for zirconia suspensions. By using optimised conditions (e.g., 30 vol% solid loading and 0.75 wt% agarose), the sintered material reached a density > 99%, producing a fine and homogeneous microstructure. The sintered samples were submitted to 4-point bending tests and the failure probability was calculated by Weibull statistics. The analysis showed that two major flaw populations were present in the cast materials. In the range between 300 and 400 MPa, the fracture origin was related to the presence of larger pores (size ~ 100 μm) not successfully removed from the suspension during evacuation. In the range between 500 and 800 MPa, the major flaws originated from agglomerates.

A further key aspect in gelcasting to achieve high-strength ceramics is powder dispersion. In a recent work [91], the Authors investigated the role of dispersion of hydroxyapatite (HA) powder and prior gelcasting on sinterability and microstructural evolution. The particle size distribution was tailored through two different milling procedures: a dry milling process, which produced particles with a mean size of 1.7 μm, and a wet milling process, which yielded finer particles (mean size of 1 μm) with a narrower size distribution. Gelcast green bodies, sintered under the same conditions, gave rise to poorly densified (~79%) materials when dry-milled powders were used, while full densification (99.9%) and fine microstructure (grain size of 1.3 μm) were achieved with wet-milled powders. The compressive strength of this last material was 300 MPa, which was five times greater than the strength achieved by the dry milled samples.

A number of recent papers deal with the use of the novel ISOBAM gelling agent to produce dense gelcast ceramics. Dense $Yb_3Al_5O_{12}$ samples have been successfully produced by optimising both solid loading (50 vol%) and the ISOBAM amount (2.6 wt% with respect to water) [43]. In this condition, the sample achieved high density (> 94%) and proper flexural strength (160 MPa). In addition, the dried green body exhibited high strength, which enabled handling by metalworking tools without any cracking or chipping.

Transparent polycrystalline $Y_3Al_5O_{12}$ (yttrium aluminium garnet, YAG) has also been fabricated by gelcasting with ISOBAM as a gelling agent [22]. First, the optimal solid loading was fixed at

68 vol% based on rheological behaviour and optimal flow of the suspensions. Then, different ISOBAM amounts (in the range 0.3 – 1.5 wt%) were tested and their effect on optical properties was established. As shown in **Figure 11**, the optimal ISOBAM concentration was determined to be 0.5 wt%, corresponding to higher optical transparency (75.7% at a wavelength of 1064 nm). Lower ISOBAM contents were not sufficient to induce proper densification behaviour (carried out at 1780 °C for 6 h, under a vacuum of 10^{-3} Pa), thus reducing the optical behaviour, while higher ISOBAM amounts increased the number and size of residual pores during the de-binding process, again affecting the transmission of light.

A similar process has been developed to produce transparent polycrystalline $MgAl_2O_4$ ceramics, sintered at 1600 °C under vacuum [20,21]. Here, the suspension solid loading, kept in the range 43–50 vol%, played a key role. The best performance was achieved at 50 vol% solid loading, where green bodies were characterised by a relative density of 60.5% and flexural strength of 2.62 MPa, while sintered bodies were fully dense (> 99.5%) and highly transparent (in-line transmittance of 86.9% at a wavelength of 1100 nm) [21].

In [92], transparent $MgAl_2O_4$ ceramics were developed as well, but in this case, gelcast samples were densified by Spark Plasma Sintering (SPS). Casting and gelling conditions were optimised as follows: 85 wt% solid loading, 0.7 wt% ISOBAM and gelation time of 350 s. This led to green bodies characterised by a density of 65% and strength of approximately 14.5 MPa. After the SPS process was carried out at 1350 °C, the sintered samples achieved full densification (99.97%) and high in-line transmittance (86.7% at a wavelength of 1100 nm).

An overview of some dense ceramics developed by the gelcasting technique using low-toxic gelling agents and eco-friendly processes is presented in **Table 2**. For the presented compositions, slurry solid loadings and gelling agent contents are given, along with some physical and mechanical data related to both green and sintered materials.

Finally, it should be mentioned that gelcasting enables the development of complex microstructures, such as those characterised by textured grains. An example is provided in [93], where textured alumina ceramics were fabricated with the aim of improving electrical, piezoelectric and mechanical properties by tailoring the microstructure. As an innovation, a highly textured microstructure was achieved owing to the combination of gelcasting with magnetic alignment followed by sintering. A scheme of the process is given in **Figure 12**. A key factor in this work was the proper dispersion of the alumina particles, which was achieved by carefully controlling solid loading, dispersant and gelling agents. Particles should be well dispersed in the ceramic slurry, characterised by a viscosity low enough to enable the rotation of the particles by low energy application, while magnetic energy should be higher than the thermal motion energy. If particles are strongly agglomerated, their interaction hinders their rotation. Thus, loosely dispersed particles were mixed with a low-toxic monomer (6-O-acryloyl-d-galactose (6-Akr-Gal)) in 30 wt% aqueous solution. Particle orientation was induced by the magnetic field, followed by a polymerisation reaction initiated by ammonium persulfate (APS) to lock the aligned particles. With this process, a very high degree of crystalline orientation (0.92) was achieved, as shown in **Figure 13**. The morphology of the surfaces parallel and perpendicular to the magnetic field direction was significantly different. Large platelet-like grains were visible on the top surface, with a mean diameter of 6.2 μm, while the side surface included grains of oblong shape and smaller average size of ~ 4.5 μm.

As a last example of innovation, it is worth mentioning the development of gelcast composite materials. The Authors in [69] produced both dense and foamed alumina-zirconia composites (ZTA) by the gelcasting process using agar as a gel-former. Composite powders were developed by an innovative *surface modification route*, recently set-up by the Authors, in which well-dispersed alumina powders were doped with inorganic second-phase precursors [94,95]. Upon controlled thermal treatments, *in-situ* crystallisation of nano-sized zirconia particles on the surface of the alumina powders was produced. Use of this route was able to produce fully dense and fine-grained ceramics, characterised by a perfect distribution of second-phase particles within the matrix [96]. In traditional processes used to develop composite materials, extensive milling is normally required to obtain a proper mix of the different ceramic particles. Such issue is completely overcome by the surface modification route, where a completely homogeneous dispersion of zirconia-modified alumina particles is easily achieved. With reference to gelcasting, this is a point of strength in the process, because achieving a proper dispersion of particles in the starting slurry is the key to fabricate highly dense and fine-grained gelcast materials, as we have recently demonstrated in [90]. In § 3.3, the development and mechanical characterisation of gelcast ZTA composite materials at different porosity amounts will be described.

2.5 General remarks on dense materials

As clearly evidenced in **Table 1**, during the last 15 years of gelcasting processing, a substantial step forward has been achieved, mainly in the area of health. Research and innovation is moving away from the widespread use of acrylamide-based gelling systems, which are recognised as carcinogens and germ cell mutagens, and is moving towards a number of non-hazardous agents. Two types of low-toxicity gel formers are of particular relevance to this study: the first is a patented water-soluble co-polymer of isobutylene and maleic anhydride, commercially known as ISOBAM®; and the other involves (different) food-grade biopolymers, including polysaccharides and proteins. As a key feature, ISOBAM® has the twofold role of being a gelling agent and dispersant, which reduces the total organic matter to very low concentrations. ISOBAM®-derived materials are unique examples of gelcast transparent polycrystalline ceramics ($MgAl_2O_4$, $Y_3Al_5O_{12}$, $Yb_3Al_5O_{12}$). With biopolymers, especially agaroids, gelatine, curdlan and egg white proteins, it is possible to achieve fully dense, high-strength ceramics, whose properties are in line with those derived by traditional processing, such as slip casting and uniaxial pressing, as well as by acrylamide-based gelcasting [97]. As a low amount of these natural gel formers is needed to achieve proper green strength and machinability, debinding prior to sintering is not required. Such features, as well as their low toxicity, make these natural systems potentially exploitable at an industrial scale.

However, despite the above-mentioned advances, some limitations still exist when using low-toxicity gelling agents, as summarised in the following:

i) The high viscosity and low solubility of natural gelling agents limit the solid loading within the ceramic slurries. Therefore, the green density is often low, making drying a rather long step that must be carefully controlled to avoid cracking and deformations. Moreover, sintering shrinkage is likely to be high and some porosity may remain.

ii) Some natural gelling agents show a certain tendency to foam, thus requiring a proper outgassing step prior to or/and during casting, as well as the addition of specific antifoaming agents.

iii) Most of these natural systems require heating (normally > 60 °C) to undergo complete dissolution, while gelation is achieved during cooling. Such a behaviour requires the simultaneous heating of the ceramic slurry, as well as casting under temperature-controlled conditions, thus increasing the complexity of the casting operation.

iv) Most of the natural gelling agents are highly hydrophilic and absorb environmental moisture. Therefore, green parts must be stored in relatively low humidity conditions, as they are susceptible to degradation, and require that a debinding or sintering step be performed within a reasonable time.

All these issues can be largely reduced through careful control of all processing steps and specifications, such as the rheological behaviour of the slurry, the concentration of the polymer solution, the outgassing and casting conditions, and the demoulding and drying operations.

Further drawbacks which should be mentioned are:

v) The very high cost of some natural gelling agents, such as agarose [98], which makes its use prohibitive for large-scale production.

vi) The preferred implementation of gelcasting as a batch process [17], which contributes to limiting the development of this shaping technique at the industrial scale.

However, with respect to the latter drawback, the concept of associating gelcasting with rapid and continuous prototyping techniques is promising [99, 100,101]. A smart processing route for the continuous extrusion of ceramic parts has been proposed in [100], in which agaroids were used as gelling agents. After mixing with the ceramic suspension, the slurry achieved a low viscosity at a temperature above T_g and a sharp increase in viscosity when cooled (up to one order of magnitude), thus forming a strong gel. For this gel-extrusion process, a special apparatus was designed and fabricated, consisting of a closed reservoir for the slurry, having a conical shape to allow free flow of the slip towards the die, which is refrigerated with tap water, thus allowing the slurry to gel. Pressure is applied to the constantly stirred slurry to facilitate its flow and to allow continuous bodies to leave the die.

Finally, a gelcasting-based 3D printing method has been very recently proposed in [101]. A laser-wise slurry deposition (LSD) method was used to spread ceramic slurry (instead of using dry powders as in the traditional processes) on a base substrate by means of a doctor blade. Each deposited layer was then dried and treated by a printing head with the proper ink. Here, an alumina slurry was mixed with sodium alginate, while bivalent cations (Cu^{2+}) necessary to react with alginate and induce gel formation (see Section 2.1) were provided by the ink. At the end of the process, the powder bed was washed with water and excess powder was removed, while the printed part was jellified and extracted. In this process, alginate plays some key roles: as a gel former to prevent the gel part from being removed during washing; as a viscosity agent to improve the rheological properties of the slurry for the deposition process; and as a binder in the green layers, preventing cracking during drying.

3. Porous materials

Traditionally, ceramics are made as dense as possible to reduce the possibility of unexpected failures and fractures in these brittle materials. However, owing to the combination of their unique, remarkable properties and cellular structure, ceramic foams have a high potential for many applications, such as molten metals filtration, high-temperature thermal insulation, support for catalytic reactions, filtration of particulates from diesel engine exhaust gases and hot corrosive gases in various industrial processes, lightweight materials, as well as bone substitutes. Thus, interest in foam ceramics has rapidly grown during the past decades [102-104].

Ceramic foams are lightweight materials with a cellular structure, struts and windows. “Open cell” foams have solid material only on the cell edges with the remainder of the cell being empty, and “closed-cell” foams have solid materials on their faces as well [105]. In the latter, cells are isolated from one another. In fact, foams often possess both open and closed cell features [105]. Porous features influence the properties of the produced components, where two crucial steps are involved in the production of cellular materials. On one hand, the selection and set-up of a reliable forming method is needed to strictly control pore size, volume, distribution and morphology, and on the other hand, a proper characterisation of the porosity features as well as the mechanical/functional performances is needed [103,104].

