2. An overview of gelcasting

The gelcasting method was first developed to produce dense ceramics, according to the increasing demand of new forming methods for advanced materials with complex shapes [1]. In fact, this technique allowed to overcome some drawbacks of other methods commonly employed for producing complex – shaped, dense ceramic components, such as injection molding and slip casting [2–4]. More precisely, the injection molding technology usually implies:

- defects due to the competition between heating necessary to completely fill the mould and following cooling to harden the green component; in fact a fast temperature decrease implies knit lines, short shots and voids within the final material, while with a slow cooling flashing, jetting and sink marks are present in sintered bodies [2–5];
- long vehicle – removal times due to the high polymer content [2, 3, 5–7];
- low green strength after binder removal [2, 3];
- warpage during binder removal due to the melting of the vehicle at high temperatures with consequent loss of its stiffness; the green component undergoes a strength decrease and residual gas causes defects formation [1, 2, 3];
- differential binder removal [2, 3];
- thick – section limitations [2–4].

On the other hand, dense materials obtained by slip casting can present:

- inhomogeneous distribution of soluble species present in suspension [4, 7];
- density gradient development in green body [2, 4, 7];
- low green strength [2, 5];
- long forming time [1, 2, 4, 5].

2.1. Gelcasting of dense and porous ceramics

The gelcasting was developed in the Oak Ridge National Laboratory (ORNL) by Janney and Omatete [1, 2, 4]. This process is based on the combination of wet ceramic processes and polymer chemistry. It provides the polymerization reaction of a monomer solution containing a ceramic powder to form green ceramic bodies in which the organic network holds the ceramic particles together [1].

In particular, the basic idea of the gelcasting technology is to exploit the monomer solution as a low-viscosity vehicle for casting the ceramic suspension and the cross-linked polymer gel for immobilizing the ceramic slurry in the mould. For this reason, gelcasting can be exploited also to produce components having complex shapes: in fact, thanks to its low viscosity, the ceramic suspension is able to fully fill moulds even showing a very complicated geometry [1–4, 6].
The gelcasting allows to preserve the high degree of homogeneity of the ceramic suspension [7] and of the organic binders [8]. Moreover, the presence of the polymeric gel in green components gives them a high strength so that easy handling and machining are allowed [1 – 4, 9]. This implies also a beneficial consequence on the economic point of view: in fact, the machining of ceramics is a very expensive process that represents about 50 – 80 % of the production costs [10].

A typical flow-chart of the gelcasting procedure exploited to produce dense materials is reported in Figure 2.1 [4].

![Figure 2.1 - A typical flow-chart of gelcasting process](image)

Generally, the ceramic powder is added in the monomers solution containing a dispersant [1 – 3, 9]. The obtained suspension is then dispersed by magnetic stirring [1, 3] or by ball-milling [11], in order to break powder agglomerates [2]. The mixing step involves the formation of air bubbles in the suspension. Their elimination is carried out through vacuum deairing in rotary evaporator at a controlled temperature [1 – 3], or under vacuum at a reduced pressure lower than the vapour pressure of the solvent via vacuum pumping [8, 9], or by mechanical vibration [11]. The beneficial effect of the deairing step on the gelcast products is shown in Figure 2.2 [12]. The deairing conditions depend on several factors, such as for instance solid content and viscosity of the suspension [13]. It is important to underline that a high deairing time implies evaporation of the solvent and a consequent development of cracks in green bodies [13].
After that, initiator and catalyst are added and the suspension is further degassed and cast into a mould at R.T. Moulds employed in the gelcasting can be made of metals, glass, plastic or wax [1 – 4, 12] and, unlike the slip casting, they are non porous [12].

During the casting operation, when the suspension fills the mould, the air entrapment can take place. As in the case of the voids due to the air bubbles formed during the mixing step, these phenomena can be avoided through the casting under vacuum. Otherwise, in order to outgas the cast suspension, the mould can be also submitted to mechanical vibration [2]. Moreover, to improve the bubbles removal, a defoamer can be added to the suspension [9]. In the case of a thermally-driven polymerization or to accelerate the gel formation, after casting the mould is heated at the temperature of gelification [1, 3, 6, 9, 11]. After polymerization, ceramic green components are demoulded and dried at R.T. with controlled relative humidity [1, 11, 12]. The drying step is a tricky unit operation in gelcasting procedure: it is important to avoid warpage and cracking in green materials [1, 2]. At R.T. humidity is the dominant variable and it is gradually lowered by using a series of controlled-humidity drying chambers starting from 95% relative humidity (R.H.) [1, 3, 4, 14]. The R.H. is lowered when shrinkage and weight change of samples are almost completed [1]. The drying step can be also affected and controlled by temperature [3, 4, 9, 14].

