Alternative gelling agents for the gelcasting of ceramic foams

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Abstract

In recent years, a new class of ceramic foams with porosity levels up to 90% was developed as a result of the association of the gelcasting process to the aeration of a suspension containing foaming agents. The gelation of foamed suspensions results from the in situ polymerization of water-soluble monomers. Nearly spherical pores and highly dense struts characterize the structure of these foams, which results in unprecedented properties, such as high permeability, low thermal conductivity, high specific surface area and high mechanical strength. The main drawbacks of this process are the inhibition of the polymerization in the presence of oxygen and the toxicity of the monomers. This work investigates two harmless alternative gelling agents that do not require atmosphere control to set foamed suspensions. The first route consists in the crosslinking of a previously dissolved polyvinyl-alcohol with the addition of an organotitanate. The other approach assessed the use of gelatin as a setting agent. This polymer gels the suspension due to changes in the structure of polypeptidic chains induced by temperature reduction. Gelatin-based systems presented higher storage modulus (G') than the systems with crosslinked polyvinyl-alcohol chains. This characteristic prevented the formation of cracks during drying of gelatin-based samples, which constituted a limitation of PVAl-based systems. The results point out gelatin as a promising gelling agent to produce ceramic foams without the disadvantages of monomeric systems, such as the toxicity and the necessity of atmosphere control. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Al$_2$O$_3$; Gelatin; Gelcasting; Foams; Gels; Polyvinyl-alcohol

1. Introduction

In the last decade several consolidation techniques have been investigated with the aim of shaping dense ceramic bodies directly from a stable colloidal suspensions.[1–3] These techniques combine advantages such as the microstructural homogeneity provided by colloidal processing[4] and the ability of directly forming complex-shaped ceramic parts. Recently, the gelcasting process was used to set foamed ceramic suspensions, giving a new class of ceramic foams, with porosity levels up to 90%.[5] This process consists in vigorously stirring a colloidal ceramic suspension containing water-soluble monomers and a foaming agent. After foam formation, the suspension is rapidly gelled by means of the polymerization of the monomers, giving a rigid ceramic foam. The green body is then dried and sintered, resulting in a ceramic foam with nearly spherical pores and highly dense struts. These characteristics have provided unprecedented properties, such as high permeability,[6,7] low thermal conductivity,[8] high specific surface area[9] and enhanced mechanical strength.[5,7] However, some drawbacks limit the use of this route to produce ceramic foams, since the monomers are considered to be from moderate to highly hazardous substances. Furthermore, the polymerization is inhibited by the atmosphere oxygen. This is not a serious problem for the fabrication of dense bodies. However, the production of foams is unfeasible without an atmosphere control, due to the large gas–liquid interface.

Other gelling systems such as gelatin[10] and the crosslinking of polyvinyl-alcohol (PVAl) chains with an organotitanate[11] have been described as alternative mechanisms to promote the conversion of a fluid ceramic suspension into a rigid solid. These gelling agents are non-toxic and do not require atmosphere control during gelation.

The purpose of this work is to investigate the possibility of using gelatin and the crosslinking of polyvinyl-alcohol as gelling agents for the production of ceramic

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foams. These compounds should not increase the suspension viscosity to levels that would limit the production of low-density foams. The gelation must be completed in a few minutes to prevent foam damage due to liquid drainage and cells coalescence. Moreover, the gel has to be sufficiently strong to withstand the body weight, even at the typically low solids loading used in these suspensions. The results were compared to data obtained with a monomer-based gelcasting system.

2. Experimental procedure

Aqueous solutions containing 3, 5, 7 and 9 wt.% of gelatin (Labsynth, Brazil), and 5, 7 and 9 wt.% of PVAl (Airvol 203, 88% hydrolysis, degree of polymerization between 155 and 300, Air Products, Brazil) were prepared for the experiments. Calcined alumina (A-1000 SG, Alcoa) was added to the solutions and to pure water to prepare 35 vol.% suspensions. Ammonium citrate dihydrate (Mallinckrodt, USA) was used as deflocculant for the PVAl and gelatin-based systems. The optimum deflocculant concentration and the effect of each polymer on the suspension rheology were evaluated with the help of a Brookfield LV DV-III viscometer. For this purpose, alumina suspensions prepared with solutions containing 5 wt.% of either gelatin or PVAl and different citrate concentrations were submitted to up and down sweep cycles, in a shear rate range between 0.2 and 55.0 s^{-1}. All the suspensions were ultrasonicated during 2 min prior to rheological tests in order to disrupt agglomerates. The shear stress versus shear rate curves obtained were fitted to Casson's model, giving the viscosity and yield stress, according to Eq. (1),

