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Thermogelling polysaccharides for aqueous gelcasting—part III: mechanical and microstructural characterization of green alumina bodies

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Abstract

The use of gelling additives, such as polysaccharides, in colloidal processing provides adequate mechanical properties to the green bodies to be handled. In this work, the green density and the mechanical behaviour (stress–strain relationships, elastic modulus, bend strength and fracture mechanism) at room temperature of gelcast alumina bodies are studied, in order to establish the influence of the type and the concentration of additive. Furthermore, the previous concentration of polysaccharide solutions is also taken into account as an important variable. Agar, agarose and carrageenan were used as gelling additives. Values of the bend strength up to 4 MPa are obtained, significantly higher than those corresponding to slip cast alumina without gelling additives, and they increase with the final concentration of polysaccharide, while Young's modulus values are mainly influenced by the concentration of additive in the precursor solution. For bodies with a large final concentration of additive, extensive plastic deformation during fracture is observed. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Al_2O_3; Gelcasting; Mechanical properties; Microstructure-prefiring

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1. Introduction

Machining is a fundamental step in the production cycle of a ceramic part to confer the final shape.[1] The hardness of ceramic materials strongly limits the final machining of sintered parts so green machining is preferred in the industry. This reduces costs, but might also increase the number of pieces rejected due to the weakness of the green parts.[2] Consequently, the enhancement of the mechanical properties of the green bodies is a key feature for optimising the complete processing cycle.

With the use of polysaccharides as gelling additives a significant increase in the green mechanical properties with respect to those obtained by conventional forming procedures is obtained,[3,4] hence, in principle, the parts could be easily handled and machined.[5–8] However, due to the high plasticity of these additives,[9,10] some plastic deformation during machining of green parts is expected. If extensive plastic deformation occurs, machining will be impeded. Therefore, the gelling agent addition has to be controlled in order to reach a compromise between strength improvement and the extension of plastic fracture.

In previous works,[11,12] the rheological properties and the gelling behaviour of aqueous solutions of three gelling additives and of alumina suspensions have been studied as a function of different processing parameters (additive amount and mixing process, pH, T, shearing, etc.). Furthermore, the linear shrinkage of the cast bodies and their stiffness and handleability have been discussed in order to select the optimum range of concentration of gelling additives to improve gelcasting performance.[12] Consequently, the compositions that led to an adequate combination of a suitable rheological behaviour to assure the homogeneity of the suspension and a proper gelling behaviour and stiffness of the green bodies were selected for further characterisation.

The aim of this work is to study the mechanical behaviour (elastic modulus, bend strength and fracture mechanism) of gelcast bodies at room temperature. The

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influence of the type of additive, the concentration of polysaccharide in the precursor solutions as well as its final concentration in the ceramic slurry are discussed. In order to establish the role of gelling additives in the mechanical behaviour and, in particular, in the extension of plastic phenomena during fracture, the evolution of the deformation of stressed samples, the bend strength and the elastic modulus as a function of polysaccharide content is studied, and results are correlated to observations of the fracture surfaces. Finally, the green mechanical properties are correlated with the suspension properties (rheological behaviour, solid loading, additive content) in order to select the optimum processing conditions that lead to high strength machineable green bodies.

2. Experimental

A high purity Al_2O_3 powder (Condea HPA05, USA), and agar (Grand Agar), agarose (D1 LE), and carrageenan (Secogel TC), all three supplied by Hispanagar S.A. (Burgos, Spain) were used. The gelling additives were previously dissolved at concentrations of 1.5, 2, 3 and 4 wt.%. Alumina samples were obtained by thermal gelcasting of aqueous suspensions with concentrations of gelling additives of 1.5–4 wt.% and dried at room temperature. The dimensions of the casting mould were $(60\times10\times10)$ mm. The linear shrinkage on drying was between 5 and 26% depending on the final concentration of gel and the concentration of the precursor solution.[12] Green densities were measured by the Hg immersion method.