The drying conditions depend on the nature of both inorganic powder and monomers. Generally this step can be divided in three stages [9, 14 – 17]:

- constant rate period (CRP), in which the solvent is transported to the surface by capillary forces and it evaporates at a constant rate;
- first falling rate period (FRP1), in which the drying rate is no more constant and evaporation occurs from the fluid menisci;
- second falling rate period (FRP2), in which the remaining solvent is removed by vapor-phase diffusion at a low drying rate.

In the first stage, the elimination of the liquid water implies a collapse of the polymer network: the water is transported through the gel to the component surface and the rearrangement of ceramic particles goes on until they touch each other. At this point, as shown in Figure 2.3 [15], the gel coats the ceramic particles and begins to shrink around them implying the formation of voids [15].
Then, water is transported by capillary forces to the particle surface, but it still remains in the formed voids: now, the second stage begins. When the partial pressure of water vapor in the voids reaches the saturation value, evaporation takes place through the voids present in the gelcast component. In the third stage, when the remaining water amount in the gel is lower than 20% of the total starting value, its movement to the particle surface is due to diffusion processes [15].

An alternative drying procedure provides the exploitation of a desiccant liquid such as a solution of poly(ethylene glycol) [18 – 20]. This method allows to avoid the formation of cracks and residual stresses within green components; moreover, it increases the drying rate. In fact, this alternative drying procedure requires a very short time, of few hours. The green components are immersed in the desiccant liquid creating an osmotic difference between the gelled polymer network and the liquid desiccant [19]. Finally, it is important to underline that the green parts shrink uniformly without warpage, tanks to the osmosis driving force: in Figure 2.4 it is possible to note the consequences of a different drying procedure [18].

During drying, gelcast components undergo a shrinkage depending on the solid loading of the starting suspension and on the critical packing fraction of the ceramic powder [11]. The dried green components can be then machined and thermally treated. The low amount of the organic compounds (generally about 4 wt% [11]) allows an easy burning out during sintering whose thermal cycle is set up on the basis of the thermal decomposition of the polymeric network [1]. To avoid cracks and defects in the final materials, sintering must be carried out at a low heating rate [1, 9], for an effective control and to maintain constant the internal pressure [1].

In 1990, gelcasting was first developed by using a nonaqueous solvent [2, 21]; one year later, this process was improved by the set up of an aqueous version [2, 22]. In the former case, a low vapour pressure at the polymerization temperature and a relatively low viscosity of the organic solvent are important requirements. Several classes of solvent can be employed, such as phthalate esters, dibasic esters, high-boiling point petroleum solvents, long-chain alcohols, pyrrolidones and blends of them [2, 9]. In this case, the drying step must be carried out in oven, in order to promote the solvent evaporation [2].
On the other hand, the use of water as a solvent allows an easier drying step, implies a low viscosity of the suspension and avoids environmental problems related to organic solvents [2, 3]. Moreover, in ceramic wet processes the use of water is very diffuse and preferred [2 – 4]; in fact, even if the choice of the solvent is based on its interaction with ceramic powder and influences the used monomer system [9], nevertheless, most literature describe aqueous gelcasting.

As stated above, the gelcasting method was developed to produce dense materials; however, this method was quickly extended to the case of porous ceramics for the possibility of exploiting the high strength of the green gelcast materials. Thanks to its versatility, it was possible to combine gelcasting with the main techniques already exploited to produce porous materials, such as replica, sacrificial template and direct foaming methods. These techniques have been previously described (ref. Chapt. 1, Par. 1: § Forming techniques for porous bodies); therefore, only the modifications of the above techniques and the advantages of their combination with gelcasting will be described in this Chapter.