$$\sqrt{\tau} = \sqrt{\tau_C} + \eta_C \cdot \sqrt{\dot{\gamma}} \qquad (1)$$

where: τ is the shear stress (Pa), $\dot{\gamma}$ is the shear rate (s^{-1}), η_C and τ_C are the Casson's yield stress (Pa) and viscosity (Pa s), respectively.

The gelling behavior of each system was studied by means of oscillatory rheometry, under 1% strain and a frequency of 2 s^{-1}, using a strain-controlled rheometer (ARES, Reometric Scientific, USA) with concentric cylinders configuration. For gelatin-containing suspensions, the test started at 40 °C and the temperature was decreased to 10 °C at a rate of 2 °C/min. For PVAl-containing suspensions, gelation was studied at 10 °C using samples prepared with 5 wt.% PVAl solution and varied additions of an organotitanate (Tyzor-TE, Du Pont, USA).[11] Temperatures above 10 °C were avoided because gelation occurred too fast. Alumina suspensions (35 vol.%) containing acrylic monomers as gelling agents also had their gelling behavior studied for comparison, since this system has been extensively used in

previous works.[5–9] For this purpose, an aqueous solution containing 30 wt.% of ammonium acrylate and 1 wt.% of methylenebysacrylamide was used as supplied by Allied Colloids, UK. Ammonium polyacrylate (Dispex A-40, Allied Colloids, UK, $\bar{M}_w = 10,000$ g/mol) was used as dispersing agent in this case. Gelation of suspensions with different monomer concentrations was studied at 25 °C.

Suspensions with different concentrations of either gelatine on PVAl and optimum deflocculant content were foamed with the help of a double blade stirrer, after the addition of varied amounts of a nonionic surfactant, Fongraminox KC-B (cocoalkyldimethylamine oxide, Clariant, Brazil). Foams were also produced using a fixed surfactant concentration (0.8 wt.% of the suspension) and varied gelatin concentrations, to assess the effect of suspension viscosity on foam formation. The suspensions containing PVAl were cooled to near 0 °C before foaming, in order to avoid premature gelation after the crosslinker addition. Suspensions with gelatin were foamed at 30 °C. The foamed suspensions were molded in 500 ml polypropylene beakers. Gelatin-based foams were stored at 10 °C, where the setting of suspension and drying occurred concurrently. PVAl-based foams were allowed to dry at room temperature just after molding. The foaming and characterization of monomer-containing samples were described in a previous work.[12] Cylindrical bodies were drilled out of dry gelatin-based samples. These samples were calcined at 300 °C using a heating rate of 1 °C/min. After organics elimination during 1 h at this soaking temperature, specimens were sintered at 1650 °C for 2 h. The density of sintered bodies was measured using the Archimedian immersion method. The permeability of the porous bodies was evaluated using Forchheimer's equation for compressible fluids,[13] expressed as

$$\frac{P_i^2 - P_o^2}{2PL} = \frac{\mu}{k_1} v_s + \frac{\rho}{k_2} v_s^2 \qquad (2)$$

where: P_i and P_0 are respectively the incoming and outcoming absolute pressures of the gas, P is the pressure at which v_s, μ and ρ were obtained (in this work, P is equal to P_0), L is the sample thickness, v_s is the gas velocity, i.e., the volumetric flow rate per unit area, μ and ρ are respectively the dynamic viscosity and density of the fluid. k_1 and k_2 are constants named Darcian and non-Darcian permeabilities, respectively. Eq. (2) includes an inertial term, $(\rho/k_2)v_s^2$, which is not considered by Darcy's equation, in spite of its significant effect at high-speed flows. The compressive strength was evaluated in a universal testing machine (MTS-810, USA) using a crosshead displacement speed of 0.5 mm/min. Small rubber pads were used at the top and bottom of the samples to minimize local stress concentrations.