Dried samples have been tested in 3-point bending with a 40 mm span using a universal testing machine (Microtest, Spain). Previously the samples were rectified using 600 mesh SiC paper. All tests were performed using a constant rate of crosshead displacement of 0.5 mm. min^{-1}, and the load-displacement curves were recorded. The load-displacement curves have been transformed into apparent stress–strain relations by calculation using the sample dimensions and the equations for elastic materials. In this way, an apparent Young's modulus, E_a, has been defined as the slope of the linear part of the σ_a–ϵ_a curves. Reported values of Young's modulus and fracture stress are the average of those obtained for five samples tested under identical conditions.

As a reference, five alumina bars obtained by conventional slip casting (without gelling additives) were also tested.

Fracture surfaces were observed by scanning electron microscopy, SEM (Zeiss DSM40, Germany). The microstructures of the areas close to the tension surfaces were compared to investigate the differences in the fracture mechanisms responsible for differences in the obtained mechanical parameters.

3. Results and discussion

The relative densities of green alumina bodies obtained by thermal gelation using agar, agarose and carrageenan are summarised in Table 1. In all cases the density tends to decrease for increasing total concentration of gelling binder and it is the same for different concentrations of the precursor solution. It is expected that the green density will increase when either the total gel content decreases or when the concentration of the precursor solution increases, according to the solid loading variation. However, this happens when the total gel content changes but does not occur for the variation of the precursor solution. This suggests that the resulting densities are not only determined by the solid loading, but the gel structure (i.e. the concentration of gel) plays an important role, because the increasing amount of gel is accompanied by increasing water retention (syneresis).

Characteristic apparent stress–strain curves of samples prepared using the three studied gelling additives at different final concentrations are shown in Figs. 1–3. In all cases plotted in these figures, the additive was incorporated in the alumina slip as a 3 wt.% precursor solution. Similar trends were observed for the precursor solutions with concentrations of 1.5, 2 and 4 wt.%. From these kinds of plots, apparent Young's modulus and bend strength values were calculated for all the studied green bodies, and the results are summarised in Tables 2 and 3.

Table 1
Relative density of gelcast alumina green bars (% of theoretical)

Gelling additive content (wt.%)	Concentration of the precursor solution									
	Agarose			Agar				Carrageenan		
	2 wt.%	3 wt.%	4 wt.%	1.5 wt.%	2 wt.%	3 wt.%	4 wt.%	1.5 wt.%	2 wt.%	3 wt.%
0.25	54.9	55.3	55.6	–	55.8	55.5	55.6	58.2	57.2	57.5
0.50	53.6	53.3	53.6	–	55.1	53.6	55.2	54.8	54.5	55.3
0.75	52.8	52.5	52.3	54.2	54.5	53.1	–	54.4	54.6	53.9

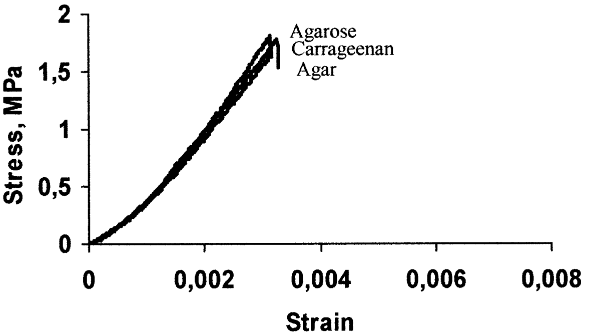

Fig. 1. Stress–strain curves of alumina samples with 0.25 wt.% of gelling additive (precursor solution concentration of 3 wt.%).

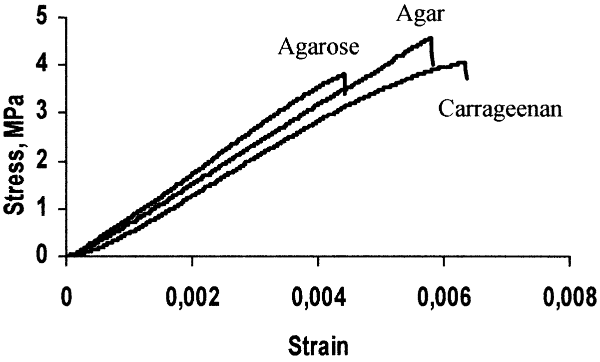

Fig. 3. Stress–strain curves of alumina samples with 0.75 wt.% of gelling additive (precursor solution concentration of 3 wt.%).