In the case of the combination involving gelcasting and replica methods, the polymeric skeleton is embedded with a ceramic suspension containing the gelling system, as shown in the flow-chart reported in Figure 2.5 [23, 24].

![Flow-chart](image)

**Figure 2.5 – The flow-chart of a combined gelcasting – replica method [24]**

Polymerization is exploited to improve the strength of the green bodies; however, the combination of gelcasting and replica methods requires a strict control of the polymerization, which must take place only after the completion of the foam impregnation procedure [24]. Moreover, particle aggregation in the slurry deposited on the polymer foam walls is limited, yielding a green component characterized by a homogeneous, thick-walled microstructure [23, 24].

The combination involving gelcasting and sacrificial template methods provides the addition of pore formers in the ceramic suspension containing the gelling system, as presented in the flow-chart of Figure 2.6 [25].
Sacrificial templates are polymeric or natural components such as poly(vinyl butyrate) [25], carbon [26, 27], natural fibers [28] and starch [29, 30]. The gelcasting suspension can be also used to coat the sacrificial template: Thijs et al. [31] used several pore formers (seeds, nuts, peas, styrene granules) having different diameters to produce a porosity gradient material, shown in Figure 2.7 [31]. Particularly, the pore formers are firstly coated by using a spray-drying apparatus or turning them around in a vessel containing the gelcasting suspension. Then, the coated templates are packed and impregnated with the gelcasting suspension in order to neck them together [31].

Also in this case, gelcasting is exploited to increase the strength of the green components; moreover, it allows to control the pore distribution [27].

The combination involving gelcasting and foaming methods was developed by Sepulveda [32]. To exploit the easiness and the inexpensiveness of the direct foaming, the gelcasting procedure was modified with the addition of a surfactant in the gelcasting suspension. The suspension was foamed through the mechanical frothing and the polymerization stabilized the
porous structure. Presently, this modified gelcasting method is the more largely used to produce porous ceramics [33, 34]. A typical flow – chart is reported in Figure 2.8 [34].

![Flow chart of a combined gelcasting – foaming method](image)

**Figure 2.8 – A typical flow-chart of a combined gelcasting – foaming method [34]**

This method allows to obtain materials having porosities ranging between 40% and 90% with spherical pores having diameters comprised between 30 μm and 2 mm [33]. The pore size depends on polymerization time, according to the growth and coalescence phenomena already described in Chapter 1. The porosity percentage depends on the surfactant amount [35]; moreover, it can be controlled by the means of the volume of the generated wet foam [33]. This parameter can be modified during a further step: after foaming, the final volume of the suspension can be increased by lowering the pressure, by a connection to a vacuum system [34].

As in the other combined methods, the presence of the polymeric network leads to an increase of the green component strength, which is particularly beneficial for highly – porous materials [32, 36]. The main drawback of this technique is a difficult control of the porosity features, precisely in terms of interconnections and pore size distribution [37].

### 2.2. Rheological behaviour of ceramic suspensions for gelcasting application

In gelcasting, as in all processes involving ceramic slurries, stable suspensions are needed and aggregation phenomena implying inhomogeneities in green components must be avoided [38]. The formation of the polymeric network is able to limit this problem, but suspension stability must be in any case achieved since gelification does not take place immediately.

Typically, in a polar medium, especially in water, ceramic powders, mostly oxides, tend to agglomerate due to the attractive Van der Waals forces [21, 39]. Moreover, in concentrated slurries, when ceramic particles are each-other closer, agglomeration becomes more probable [22]. When the distance among particles decreases, the suspension viscosity increases [40]. Therefore, considering that deairing and casting steps of these processes require a low suspension viscosity, a low solid content must be used. On the other hand, a higher amount of ceramic powder in the starting suspension implies a faster drying [4, 13, 21]. Moreover, the solid loading strongly influences the green density of the gelcast components [4, 7, 17], even if its effect is negligible at high powder amounts, which allow to reach highly packed green microstructures. On the basis of the above statements, it is clear that the suspension viscosity is a key feature in the gelcasting method. On the ground of the recent literature, a successful
gelcasting process can be carried out exploiting suspensions having a low viscosity (below 1 Pa·s at 20 s$^{-1}$) [41].