The most frequently reported manufacturing methods to produce porous ceramics with controlled properties combined with a gelcasting technique are typically classified into replication processes, burnout of pore formers (elimination of a sacrificial phase) and direct foaming. **Figure 14** depicts the main processing steps for producing gelcast porous materials, in which pores are generated by the burn-out of a sacrificial phase. We can observe that the processing steps are almost the same as for dense materials (see Figure 1 and Section 2), apart from the addition of the sacrificial porogens in the starting slurry (step 1) and their thermal decomposition (step 6) prior to sintering. This emphasises the versatility of gelcasting, as limited modifications in the process allow changing from dense to porous parts manufacturing.

The fabrication techniques can be also classified according to the pores created randomly (replication process and gelcasting) or by design (rapid prototyping) [102]. Thus, the next sections will discuss the single steps of preparation of ceramic foams while keeping the previous classification of pore formation methods:

- replica foam process,
- use of porogens,
- emulsification of a ceramic suspension,
- direct foaming of a ceramic suspension.

3.1 Pore formation

One of the simplest and oldest methods for the preparation of ceramic foams is the ‘‘replication process’’, which consists of the impregnation of a polymeric sponge (usually a polyurethane foam, but not exclusively) by a ceramic slurry, followed by a drying and a sintering step [106,107]. In the combined processing route, initially the compounds are dispersed in distilled water (the gelling agent and dispersant for natural gelling systems, or a functional monomer, crosslinker, binder and dispersant for AM systems) and mixed by means of a heating magnetic agitator until a homogeneous solution is achieved. Afterwards, the ceramic powder is added to the solution under mechanical stirring to break the agglomerates present in the powder. Next, the existing bubbles are removed from the mixture in a vacuum chamber. Once the mixture is ready, infiltration of polyurethane foams is performed under vacuum by immersion into the suspension, and the excess slurry is removed by gravity before gelling [108]. After drying, the samples can be sintered at high temperature. Because of the availability of many polymeric foams with controlled size and shape of pores, this method readily allows the preparation of ceramic components having a well-defined porosity [102]. Depending on the starting polymeric sponge, the replication technique can create open interconnected cells and anisotropic pore structures with elongated pores [102].

Surprisingly, the literature survey found no paper dealing with gelcasting techniques based on natural gelling agents combined with the replica foam process. In addition, there ~~is a priori~~ are no known technical side effects ~~to~~ for combining both processes. As already highlighted for dense component manufacturing, the production of pieces by gelcasting techniques requires a high solid content of at least 50 vol% to avoid cracks during the drying and sintering steps [25] and to reduce excessive sample shrinkage. In addition, suspensions must have a low viscosity to infiltrate the polymeric template. To this aim, for example, hydroxyapatite powders having a specific surface area of approximately 10 m^2/g are recommended to avoid undesirable agglomerates [109-111], and the mean particle size should be in the range of 4–13 μm [111,112]. Finally, the rheological behaviour of the suspensions should be pseudoplastic or shear-thinning because of the necessarily high solid loading [112]. For the infiltrated foam combined with gelcasting, the preferred quantity of dispersant to be added to the suspension is one which produces the highest value of viscosity to prevent the suspension from running out of the polymeric sponge before it is impregnated [112-115]. During the combustion of polyurethane foams, isocyanate derivatives are the main reason for the presence of hydrogen cyanide (HCN) in fire smoke [116]. The Threshold Limit Value – Short-Term Exposure Limit (TLV-STEL) of HCN is 4.7 ppm [117].

Use of porogens is a second method widely exploited to produce highly porous materials with controlled porosity features. The process is based on the decomposition of the fugitive phases (typically, polymer spheres) during thermal treatment. The shape, size, and size distribution of these spheres (made of polymethylmethacrylate (PMMA) or of polyethylene (PE)) after sieving, as well as their volume fraction with respect to the ceramic content in the slurry, can be used to perform strict control of many porosity features in the final components [69,77,88-90,118-120]. To fabricate porous ceramics, the polymeric spheres are added to the powder suspension in suitable amounts to obtain ceramic bodies with the targeted vol% porosity after a preliminary dispersion in water [69,77,88-90,118-120]. The ceramic content of the slurries is the same as adopted for dense materials (e.g., 60 wt% solid content and 3 wt% of gelatine as gelling agent) for zirconia bodies having 40 vol% porosity [90]. Then, the procedures for preparing dense and porous bodies differ for the sintering cycle.

The use of synthetic materials obtained from non-renewable resources (oil) as porogens such as PE or PMMA beads presents drawbacks connected to the toxicity of the gases formed during firing. There are no differences in the thermal degradation products of low density-PE and high density-PE [121]. Aged materials do not show any changes in the chromatogram either. Apart from CO_2 and water vapour emissions, there are also other decomposition products; amongst them, 1,12-tridecadiene, 1,13-tetradecadiene, 1,14-pentadecadiene and 1,15-hexadecadiene are specific to PE thermal decomposition [121]. For example, 1,13-tetradecadiene is known to be a skin (H315), eye (H319) and respiratory (H335) irritant, according to the Globally Harmonised System of Classification and Labelling of Chemicals (GHS) [122]. CO, CO_2, water vapour and several hydrocarbons (HCs: CH_3OH, CH_2O, CHO…) can be generated during PMMA combustion [123]. CO_2 is produced once the agents and precursors for its formation (HCs) have already formed. CO is surely the most known dangerous gas: its Threshold Limit Value- Time-Weighted Average (TLV-TWA) is 25 ppm [117]. Methanol is also known for its toxicity; it is classified as potentially toxic (Category 3) if swallowed (H301), inhaled (H331) or comes into contact with skin (H311), and it can cause damage to organs (Category 1, H370) [124]. During PE decomposition, more than 230 products were evidenced in [125]. Higher values of available oxygen led to a decrease in the yields of hydrocarbons, whereas oxygenated semi-volatile compounds and carbon oxides increased. In contrast, when increasing temperature, both cracking and pyrosynthesis reactions were enhanced, and a rise in the yields of methane, ethane, ethylene, benzene or polycyclic aromatic hydrocarbons (PAHs) was observed, whereas the production of other linear hydrocarbons, oxygenated compounds and carbon oxides decreased [125]. It has been demonstrated that PAHs can cause carcinogenic and mutagenic effects and are potent immuno-suppressants. They are known to also affect immune system development, humoral immunity and host resistance [126].

A third method to produce porous gelcast ceramics is based on emulsification of a ceramic suspension with molten paraffin [127,128]. Subsequent gelation at a temperature below the melting point of this fugitive phase allows solidification of paraffin droplets before gelcasting and drying without coarsening, thus yielding relatively strong green bodies [127,128]. In these works, an aqueous alumina suspension was prepared at 50 vol% solid loading. Dolapix PC-67 was added as a dispersant and stabilising agent and to adjust viscosity to 0.5 Pa.s. This suspension (prepared at room temperature) was then emulsified at 80 °C (above paraffin's melting temperature of 58°C), with a paraffin:suspension volume ratio of 1.5 by stirring at 1000 rpm with an overhead stirrer. Finally, sodium lauryl sulphate as a tensioactive, and collagen as a gelling agent, were added [127,128]. N-paraffins can be formed from the primary decomposition of polyethylene in cracking reactions, so at high temperatures they turn into gases and polycyclic aromatic hydrocarbons, leading to the health problems involving PE mentioned above [125].

Oil in-water (O/W) Si_3N_4 suspensions are described in [129], where oil drops (liquid paraffin) are used as sacrificial materials that leave pores in the samples after firing. Powders with a solid content of 55 wt% (95 wt% Si_3N_4 and 5 wt% Y_2O_3) were first milled with Si_3N_4 spheres for 2 h, and then were added into a sodium alginate solution. The O/W emulsion was poured into this suspension to ball-mill for another 30 min. The cast suspensions were quickly gelled by spraying calcium chloride aqueous solution onto the surface, thus the oil was enwrapped in the green bodies [129]. The solid content of the suspensions decreased with emulsion addition, which led to a decrease in viscosity. In contrast, the oil drops in the suspensions had an opposite effect on the viscosity of the suspensions; the interactions between oil drops and Si_3N_4 grains increased the flow resistance in the suspensions. These two parameters governed the viscosities of the suspensions.

These issues have driven the research to finding more environmentally friendly approaches for the development of gelcast porous ceramics, and a further eco-friendly method consists of the direct foaming technique. The process consists either of a vigorous stirring of a colloidal ceramic suspension with water-soluble monomers and a foaming agent, or by the injection of gases into ceramic suspensions. After foaming, the suspension is rapidly gelled by the polymerisation of the monomers, yielding rigid ceramic foam. Finally, green bodies are dried and sintered, resulting in ceramic foam with nearly spherical pores and highly dense struts [91,130]. In most cases, the addition of a surfactant is required to stabilise the generated foam [131]. Surfactants tend to adsorb onto gas–liquid interfaces, expelling a hydrophobic part from the solvent and leaving a hydrophilic part in contact with the liquid. Surfactants thus reduce the surface tension of the gas–liquid interfaces. However, they stabilise the liquid foam only for a limited period of time [124]. The amount of dispersant is selected according to the minimal value of viscosity needed to enhance the formation of foam [112-115].

In [130], a calcined alumina suspension at 35 vol% solid loading was prepared. Ammonium citrate dihydrate was used as a deflocculant (0.8 wt% of the suspension) for the gelatine-based system (5 wt% of the suspension). The addition of gelatine to aqueous alumina suspensions significantly increased the Casson viscosity and yield stress, but the system could be well-dispersed using ammonium citrate. Suspensions were foamed using a double blade stirrer.

Suspensions having 45.5 vol% of doped SiC powders were prepared by dispersion in water with tetramethyl ammonium hydroxide (TMAH, 0.1 wt%) and addition of Triton X-114 and Tergitol TMN-10 as foaming agents, while agar was used as the gelling agent [132]. The isoelectric point (IEP) of the doped SiC powder had a pH value of 2.5 after TMAH addition. The slurry, foaming agents and agar solution were mixed at 70 °C and stirred for 10 min. The foamed suspension was then cast in a mould.

A gelcasting technique associated with the direct foaming method was also used to recycle industrial and municipal wastes in [133] to produce construction materials. The slurry consisted of water, broken bottles 42–45 wt%, mica minerals 18–22 wt%, mining waste 18–22 wt%, and spent alumina 12–15 wt% milled together with gelatine as a binder. The suspension was heated at 80 °C and mixed vigorously to produce foam. The hot, foamed slurry was finally cast into moulds and was allowed to cool to room temperature to achieve the desired shape. The samples were then strong enough for mechanical handling.

In [134], a direct foaming-emulsification method was used to produce porous alumina. Alumina suspensions were emulsified with soybean oil at 80 °C. Sodium dodecyl sulfate (6 vol% relative to the emulsified suspension volume) and gelatine (5 wt% relative to water volume) were added as extra-emulsifying and gelling agents, respectively. The experimental results (in the range of investigated shear rates (1–600 s^{-1})), revealed pseudoplastic behaviour characteristic of concentrated systems caused by a shear-induced structural breakdown in the emulsified suspensions. The emulsions were cast in a mould, and were subsequently cooled to promote physical cross-linking of the gelatine.

Porous mullite ceramics were also prepared via foam-gelcasting using a commercial mullite powder (average particle size ~ 2.8 μm; suspension solid loading 48–54 vol%) and ISOBAM-104

(IB, 0.3–1.0 wt% with respect to mullite) as the dispersing and gelling agents, respectively, sodium carboxymethylcellulose (0.025-0.2 wt% with respect to mullite) as the foam stabilising agent, and triethanolamine lauryl sulfate (0.025–1.2 vol% with respect to slurry) as the foaming agent [135]. The IEP of the mullite slurry without any additive was at pH 6.6 and after the addition of the various additives, it shifted to below pH 2. Upon addition of 0.5 wt% of IB, the zeta potential value of the mullite slurry at pH 6.6 reached approximately 31 mV, indicating that addition of ISOBAM improved the particle dispersion in the slurry [135]. Viscosity values of the slurries with 52 vol% solid loading decreased initially by increasing the IB content from 0.3 to 0.5 wt% and increased slightly upon increasing the IB content from 0.5 to 1.0 wt%. In all cases, the viscosity values of all slurries were lower than 1 Pa.s at a shear rate of 100 s^{-1}, which was favourable for foaming. 0.5 wt% IB was considered by the authors as the optimal amount to prepare mullite slurry. After foaming, the slurry was immediately cast into moulds and gelled for 12 h at room temperature [135].

