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# Improved green properties of gelcast alumina through multiple synergistic interaction of polysaccharides

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### Abstract

Carrageenans have been proposed for the aqueous gelcasting of ceramic and metallic powders because they form strong gels on cooling that allow fast consolidation and enhanced green strength. However, for additive contents above a threshold value, extensive plastic deformation occurs during fracture. Different gums can be combined with carrageenan to obtain the desired gel properties through synergistic interaction. In this work the combination of carrageenan with locust bean gum and with mixtures of locust bean gum and xanthan gum is investigated. The rheological behaviour of solutions (2 wt.%) of these three polysaccharides and their mixtures is studied at 60 °C, as well as the evolution of viscosity on cooling. The effect of mixtures of these gums on the rheological behaviour of deflocculated alumina slurries (50 vol.%, 80 wt.%) is also studied. The additions increase the viscosity of the suspensions and the deformability of the wet bodies. However, after drying, the green strength of the alumina pieces is enhanced and the plastic deformation during fracture is significantly reduced, thus improving machineability. The fracture strengths and Young's modulus values of alumina bars prepared with the three polysaccharides are around 4 MPa and 2 GPa, respectively. Relative densities are >55% of the theoretical value in the green state and ~98% after sintering at 1500 °C/2 h.

Keywords: Al<sub>2</sub>O<sub>3</sub>; Mechanical properties; Shaping; Suspensions; Gelcasting

## 1. Introduction

Machining is a fundamental step in the production cycle of a ceramic part to confer the final shape.<sup>1</sup> 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 can also increase the number of pieces rejected due to the weakness of the green parts.<sup>2</sup> Consequently, the enhancement of the mechanical properties of the green bodies is a key feature for optimising the complete processing cycle.<sup>3</sup> Moreover, in order to avoid the failure of the pieces as well as blunting during machining, a suitable combination of stiffness and strength of the green parts is needed. In terms of laboratory mechanical characterisation of the bodies, this combination of properties is translated into steep and linear stress-strain curves.

In a previous work<sup>4</sup> the mechanical behaviour of alumina green bodies prepared using different gelling additives (agarose, agar, carrageenan) was studied. It was demonstrated that the presence of these additives strongly increased the strength of the green parts but that a threshold value for the amount of additive existed if extensive plastic deformation was to be avoided during fracture. In fact, part of the toughening effect of these gelling additives was related to large strains to fracture. A larger strength increase can be obtained by means of the synergistic interaction of carrageenan (C) with non-gelling gums.<sup>5–7</sup> The addition of locust bean gum (LBG) to carrageenan provides strengthening, as a consequence of polymer cross-linking. The processability of alumina suspensions using synergistic mixtures of C+LBG has been studied elsewhere.<sup>8</sup> The gel strength of the dried green bodies increases, due to the structure conferred by the LBG that reduces swelling of the carrageenan molecules. The adequacy of this processing method will be determined by the fracture mode of the pieces. If the responsible factor for strengthening was larger plastic deformation, the use of a C + LBG

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mixture would be limited to non machineable green parts. Conversely, if the synergistic effect of C and LBG led to the formation of a structural network in which LBG would serve as a rigid basis for the interlocking of the gelling additive, the strengthened parts would be easily machineable. On the other hand, xanthan gum (XG) also interacts with LBG,<sup>9</sup> so that its addition will contribute to further strengthening the resulting gels.

In this work the synergism of LBG with C and the double synergism of LBG with C and XG are studied. The rheological behaviour of the solutions of each polysaccharide and of their mixtures is studied, as well as their effect on the cooling viscosity of alumina suspensions. The fracture behaviour of green parts prepared using carrageenan, C + LBG, C + LBG + XG, and LBG + XG is analysed in order to determine the adequacy of these additives for the fabrication of strong and machineable green parts.