Flowable ceramic suspensions presenting as high as 50 vol% solid loading have been employed; [42] their rheology is characterized by a viscosity decrease with increasing shear rate, that is the so-called thixotropic or shear-thinning behaviour [43, 44]. At low shear rates, thermal motion prevails over the viscous forces; at high shear rates, viscous forces are predominant and the measured viscosity values correspond to the flow resistance of the suspension [39, 45].

The viscosity of the suspension can be decreased by modifying the pH or adding a dispersant [2, 14, 40, 46, 47]. Both methods involve the development of repulsive forces opposite to the Van der Waals ones.

In a polar medium, ceramic oxide particles present a surface charge: hydroxyl reactions lead to formation of negative or positive sites [48, 49], as shown in the case of alumina surfaces:

$$\equiv\text{AlOH}^0 + H^+ \leftrightarrow \equiv\text{AlOH}_2^+ \quad \text{or} \quad \equiv\text{AlOH}^0 \leftrightarrow \equiv\text{AlO}^- + H^+$$

(2.1)

where $\equiv\text{AlOH}^0$ represents a hydroxyl group linked to the alumina surface.

Adjusting the pH suspension, the surface charge changes according to the reaction 2.1. An electrical double layer is therefore developed on the particle surface generating repulsive forces among particles according to the electrostatic mechanism [17, 49, 50], schematically represented in Figure 2.9a [17].

![Figure 2.9](image)

Figure 2.9 – Schematic representation of electrostatic (a) and steric (b) repulsive forces [17]

In aqueous and nonaqueous media, large organic molecules can be exploited as dispersants: they adsorb on particle surface and the resulting polymer layer involves repulsion among particles due to the steric hindrance [17, 22, 49], as shown in Figure 2.9b, or to an electrosteric mechanism. In this latter case, polyelectrolytes are used. They are made of a hydrocarbon chain containing polar, ionic groups [22] so that they can contrast the Van der Waals forces according to both electrostatic and steric mechanisms [17, 38, 48, 50].

The addition of a dispersant involves a lower suspension viscosity and consequently the possibility to reach higher solid contents. The choice of the dispersant must take into account both the dispersion medium and the gelling system; since it must not react with the monomers or the initiator, inhibiting the polymerization [1, 51]. Moreover, it is important to remind that the suspension solid loading is also influenced by the particle size, shape and surface characteristics. These features cannot be neglected during the optimization of the rheological behaviour of the suitable ceramic slurry [9].

### 2.3. Gelling agents and their polymerization

Monomers are a crucial component in a gelcasting system: generally monofunctional and difunctional organic monomers are used. The former are characterized by in presence of only one double bond leading to a gel network made of only linear chains. The latter are needed for crosslinking and therefore they must contain at least two double bonds [7, 9, 52].

The polymerization can require the addition of an initiator and a catalyst. These two compounds must be chosen according to the gelling system. They must be added in the gelcasting suspension before casting and the polymerization takes place in the mould [1].
Generally, any organic compound soluble in the selected medium and able to undergo a liquid-to-solid transition, yielding a polymer, can be used as monomer [7]. As a consequence, the principal classification of the gelling agent systems is based on the nature of the solvent. In the case of nonaqueous gelcasting, a free-radical mechanism is usually exploited. In the system developed by Omatete and Janney, the acrylate monomers contained vinyl groups able to polymerize [2, 4]. It is clear that the choice of the initiator and of the catalyst depends on the nature of the monomers and on the polymerization mechanism, but also the dispersant must be selected previously considering its possible interaction with the gelling systems. As a consequence, Omatete and Janney suggested a list of dispersants and initiators for nonaqueous gelcasting based on the polymerization of trimethylolpropane triacrylate and 1,6-hexanediol diacrylate [2].