Ceramic shell (mullite source), an industrial solid waste produced by the lost-wax casting process, was proposed after crushing and milling steps as an alternative raw material source in [136]. The aqueous suspension was prepared with 35 or 42 vol% of ceramic shell powder and 1.5 vol% of a polyacrylic acid (Dolapix CE 64, Zschimmer & Schwarz). Homogenisation was performed in a laboratory mixer operating at a stirring speed of 2000 rpm for 20 min. Foam was obtained by adding 0.1 vol% of Tergitol TMN-10 (Sigma-Aldrich) as surfactant, and 5 wt% (based on solid content) of ovalbumin (Sigma-Aldrich) as gelling agent to ceramic suspensions containing different solids loading under mechanical stirring for 5 min. The wet foams were cast in cylindrical aluminium moulds and were subjected to low vibration to eliminate defects. Finally, the foams were consolidated at 80 °C for 20 min in an oven.

Recently, a combined foam-gelcasting and microwave heating method was developed for low temperature rapid preparation of high quality porous mullite ceramics [137]. Slurries at 52 vol%

solid loading, with 0.5 wt% ISOBAM 104 and 0.1 wt% sodium carboxymethyl cellulose (CMC) (both with respect to solid powder) were initially prepared under mechanical stirring. Then, 1.0 vol% triethanolamine lauryl sulfate (TLS) (with respect to the slurry) was added to the slurry to generate foam under mechanical stirring [137].

Recently the Authors developed hydroxyapatite foams by gelcasting coupled with a direct foaming technique, with the aim of producing scaffolds for bone replacement applications [91]. Agar was dissolved in deionised water (2 wt%) at 90 °C to ensure complete dissolution. Then, the agar solution was cooled to 60 °C and added to the dispersed ceramic slurries heated to the same temperature. Foaming was carried out at 60 °C under vigorous stirring of the slurries by using a double-blade mixer. Addition of an anionic surfactant (sodium dodecyl sulfate, 1.2 wt%) was necessary to stabilise the foam. The suspensions were cast under vacuum (10^{-2} Pa) to remove air bubbles entrapped in the ceramic suspensions. Gelation of the samples occurred during slow cooling to room temperature.

3.2 Shaping, drying and thermal treatment

In the replica process, drying is not a critical step and it can be conducted first at room temperature for 24 h to eliminate excess water and then is carried out in an oven at 70 °C for several hours, thus giving samples sufficient mechanical strength to be handled [108,112]. Drying can also be fully performed at room temperature [113].

Usually, the viscosity of the suspensions containing transient porogens is low because of the high temperature needed to dissolve natural gelling agents into water and because of the previous optimisation of the solutions. This obviously enables efficient casting into moulds and allows fast migration of residual bubbles to the top of the solution by enhanced flotation–separation [118].

In the case of sacrificial templates, drying is a critical step and humidity must be controlled and reduced progressively during the entire process. When too fast a drying rate is applied, the surface of the samples dries just after suspension casting and this dried surface blocks diffusion paths for water molecules. Consequently, density gradients inside the body generate stresses leading to cracks. Therefore, a long-term (8–10 days) humidity-controlled drying process at room temperature must be performed [69,77,88-90,118-120]. This was also confirmed when using paraffin, where drying of the green ceramic phase required three days in an oven at 50 °C (below the melting temperature of paraffin) to prevent coarsening of paraffin droplets [127].

Pyrolysis of a polymer is critical in sintering ceramics using the polymer sponge method. Sufficient time should be provided for the polymer burnout before sintering of the ceramic coating starts to avoid cracks in the microstructure due to gas overpressure when the polyurethane foam decomposes [107,113,137]. To this aim, thermogravimetric analysis (TGA) is used to determine the temperature at which complete burnout of the polyurethane foam occurs before introducing several heating and isothermal steps below 600 °C needed in the thermal cycling of the foam [107,113,138].

Furthermore, in the case of sacrificial templates, the thermal decomposition of the PE and of the PMMA spheres must be controlled so as not to affect the integrity of the green bodies [69,77,88-90,118-120]. Burnout conditions must be controlled to avoid overpressure of burnout gases resulting from the pore former (paraffin droplets), gelling additive (dried gelatine), tensioactive additives, etc., after emulsification of a ceramic suspension with molten paraffin [127,128]. TGA of organic precursors helps in solving the problem in both cases by understanding when to introduce step-wise isothermal steps and to slow heating ramps during thermal treatment. The positive effect of adding PMMA beads during the critical step of polymer burnout is related to the influence of this dispersed template phase on the microstructure (**Figure 15**), which hinders shrinkage of the matrix. This leads to an increased void volume between the templates at the beginning of the burnout process. Additionally, this effect may be enhanced by a pore stabilisation mechanism; the volume fraction of the filler beads offers an intermediate reservoir for the gaseous products to be released, thus decreasing the internal gas pressure and stabilising the macro-structure [118].

Finally, in common with other casting operations, highly fluid systems are required in direct foaming to enable foaming and to fill small details in moulds for production of high-complexity shapes [135]. The high viscosity features of foamed systems at low shear rates can thus be a critical factor for the production of complex foamed body shapes [135].

Their strength after gelation and their resistance to crack formation during demoulding, handling and drying operations are determined by the gel strength. A high gel strength is essential in the case of foamed suspensions because the high porosity and the low solids loading (30–40 vol%) tend to weaken the body [130].

Increasing the gelatine concentration in the liquid phase from 3 to 9 wt% led to an increase of the diametral compressive strength of dry samples from 1.7 to 5 MPa. However, these values are lower than the dry strength of green samples produced with suspensions containing 25 wt% of monomer in the liquid phase, which can reach up to 20 MPa [139]. Nonetheless, the obtained samples resisted demoulding and drying stresses; dry samples had no cracks and were strong enough to be core drilled, yielding cylinders with good surface finish [130]. Drying can be performed in an oven at 50 °C [131] or even 100 °C [135].

Table 3 summarises the advantages and challenges of the previously described fabrication techniques.

3.3 Green and fired bodies: microstructural features and properties

Because of inherent drawbacks, none of the presented techniques can completely satisfy the structural features required, for example, perfectly acceptable highly porous scaffolds having fully interconnected pores in the order of several hundreds of microns with reasonable mechanical strength [140]. The polymer replica method can produce the desirable porous morphology with highly interconnected and large-sized pores. However, the porous scaffolds obtained from this process commonly have insufficient mechanical strength for load-bearing in tissue engineering applications [140]. The classic defects of ceramic foams are the following: voids inside the struts caused by burnout of the polymer, and cracks between the pore walls caused by the expansion difference between the polymer and ceramic powder during the initial heating stage of the pyrolysis of the polymer [107,137]. The triangular form of the voids inside the struts generated by the shape of the polymer preform sponge is also detrimental to the mechanical properties of these foams [107,137].

Nonetheless, SEM micrographs usually show open and interconnected pores inside the foams obtained by the replication technique. They can have pore sizes between 100 and 600 μm with irregular geometry, as well as internal pores in the range 50–100 μm, which suggests the existence of an interconnected internal microporous structure in the ceramic material (**Figure 16**) [108,140].

Finally, rough surfaces can be obtained in the porous bodies, which are favourable for cellular adhesion and new bone formation in tissue engineering applications [108,112].

The Authors in [88] prepared green alumina porous materials with gelatine as a gelling agent having a highly homogeneous distribution of PE spheres in the ceramic matrix and the green microstructure, similar to that observed for dense components. However, some PE clusters were also observed, as reported in [90]. PMMA beads are usually more regular. PE decomposition yields pores having a spherical shape, which appear to be homogeneously distributed in the sintered microstructures (**Figure 17** [141]), where pores are surrounded by ceramic walls and struts showing a dense and fine microstructure. However, a limited number of interconnections amongst pores was observed as a consequence of the volume amount of PE spheres (40 or 50 vol%) and of final density of the foams (68%). By using the same process, the Authors in [69] developed alumina-10 vol% zirconia composites having 56-73% total porosity. Agar was used as a gelling agent. The SEM observations of the porous materials revealed a uniform distribution of the macro-pores and the presence of diffuse micro-porosity with dimensions of approximately 1 μm, as already observed by the same Authors in dense gel-cast samples without pore formers. The porous composite samples showed a higher compressive strength compared to the pure alumina ones, probably because of smaller pores due to higher shrinkage during the sintering step. In fact, the small size of tetragonal grains as well as their low tensile residual stress after sintering probably reduced their transformability to the monoclinic phase under the applied stress, thus limiting the well-known reinforcing and toughening mechanisms.

Figure 18 depicts the SEM microstructures of sintered cellular ceramics made from paraffin emulsified suspensions having well defined cells. Cell walls are relatively thin, with a thickness of approximately 1 μm [127].

Silicon nitride foams made with O/W emulsions had an open porosity of 60.1–63.9% and a flexural strength ranging from 34.6 to 44.5 MPa after sintering at 1690 °C for 2 h in a graphite furnace under a N_2 atmosphere [129].

After firing at 1100 °C, the fabricated porous ceramic tiles from industrial and municipal wastes described in [133] were compared to six commercially available porous tiles in terms of sound absorption and thermal conductivity. The prepared porous ceramics from wastes are a potential sound insulator, because of their better sound absorption characteristics when compared with the six commercially available porous materials. Moreover, these new porous materials are good thermal insulators, which provide natural cooling and ventilation. In addition, gelcasting from waste materials offers the possibility to obtain products with a soil structure; the resulting microstructure reveals a well inter-connected pore structure that allows grass roots to penetrate it as they would penetrate natural soil. This material can retain water and release it during hot weather, making it attractive for roof gardens and wall material, where vegetation can be grown on it.

In the direct foaming process, variation of the porosity content, pore size (bubble size), and shape is possible by changing different processing parameters such as the liquid-to-powder ratio, the concentration, the composition of the foaming agent in solution, the particle sizes of the starting powders, and the stirring conditions [105]. These characteristics provide unprecedented properties, such as high permeability [142,143], low thermal conductivity [144], high specific surface area and enhanced mechanical strength [127,143]. For instance, as investigated by the Authors in a recent work [91], in sintered HA foams depicted in **Figure 19,** a certain residual porosity is present in HA_{dry} (poorly dispersed hydroxyapatite powders, see § 3.2) while a dense and compact structure characterises the struts in HA_{wet} (well dispersed hydroxyapatite powders)-foam. The higher linear shrinkage during sintering of HA_{wet} (21% for HA_{wet}) as compared to HA_{dry} (15%) explains the much more compact struts in the last sample. However, as these materials can be potentially used as scaffolds for bone tissue engineering, the presence of residual micropores can have a positive role in the bone regeneration process, as it allows protein interactions responsible for bioactivity. On the other hand, thickness and density of the struts play a pivotal role in the mechanical properties of such highly porous materials.

To conclude, **Table 4** summarises the main features of the obtained foams by the previously described fabrication techniques.

Finally, it should be mentioned that the versatility of gelcasting processes allows the development of unconventional architectures, such as functionally graded structures. For instance, the Authors have recently developed a novel calcium phosphate (CaP)/polycaprolactone (PCL) scaffold for bone tissue engineering, achieving a gradation in both composition and porosity fraction [145]. The scaffold is made of (*i*) a dense hydroxyapatite (HA)/β-tricalcium phosphate (β-TCP) core, (*ii*) a macro-porous HA/β-TCP transition layer and (*iii*) a macro-porous PCL/(HA/β-TCP) external layer. Both the porosity and β-TCP/HA ratio increased from the inner to the outer layer, providing modulation of mechanical properties as well as biodegradation behaviour. The two ceramic layers were fabricated by gelcasting, in which agar was used as the gel-former. The outer polymer/CP layer, obtained by a solvent casting/particle leaching process, was strongly joined with the ceramic layer, highlighting the potential of gelcasting to be combined with other forming techniques, thus opening the way to the design and fabrication of further innovative architectures with targeted multi-functionalities.