### 2. Background

Gums are hydrophobic or hydrophilic high-molecular weight molecules wich when immersed in an appropriate solvent produce gels or high viscosity suspensions or solutions.<sup>10</sup> However, the term gum is technically employed for plant or microbial polysaccharides that are dispersable in water. Gums can be exuded from plants (e.g. arabic gum), extracted from seeds (e.g. locust bean gum, LBG) or from seaweeds (e.g. agaroids, carrageenan) or produced by microorganisms (e.g. xanthan gum, XG). Properties of gums are largely determined by the interaction of the polysaccharide molecules with themselves and with water molecules. Polysaccharides occur as linear or branched chains composed of glycosyl units. Linear molecules need a greater space for gyration, thus providing higher viscosities. On the other hand, linear molecules tend to join to form an association of segments through hydrogen bonds. Regions where molecules join together are referred to as junction zones. The strength and stability of the association is larger when the junction zones are longer. Hence, linear molecules have also a higher tendency to form gels. There are different types of chainchain interactions in polysaccharide solutions that can lead to gel formation, such as the interpenetration of flexible coils, the weak association of rigid rod-like structures or the formation of inter-chain tertiary structures.<sup>11</sup>

Carrageenans are linear polysaccharides built up of alternating 1,3-linked  $\beta$ -D-galactopyranosyl and 1,4-linked  $\alpha$ -D-galactopyranosyl units with hemiester sulphate groups. In  $\kappa$ -carrageenan the 1,3- and 1,4-linked units are D-galactose-4-sulphate and 3,6-anhydro-D-galactose, respectively. The structure of the repeating unit of carrageenan is shown in Fig. 1a. Carrageenans

form rigid, thermoreversible gels through the cooperative association of double helices.<sup>12</sup>

Gums (arabic, xanthan, locust bean, etc.) do not form gels but contribute to enhance the viscosity of their solutions. LBG is a galactomannan with a backbone of 1,4linked  $\beta$ -D-mannopyranosil units having side stubs of 1,6linked α-D-galactopyranosyl groups (Fig. 1b). LBG has a typical molecular weight of  $30-35\times10^4$ . Xanthan gum is composed of a backbone of 1,4-linked  $\beta$ -D-glucose with side chains containing two mannose and one glucuronic acid (Fig. 1c). XG is one of the stiffest natural biopolymers. This is attributed to the adoption of a double helix structure but experimental evidence supports the hypothesis that there is a disordered structure consisting of a dimerized expanded coil that retains some double helical segments. XG dispersions contain weakly associated microgel particles or aggregates.<sup>9</sup> Estimates of molecular weight range from  $15-50 \times 10^6$ .

Different gums can be combined to obtain desired gel properties. Pure k-carrageenan gives relatively low Young's modulus and low strength gels. However, the properties of these gels can be modified by addition of other, non-gelling polysaccharides. One of the most widely used mixtures is that of carrageenan with LBG, which provides unique strength and capacity to retain shape. Ainsworth et al.<sup>13</sup> observed that the elastic modulus of a 1 wt.% solution of C was lower than that of a mixture with 0.5 wt.% C-0.5 wt.% LBG. Williams et al.14 showed by DSC and ESR that no peak (no gel) appeared for LBG, while a peak centred at 40 °C occurred for C. The mixture showed a peak at 44 °C. When C was in excess, two peaks appeared, relative to the C gel and to the mixture, respectively. There is an open debate regarding the mechanisms of such synergistic interaction, but it has been proposed that on cooling the carrageenan chains shift from random coils to double helices, as a result of the potassium ions. This reduces the number of carrrageenan-water contacts and thus, the interfacial energy. The helices can either self-aggregate or associate with the mannan chains of LBG, the last being preferred because the mannan molecules are uncharged.

On the other hand, LBG also interacts with XG, leading to rubbery gels that transform into stiff structures on drying, at a total concentration of 0.5 wt.%, with the optimum LBG/XG ratio being  $3:1.^5$  Although there is still debate, it is believed that interaction involves ordered XG chains that reduce the polymer-water contacts and the interfacial energy. The inner mannose residue of a XG side chain interacts with a OH<sup>-</sup> group on the adjacent mannose of the LBG via H-bonding. In the presence of K<sup>+</sup>, ionic association with the carbonyl oxygen of the glucuronic acid of the side chain and an adjacent hemiacetal oxygen of the mannan may occur.<sup>15</sup>

Hence, it can be expected that mixtures of the three polysaccharides provide specific properties to the resulting gels due to the two synergistic interactions



Fig. 1. Structure of  $\kappa$ -carrageenan (a), locust bean gum (b) and xanthan gum (c).