In the case of aqueous gelcasting, two major monomer systems are exploited in literature: the acrylates and the acrylamides [2, 6, 9]. Nevertheless, in the case of acrylate monomers a complete solubility of the gelling agents in water cannot be reached. For this reason, the system mainly described and used in the recent literature is based on acrylamide and, among the many monomers exploitable, the most frequently used are methacrylamide (MAM) or acrylamide (AM) with methylenebisacrylamide (MBAM). These monomers polymerize according to a free-radical mechanism [2, 17], thanks to the addition of ammonium persulfate (APS) and N, N, N', N'-tetramethylethylene diamine (TEMED) as initiator and catalyst, respectively [2, 53 – 56]. When a catalyst is not employed [2], the reaction is often accelerated by a temperature increase, which implies the formation of initiator radicals [1, 51, 54, 55], as follows:

\[(NH_4)_2S_2O_8 \rightarrow 2NH_4^+ + 2SO_4^-\]  \hspace{1cm} (2.2)

During the first stage of the polymerization reaction, these free radicals react with the monomer molecules, yielding monomer free radicals. In this stage, named initiation, the viscosity remains constant [53]. After that, a propagating radical is formed [51, 54, 55, 56], yielding polymer chains. They can then react with the crosslinking monomers, which induce bridging effects. At the same time, the polymerization can end due to the crosslinking of two PAM chains [55, 56]. In the second stage, when the gel is formed, many factors can affect the polymerization and its rate. First of all, polymerization rate depends on the concentration of monomers, initiator and catalyst [1, 52, 55, 57] according to the equation:

\[R_p = K [I]^n [M]^m\]  \hspace{1cm} (2.3)

where \(R_p\) is the polymerization rate, \(K\) is a temperature dependent constant, \([I]\) is the initiator concentration, \([M]\) is monomer concentration [57]. As a consequence, a high concentration of \(I\) and \(M\) implies an increase in reaction rate [55]. However, high polymerization rates can promote the formation of voids or defects in gelcast green bodies. In fact, the growth of the polymer chains induced an increase of the slurry viscosity, thus contrasting an easy casting.

Moreover, also the monomer concentration affects the properties of green components. In fact, the amount of both monomers and crosslinking can influence some gel features, particularly its strength [1, 8, 58], stiffness, toughness and consequently the machinability of the green bodies [17, 51]. The monomer amount also influences the density of the fired gelcast materials [8, 57]. In fact, in green components, the ceramic particles are surrounded by the polymeric network, as schematically shown in Figure 2.10 [59].
After the burn-out of the polymer, the ceramic microstructure is characterized by residual porosity whose percentage increases with increasing polymer content. If the monomer concentration is high, the porosity inhibits the effective densification of the ceramic structure [8, 57]. Finally the content of the gelling agents depends on the particle size of the ceramic powder; it was demonstrated that fine powders require a higher polymer concentration [57]. The polymerization of AM and MAM monomers is inhibited in the presence of oxygen, that easily reacts with the radicals [39]; for this reason, gelcasting must be carried out in an inert atmosphere, for instance under nitrogen [1, 3, 12, 46, 47, 55, 60] or argon [47, 55], or under higher-vacuum conditions [60]. As presented in Figure 2.11 [60], the presence of oxygen during casting in air or under low vacuum conditions implies exfoliation of the surfaces. An unaffected surface is presented by the sample prepared under nitrogen.

To work in an inert atmosphere is a strong limitation for gelcasting method, especially for the relevant increase of the associated costs [40, 44, 61]. To avoid this drawback, some water-soluble polymers such as poly(ethylene glycol) PEG [40, 46, 51, 54, 61] poly(vinylpyrrolidone) PVP [44, 46], polyacrylamide PAM [46, 62], poly(ethylene oxide) PEO [46] can be used, since they are able to prevent the reaction between oxygen and monomer free radicals, as shown in the Figure 2.12 [61].

Then, at the beginning, gelcasting was not industrially exploited because polymerization is inhibited by oxygen and the inert atmosphere working conditions were not economically acceptable. In addition, gelcasting was also rejected due to the toxicity of the acrylamide monomers [2, 6, 62]. Many studies were therefore devoted to the development of gelcasting procedures to be performed by using less or no toxic monomers. As concerns low toxicity, research was
focused on monomers containing one of the following four functional groups: acrylamide, acrylate, vinyl and allyl [63]. Some of these monomers are listed in Table 2.1 [63].

On the grounds of the rheological behaviour of the suspension and the strength of the polymerized gel, as well as the toxicity aspects, the acrylic acid-based systems were selected as the best performing gelling agent [64 – 66]. In comparison to the acrylamide monomers, the acrylic acid systems are less toxic; moreover they are highly water soluble and they form very strong gel thanks to the interactions of the acrylic acid groups with ceramic particles and among polymer chains [41].