3.4 General remarks on porous materials

As mentioned in § 3.1, the literature survey found no paper dealing with gelcasting techniques based on natural gelling agents combined with the replica foam process. In addition, there are no known technical side effects for combining both processes. As already highlighted for dense component preparation, the production of pieces by gelcasting techniques requires a high solid content of at least 50 vol% to avoid cracks during the drying and sintering steps [25] and to reduce excessive sample shrinkage. Depending on the starting polymeric sponge, the replication technique can create open and interconnected cells and anisotropic pore structures with elongated pores [102].

A modified gel-casting process can also produce highly porous materials with controlled porosity features from fugitive phases (mainly, the PE and PMMA beads) that decompose during the thermal treatment. The shape, size, and size distribution of these spheres (made of PMMA or PE) after sieving, as well as their volume fraction with respect to the ceramic content in the slurry, can be used to perform strict control of many porosity features in the final components [69,77,88-90,118-120]. However, the use of synthetic materials obtained from non-renewable resources (oil) as porogens such as PU foams, as well as PE or PMMA beads and paraffin, present drawbacks connected to the toxicity of gases that develop during firing. These can be overcome using the direct foaming process, where a much lower amount of organic compounds is necessary. In addition, the direct foaming technique is able to produce higher-porosity samples compared to the porogen techniques. In spite of the continuous advances of gelcasting in the fabrication of porous materials, none of the presented techniques can totally satisfy the structural features required (for example) for perfectly acceptable highly porous scaffolds with fully interconnected pores in the order of several hundreds of microns with reasonable mechanical strength [140]. However, a point of strength of gelcasting is the versatility of this shaping method, which allows the development of unconventional architectures, such as functionally graded structures. Some attempts to further mitigate the environmental impact of gelcasting relate to the use of waste (glass bottles, mining waste, ceramic shell waste) as raw material for the fabrication of porous tiles or mullite foams. Although few data are available, the properties of a developed structure show comparable properties to commercially available products, thus underlining the great potential of this approach, not only for achieving desirable physical-mechanical properties, but also for recycling of waste resources.

4. Conclusions and Perspectives

Recent trends in near-net-shaping methods for dense and porous ceramic materials have been presented in this work, focusing on natural gelling agents in gelcasting techniques. The search for low-toxicity precursors has been successful in that these gelling agents have been demonstrated as competitive with AM original monomers. However, to achieve this competitiveness, extensive research was necessarily dedicated to optimising many of the processing parameters related to natural gelling agents, such as ceramic slurries and the shaping, drying and firing conditions, as reviewed in this study.

This work aims to highlight the low-toxicity and versatility aspects of gelcasting. The process can be considered as environmentally friendly because most of the non-toxic/natural gel-formers can be processed in an aqueous medium. Furthermore, they are used in extremely low concentrations, thus not requiring a separate binder removal cycle during firing. With such natural processes, many successful case studies – here reported – have demonstrated the versatility of this technique towards the development of both fully dense ceramics with simple and complex-shapes, and porous/foamed materials with well-controlled porosity features. The potential to join dense structures with porous layers, leading to functionally graded ceramics, has been demonstrated as well. In addition, this technique has allowed the successful fabrication of advanced materials such as transparent polycrystalline ceramics, textured ceramics, and nanocrystalline and nanocomposite ceramics.

It is clear that there is significant promise in this technology. However, the application of aqueous-based gelcasting is in its early stages and is largely limited to academic studies at present. This is, in fact, a key difference from acrylamide-based gelcasting, as this process has already achieved a technology readiness level approaching industrialisation requirements. As an example, in the 2000s, AlliedSignal Incorporated was engaged in the production of turbomachinery parts in gelcast silicon nitride through the installation of an automated production line consisting of a series of specialised stations assigned to perform the gelcasting process [16,17]. This automated system was designed to have the capability to fabricate AM-MBAM-based gelcast components at the rate of 10,000 parts per year [8]. In the case of natural gelcasting, some major drawbacks in the process limit its development at a larger scale. As mentioned in Section 2.5, to successfully process such natural-based systems, careful control of many processing parameters has to be carried out, such as the rheological behaviour of the slurries, the casting operation, and the drying and storing conditions. Furthermore, the price of some biopolymers is high. Just to give an indication, the cost of carrageenan and gelatine is twice or triple that of the AM-MBAM system [146,147], while agarose's cost can be more than one order of magnitude higher [98].

Efforts to increase the environmental and economic sustainability of gelcasting relate to the use of waste as ceramic raw material in natural gelling systems. Although the few data available show that this approach is promising, further investigations are needed to understand the true potential of this approach and to bring it to an industrial scale.

A step forward towards the industrialisation of gelcasting can be accomplished owing to the new 3D printing technologies, which represent an almost unexplored field when using natural gelling agents. The rare examples of gel-extrusion or gel-assisted layerwise slurry deposition open the way to the development of continuous and automated processes as a new challenge to move the technology from the laboratory to industrial scale.

5. References

[1] A.C. Young, O.O. Omatete, M.A. Janney, P.A. Menchhofer, Gelcasting of alumina, J. Am. Ceram. Soc. 74 (1991) 612-618. https://doi.org/10.1111/j.1151-2916.1991.tb04068.x

[2] M.A. Janney, 1990. Method for molding ceramic powders. U.S. Patent No. 4894194, January 16.

[3] M.A. Janney, O.O. Omatete, 1991. Method for molding ceramic powders using a water-based gel casting. U.S. Patent No. 5028362, July 2.

[4] J. Yang, J. Yu, Y. Huang, Recent developments in gelcasting of ceramics, J. Eur. Ceram. Soc. 31 (2011) 2569-2591. https://doi.org/10.1016/j.jeurceramsoc.2010.12.035

[5] J. Yu, J. Yang, Y. Huang, The transformation mechanism from suspension to green and the development of colloidal forming, Ceram. Int. 37 (2011) 1435-1451. https://doi.org/10.1016/j.ceramint.2011.01.019

[6] C. Tallon, G.V. Franks, Recent trends in shape forming from colloidal processing: A review, J. Ceram. Soc. Jpn. 119 (2011) 147-160. https://doi.org/10.2109/jcersj2.119.147

[7] G.V. Franks, C. Tallon, A.R. Studart, M.L. Sesso, S. Leo, Colloidal processing: enabling complex shaped ceramics with unique multiscale structures, J. Am. Ceram. Soc. 100 (2017) 458-490. https://doi.org/10.1111/jace.14705

[8] O.O. Omatete, M.A. Janney, S.D. Nunn, Gelcasting: from laboratory development to industrial production, J. Eur. Ceram. Soc. 17 (1997) 407-413. https://doi.org/10.1016/S0955-2219(96)00147-1

[9] S.K. Swain, D.K. Sengupta, B.P. Singh, S. Bhattacharjee, Gelcasting – a versatile process, Part 1, InterCeram 54 (2005) 174-177.

[10] R. Gilissen, J.P. Erauw, A. Smolders, E. Vanswijgenhoven, J. Luyten, Gelcasting, a near net shape technique, Mater. Des. 21 (2000) 251-257. https://doi.org/10.1016/S0261-3069(99)00075-8

[11] A. Kaşgöz, Z. Özbaş, H. Kaşgöz, I. Aydin, Effects of monomer composition on the mechanical and machinability properties of gel-cast alumina green compacts, J. Eur. Ceram. Soc. 25 (2005) 3547-3552. https://doi.org/10.1016/j.jeurceramsoc.2004.09.013

[12] K.T. Faber, N.O. Shanti, Gelcasting of ceramic bodies, in: N.P. Bansal, A.R. Boccaccini (Eds.), Ceramics and Composites Processing Methods, Wiley, Hoboken, NJ, 2012, pp. 199-234.

[13] M. Huang, P. He, J. Yang, F. Duan, S.C. Lim, M.S. Yip, Fabrication and characterization of mini alumina ceramic turbine rotor using a tailored gelcasting process, Ceram. Int. 40 (2014) 7711-7722. https://doi.org/10.1016/j.ceramint.2013.12.112

[14] H. Zhao, C. Ye, Z. Fan, A simple and effective method for gel casting of zirconia green bodies using phenolic resin as a binder, J. Eur. Ceram. Soc. 34 (2014) 1457-1463. https://doi.org/10.1016/j.jeurceramsoc.2013.11.021

[15] Z. Lu, K. Miao, W. Zhu, Y. Chen, Y. Xia, D. Li, Fractions on of irregular particles in suspensions for the fabrication of multiscale ceramic components by gelcasting, J. Eur. Ceram. Soc. 38 (2018) 671-678. https://doi.org/10.1016/j.jeurceramsoc.2017.08.002

[16] J.J. Nick, D. Newson, B. Draskovich, O.O. Omatete. Gelcasting advancement for manufacturing scale-up, 23rd Annual Cocoa Beach International Conference on Engineering Ceramics and Structures. Cocoa Beach, Florida, January 24–29, 1999.

[17] J.J. Nick, D. Newson, R. Masseth, S. Monette, Gelcasting automation for high-volume production of silicon nitride turbine weels, 23rd annual Cocoa Beach International Conference on Engineering Ceramics and Structures. Cocoa Beach, Florida, January 24–29, 1999, 225-232.

[18] B. Su, S. Dhara, L. Wang, Green ceramic machining: A top-down approach for the rapid fabrication of complex-shaped ceramics, J. Eur. Ceram. Soc. 28 (2008) 2109-2115. https://doi.org/10.1016/j.jeurceramsoc.2008.02.023

[19] W.H. Kok, W.K.C. Yung, D.T.C. Ang, Green gelcasting of aluminum nitride using environmental sustainable ovalbumin natural binder, J. Aust. Ceram. Soc. (2018) 1-9. https://doi.org/10.1007/s41779-018-0222-3

[20] P. Zhang, P. Liu, Y. Sun, X. Peng, Z. Wang, J. Zhang, Aqueous gelcasting of the transparent $MgAl_2O_4$ spinel ceramics, J. Alloys Compd. 646 (2015) 833-836. https://doi.org/10.1016/j.jallcom.2015.05.275

[21] P. Zhang, P. Liu, Y. Sun, X. Peng, Z. Wang, J. Zhang, Microstructure and properties of transparent $MgAl_2O_4$ ceramic fabricated by aqueous gelcasting, J. Alloys Compd. 657 (2016) 246-249. https://doi.org/10.1016/j.jallcom.2015.10.113

[22] Q. Yao, L. Zhang, Z. Jiang, G. Huang, T. Zhou, Y. Ben, S. Wei, R. Sun, H. Chen, Y. Wang, Isobam assisted slurry optimization and gelcasting of transparent YAG ceramics, Ceram. Int. 44 (2018), 1699-1704. https://doi.org/10.1016/j.ceramint.2017.10.098

[23] H. Zhang, H. Wang, H. Gu, X. Zong, B. Tu, P. Xu, B. Wang, W. Wang, S. Liu, Z. Fu, Preparation of transparent $MgO \cdot 1.8Al_2O_3$ spinel ceramics by aqueous gelcasting, presintering and hot isostatic pressing, J. Eur. Ceram. Soc. 38 (2018) 4057-4063. https://doi.org/10.1016/j.jeurceramsoc.2018.04.057

[24] F. Chena, K. Liua, H. Suna, Z. Shuic, C. Liuc, J. Chend, Y. Shie, Fabrication of complicated silicon carbide ceramic components using combined 3D printing with gelcasting, Ceram. Int. 44 (2018) 254-260. https://doi.org/10.1016/j.ceramint.2017.09.166