C+LBG, and LBG+XG. The interaction of the different polymers should promote extensive cross-linking that would enhance the network structure where the polymer chains come in closer contact. As a result, the stiffness as well as the strength of the obtained dry gels should increase, and the ceramic parts shaped from these mixtures should exhibit a higher machineability.

## 3. Experimental procedure

As ceramic powder a commercial  $Al_2O_3$  was used (Condea HPA05, USA) with a mean particle size of 0.35 µm (measured by laser diffraction, Malvern, Mastersizer S, UK) and a specific surface area of 9.5 m<sup>2</sup>/g (measured by N<sub>2</sub> adsorption, BET, Monosorb, Quantachrome, USA). Aqueous suspensions were prepared to a solid loading of 80 wt.% (50 vol.%,) by ball milling for 6 h with an alumina jar and balls. As deflocculant an ammonium salt of polyacrylic acid (Duramax D3005, Rohm & Haas, USA) was used at a fixed concentration of 0.8 wt.% referred to dry solids. The resulting pH value was  $9.0\pm0.1$ . These suspensions were shaken in closed flasks for 16 h prior to binder addition in order to reach an adequate surface equilibrium.

As gelling additives, the following commercial polysaccharides were selected: (a)  $\kappa$ -carrageenan (Secogel TC, Hispanagar S.A., Spain), (b) locust bean gum (Palgum AG, Carob S.A., Spain), and (c) xanthan gum (P-X200, Carob S.A., Spain).

Aqueous solutions of carrageenan (C), locust bean gum (LBG), and xanthan gum (XG) were first prepared independently to a concentration of 2 wt.%. Carrageenan solutions were prepared by mixing the as-received carrageenan powder with water at room temperature and subsequently heating to 90-92 °C, to allow the powder to fully dissolve. Then, the solution was maintained at a temperature of 60-65 °C. The LBG solutions were prepared at the same concentration by mixing with water and further heating up to 85 °C for 15 min, and it was also maintained at 60-65 °C. The XG solutions were prepared by incorporating the polysaccharide powder into water at room temperature. Five different mixtures of additives were prepared by mixing the proper amounts of the corresponding solutions whose compositions are shown in Table 1. The parenthesis indicates how the mixture was prepared; for instance, in composition (3), a mixture of 1 part of LBG and 1 part of XG was added to 2 parts of C solution, so that the total content of C equals that of the gums. Mixtures (3) and (4) were prepared by dissolving the gums together, and mixing this solution with the carrageenan solution. Composition (5) was prepared by combining a mixture of C and LBG with a mixture of LBG + XG.

In order to prepare the gelcasting suspensions, welldispersed alumina suspensions (80 wt.%) were heated to 60 °C, and the binder solutions were then added at this temperature. In all cases the total amount of polysaccharides into the ceramic slurries was 0.5 wt.% with regard to dry solids. Since they were introduced as 2

 Table 1

 Composition of the different mixtures of additives

Solution	Composition	Relative ratios		
		С	LBG	XG
1	C + LBG(1:1)	0.5	0.5	0
2	LBG + XG(1:1)	0.0	0.5	0.5
3	C + (LBG + XG)(2:1:1)	0.5	0.25	0.25
4	C + (LBG + XG)(4:3:1)	0.5	0.375	0.125
5	(C+LBG)+(LBG+XG)	0.25	0.5	0.25

wt.% solutions, the total solid loading of the suspensions decreased to 68.6 wt.% (35.5 vol.%).