For similar processing parameters—final content and concentration of the precursor solution —, the apparent Young's modulus values, E_a, are coincident for the three additives (Table 2). For the same concentration of additive in the precursor solution, no significant differences between E_a values were found when the final content of gelling additive changed. Conversely, a significant decrease ($\approx$30%) of E_a values occurred when the precursor solution concentrations changed from lower (1.5 and 2 wt.%) to higher (3–4 wt.%) concentrations. This trend cannot be related to density changes, as density values remain the same for different concentrations of the precursor solution, but seems to indicate that a threshold value between 2 and 3 wt.% for concentration of precursor solution exists, which dominates the elastic behaviour.

The presence of a film of additive between the particles in the fracture surfaces of samples prepared from concentrated solutions ($\geqslant$3wt.%) can be appreciated in the micrograph shown in Fig. 4, which suggests the formation of a denser network of the gelling agent in which the ceramic particles are embedded. The scarce and inconsistent presence of this film in samples from low concentrated solutions indicates that the number of alumina–alumina contacts is higher in this case. This can be explained considering that the cell size of the gel net would be smaller for larger concentrations in the precursor solution, so that a lower number of alumina particles will be embedded in each cell.

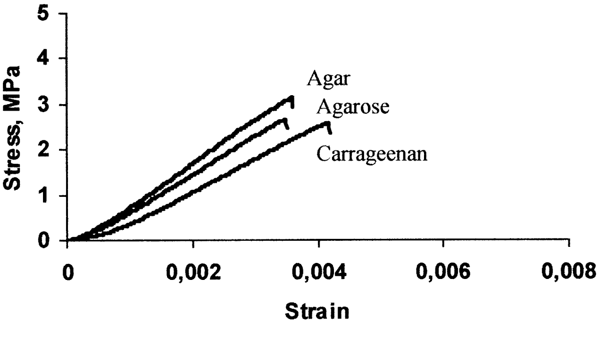

Fig. 2. Stress–strain curves of alumina samples with 0.50 wt.% of gelling additive (precursor solution concentration of 3 wt.%).

Deformation behaviour in the elastic region and, therefore, apparent Young's modulus values are determined by the nature of the alumina-alumina interfaces. In samples prepared from high concentrated solutions, the film of low modulus gelling agent would be the controlling factor and, therefore, these samples present the lowest E_a values. In the samples obtained from low concentrated solutions, the larger number of direct contacts between the high modulus alumina particles is responsible for the rigidity increase.

Bend strength values (Table 3) are very similar to those obtained for aqueous injection of alumina with similar content of agarose by Rak et al.[4] The obtained value for slip cast alumina samples without gelling additives was 0.5±0.2 MPa, significantly lower that all other values, indicating that the three gelling agents confer a mechanically resistant structure to the green bodies.

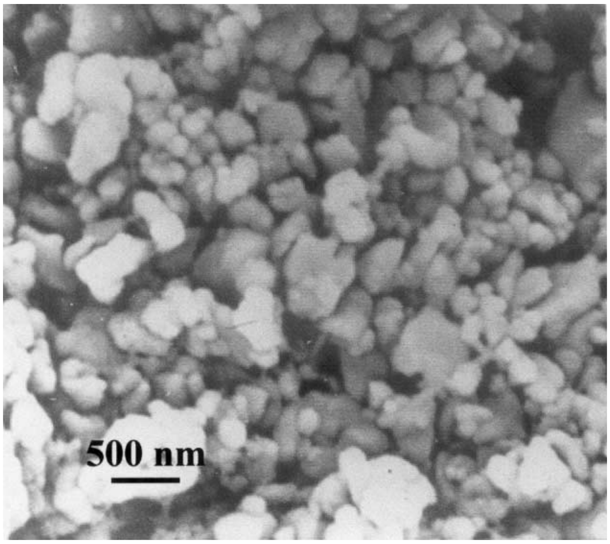

Fig. 4. SEM fracture surface of green alumina sample with 0.50 wt.% of agarose prepared from a 3 wt.% concentration of precursor solution.