3. Results and discussion

The addition of either gelatin or PVAl to aqueous alumina suspensions increased significantly the Casson's viscosity and yield stress, as shown in Fig. 1. This effect was expected, since polymer solutions have generally higher viscosity than pure solvents. Nonetheless, both systems could be well dispersed using ammonium citrate. The deflocculation of a previously studied[12] monomer-containing suspension dispersed with ammonium polyacrylate was included in Fig. 1 for comparison. It also presented Casson's viscosity and yield stress values higher than those of aqueous suspensions. But in this case, this behavior was related to a double layer compression due to the presence of the acrylic monomers, as discussed in a previous work.[12]

The effect of polymer concentration on the suspension viscosity may be best observed in well-dispersed suspensions, where the effect of particle aggregation is minimized. Fig. 2 displays the rheological behavior of suspensions prepared with an optimum citrate concentration of $2.06 \cdot 10^{-4}$ g/m^2 (Fig. 1) and varied concentrations of gelatin or PVAl. The rheological behavior of a monomer-containing suspension ([mon.]$_{liq.}$ = 30 wt.%) was included in Fig. 2 for comparison.[12]

The suspensions containing PVAl presented higher viscosity than those prepared with gelatin, in spite of the low molecular weight and partial hydrolysis of the polyvinyl alcohol used, which were expected to display a less pronounced impact on the suspension viscosity. The apparent viscosity of a suspension with 9% of gelatin in the liquid phase was similar to that of a suspension with 5% of PVAl. Conversely, suspensions with low viscosity have been prepared using 30 wt.% monomer

solutions.[5,7,9,12] This is possible due to the low molecular weight of the monomers, which renders solutions with low viscosity. It is of prime importance to understand the effect of powder dispersion and polymer concentration on the rheological properties of the suspension, because these properties exert a dramatic influence on the slurry ability to form foam.

The sample strength after gelation and its resistance to crack formation during demolding, 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. Fig. 3 shows the evolution of the storage modulus (G') during the gelation of suspensions.

Increasing the addition of crosslinker solution from 0.095 to 0.15 wt.% caused the storage modulus of gelled
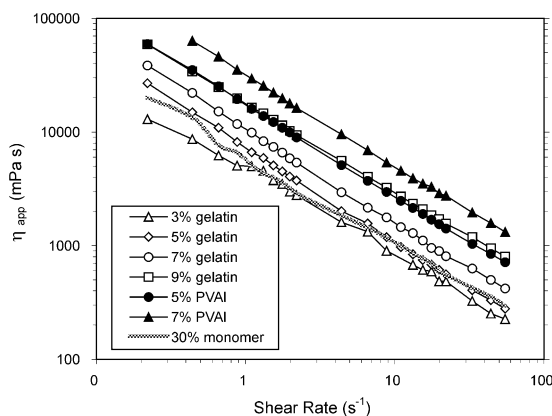
Fig. 2. Apparent viscosity of well dispersed suspensions containing different concentrations of either gelatin or PVAl in the liquid phase. The behavior of a suspension with acrylic monomers was included for comparison.[12]
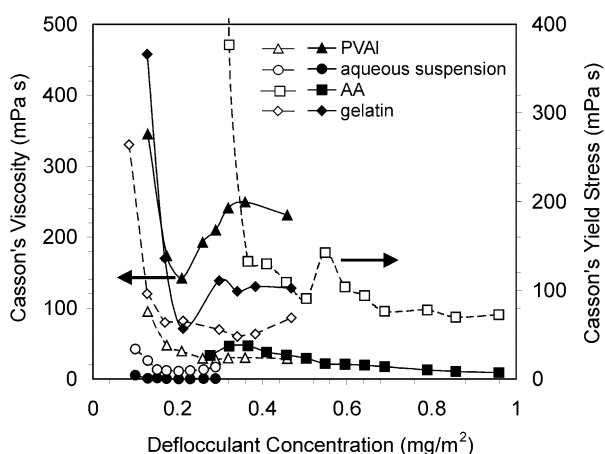
Fig. 1. Effect of deflocculant concentration on Casson's viscosity (full symbols) and yield stress (open symbols) of suspensions containing 35 vol.% of alumina in water ($\bigcirc$ $\bullet$), in 5 wt.% solutions of either gelatin ($\diamond$ $\blacklozenge$) or PVAl ($\triangle$ $\blacktriangle$) and in 30 wt.% solutions of acrylate monomers ($\square$ $\blacksquare$).[13] Ammonium citrate dihydrate was used as dispersant in the gelatin and PVAl-containing suspensions, while ammonium polyacrylate was used to disperse monomer-containing suspensions.
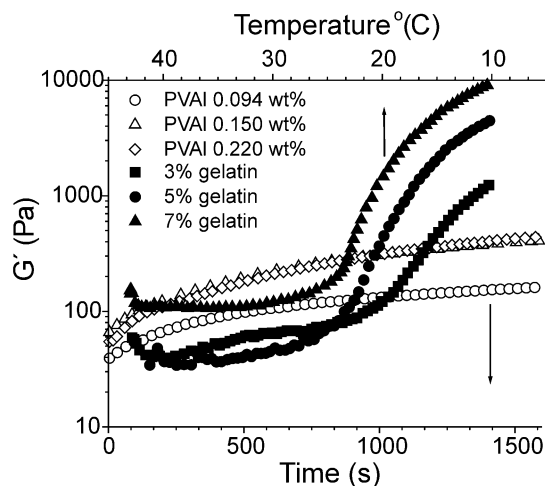
Fig. 3. Evolution of the storage modulus (G') during gelation as a function of temperature (for gelatin-containing suspensions) or time (for PVAl-containing suspensions with different crosslinker additions, at 10 °C).