The rheological behaviour of the solutions of polysaccharides and the ceramic suspensions with binders was studied using a rheometer (Haake RS50, Germany) operating with a double cone and plate system (60 mm in diameter, cone angle 2°) and at 60 °C. A solvent trap was coupled to the measuring unit to reduce evaporation. The evolution of viscosity on cooling was measured at temperatures ranging from 65 to 25 °C using a probe of temperature, which enables the continuous recording of viscosity data on cooling. These tests were made at a constant shear rate of 5 s<sup>-1</sup> because the arrangement of locust bean gum molecules can be altered at higher shear rate.<sup>8</sup>

Alumina green bodies were obtained by gelcasting, pouring the heated suspensions (60/65 °C) into stainless steel moulds at the same temperature, and further cooling with tap water. The dimensions of the moulds were  $80 \times 10 \times 10$  mm<sup>3</sup>. After residence times of a few min (<5 min), the test bars were demoulded and dried at room conditions for 48 h. Green densities were measured by Archimedes' method in Hg. Drying shrinkage and weight loss were also measured.

Green bars were squared off with a 600 mesh SiC paper and loaded in 3-point bending (40 mm span and constant rate of cross head displacement of 0.5 mm min<sup>-1</sup>) using an universal testing machine (Microtest, Spain). The load-displacement curves were transformed into apparent stress-strain relations and the slope of the linear part of the  $\sigma_a$ - $\varepsilon_a$  curves was defined as the apparent Young's modulus,  $E_a$ .

The fracture surfaces were observed by scanning electron microscopy, SEM (Zeiss DSM40, Germany) to investigate the fracture mechanisms responsible for the obtained strength values.

Due to the small amount of binder used to make the bars, sintering was performed in a single step heating ramp up to 1500 °C, at a heating rate of 5 °C/min., with 2 h dwell. Cooling was made in two steps, from 1500 to 1200 °C at a cooling rate of 5 °C/min., and then to room temperature at a cooling rate of 2 °C/min in order to avoid thermal stresses. The sintered densities were measured by immersion in water.

#### 4. Results and discussion

The rheological behaviour of solutions of gums was first evaluated by measuring the flow curves at the mixing temperature (60 °C). Fig. 2 shows the flow curves at 60 °C of 2 wt.% solutions of each gum and that of the (1:1) mixture. The gums show a thixotropic cycle at shear rates below 500 s<sup>-1</sup> related to their high deformability. The shape of the LBG curve is very irregular and a significant discontinuity among neighbour data points is registered. The viscosity largely increases for the mixture, as well as the thixotropy below 500 s<sup>-1</sup>, which disappears at higher shear rates, thus suggesting a helix to coil transition on shearing. Fig. 3 shows the variation of viscosity on cooling of 2 wt% solutions of each gum and of the mixture at a shear rate of 5 s<sup>-1</sup>. XG solution is not affected by temperature between 65 and 25 °C, while the viscosity of LBG increases on cooling. None of the gums forms a gel structure on cooling. When mixed, there is a sharp viscosity increase at ~50 °C, but viscosity still increases on further cooling. This demonstrates the synergistic interaction between both gums.

Therefore, solutions containing the three polymers were rheologically characterised. The flow curves of these three-components solutions are shown in Fig. 4. All the curves show a regular evolution without the discontinuities observed in Fig. 2, although the curves corresponding to mixtures (4) and (5) still show a broad thixotropic cycle below 600 s<sup>-1</sup> due to the higher content of LBG.<sup>8</sup> The thixotropy is negligible in mixture (3), in which both gums are in the same proportion, i.e. the relative content of LBG is lower, but this solution has the highest viscosity at high shear rates. In such case, both synergisms act without competition and the mixture becomes sticky and more deformable. This effect is not interesting for ceramic forming processes, because distortion of the shaped wet parts will occur before drying.

The evolution of viscosity on cooling at 5 s<sup>-1</sup> for the different (C+LBG+XG) solutions is plotted in Fig. 5, where two steps in viscosity can be seen, at ~55 and 30 °C. The first is related to the gums and the second to carrageenan gelation. The  $T_g$  of carrageenan solutions is near 37 °C for this solution concentration.<sup>16</sup> However, the high concentration of gums in mixture (5) reduces the  $T_g$  to ~30 °C. It should be noted that mixtures (3) and (4) follow a similar trend with a sharp viscosity increase below 40 °C that reaches a maximum value of about 12,000 and 14,000 mPa.s respectively. The best results are obtained for mixture (4), where the change of viscosity at 50–55 °C due to the gums is small and the viscosity gap due to gelation is higher.