Table 2
Apparent elastic modulus of green gelcast alumina bars (GPa)

Gelling additive content (wt.%)	Concentration of the precursor solution									
	Agarose			Agar				Carrageenan		
	2 wt%	3 wt.%	4 wt.%	1.5 wt.%	2 wt.%	3 wt.%	4 wt.%	1.5 wt.%	2 wt.%	3 wt.%
0.25	–	0.7±0.1	0.8±0.2	–	–	0.7±0.1	0.6±0.4	–	–	0.8±0.2
0.50	1.2±0.2	0.9±0.1	0.8±0.1	–	1.0±0.3	0.9±0.1	0.6±0.1	1.2±0.1	1.1±0.1	0.8±0.1
0.75	1.6±0.3	0.9±0.2	0.7±0.1	1.2±0.1	1.4±0.4	0.9±0.1	–	1.3±0.1	1.2±0.2	0.9±0.1

The dependence of bend strength on the two processing parameters considered here is completely different from that of Young's modulus, as strength is strongly affected by the gelling additive content and not by the concentration of the precursor solution. In general, two factors affect the strength of materials, the nature of the bonding, which determines toughness, and the presence of defects, such as pores, acting as stress intensity concentrators. In particular, numerous relations between total porosity and strength have been found for low strength - highly porous materials. This dependence is not found in the samples studied here, in which higher relative density values, correspond to samples with lower strength. Therefore, the behaviour of strength is not related to porosity and should be determined by the nature of the gel bonding. The increase of strength for different gels formed from solutions of increasing agar concentration has been described by Zhang et al.[3] This dependence is weaker for samples with carrageenan (e.g. for 3 wt.% precursor concentration, the green strength increases by about 110% for agarose and agar, but only by 56% for carrageenan when final concentration increases from 0.25 to 0.75%), which confers the largest strength to the samples with the lowest total concentration (2.5 vs 1.7 and 1.9 for carragenan, agarose and agar, respectively, for 3 wt.% precursor concentration).

The deformation behaviour of the samples with lower content of polysaccharide (0.25 wt.%) is fairly coincident for the three additives (Fig. 1); all samples experience low and coincident total strains of about 0.2%. Differences between the curves corresponding to the three gelling agents appear for final concentrations of additive of 0.5 and 0.75 wt.% (Figs. 2 and 3), as fracture strain values increase differently with final concentration. Carrageenan samples were the ones for which fracture strain increased more and monotonously, from ≈0.3 to ≈0.63% as final concentration changes from 0.25 to 0.75 wt.%, in the cases plotted in Figs. 1–3. Agarose samples were the less sensible to final concentration in terms of fracture strain (≈0.3–0.4%, in Figs. 1–3). Agar samples behaved similarly to those of agarose for the intermediate final concentration (0.5 wt.%, Fig. 2) whereas they experienced strains close to those of carragenan samples for the largest final concentration (≈0.60%, Fig. 3).

Figs. 5–7 show characteristic low magnification SEM micrographs of fracture surfaces of bend samples. The fracture surfaces of all gelcast samples (Figs. 5 and 6) were rough when compared to the slip cast ones (Fig. 7), which has to be related to the presence of a plastic binder.

In the samples containing carrageenan (Fig. 5) no differentiated defects and fast fracture zone close to the tension surface were observed and roughness increased sharply with higher concentrations. In the fracture surfaces of the samples with 0.5 and 0.75 wt.%, large areas which appear to be plastically deformed were observed [Fig. 5(b) (c)]. Larger magnification of these areas (Fig. 8) reveals the presence of regions with a higher densification which demonstrates that plastic deformation has occurred. The extension of this phenomenon increased with increasing content of additive, in agreement with the sharp increase of fracture strain of carragenan samples with the same processing parameter (Figs. 1–3) discussed above. Conversely, the roughness of the fracture surfaces of the samples with agarose (Fig. 6) was similar for increasing contents and always smaller than that of carrageenan samples. The micro-

Table 3
Bend strength of green gelcast alumina bars (MPa)