[25] M.A. Janney, O.O. Omatete, C.A. Walls, S.D. Nunn, R.J. Ogle, G. Westmoreland, Development of low-toxicity gelcasting systems, J. Am. Ceram. Soc., 81 (1998) 581–91. https://doi.org/10.1111/j.1151-2916.1998.tb02377.x

[26] I. Ganesh, Hydrolysis-Induced Aqueous Gelcasting: The Latest Concept for Net-Shape Consolidation of Ceramics—A Review, Mater. Manuf. Processes, 27 (2012) 233–241. https://doi.org/10.1080/10426914.2011.585494

[27] C. Zhang, J. Yang, T. Qui, J. Guo, Preparation of ZTA ceramic by aqueous gelcasting with a low-toxic monomer DMAA, Ceram. Int. 38 (2012) 3063-3068. https://doi.org/10.1016/j.ceramint.2011.12.004

[28] W. Xu, J. Yang, J. Yin, T. Qiu, Aqueous gelcasting of yttrium iron garnet, J. Eur. Ceram. Soc. 33 (2013) 1023-1028. https://doi.org/10.1016/j.jeurceramsoc.2012.11.002

[29] J. Zhang, D. Jiang, Q. Lin, Z. Chen, Z. Huang, Gelcasting and pressureless sintering of silicon carbide ceramics using Al_2O_3-Y_2O_3 as the sintering additives, J. Eur. Ceram. Soc. 33 (2013) 1695-1699. https://doi.org/10.1016/j.jeurceramsoc.2013.02.009

[30] J. Zhang, D. Jiang, Q. Lin, Z. Chen, Z. Huang, Properties of silicon carbide ceramics from gelcasting and pressureless sintering, Mater. Des. 65 (2015) 12-16. https://doi.org/10.1016/j.matdes.2014.08.034

[31] D.C. Jana, G. Sundararajan, K. Chattopadhyay, Effect of monomers content in enhancing solid-state densification of silicon carbide ceramics by aqueous gelcasting and pressureless sintering, Ceram. Int. 43 (2017) 4852-4857. https://doi.org/10.1016/j.ceramint.2016.12.117

[32] W. Wan, J. Yang, J. Zeng, L. Yao, T. Qiu, Aqueous gelcasting of silica ceramics using DMAA, Ceram. Int. 40 (2014) 1257-1262. https://doi.org/10.1016/j.ceramint.2013.06.048

[33] F.S. Ortega, F.A.O. Valenzuela, C.H. Scuracchio, V.C. Pandolfelli, Alternative gelling agents for the gelcasting of ceramic foams, J. Eur. Ceram. Soc. 23 (2003) 75-80. https://doi.org/10.1016/S0955-2219(02)00075-4

[34] K.P. Plucknett, C.D. Munro, Bio-polymer based gel casting of ferroelectric ceramics, Adv. Eng. Mater. 16 (2014) 684-698. https://doi.org/10.1002/adem.201400084

[35] Y. Chen, Z. Xie, J. Yang, Y. Huang, Alumina casting based on gelation of gelatine, J. Eur. Ceram. Soc. 19 (1999) 271-275. https://doi.org/10.1016/S0955-2219(98)00201-5

[36] A.J. Millán, M.I. Nieto, R. Moreno, Near-net shaping of aqueous alumina slurries using carrageenan, J. Eur. Ceram. Soc. 22 (2002) 297-3030. https://doi.org/10.1016/S0955-2219(01)00283-7

[37] Y. Jia, Y. Kanno, Z.P. Xie, New gelcasting process for alumina ceramics based on gelation of alginate, J. Eur. Ceram. Soc. 22 (2002) 1911-1916. https://doi.org/10.1016/S0955-2219(01)00513-1

[38] I. Santacruz, M.A. Nieto, R. Moreno, Alumina bodies with near-to-theoretical density by aqueous gel casting using concentrated agarose solutions, Ceram. Int. 31 (2005) 439-445. https://doi.org/10.1016/j.ceramint.2004.06.007

[39] X. He, B. Su, X. Zhou, J. Yang, B. Zhao, X. Wang, G. Yang, Z. Tang, H. Qiu, Gelcasting of alumina ceramics using egg white protein binder system, Ceram. Silik. 55 (2011) 1-7.

[40] Y. Zhang, J. Xu, Y. Qu, X. Xi, J. Yang, Gel casting of alumina suspension using gellan gum as gelling agent, Ceram. Int. 40 (2014) 5715-5721. https://doi.org/10.1016/j.ceramint.2013.11.010

[41] J. Xu, Y. Zhang, K. Gan, X. Zhang, Y. Qu, N. Ma, J. Yang, A novel gelcasting of alumina suspension using curdlan gelation, Ceram. Int. 41 (2015) 10520-10525. https://doi.org/10.1016/j.ceramint.2015.04.144

[42] C.A. Moorehead, V.L. Blair, J.W. Adams, Characterization of novel gel-casting system to make complex-shaped aluminum oxide (Al_2O_3) Parts, U.S. Army Research Laboratory ARL-TR-7620 (march 2016).

[43] X. Wang, H. Xiang, J. Liu, F. Hou, Y. Sun, Y. Zhou, Gelcasting of $Yb_3Al_5O_{12}$ using a non-toxic water-soluble copolymer as both dispersant and gelling agent, Ceram. Int. 42 (2016) 421-427. https://doi.org/10.1016/j.ceramint.2015.08.126

[44] S. Shimai, Y. Yang, S. Wang, H.Kamiya, Spontaneous gelcasting of translucent alumina ceramics, Opt. Mater. Express 3 (2013) 1000-1006. https://doi.org/10.1364/OME.3.001000

[45] Y. Sun, S. Shimai, X. Peng, G. Zhou, H. Kamiya, S. Wang, Fabrication of transparent Y_2O_3 ceramics via aqueous gelcasting, Ceram. Int. 40 (2014) 8841-8845. https://doi.org/10.1016/j.ceramint.2014.01.106

[46] H.A. Tilson, P.A. Cabe, The effects of acrylamide given acutely or in repeated doses on fore-and hindlimb function of rats. Toxicol. Appl. Pharmacol. 47 (1979) 253-260. https://doi.org/10.1016/0041-008X(79)90319-3

[47] K. Cai, Y. Huang, J.L. Yang, Alumina gelcasting by using HEMA system. J. Eur. Ceram. Soc. 25 (2005) 1089-1093. https://doi.org/10.1016/j.jeurceramsoc.2004.04.024

[48] K. Cai, Y. Huang, J.L. Yang, A Synergistic Low-Toxicity Gelcasting System by Using HEMA and PVP. J. Am. Ceram. Soc. 88 (2005) 3332-3337. https://doi.org/10.1111/j.1551-2916.2005.00602.x

[49] Y. Zhang, Y.-B. Cheng, Use of HEMA in Gelcasting of Ceramics: A Case Study on Fused Silica. J. Am. Ceram. Soc. 89 (2006) 2933–2935. https://doi.org/10.1111/j.1551-2916.2006.01152.x

[50] X. Shu, J. Li, M. Zhang, M. Dong, S. Shunzo, Gelcasting of aluminum nitride using a water-soluble copolymer, J. Inorg. Mater. 29 (2014) 327–330. https://doi.org/10.3724/SP.J.1077.2014.13488

[51] Y. Wang, Y.J. Zhou, H.F. Cheng, J. Wang, Gelcasting of sol-gel derived mullite based on gelation of modified poly (isobutylene-alt-maleic anhydride). Ceram. Int. 40 (2014) 10565–10571. https://doi.org/10.1016/j.ceramint.2014.03.034

[52] Y. Yang, S. Shimai, S.W. Wang, Room-temperature gelcasting of alumina with a water-soluble copolymer. J. Mater. Res. 28 (2013) 1512–1516. https://doi.org/10.1557/jmr.2013.132

[53] X.P. Qin, G. Zhou, Y. Yang, J. Zhang, X. Shu, S. Shimai, S. Wang, Gelcasting of transparent YAG ceramics by a new gelling system. Ceram. Int. 40 (2014) 12745–12750. https://doi.org/10.1016/j.ceramint.2014.04.125

[54] Y. Lu, K. Gan, W. Huo, L. Lv, J. Liu, X. Zhang, S. Yan, J.L. Yang, Dispersion and gelation behavior of alumina suspensions with Isobam, Ceram. Int. 44 (2018) 11357-11363. https://doi.org/10.1016/j.ceramint.2018.03.185

[55] A.J. Millán, R. Moreno, M.I. Nieto, Thermogelling polysaccharides for aqueous gelcasting – Part I: comparative studies of gelling additives, J. Eur. Ceram. Soc. 22 (2002) 2209-2215. https://doi.org/10.1016/S0955-2219(01)00532-5

[56] M. Djabourov, J. Leblond, P. Papon, Gelation of aqueous gelatin solutions.I. Structural investigation. Journal de Physique, 49 (1988) 319-332. https://doi.org/10.1051/jphys:01988004902031900

[57] S.B. Ross-Murphy, Structure and rheology of gelatin gels. Recent progress, Polymer 33 (1992) 2622-2627. https://doi.org/10.1016/0032-3861(92)91146-S

[58] Z.-P. Xie, Y. Huang, Y.-L. Chen, Y. Jia, A new gel casting of ceramics by reaction of sodium alginate and calcium iodate at increased temperatures. J. Mater. Sci. Lett. 20 (2001) 1255-1257. https://doi.org/10.1023/A:1010943427450

[59] C.K. Siew, P.A. Williams, New Insights into the Mechanism of Gelation of Alginate and Pectin: Charge Annihilation and Reversal Mechanism. Biomacromolecules 6 (2005) 963-969. https://doi.org/10.1021/bm049341l

[60] I. Braccini, S. Pérez, Molecular Basis of Ca^{2+}-Induced Gelation in Alginates and Pectins: The Egg-Box Model Revisited. Biomacromolecules 2 (2001) 1089-1096. https://doi.org/10.1021/bm010008g

[61] E.R. Morris, D.A. Rees, D. Thom, J. Boyd, Chiroptical and stoichiometric evidence of a specific, primary dimerization process in alginate gelation. Carbohyd. Res. 66 (1978) 145–154. https://doi.org/10.1016/S0008-6215(00)83247-4

[62] Y. Huang, J. Yang, Gelation forming process for low toxicity system, in: Novel Colloidal Forming of Ceramics. Springer, Tsinghua University Press, Beijing and Springer-Verlag Berlin Heidelberg, 2010, pp. 74-128.

[63] Y. Mine, Recent advances in the understanding of egg white protein functionality, Trends Food. Sci. Technol., 6 (1995) 225-232. https://doi.org/10.1016/S0924-2244(00)89083-4

[64] D.J. McClements, Food Emulsions: Principles, Practice, and Techniques, Florida, USA, CRC Press, 1999.

[65] Y. Huang, J. Yang, Generation, Development, Inheritance, and Control of the Defects during the Transformation from Suspension to Green Body, in: Novel Colloidal Forming of Ceramics. Springer, Tsinghua University Press, Beijing and Springer-Verlag Berlin Heidelberg, 2010, pp. 129-210.

[66] C.G. Ha, Y.G. Jung, J.W. Kim, C.Y. Jo, U. Paik, Effect of particle size on gelcasting process and green properties in alumina, Mat. Sci. Eng. A-Struct. 337 (2002), 212-221. https://doi.org/10.1016/S0921-5093(02)00034-5

[67] J. Yang, Z. Xie, Q. Tang, Y. Huang, Studies on rheological behavior and gelcasting of α-Al_2O_3 suspension, J. Chi. Ceram. Soc. 26 (1998) 41.