Table 2.1 – Low-toxicity monomers [63]

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Abbreviation</th>
<th>Functionality</th>
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<tbody>
<tr>
<td>Acrylic acid</td>
<td>AA</td>
<td>Acrylate</td>
</tr>
<tr>
<td>Dimethyl aminoethyl methacrylate</td>
<td>DMAEMA</td>
<td>Acrylate</td>
</tr>
<tr>
<td>Dimethyl aminoethyl methacrylamide</td>
<td>DMAPMAM</td>
<td>Acrylamide</td>
</tr>
<tr>
<td>Hydroxyethyl acrylate</td>
<td>HEA</td>
<td>Acrylate</td>
</tr>
<tr>
<td>Hydroxyethyl methacrylate</td>
<td>HEMA</td>
<td>Acrylate</td>
</tr>
<tr>
<td>Hydroxypropyl acrylate</td>
<td>HPA</td>
<td>Acrylate</td>
</tr>
<tr>
<td>Hydroxypropyl methacrylate</td>
<td>HPMA</td>
<td>Acrylate</td>
</tr>
<tr>
<td>Methoxy poly(ethylene glycol) monomethacrylate</td>
<td>MPEGMA</td>
<td>Acrylate</td>
</tr>
<tr>
<td>Methacrylic acid</td>
<td>MAAM</td>
<td>Acrylamide</td>
</tr>
<tr>
<td>Methacryloxyethyl trimethyl ammonium chloride</td>
<td>MAETAC</td>
<td>Acrylate</td>
</tr>
<tr>
<td>Methacrylamidopropyl trimethyl amonium chloride</td>
<td>MAPTAC</td>
<td>Acrylate</td>
</tr>
<tr>
<td>Methacrylic acid</td>
<td>MAA</td>
<td>Acrylate</td>
</tr>
<tr>
<td>p-Sterile sulfonic acid (sodium salt)</td>
<td>SSA</td>
<td>Sulfonic</td>
</tr>
<tr>
<td>n-vinyl pyrrolidone</td>
<td>NVP</td>
<td>Vinyl</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Abbreviation</th>
<th>Functionality</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diallyl tartardiamide</td>
<td>DATDA</td>
<td>Allyl</td>
</tr>
<tr>
<td>N,N’-methylene bisacrylamide</td>
<td>MBAM</td>
<td>Acrylamide</td>
</tr>
<tr>
<td>Poly(ethylene glycol XXX) diacrylate</td>
<td>PEGXXxD</td>
<td>Acrylate</td>
</tr>
<tr>
<td>Poly(ethylene glycol XXX) dimethacrylate</td>
<td>PEGXXxDMA</td>
<td>Acrylate</td>
</tr>
<tr>
<td>Triallyl amine</td>
<td>TAA</td>
<td>Allyl</td>
</tr>
</tbody>
</table>

To meet the industrial demand of no toxic gelcasting, natural polymers such as polysaccharides and proteins were also studied [2, 7, 65]. Generally, these alternative gelling systems form rigid gels through mechanisms driven by temperature; unlike the organic monomers, the polymerization occurs during cooling [43, 59, 67].

Most gelling agents used in gelcasting are water-soluble polysaccharides. These molecules are constituted by chains of glycosyl units formed from hexoses and pentoses. Their water solubility is due to the presence of oxygen atoms and hydroxyl groups in the chains, which are able to form hydrogen bonding with water molecules. Generally, when the polysaccharides molecules bond together the access of the water is blocked forming a three-dimensional network [68, 69]. Gelation process takes place at temperature below the glass-transition temperature with the development of double helix structures, as shown in Figure 2.13 [68].

Figure 2.13 – Gelification of polysaccharides [68]

If the gel is reheated, it melts: the polymer network breaks down and the polysaccharides chains become isolated; the gelation is therefore thermo-reversible [68]. It is important to
underline that the dissolution and gelation temperatures strongly differ. This temperature hysteresis is broader for the agaroids [68].

An advantage of the water-soluble polysaccharides is their ability to yield a gel even at a very low concentration (about 0.5 wt% on a dry solid basis) [70].

Among the polysaccharides, the most investigated for gelcasting applications are agar [68, 71], agarose [68, 69, 72] and carrageenan [68, 73].