Gelling additive content (wt.%)	Concentration of the precursor solution									
	Agarose			Agar				Carrageenan		
	2 wt%	3 wt.%	4 wt.%	1.5 wt.%	2 wt.%	3 wt.%	4 wt.%	1.5 wt.%	2 wt.%	3 wt.%
0.25	–	1.7±0.1	1.8±0.2	–	–	1.9±0.2	2.0±0.1	–	–	2.5±0.8
0.50	2.6±0.1	2.6±0.1	3.0±0.1	–	3.0±0.1	3.1±0.1	3.0±0.1	3.3±0.1	3.0±0.1	3.1±0.3
0.75	3.5.±0.1	3.6±0.2	4.2±0.1	3.8±0.3	4.0±0.1	4.0±0.5	–	3.9±0.2	4.0±0.1	3.9±0.3

structure of the zones close to the tension surfaces was open, and no highly dense zones such as those observed in carrageenan-containing samples were found, as shown in the larger magnification micrographs of the Fig. 9. These observations agree with the facts that agarose samples experienced the lowest values of fracture strains and that their dependency on additive concentration was the lowest (Figs. 1–3). For agar samples to experience extensive plastic deformation final contents larger than 0.5 wt.% were needed.

Many agglomerates of agarose were found in samples with high concentration of the additive (0.75 wt.%), such as the one observed in the micrograph in Fig. 10, but no agglomerates were found in the samples with carrageenan. The agglomerates originate because agarose is not completely dissolved at the temperature required for gelcasting, as described elsewhere.[11] In the fracture surfaces of the samples containing 0.5 and 0.75 wt.% of agarose differentiated defects due to the agglomerates were found as origin of fracture (Fig. 6) and the strength of these samples was lower than that of the carrageenan samples (Table 3). Therefore, uncompleted dissolution of the gelling agent leads to the weakening of the green compact. Moreover, these defects would evolve during sintering becoming fracture origins in the sintered material.

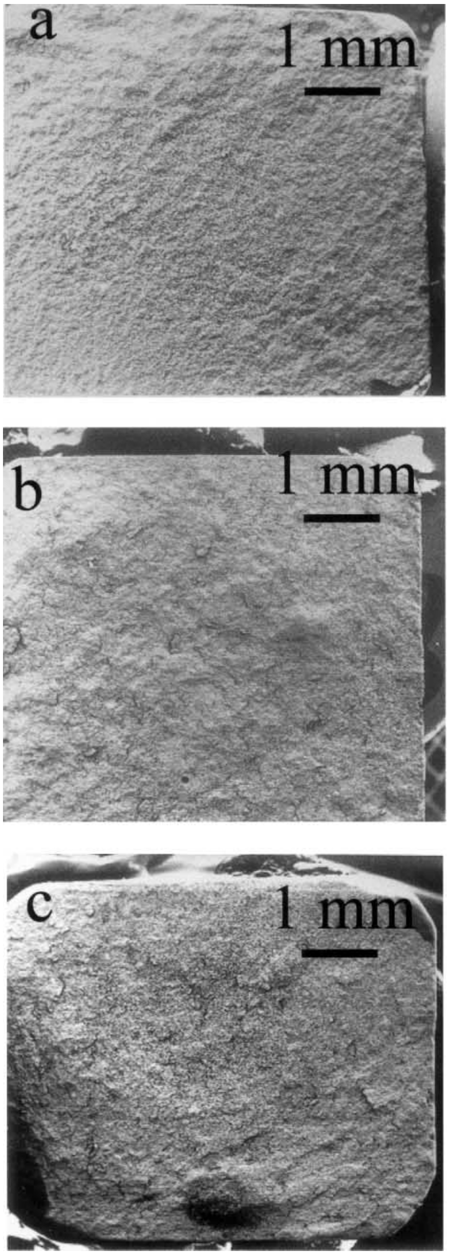

Fig. 5. SEM fracture surfaces of samples with carrageenan: (a) 0.25 wt.%; (b) 0.50 wt.%; (c) 0.75 wt.%.