[68] L. Chen, X.L. Song, J.D. Ye, B. Li, Colloidal in-situ consolidation forming of Al_2O_3 ceramics using modified starch. In Key Engineering Materials 280 (2005) 1027-1032. https://doi.org/10.4028/www.scientific.net/KEM.280-283.1027

[69] J.M. Tulliani, M. Lombardi, P. Palmero, M. Fornabaio, L.J. Gibson, Development and mechanical characterization of novel ceramic foams fabricated by gel-casting, J. Eur. Ceram. Soc. 33 (2013) 1567-1576. https://doi.org/10.1016/j.jeurceramsoc.2013.01.038

[70] E. Adolfsson, Gelcasting of Zirconia Using Agarose, J. Am. Ceram. Soc., 89 (2006) 1897–1902. https://doi.org/10.1111/j.1551-2916.2006.01040.x

[71] J. Xu, K. Gan, M. Yang, Y. Qu, J. Wu, J. Yang, Direct coagulation casting of yttria-stabilized zirconia using magnesium citrate and glycerol diacetate, Ceram. Int. 41 (2015) 5772-5778. https://doi.org/10.1016/j.ceramint.2014.12.163

[72] S.M. Olhero, G. Tarı, M.A. Coimbra, J.M.F. Ferreira, Synergy of polysaccharide mixtures in gelcasting of alumina, J. Eur. Ceram. Soc., 20 (2000), 423-429. https://doi.org/10.1016/S0955-2219(99)00182-X

[73] V.C. Colonetti, M.F. Sanches, V.C. de Souza, C.P. Fernandes, D. Hotza, M.G.N. Quadri, Cellular ceramics obtained by a combination of direct foaming of soybean oil emulsified alumina suspensions with gel consolidation using gelatin. Ceram. Int. 44 (2018), 2436-2445. https://doi.org/10.1016/j.ceramint.2017.10.215

[74] M.F. Sanches, N. Vitorino, C. Freitas, J.C.C Abrantes, J.R. Frade, J. R. Neto, D. Hotza, Cellular ceramics by gelatin gelcasting of emulsified suspensions with sunflower oil. J. Eur. Ceram. Soc. 35 (2015), 2577-2585. https://doi.org/10.1016/j.jeurceramsoc.2015.03.008

[75] M. Huang, D.Q. Zhang, Z.H. Liu, J. Yang, F. Duan, C.K. Chua, S.C. Lim, M.S. Yip, Comparison study of fabrication of ceramic rotor using various manufacturing methods. Ceram. Int. 40 (2014) 12493-12502. https://doi.org/10.1016/j.ceramint.2014.04.104

[76] S. Dhara, R.K. Kamboj, M. Pradhan, P. Bhargava, Shape forming of ceramics via gelcasting of aqueous particulate slurries. Bull. Mater. Sci., 25 (2002) 565–568. https://doi.org/10.1007/BF02710552

[77] J.-M. Tulliani, C. Bartuli, E. Bemporad, A. Cavalieri, J. Tirillò, G. Pulci, M. Sebastiani, Dense and Porous Zirconia Prepared by Gelatine and Agar Gel-Casting: Microstructural and Mechanical Characterization. Ceramic Materials 63 (2011), 109-116.

[78] E.C. Hammel, J.A. Campa, C.E. Armbrister, M.V. Scheiner, O.I. Okoli, Influence of osmotic drying with an aqueous poly(ethylene glycol) liquid desiccant on alumina objects gelcast with gelatin. Ceram. Int. 43 (2017), 16443-16450. https://doi.org/10.1016/j.ceramint.2017.09.024

[79] J.-M Wu, W.-Z Lu, W. Lei, X-C. Wang, Preparation of $ZnAl_2O_4$-based microwave dielectric ceramics and GPS antenna by aqueous gelcasting. Mater. Res. Bull. 46 (2011) 1485–1489. https://doi.org/10.1016/j.materresbull.2011.04.026

[80] A. Barati, M. Kokabi, M.H.N. Famili, Drying of gelcast ceramic parts via the liquid desiccant method, J. Eur. Ceram. Soc. 23 (2003) 2265–2272. https://doi.org/10.1016/S0955-2219(03)00045-1

[81] N.O. Shanti, G.C. DeNolf, K.R. Shull, K.T. Faber, Liquid desiccant solvent extraction of alumina-filled thermoreversible gels, J. Am. Ceram. Soc. 95 (2012) 509–514. https://doi.org/10.1111/j.1551-2916.2011.04884.x

[82] M. Trunec, Osmotic drying of gelcast bodies in liquid desiccant, J. Eur. Ceram. Soc. 31 (2011) 2519–2524, https://doi.org/10.1016/j.jeurceramsoc.2011.02.015

[83] X. Peng, S. Shimai, Y. Sun, G. Zhou, S. Wang, Correlation between microstructure evolution and drying behavior of gelcast alumina green bodies, Ceram. Int. 41 (2015) 11870-11875. https://doi.org/10.1016/j.ceramint.2015.06.001

[84] R. He, R. Zhang, X. Zhu, K. Wei, Z. Qu, Y. Pei, D. Fang, Improved green strength and green machinability of ZrB2–SiC through gelcasting based on a double gel network, J. Am. Ceram. Soc. 97 (2014) 2401-2404. https://doi.org/10.1111/jace.13076

[85] J.T. Oliveira, L. Martins, R. Picciochi, P.B. Malafaya, R.A. Sousa, N.M. Neves, J.F. Mano, R. L. Reis, Gellan Gum: a new biomaterial for cartilage tissue engineering applications, J. Biomed. Mater. Res. 93A (2010) 852–863. https://doi.org/10.1002/jbm.a.32574

[86] E. Ogawa, R. Takahashi, H. Yajima, K. Nishinari, Effects of molar mass on the coil to helix transition of sodium-type gellan gums in aqueous solutions, Food Hydrocoll. 20 (2006) 378–385. https://doi.org/10.1016/j.foodhyd.2005.03.016

[87] D.M. Kirchmajer, B. Steinhoff, H. Warren, R. Clark, M. in het Panhuis, Enhanced gelation properties of purified gellan gum, Carbohyd. Res. 388 (2014) 125-129. https://doi.org/10.1016/j.carres.2014.02.018

[88] M. Lombardi, V. Naglieri, J.-M. Tulliani, L. Montanaro, Gelcasting of dense and porous ceramics by using a natural gelatine. J. Porous Mater. 16 (2009) 393–400. https://doi.org/10.1007/s10934-008-9212-0

[89] J.-M. Tulliani, E. Bemporad, Sebastiani M., Pulci G., Tirillò J., C. Bartuli, Dense and Cellular Zirconia Produced by Gel Casting with Agar: Preparation and High Temperature Characterization. J. Nanomater., 2013 (2013), 1-11. http://dx.doi.org/10.1155/2013/108076

[90] J.-M. Tulliani, C. Bartuli, E. Bemporad, V. Naglieri, M. Sebastiani, Preparation and mechanical characterization of dense and porous zirconia produced by gel casting with gelatin as a gelling agent. Ceram. Int. 35 (2009) 2481-2491. https://doi.org/10.1016/j.ceramint.2009.02.017

[91] M. Mohammadi, J.-M. Tulliani, P. Palmero, Fabrication of dense and porous hydroxyapatite: effect of dispersion conditions on sinterability and microstructural development. Int. J. Appl. Ceram. Tech. (*submitted*)

[92] H. Shahbazi, H. Shokrollahi, M. Tataei, Gel-casting of transparent magnesium aluminate spinel ceramics fabricated by spark plasma sintering (SPS), Ceram. Int. 44 (2018) 4955–4960. https://doi.org/10.1016/j.ceramint.2017.12.088

[93] A. Szudarska, T. Mizerski, Y. Sakka, T.S. Suzuki, M. Szafran, Fabrication of textured alumina by magnetic alignment via gelcasting based on low-toxic system, J. Eur. Ceram. Soc. 34 (2014) 3841–3848. https://doi.org/10.1016/j.jeurceramsoc.2014.05.017

[94] V. Naglieri, P. Palmero, L. Montanaro, Preparation and characterization of alumina-doped powders for the design of multi-phasic nano-microcomposites. J. Therm. Anal. Calorim., 97 (2009) 231-237. https://doi.org/10.1007/s10973-009-0261-7

[95] P. Palmero, V. Naglieri, L. Spina, M. Lombardi, Microstructural design and elaboration of multiphase ultra-fine ceramics, Ceram. Int. 37 (2011) 139-144. https://doi.org/10.1016/j.ceramint.2010.08.031

[96] P. Palmero, Montanaro L., Reveron H., Chevalier J., Surface coating of oxide powders: A new synthesis method to process biomedical grade nano-composites. Materials 7 (2014) 5012-5037. https://doi.org/10.3390/ma7075012

[97] R.R. Rao, L. Mariappan, H.N. Roopa, Fabrication of micro-featured shapes of alumina ceramics, Proc. Mat. Sci. 5 (2014) 2595-2604. https://doi.org/10.1016/j.mspro.2014.07.520

[98] A.J. Millàn, M.I. Nieto, R. Moreno, Aqueous Gel-Forming of Silicon Nitride Using Carrageenans, J. Am. Ceram. Soc. 84 (2001) 62-64. https://doi.org/10.1111/j.1151-2916.2001.tb00608.x

[99] F.-Z. Zhang, T. Kato, M. Fuji, M. Takahashi, Gelcasting fabrication of porous ceramics using a continuous process, J. Eur. Ceram. Soc. 26 (2006) 667-671. https://doi.org/10.1016/j.jeurceramsoc.2005.07.021

[100] A.J. Millàn, I. Santacruz, A.J. Sánchez-Herencia, M.I. Nieto, R. Moreno, Gel-extrusion: a new continuous forming technique. Advanced Engineering Materials 12 (2002) 913-915. https://doi.org/10.1002/adem.200290002

[101] A. Zocca, P. Lima, J. Günster, LSD-based 3D printing of alumina ceramics. J. ceram. Sci. Tech. 8 (2017) 141-148. https://doi.org/10.4416/JCST2016-00103

[102] A.R. Studart, U.T. Gonzenbach, E. Tervoort, L.J. Gauckler, Processing Routes to Macroporous Ceramics: A Review, J. Am. Ceram. Soc. 89 (2006) 1771–89. https://doi.org/10.1111/j.1551-2916.2006.01044.x

[103] P. Colombo, Conventional and novel processing methods for cellular ceramics, Philos. Trans. Royal Soc. A, 364 (2006) 109–24. https://doi.org/10.1098/rsta.2005.1683

[104] J. Luyten, S. Mullens, J. Cooymans, A.M. De Wilde, I. Thijs, New processing techniques of ceramic foams, Adv. Eng. Mater., 5, 10 (2003) 715-718. https://doi.org/10.1002/adem.200300381

[105] E. Babaie,S. B. Bhaduri, Fabrication Aspects of Porous Biomaterials in Orthopedic Applications: A review, ACS Biomater. Sci. Eng. 4 (2018) 1–39. https://doi.org/10.1021/acsbiomaterials.7b00615

[106] H. Schwartzwalder, A. V Somers, Method of making porous ceramic articles, US Patent 3,090,094A, May 21, 1963

[107] F. F. Lange and K. T. Miller, Open-Cell, Low Density Ceramics Fabricated from Reticulated Polymer Substrates, Adv. Ceram. Mater. 2, 4 (1987) 827–31. https://doi.org/10.1111/j.1551-2916.1987.tb00156.x

[108] J. González Ocampo, D.M. Escobar Sierra, C.P. Ossa Orozco, Porous bodies of hydroxyapatite produced by a combination of the gel-casting and polymer sponge methods, J. Adv. Res. 7 (2016) 297–304. https://dx.doi.org/10.1016/j.jare.2015.06.006

[109] F. Lelièvre, D. Bernache-Assolant, T. Chartier, Influence of powder characteristics on the rheological behaviour of hydroxyapatite slurries, J. Mater. Sci.: Mater. Med. 7 (1996) 489-494. https://doi.org/10.1007/BF00705430

[110] L.M. Rodriguez-Lorenzo, M. Vallet-Regí, J.M.F. Ferreira, Colloidal processing of hydroxyapatite, Biomater. 22 (2001) 1847-1852. https://doi.org/10.1016/S0142-9612(00)00366-5