Agar is derived from the red algae class of seaweed; it is employed in food industry as a thickener and gelling agent [74]. It is a polygalactoside made of agarose and agaropectine; its structure is reported in Figure 2.14 [68].

![Figure 2.14 – The structure of the agar](image)

**Agarose** is the gelling fraction of agar; its repeating units (agarobiose) are β-D-galactopyranosyl and 3,6-anydro-α-L-galactopyranosil groups. Its structure is presented in Figure 2.15 [68].

![Figure 2.15 – The structure of the agarose](image)

Negative effects of agaroids in gelcasting applications are the increase of the suspension viscosity when the gelling agent is added and the low strength of the gels [69, 71, 72]. This latter problem can be solved by using a higher agaroid content or by combining them with other polysaccharides [69], such as the locust bean gum [71]. This compound is made of galactomannan, a polysaccharide able to improve the gel strength in the presence of other polysaccharides [71].

**Carrageenan** is a hydrocolloid obtained from red seaweed of the Euclima order and it is used in food industry as stabilizing system [75]. Carrageenan is a linear sulphonated polysaccharide constituted by β-D-galactopyranosyl and 1,4-linked α-L-galactopyranosyl groups. There are several fractions of carrageenans that can link different cations on the basis of their semi-ester sulphate groups. Among these, the less viscous solution and the strongest gel were obtained by κ-carrageenan in presence of K⁺ cations, whose structure is shown in Figure 2.16 [68, 75].

![Figure 2.16 – The structure of the κ-carrageenan](image)

The cations linked to the sulphate group of carrageenans influenced their gelation mechanism, controlling the angle between monomers and consequently the structure of the double helices
The strength of the gel obtained from carrageenans can be increased by adding gums such as locust bean gum [70, 76].

The polysaccharides used in gelcasting do not influence the strength of the green components [77]. Moreover, as far as the gelation temperature is concerned, there is not a relevant difference between carrageenan and agaroids, since gelation occurs in the range 30°C – 40°C. On the other hand, the carrageenan presents a lower dissolution temperature than agar and agarose (70°C and 90°C, respectively). This feature represents an advantage in gelcasting application because, increasing the working temperature, the risk of an uncontrolled solvent evaporation increases [68, 75]. In addition, agarose is more expansive [75].

Other polysaccharides showing different gelation mechanism, such as alginate [78 – 80] and starch [29] have been also tested. Alginate is an unbranched binary copolymer of 1,4-β-D-marrunoric acid (β-D-M unit) and α-L-guluronic acid (α-L-G unit), (Figure 2.17), extracted from marine brown algae [81].

Gelation of alginate solutions is obtained at R.T. in the presence of several cations, mainly Ca²⁺, able to chelate the α-L-guluronic acid blocks, particularly the ring and the hydroxyl oxygen atoms. Moreover, the buckled chains of polysaccharide form ionic bonds with the cations through the carboxyl groups, leading to a typical structure named “egg-box” enclosing the calcium ions [78, 81]. This structure is schematized in Figure 2.18 [78].
However, alginate as gelling agent presents two main disadvantages: first of all, the gelation is irreversible and immediate. The reaction can be controlled by using a chelator for calcium ions, such as sodium hexametaphosphate, so that chelate complexes are formed before casting. When the mould is filled, chelate complexes are decomposed by adding an appropriate compound, such as hexanedioic acid, the calcium ions are therefore released and gelation occurs [79, 82]. The second problem is represented by the introduction of Ca ions in ceramic matrix, which induces a deleterious effect on the grain growth. Other cations can be used, such as Ba, Sr, Ce, Y, La, but the respective gel is characterized by a lower strength [80].

Starch is made of glucose units, as shown in Figure 2.19 [29]; it is a mixture of two polysaccharides: amylase, which is the gelling unit, and amylopectin [29].

![Figure 2.19 – The structure of the starch [29]](image)

At a temperature below the gelling one, the starch is insoluble in water but a limited water adsorption takes place. This phenomenon leads to a slight swelling that rises by heating at 60°C – 80°C. The starch swelling implies the consolidation of the ceramic green components having a high strength [29].