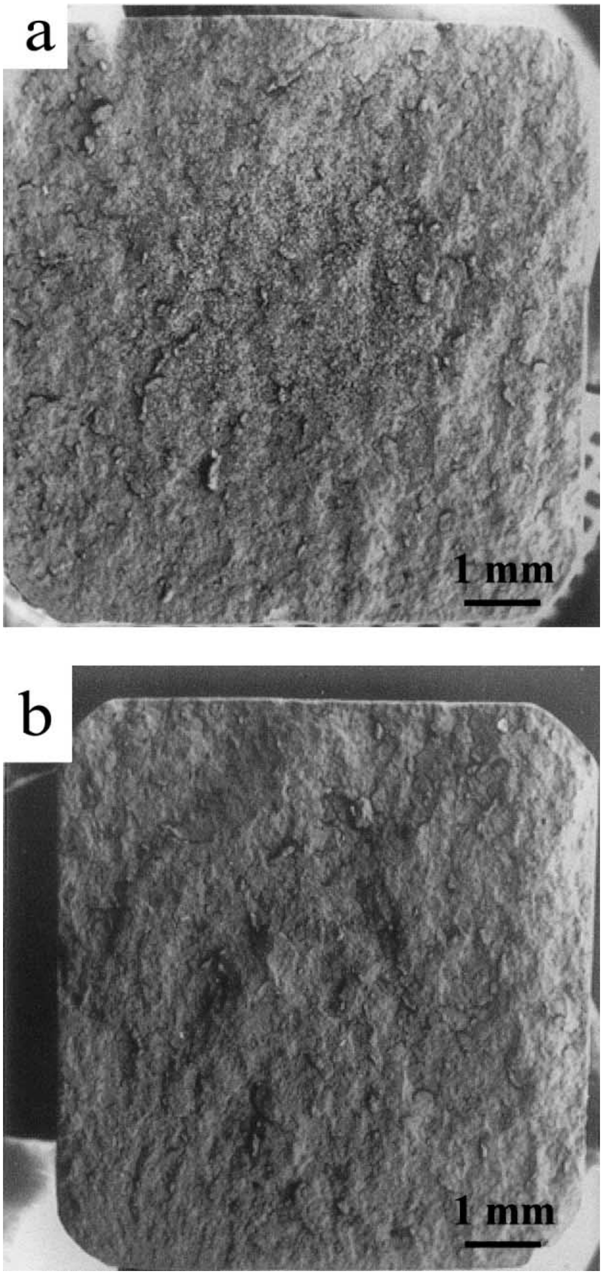

Fig. 6. SEM fracture surface of samples with agarose: (a) 0.50 wt.%; (b) 0.75 wt.%.

Considering all results, it is possible to establish that optimum gelling is achieved when the concentration of precursor solution is greater than 2 wt.%, where the polysaccharide forms a denser net that reduces the number of alumina–alumina contacts. In previous work,[12] the evolution of the viscosity of the slurries with precursor solution suggested that the large volume of particles in the slurry makes it difficult for the formation of the gel network. Hence, for low concentrations of polysaccharide (<2 wt.%), the coil helices remain isolated at the shape forming temperatures, while for higher concentrations of polysaccharide the separation distance among coil helices decreases leading to a larger linking among macromolecular chains on gelling. The mechanical behaviour confirms this hypothesis. In Fig. 11 the relationship between the apparent Young's modulus

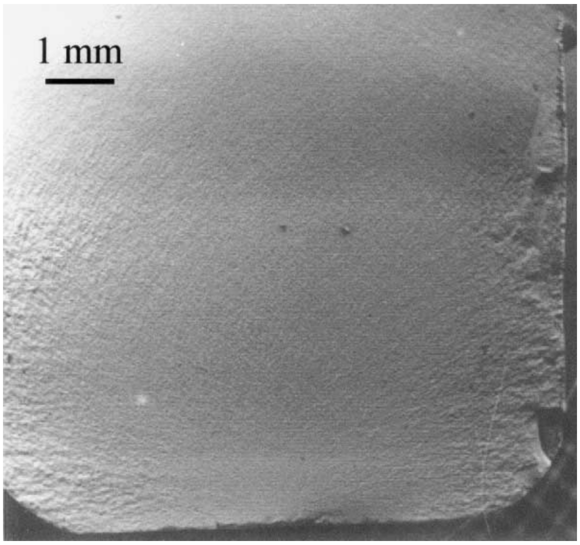

Fig. 7. SEM fracture surface of slip cast alumina green body without gelling additive.