[111] S. Padilla, J. Román, M. Vallet—Regí, Synthesis of porous hydroxyapatites by combination of gelcasting and foams burnout methods, J. Mater. Sci.: Mater. Med. 13 (2002) 1193-1197. https://doi.org/10.1023/A:1021162626006

[112] J. González Ocampo, M. Escobar Jaramilo, D. Escobar Sierra, C. Ossa Orozco, Suspension Rheology, Porosity and Mechanical Strength of Porous Hydroxyapatite Obtained by gel-casting and Infiltration, J. Mater. Eng. Perf. 25, 2 (2016) 431-442. https://doi.org/10.1007/s11665-015-1855-9

[113] H. Ramay, M. Zhang, Preparation of Porous Hydroxyapatite Scaffolds by Combination of the Gel-Casting and Polymer Sponge Methods, Biomater. 24 (2003) 3293-3302. https://doi.org/10.1016/S0142-9612(03)00171-6

[114] S. Teixeira, M. Rodriguez, P. Pena, H. de Aza, S. De Aza, M. Ferraz, F. Monteiro, Physical Characterization of Hydroxyapatite Porous Scaffolds for Tissue Engineering, Mater. Sci. Eng. C, 29 (2009) 1510-1514. https://doi.org/10.1016/j.msec.2008.09.052

[115] I. Sopyan, J. Kaur, Preparation and Characterization of Porous Hydroxyapatite Through Polymeric Sponge Method, Ceram. Int., 35 (2009) 3161-3168. https://doi.org/10.1016/j.ceramint.2009.05.012

[116] Q. Zhang, W. Han, J. Wang, D. Liu, X. Jin, G. Wang, Thermal behavior and combustion behavior of polymer-based thermal insulation materials for buildings, Jianzhu Cailiao Xuebao/Journal of Building Materials 18 (2015) 1077-1083 https://doi.org/10.3969/j.issn.1007-9629.2015.06.029

[117] http://www.mathesongas.com/pdfs/products/Threshold-Limit-Values-(TLV).pdf

[118] H. Santa Cruz, J. Spino, G. Grathwohl, Nanocrystalline ZrO2 ceramics with idealized macropores, J. Eur. Ceram. Soc. 28 (2008) 1783–1791. https://doi.org/10.1016/j.jeurceramsoc.2007.12.028

[119] M. Lombardi, P. Palmero, K. Haberko, W. Pyda, L. Montanaro, Processing of a natural hydroxyapatite powder: From powder optimization to porous bodies development, J. Eur. Ceram. Soc. 31 (2011) 2513–2518. https://doi.org/10.1016/j.jeurceramsoc.2011.02.017

[120] S. Alonso-Sierra, R. Velázquez-Castillo, B. Millán-Malo, R. Nava, L. Bucioc, A. Manzano-Ramírez, H. Cid-Luna, E.M. Rivera-Muñoz, Interconnected porosity analysis by 3D X-ray microtomography and mechanical behavior of biomimetic organic-inorganic composite materials, Mater. Sci. Eng. C. 80 (2017) 45–53. https://doi.org/10.1016/j.msec.2017.05.106

[121] E. Dümichen, P. Eisentraut, C.G. Bannick, A.K. Barthel, R. Senz, U. Braun, Fast identification of microplastics in complex environmental samples by a thermal degradation method, Chemosphere 174 (2017) 572-584. https://doi.org/10.1016/j.chemosphere.2017.02.010

[122] MSDS of 1,13-Tetradecadiene (CAS n° 21964-49-8)

[123] R.N. Ghosh, I.S. Wichman, C.A. Kramer, R. Loloee, Time-resolved measurements of pyrolysis and combustion products of PMMA, Fire Mater. 37 (2013) 280-296. https://doi.org/10.1002/fam.2129

[124] MSDS of Methanol (CAS n° : 67-56-1)

[125] R. Font, I. Aracil, A. Fullana, J.A. Conesa, Semivolatile and volatile compounds in combustion of polyethylene. Chemosphere 57 (2004) 615-627. https://doi.org/10.1016/j.chemosphere.2004.06.020

[126] K.H. Kim, S.A. Jahan, E. Kabir, R.J. Brown, A review of airborne polycyclic aromatic hydrocarbons (PAHs) and their human health effects. Environ. Int. 60 (2013) 71-80. https://doi.org/10.1016/j.envint.2013.07.019

[127] M.F. Sanches, N. Vitorino, J.C.C. Abrantes, J.R. Frade, J.B. Rodrigues Neto, D.Hotza, Effects of processing parameters on cellular ceramics obtained by paraffin emulsified suspensions, Ceram. Int. 40 (2014) 9045-9053. https://doi.org/10.1016/j.ceramint.2014.01.117

[128] C. Freitas, N. Vitorino, J.C.C. Abrantes, J.R. Frade, Burnout effects on cellular ceramics obtained from gelatine gelcasted emulsified suspensions, J. Eur. Ceram. Soc. 35 (2015) 971-979. https://doi.org/10.1016/j.jeurceramsoc.2014.10.021

[129] F. Wang, J. Yin, D. Yao, Y. Xia, K. Zuo, H. Liang, Y.P. Zeng, Effects of oil on gelcasting of oil-in-water Si3N4 suspensions, J. Alloy. Compd. 699 (2017) 268-273. https:// dx.doi.org/10.1016/j.jallcom.2016.12.377

[130] F.S. Ortega, F.A.O. Valenzuela, C.H. Scuracchio, V.C. Pandolfelli, Alternative gelling agents for the gelcasting of ceramic foams. Journal of the European Ceramic Society 23 (2003) 75–80. https://doi.org/10.1016/S0955-2219(02)00075-4

[131] P. Sepulveda, J.G.P. Binner, Processing of Cellular Ceramics by Foaming and in situ Polymerisation of Organic Monomers, J. Eur. Ceram. Soc. 19 (1999) 2059-2066. https://doi.org/10.1016/S0955-2219(99)00024-2

[132] R. Mouazer, I. Thijs, S. Mullens, J. Luyten, SiC foams produced by gel casting: synthesis and characterization. Adv. Eng. Mater. 6 (2004) 340-343. https://doi.org/10.1002/adem.200400009

[133] M. Takahashi, R. L. Menchavez, M. Fuji, H. Takegami, Opportunities of porous ceramics fabricated by gelcasting in mitigating environmental issues, J. Eur. Ceram. Soc. 29 (2009) 823–828. https://doi:10.1016/j.jeurceramsoc.2008.07.030.

[134] V.C. Colonetti, M.F. Sanches, V.C. de Souza, C.P. Fernandes, D. Hotza, M.G.N. Quadri, Cellular ceramics obtained by a combination of direct foaming of soybean oil emulsified alumina suspensions with gel consolidation using gelatin, Ceram. Int. 44 (2018) 2436-2445. https://doi.org/10.1016/j.ceramint.2017.10.215

[135] X. Deng, J. Wang, J. Liu, H. Zhang, F. Li, H. Duan, L. Lu, Z. Huang, W. Zhao, S. Zhang, Preparation and characterization of porous mullite ceramics via foam-gelcasting, Ceram. Int. 41 (2015) 9009-9017. https://doi.org/10.1016/j.ceramint.2015.03.237

[136] N. P. Stochero, E. Guzi de Moraes, A. P. Novaes de Oliveira, Cellular Ceramics Produced from Ceramic Shell: Processing and Characterization, Mater. Res. 20 (2017) 549-554. https://dx.doi.org/10.1590/1980-5373-MR-2016-1093.

[137] L. Han, X. Deng, F. Li, L. Huang, Y. Pei, L. Dong, S. Li, Q. Jia, H. Zhang, S. Zhang, Preparation of high strength porous mullite ceramics via combined foam gelcasting and

microwave heating, Ceram. Int. 44 (2018) 14728-14733. https://doi.org/10.1016/j.ceramint.2018.05.101

[138] J.M. Tulliani, L. Montanaro, T.J. Bell, M.V. Swain, Semiclosed-Cell Mullite Foams: Preparation and Macro- and Micromechanical Characterization, J. Am. Ceram. Soc. 82,4 (1999) 961-968. https://doi.org/10.1111/j.1151-2916.1999.tb01860.x

[139] F.S. Ortega, P. Sepulveda, V.C. Pandolfelli, Monomer systems for the gelcasting of foams. J. Eur. Ceram. Soc. 22 (2002) 1395-1401. https://doi.org/10.1016/S0955-2219(01)00486-1

[140] J.H. Lee, H.J. Choi, S.Y. Yoon, B.K. Kim, H.C. Park, Processing of porous hydroxyapatite scaffolds containing calcium phosphate glassceramics for bone tissue engineering, J. Ceram. Proc. Res. 14, 4 (2013) 544-548. https://doi.org/10.1007/s12540-014-1007-z

[141] P. Palmero, L. Lombardi, L. Montanaro, J. Tirillò, C. Bartuli, T. Valente, P. Marcassoli, M. Cabrini, Development and mechanical characterization of hydroxyapatite micro/macro-porous scaffolds by an innovative gel-casting process. 11th International Conference and Exhibition of the European Ceramic Society 1 (2009) 448-455.

[142] M.D.M. Innocentini, P. Sepulveda, V.R. Salvini, V.C. Pandolfelli, Permeability and structure of cellular ceramics: a comparison between two preparation techniques, J. Am. Ceram. Soc. 81 (1998) 3349–3352. https://doi.org/10.1111/j.1151-2916.1998.tb02782.x

[143] F.S. Ortega, P. Sepulveda, M.D.M. Innocentini, V.C. Pandolfelli, Surfactants: a necessity for producing porous ceramics, Am. Ceram. Soc. Bull., 80 (2001) 37–42.

[144] P. Sepulveda, W.N. Santos, V.C. Pandolfelli, J.C. Bressiani, R. Taylor, Thermal conductivity of porous alumina produced by different routes, Am. Ceram. Soc. Bull., 78 (1999) 61– 66. https://doi.org/10.1111/j.1551-2916.1954.tb20107.x

[145] C. Petit, J.M. Tulliani, S. Tadier, S. Meille, J. Chevalier, P. Palmero, Novel calcium phosphate/PCL graded samples: design and development in view of biomedical applications. Mater. Sci. Eng. C (*submitted*)]

[146] https://www.sigmaaldrich.com/italy.html

[147] http://www.hispanagar.com

6. Figure captions

Figure 1. Schematic representation of the gelcasting process towards the fabrication of dense ceramics.

Figure 2. Schematic drawing of: **(a)** double helix structure formed on cooling of polysaccharides (reprinted from [55] with the permission of Elsevier under the license n° 4395200573113); **(b)** "egg box model", as described for the pair of guluronate chains in calcium alginate junction zones. Dark circles represent the oxygen atoms involved in the coordination of the Ca ions. Reprinted with permission from [60]. Copyright (2001) American Chemical Society).

Figure 3. Evolution of viscosity with temperature of aqueous solutions of agar at different concentrations. Reprinted from [34] with the permission of John Wiley and Sons under the license n° 4395201366912).

Figure 4. Rheological behavior of aqueous alumina suspensions with different solid loadings **(a)** from 40 to 50 vol% and **(b)** from 51 to 55 vol%. Reprinted from [65] with the permission of Springer Nature under the license n° 4395340039610.

Figure 5. Optimal casting conditions as a function of gelling agent content and solid loading. Reprinted from [70] with the permission of John Wiley and Sons under the license n° 4395210697658).

Figure 6. SEM micrographs of two sintered zirconia samples produced without **a)** and **b)** with PEG addition, used as anti-foaming agent [77].

Figure 7 (a): Mass losses of gelcast alumina disc immersed in water solutions of PEG with different molecular weights. The osmotic pressure was kept the same (4.9MPa) in all desiccants; **(b)**: Images comparing test sample (dia. 60mm – thickness 4 mm) dried in a liquid desiccant followed by air-drying with sample dried out in air at room temperature and humidity. Reprinted from [82] with the permission of Elsevier under the license n° 4395321039509.