PVAl-containing suspensions to increase from 180 to 400 Pa. But no additional increase was observed when 0.22 wt.% of crosslinker solution was added. This suggests that a crosslink limit was reached after adding 0.15 wt.% of the organotitanate, and further additions of this reagent could not increase the crosslink density.

The storage moduli of gelatin-containing suspensions reached values about 10 times higher (10^3–10^4 Pa) than those obtained with PVAl-containing suspensions (10^2–10^3 Pa), depending on the gel concentration. A gelled suspension with 7 wt.% of gelatin in the liquid phase (Fig. 3) reached a storage modulus (10^4 Pa) comparable to that obtained after the gelation of a suspension with 15 wt.% of monomers in the liquid phase (Fig. 4). Nonetheless, G' values as high as 10^5 Pa may be reached by gelling low viscosity suspensions having 30 wt.% of monomers in the liquid phase (Fig. 4). None of the alternative gelling agents reached such high values.

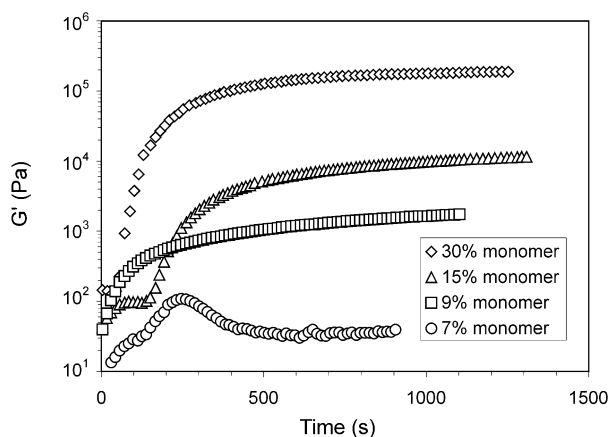As occurred to the storage modulus, the green strength after drying was strongly affected by the gel

Fig. 4. Evolution of the storage modulus (G') during gelation by in situ polymerization of suspensions containing different concentrations of monomer.
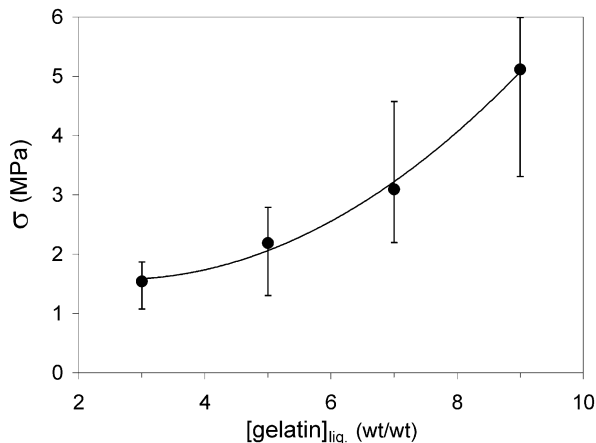

Fig. 5. Dry strength of green dense samples tested under diametral compression as a function of gelatin concentration.