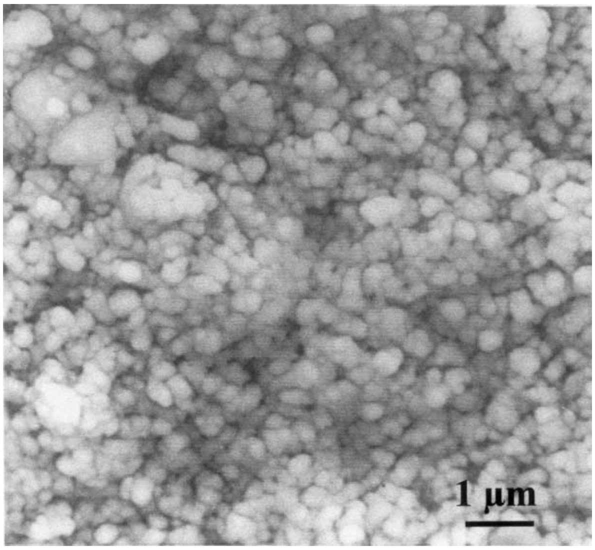

Fig. 8. SEM microstructure of 0.75 wt.% carrageenan alumina sample.

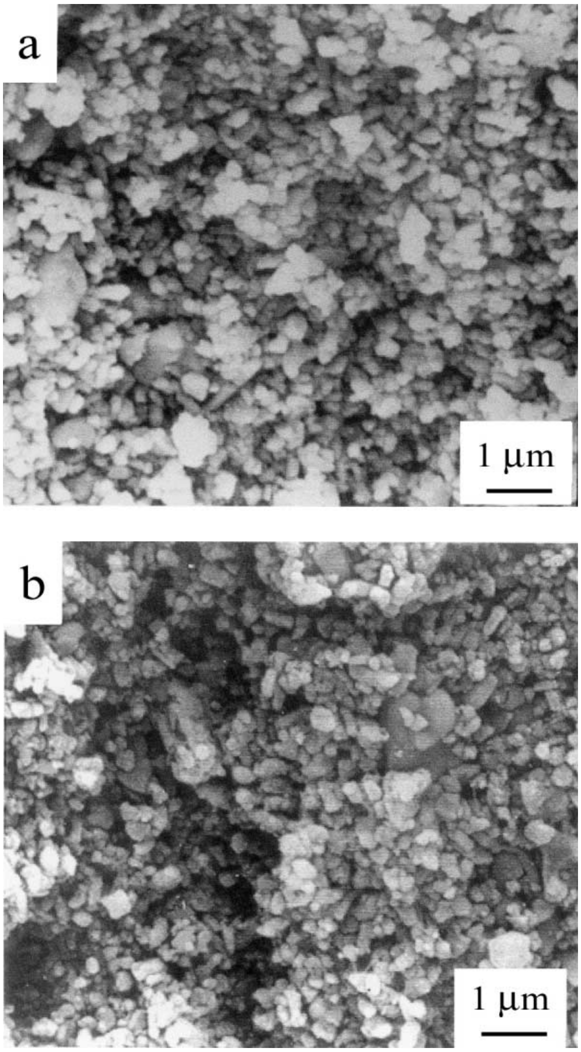

Fig. 9. SEM microstructure of 0.75 wt.% agarose alumina samples from a precursor solution concentration of: (a) 2 wt.%; (b) 4 wt.%.