As natural gelling agents, proteins showed attractive features; among them, the most used compounds are gelatine [31, 83 – 86] and albumin [87]. Generally the proteins are condensation products of amino acids, and their origins affect their structures. In their main chains covalent peptide bonds are present; however, the chemical and physical properties of these materials depend on the weak non-covalent bonds present between the chains. The gelation mechanism is based on the denaturation of the proteins, in which secondary bonds, such as hydrogen bridges and ionic bonds, are formed leading to the structure consolidation [88]. The denaturation can be induced by temperature changes [31, 83 – 87], or with the addition of nitric acid in the case of albumin [89]. Moreover, proteins show an amphiphilic character that allows their exploitation also as foaming agent in the production of the porous materials. This property depends on the amino acid sequence, the number of polar and apolar chains and the molecule flexibility. Ceramic foams produced by exploiting the foaming and the gelling properties of albumin are described as a very simple process [88, 89].

Gelatin is extracted from collagenous raw materials such as skin, white connective tissue and animal bones [85]. It is able to undergo a thermo-reversible gelation [90], during which the main chains form helices [85]. Gelatin, like agaroids and carrageenans, presents a hysteresis between gelation and melting temperature [90]. The exploitation of gelatin as gelling agent implies long drying steps [85], production of less strong gels than in the case of agarose [83] and a high casting temperature which can promote water evaporation [86]. This latter disadvantage can be overcome by using urea and urease in combination with gelatin. On one side, urea does not allow the formation of the hydrogen bonds among the gelatin chains during cooling; on the other, the addition of the urease leads to the decomposition of the urea and gelation occurs at room temperature [86].

Finally, gelatin, like all the other natural gelling systems, implies a higher viscosity in gelcasting suspensions [2], but in any case lower than 1 Pa·s at 20 s⁻¹, so that a suitable casting is possible [41, 83]. On the other hand, they are more environmentally friendly, low-cost binders.
2.4. Dense and porous gelcast materials

Gelcasting was successfully applied for producing dense and porous components starting from many different ceramic powders, such as alumina [1, 2, 5, 13, 18 – 20, 26 – 29, 31, 33, 34, 39 – 41, 43, 44 – 47, 51, 52, 54, 57, 59, 60, 62 – 67, 70 – 72, 75 – 78, 80, 82 – 89, 91 – 93], hydroxyapatite [23 – 25, 35, 37, 94 – 100], silicon carbide [8, 11, 61, 79, 101], silicon nitride [16, 58, 63], NiO/YSZ [30], PZT [42, 102], zirconia [43, 69, 103], Ni/Al₂O₃ composites [14, 73], Al₂O₃/ZrO₂ composites [104], Al₂O₃/SiC composites [105], cordierite [36], mullite [106, 107], and many others. Generally, literature studies are extensively devoted to the green state, discussing in details microstructural and mechanical properties of green components. Particularly, these features were investigated to state the feasibility of gelcasting applications exploiting low or no toxic gelling agents. Typical microstructures of the green materials, shown in Figure 2.20, are characterized by a homogeneous packing of the particles [57, 100, 101].

Few papers reported the mechanical data of sintered gelcast materials, mostly investigating by bending or compressive tests or by Vickers microhardness measurements. In this paragraph attention will be focused only on alumina-based and hydroxyapatite-based gelcast materials since these two ceramics have been investigated in the present work.

Figure 2.21 – Dense gelcast alumina material [44]
Alumina components (Figure 2.21) obtaining by gelcasting having densities higher than 90% of the theoretical value (TD) showed flexural strengths of about 300 – 350 MPa [44, 57, 62, 82, 83, 91, 92].

In the case of porous alumina (Figure 2.22), flexural strengths, ranging between 2 and 26 MPa, were reported for materials showing densities from 10 to 30 %TD [34, 93]. Compared with the porous alumina obtained by replica method, gelcast foams present higher strength, as shown in Figure 2.23 [33].

In the case of hydroxyapatite (Figure 2.24), samples having densities higher than 90 %TD presented bending strengths of about 50 MPa [94, 97] and Vickers microhardness of about 250 HV [94, 95] (or about 5 GPa [96, 98]). Also compressive strength values s of about 85 MPa were measured [98].
Finally, porous hydroxyapatite components (Figure 2.25) were submitted to compressive tests: components having densities ranging between 10 and 30 %TD showed strengths from 2 to 7 MPa [24, 35, 99].