concentration. Fig. 5 shows the green strength of dry dense samples with different gelatin concentrations tested under diametral compression. Samples with crosslinked PVAl were not tested because the low gel strength and adhesion to the mold surface caused the samples to crack severely during drying. Increasing the gelatin concentration in the liquid phase from 3 to 9 wt.% caused the diametral compressive strength of dry samples to increase from 1.7 to 5 MPa. These values are far below the dry strength of green samples produced with suspensions containing 25 wt.% of monomer in the liquid phase, which can reach 20 MPa.[12] Nonetheless, foamed samples could be produced using the gelatin-based system. The samples resisted satisfactorily to demolding and drying stresses. Dry samples had no cracks and were strong enough to be core drilled, giving cylinders with good surface finishing.

Foams were also produced from suspensions with 7 wt.% of PVAl in the liquid phase. However, the low strength of crosslinked PVAl network was not enough to resist to drying tensions. As a result, large cracks were formed at the center of all PVAl-based foams. Additionally, the higher viscosity of suspensions with PVAl resulted in foams with lower volume, comparatively to gelatin-containing suspensions. A photograph of typical ceramic foams produced with suspensions containing PVAl and gelatin is shown in Fig. 6.

Although crosslinking PVAl chains has been successfully used to set non-foamed, high solids loading suspensions,[11] the low values of G' and green strength in systems with low solids loading prevent its application to porous, foamed ceramics.

The foaming agent concentration and the suspension viscosity affected the foam volume, consequently the sample final density, as shown in Fig. 7. The foam relative density scaled with gelatin concentration, due to the increase of suspension viscosity (Fig. 2). On the other hand, the increase of the surfactant concentration decreased the foam density, because of the lower surface tension at the gas–liquid interface. Changing these variables allowed the production of ceramic foams in a wide

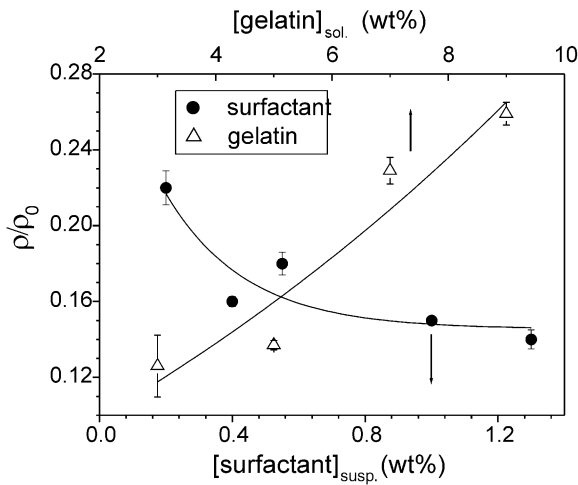Fig. 6. Samples gelled after crosslinking of PVAl (left) and using gelatin (right).

Fig. 7. Effect of gelatin (for [surfactant]$_{susp.}$ = 0.8 wt.%) and surfactant (for [gelatin]$_{sol.}$ = 7 wt.%) concentrations on the relative density (ρ/ρ_0) of sintered alumina ceramic foams (ρ_0 = 3.98 g/cm^3).

Fig. 9. Compressive strength of sintered ceramic foams as a function of relative density (ρ/ρ_0). Foam density was varied by changing either surfactant ($\triangle$) or gelatin ($\bullet$) concentration. Data of previously studied monomer-based gelcast foams[7] were plotted for comparison.
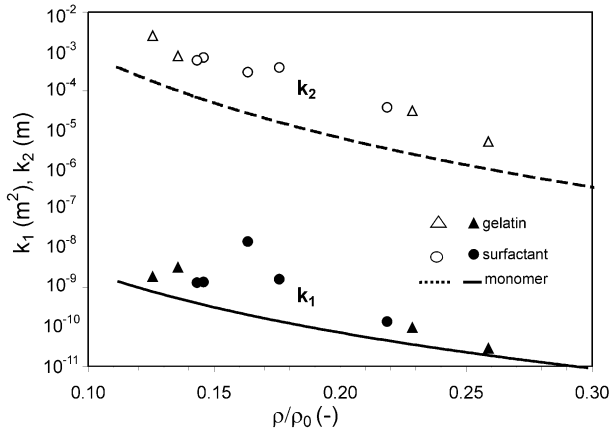

Fig. 8. Permeability constants, k_1 (full symbols) and k_2 (open symbols) of ceramic foams produced with gelatin as a function of relative density (ρ/ρ_0), which was varied by changing either the gelatin ($\triangle\blacktriangle$) or the surfactant ($\bigcirc$ $\bullet$) concentration. The lines represent a tendency calculated from the permeability constants of samples produced with monomer-based system.[7]

range of densities. However, the use of low gelatin concentrations resulted in low green strengths, and the samples were more susceptible to handling damages.