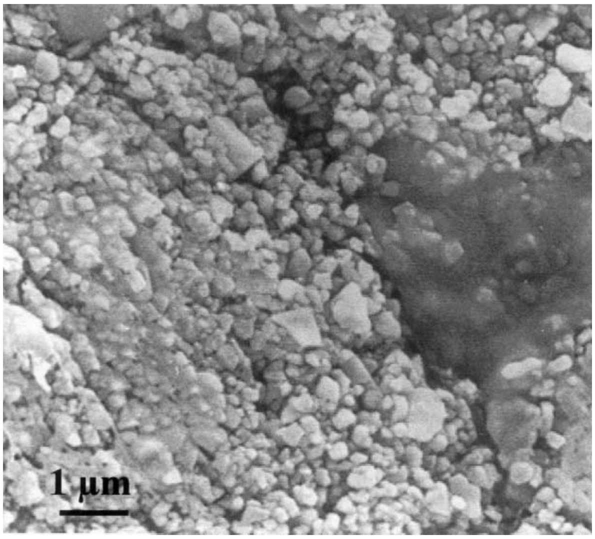

Fig. 10. SEM microstructure of 0.75 wt.% agarose alumina sample from a 3 wt.% precursor solution of additive.

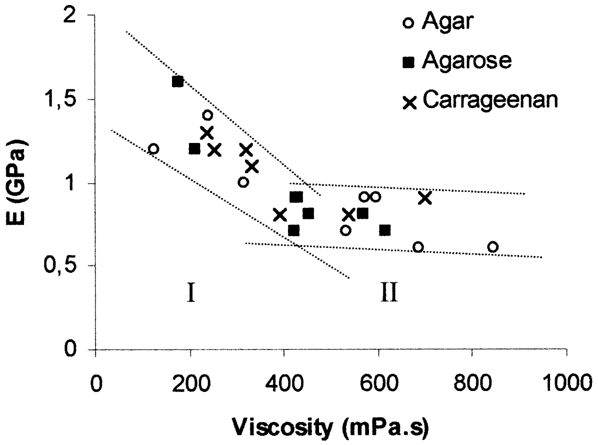

Fig. 11. Relationship between Young's modulus of the green and the viscosity of the starting suspensions for all the studied samples.

of the greens and the viscosity of the starting suspensions is plotted. It can be seen that E_a decreases with increasing viscosities. However, the experimental values can be fit in two regions with a different slope. Region I equates to samples with $\leqslant 2$ wt.% precursor solutions, whereas higher concentrations are located in region II, with a much lower variation of the modulus. The sharp decrease of E_a demonstrates that viscosity increase is due to the formation of a continuous channel of helical aggregates in the ceramic slurries which is the origin of the gel structure observed in the fracture surfaces of dried green bodies containing $\geqslant 3$wt.% gelling additive.

The use of concentrated precursor solutions is also better for other green properties (e.g. density and shrinkage). On the other hand, the increase in bend strength with the final concentration of gelling additive is accompanied by an increase in fracture strain, which extent depends on the nature of the binder, due to extensive plastic deformation. When a concentration of 0.5 wt.% is used, reasonable strength and strain values are obtained for all gelling additives studied here. Conversely, for carrageenan and agar samples, even tough the strength of samples containing 0.75 wt.% is larger, this increase is accompanied by a large increase in the extent of plastic deformation. Consequently, if the green parts have to be machined, a concentration of gelling agent of 0.5 wt.% is sufficient to prevent damage by plastic deformation. It has also the advantage that the drying shrinkage is lower. Only in the case of manufacturing near-net shaped parts, gelling additive concentrations of 0.75 wt.% can be used in order to increase the mechanical properties of green bodies and to avoid deformation during handling.

4. Conclusions

In the gelcast alumina bodies, deformation and fracture are determined by the presence, final concentration and type of gelling additive, as well as by the characteristics of the precursor solution.

Young's modulus values are mainly influenced by the concentration of the additive in the precursor solution, which determines the size of the cells that constitute the gel net in which the ceramic particles are embedded.

Bend strength values are significantly higher than those corresponding to slip cast alumina without gelling additives, and increase with the final concentration of additive. The effect of this parameter overcomes other microstructural effects such as porosity.

For the three studied additives, larger final concentrations of additive lead to increasing plastic deformation during fracture. The nature of the additive determines the concentration needed for extensive plastic deformation to occur. In order to chose the optimum concentration of gelling agent, a compromise must be reached between strength improvement and plastic deformation.

Considering all properties, for the additives studied here, a concentration of gel of 0.5 wt.% from a 3 wt.% precursor solution have been proved to reach a compromise between sufficient low Young's modulus and high strength without extensive plastic deformation.

Acknowledgements

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