Figure 8. Dried alumina green bodies (400 mm X 50 mm X 5 mm) using **(a)** ISOBAM and **(b)** EA gel system. Reprinted from [83] with the permission of Elsevier under the license n° 4395321203773.

Figure 9. Complex shaped green bodies prepared by curdlan gelation. Reprinted from [41] with the permission of Elsevier under the license n° 4395321399544.

Figure 10. SEM micrographs of **(a)** green alumina body (reprinted from (a) [88] with the permission of Springer Nature under the license n° 4395330713833) and **(b)** dense ZrO_2 sample derived [77].

Figure 11. The in-line transmission of polycrystalline YAG (thickness of 2.5 mm) with different ISOBAM contents and related photographs (inset). Reprinted from [22] with the permission of Elsevier under the license n° 4395331055618.

Figure 12. The idea of magnetic field alignment method combined with gelcasting: **(a)** Randomly oriented particles dispersed together with monomers molecules, **(b)** influence of high magnetic field makes the particles oriented, **(c)** polymerization reaction during the exposure to magnetic field, and **(d)** oriented particles locked by the polymer macromolecular network. Reprinted from [93] with the permission of Elsevier under the license n° 4395331282084.

Figure 13. SEM images top and side surfaces of sintered at 1600 °C, polished and thermally etched samples gelcast in magnetic field 12 T by using 0.5 wt.% APS. Top surface is perpendicular to the magnetic field, side surface is parallel. Reprinted from [93] with the permission of Elsevier under the license n° 4395331282084.

Figure 14. Schematic representation of the gelcasting process towards the fabrication of porous ceramics by means of transient porogens.

Figure 15. Schematic model of gas release process in a dense sample with the formation of a network of cracks (upper row) and (with PMMA) in crack-free microporous body (lower row) (small arrows in the figure indicate dominant intermediate position of the gas). Reprinted from Ref. [118] with the permission of Elsevier under the license n° 4397030471711

Figure 16. SEM micrographs of porous HA scaffolds sintered at: (a, b) 1050°C; (c, d): 1150°C, and (e, f): 1250°C. Reprinted from Ref. [140] with the permission of Springer Nature under the license n° 4397050398829

Figure 17. SEM micrographs of a cellular hydroxyapatite sintered ceramic [141]

Figure 18. SEM micrographs of cellular ceramics made from paraffin emulsified suspensions. Reprinted from Ref. [127] with the permission of Elsevier under the license n° 4397080806107

Figure 19. SEM micrographs of foamed samples at different magnifications: HA_{dry}- (A) having 77% porosity and HA_{wet}- (B), with 73% porosity.

7. Table captions

Table 1. Common gelcasting constituents and related health and safety information (according to European regulation n° 1272/2008)

Table 2. Examples of dense ceramics produced by gelcasting process, by using eco-friendly and toxic-free gelling agents

Table 3. Advantages and challenges of the different fabrication techniques. Adapted from Ref. [102]

Table 4. Porosity, pore size and mechanical strength of porous samples produced by different methods

8. Tables

Table 1

Product name	CAS-No.	Classification according to Regulation (EC) N° 1272/2008	LD50		LC50 (mg/m^3)	Ref.
			Oral (mg/kg)	Dermal (mg/kg)		
- Monomer, cross-linker						
Acrylamide (AM)	79-06-1	Carcinogenicity (Category 1B), H350 Germ cell mutagenicity (Category 1B), H340 Reproductive toxicity (Category 2), H361f Acute toxicity, Oral (Category 3), H301 Specific target organ toxicity - repeated exposure (Category 1), H372 Acute toxicity, Inhalation (Category 4), H332 Acute toxicity, Dermal (Category 4), H312 Eye irritation (Category 2), H319 Skin irritation (Category 2), H315 Skin sensitisation (Category 1), H317	177	1500	1141	[1,66,79,80]
Methacrylamide (MAM)	79-39-0	Acute toxicity, Oral (Category 4), H302 Skin irritation (Category 2), H315 Eye irritation (Category 2), H319 Specific target organ toxicity - single exposure (Category 3), Respiratory system, H335	1815	> 5000	-	[76]
Poly(isobutylene-alt-maleic anhydride) (ISOBAM)	26426-80-2	Not a hazardous substance	No data available			[21,43,51,64]
N,N′-Methylenebis(acrylamide) (MBAM)	110-26-9	Acute toxicity, Oral (Category 4), H302	390	No data available		[1,47,66,76,79, 80]
N,N,N',N'-Tetramethyl ethylenediamine (TEMED)	110-18-9	Flammable liquids (Category 2), H225 Acute toxicity, Oral (Category 4), H302 Acute toxicity, Inhalation (Category 4), H332 Skin corrosion (Category 1B), H314	268	5390	6264	[1,47,66,79,80]
Poly(ethyleneimine) (PEI)	9002-98-6	Acute toxicity, Oral (Category 4), H302 Chronic aquatic toxicity (Category 2), H411	No data available			[51]
2-Hydroxyethyl methacrylate (HEMA)	868-77-9	Skin irritation (Category 2), H315 Eye irritation (Category 2), H319 Skin sensitisation (Category 1), H317	5564	-	> 5000	[47]
Ammonium persulfate (APS)	7727-54-0	Oxidizing solids (Category 3), H272 Acute toxicity, Oral (Category 4), H302 Skin irritation (Category 2), H315 Eye irritation (Category 2), H319 Respiratory sensitisation (Category 1), H334 Skin sensitisation (Category 1), H317 Specific target organ toxicity - single exposure (Category 3), Respiratory system, H335	689	> 2000	-	[1,47,66,79, 80]
- Gelling agent						
Gelatine/Collagen	9000-70-8	Not a hazardous substance	No data available			[35,73,74,78, 88, 117]
Agarose	9012-36-6	Not a hazardous substance	No data available			[38,70]
Agar	9002-18-0	Not a hazardous substance	11000	No data available		[69,72]
Locust bean gum	9000-40-2	Not a hazardous substance	13000	No data available		[72]
Curdlan	54724-00-4	Not a hazardous substance	No data available			[41]
Magnesium citrate	144-23-0	Skin irritation (Category 2) Eye irritation (Category 2) Specific target organ toxicity - single exposure (Category 3)	No data available			[71]
- Additives						
DARVAN® 7-N	7732-18-5 (water) 54193-36-1 (sodium polymethacrylate)	Not a hazardous substance	> 20000	> 5000	-	[78]
Ammonium polyacrylate (solution in water) (PAA-NH_4)	7732-18-5 (water) 9003-03-6 (ammonium polyacrylate)	Not a hazardous substance	No data available			[64,71]
Sodium dodecyl sulfate/Sodium Lauryl Sulfate	151-21-3	Flammable solids (Category 2), H228 Acute toxicity, Oral (Category 4), H302 Acute toxicity, Inhalation (Category 4), H332 Skin irritation (Category 2), H315 Serious eye damage (Category 1), H318 Specific target organ toxicity - single exposure (Category 3), Respiratory system, H335 Chronic aquatic toxicity (Category 3), H412	977	> 2000	3900	[73,117]
Glycerol diacetate	25395-31-7	Not a hazardous substance	8500	No data available		[71]
Triammonium citrate (TAC)	3458-72-8	Skin irritation (Category 2), H315 Eye irritation (Category 2), H319 Specific target organ toxicity - single exposure (Category 3), H335	No data available			[41,64,69]
Surfynol CT-136	111-76-2 (2-Butoxyethanol) 126-86-3 (2,4,7,9-Tetramethyldec-5-yne-4,7-diol) 107-21-1 (Ethane-1,2-diol) Ester/Styrene Maleic Anhydride Copolymer Alkylarylalkoxylate	Acute toxicity (Inhalation) Category 4 H332 Serious eye damage Category 1 H318 Reproductive toxicity Category 2 H361 Specific target organ toxicity - repeated exposure (Oral, Kidney) Category 2 H373	> 2000	-	> 20000	[51]
Soybean oil	8001-22-7	Not a hazardous substance	16500 (Intravenous)		-	[73]

Table 2

Powder (solid loading, vol%)	Gelling agent (wt%)*	Green density (%)	Green strength (MPa)°	Fired density (%)	Flexural strength (MPa)	Ref.
Al_2O_3 (50.4)	Agarose (1.01)	63	nr	> 99	nr	[38]
Al_2O_3 (50.55)	Gellan gum (0.5-1.0)	55.1 - 59.6	~ 4-5 MPa°°	97.1 - 98.5	274 - 327	[40]
Al_2O_3 (50)	Curdlan (2.5)	56.5	3.7 ± 1.2°°	98.3	347 ± 14	[41]
Al_2O_3 (55)	Egg white (6)	> 60	7.3	~ 98	314	[39]
Al_2O_3 (53)	Gelatin (4.5)	nr	> 8°°°	96.5	~305	[35]
Hydroxyapatite (41.4)	Agar (1.5)	52.7	nr	99.9	~300'	[91]
ZrO_2 (20-39)	Agarose (0.25-1.0)	46-52	nr	> 99	300-800	[70]
$Yb_3Al_5O_{12}$ (50)	Isobam (0.4-0.8)**	52-63	14.2-18.7	94	159	[43]
$MgAl_2O_4$ (50)	ISOBAM (0.1 - 0.7)	60.5	2.62°°°°	99.5	nr	[21]
$MgAl_2O_4$ (61)	ISOBAM (0.8)^	65	14.5	99.97	nr	[92]

*Referred to water; **Referred to powder

°By flexural tests; °°By compressive test; °°°Determined by using a specific device for green body strength determination described in [35]; °°°°mechanical test not specified;

^0.7 wt% Ib600 + 0.1 wt% Ib104

'By compressive test

Table 3

Fabrication route	Advantage	Challenge
Replication technique	Can lead to open and interconnected cells, can create anisotropic pore structure with elongated pores	Slurry rheology and homogeneity
Porosity created by transient porogens	Controlled porosity, graded porosity, can create complex shapes	Low interconnectivity, isotropic structures
Direct foaming	High porosity when combined with salt leaching improves interconnectivity	Low mechanical strength, normally leads to small pore size
Gelcasting	Near net shape, high homogeneity, good interconnectivity when combined with foaming	Slurry rheology and homogeneity

Table 4

Fabrication route and material	Porosity (%)	Pore size (μm)	Interconnectivity (%)	Green strength (MPa)	Compressive strength after firing (MPa)	Ref.
Gelcasting + replication method (HA)	84.9-89.2	50-600	55.8-79.2	n.d.	n.d.	[108]
Gelcasting + replication method (HA)	n.d.	30.8-58.6	n.d.	n.d.	n.d.	[111]
Gelcasting + replication method (HA)	84.9-89.2	100-600	n.d.	n.d.	0.07-0.12	[112]
Gelcasting + replication method (HA)	70.0-76.9	200-400	n.d.	n.d.	0.55-5.00	[113]
Gelcasting + sacrificial template (4 mol%Y-ZrO_2)	> 20%	100-200 nm and 2 μm	none	n.d.	n.d.	[118]
Gelcasting + sacrificial template (HA)	52%	100-350	n.d.	n.d.	n.d.	[119]
Gelcasting + sacrificial template (HA)	16.72	20-40	15.33	n.d.	13.2-18.0	[120]
Gelcasting + sacrificial template (Al_2O_3)	55-75	8.9-25.6	n.d.	n.d.	24-46	[127]
Gelcasting + sacrificial template (Al_2O_3)	65-67	14-24	n.d.	n.d.	35-65	[128]
Direct foaming w agar (SiC)	78-88	100-1,300	n.d.	n.d.	2.5-10.8*	[132]
Direct foaming w gelatin (Al_2O_3)	63.6-66.0	5.3-38.7	n.d.	n.d.	15.2-62.2	[134]
Direct foaming w agar (HA)	73-77	50-350	n.d.	n.d.	n.d.	[91]
Direct foaming w IB (mullite)	17-76	57-313	n.d.	n.d.	3.7-15.3	[135]

n.d.: not determined

*: Flexural strength (MPa)