The permeability constants of ceramic foams produced with gelatin and with monomers[7] are compared in Fig. 8, as a function of the relative density. Gelatin-based foams presented higher permeability than monomer-based foams, in the range of relative densities assessed. This suggests that the macrostructures obtained in each case were slightly different. This difference may be associated to the substitution of a chemically-induced by a thermally-induced gelation mechanism, which allows some foam drainage and cell coalescence before gelation is completed. Other factors such as the higher suspension viscosity and lower green strength
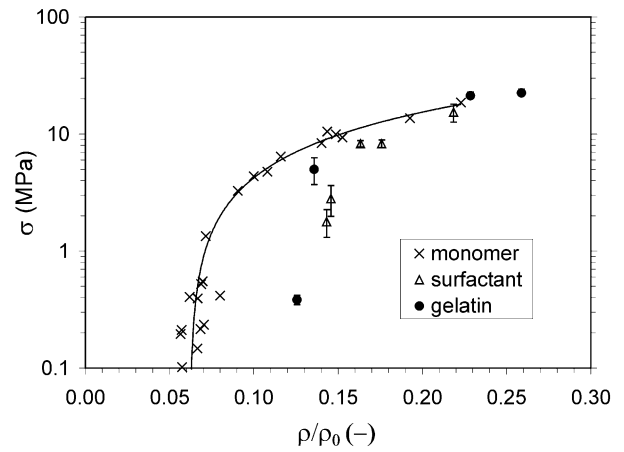
may have affected the final macrostructure, therefore, the properties of gelatin-based foams.

Fig. 9 shows the compressive strength of sintered ceramic foams as a function of relative density, which was varied by changing either gelatin or surfactant concentration. Data of previously studied foams gelled with the polymerization of monomers[7] were included for comparison.

At low densities, the compression strength of gelatin-based systems was lower than that achieved by monomer-based systems. However, samples with relative density higher than 0.20 showed strengths at the same level of those produced with monomers. It is difficult to establish definite conclusions based on this behavior, since the monomer-containing suspensions were ball-milled before being foamed. Further experiments are necessary to understand the reasons that led to the degradation of foam strength at low densities, as well as the higher permeability of gelatin-based foams, comparatively to monomer-based foams. Nonetheless, the advantages of using gelatin in the place of monomers encourage further investigations of this process.

4. Conclusions

The use of gelatin and the crosslinking of poly-vinylalcohol chains were studied as alternative mechanisms to gel foamed ceramic suspensions, in substitution to monomer polymerization. The addition of these gelling agents to aqueous ceramic suspensions increased slightly the slurry viscosity. This effect was more pronounced for suspensions containing PVAl, limiting the production of highly porous foams with this system. The viscosity of gelatin-containing and monomer-con-

taining suspensions were similar. The storage modulus of gelled PVAl-based systems (10^2–10^3 Pa) was about 10 times lower than that of gelatin-based systems (10^3–10^4 Pa). Higher values of storage modulus could not be reached because for higher polymer concentrations the suspension viscosity increased to unacceptable levels. None of the systems reached the storage modulus of suspensions gelled by the in situ polymerization of monomers (10^5 Pa). The foams gelled by crosslinking PVAl cracked severely during the drying step due to their low storage modulus and low green strength, while gelatin-based foams resisted to crack formation during demolding, drying, green machining and sintering. The dry strength of green samples scaled up with the gelatin concentration. The permeability constants of sintered gelatin-based foams were slightly higher than the permeability constants of monomer-based foams. When compared to previously studied monomer-based foams, the strength of sintered bodies produced with gelatin reached similar values for relative densities above 0.20. For relative densities below 0.20 the strength was lower than that of monomer-based gelcasting systems. These results, as well as the advantages of using a non-toxic, cheaper system that does not require atmosphere control encourage additional efforts to optimize the use of gelatin-based gelcasting to produce ceramic foams.

Acknowledgements

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