Fig. 2. Flow curves at 60  $^{\circ}$ C of 2 wt.% solutions of locust bean gum, LBG (a), xanthan gum, XG (b), and a (1:1) mixture of locust bean gum/xanthan gum, LBG + XG (c).



Fig. 3. Evolution of viscosity on cooling of 2 wt.% solutions of locust bean gum (LBG), xanthan gum (XG) and a (1:1) mixture of locust bean gum/xanthan gum (LBG+XG) at a shear rate of 5 s<sup>-1</sup>.



Fig. 4. Flow curves at 60 °C of the synergistic mixtures C + LBG + XG (3), (4) and (5).



Fig. 5. Evolution of viscosity on cooling of the synergistic mixtures C+LBG+XG (3), (4), and (5) (shear rate: 5 s<sup>-1</sup>).

On the other hand, mixture (5) shows much higher viscosities over the whole range of temperatures and a sharper increase of viscosity at 50 °C, as was found for the mixture LBG + XG (1:1), Fig. 3. This suggests that in mixture (5) the intensity of the synergism between LBG and XG is higher than that of C with LBG, in agreement with the fact that the concentration of gelling agent is three times lower than that of the gums, while in the other mixtures the total quantity of gums equals that of carrageenan. In shape forming a fast consolidation is needed, so a sharp viscosity increase at the  $T_g$  is desired, as occurs for mixtures (3) and (4), and less so for solution (5), which does not form a rigid gel but a deformable structure very difficult to handle before drying.

The gelcasting alumina suspensions were prepared with 0.5 wt.% of polysaccharides (with regard to solids) by adding the required amounts of 2 wt.% solutions. A first step was to study the rheological behaviour of suspensions containing the gums at 60 °C. Fig. 6 shows the flow curves at 60 °C of the alumina suspensions with carrageenan, with the mixture of gums and with the gums and carrageenan [mixture (4)]. This plot shows that at low shear rates, the lowest viscosity is presented for the suspension with only carrageenan. The alumina suspension with mixture (4) shows the highest viscosity at any shear rate in agreement with the higher viscosity of the previous solution.

Fig. 7 shows the viscosity vs. temperature curves of alumina suspensions with mixtures (2) and (4). The suspension with gums (2) shows an increase of viscosity at temperatures between 50-60 °C, as observed in Fig. 3 for the solution. However, suspension of mixture (4) shows a first increase of viscosity below 60 °C and a second slight increase below 45 °C. In this case, the increase of viscosity on gelation starts at higher temperature and the gel formation needs longer times, but the decrease of viscosity below 30 °C suggests that a soft gel is formed that separates from the rotor. Hence, it

can be predicted that longer residence times will be needed for consolidation.

After casting these suspensions, the demoulded bars containing gums were easily deformed in the wet state. Drying times of 48 h were needed to obtain dry and handleable testing bars. Table 2 summarises the characteristics of the dry casts obtained with the different additive mixtures. The green densities were similar to those found in previous works for alumina bodies obtained by gelcasting using only carrageenan or agaroids,<sup>4</sup> but they tend to increase as the content of gums increases. The highest average density (>60% of theoretical) was found for the bars prepared with the A + (2)suspension, but variability was the highest and these samples presented also the largest variability in all the microstructural and mechanical parameters. In fact, large defects were found in these samples which originated during forming due to the absence of gelling agent and the need for longer residence times in the mould. The linear shrinkage on drying of the bars containing gums was much lower and the weight loss was slightly lower than that of the samples containing only carrageenan. This behaviour may be related to the synergistic interaction that causes a reduction in syneresis and consequently, greater water retention. However, the actual errors associated with the measurement of linear shrinkage are larger than the average calculated errors, because of the deformability of the bars.

Characteristic apparent stress-strain curves of samples prepared from alumina suspensions with only carrageenan, and with mixtures (1), (2) and (4) are shown in Fig. 8. Apparent Young's modulus and bend strength values are summarised in Table 2. Fig. 9 shows characteristic low magnification SEM micrographs of fracture surfaces of bend samples. Homogeneous microstructures with some residual porosity are observed for the samples containing carrageenan (Fig. 9a and b), whereas large defects were detected in the samples containing only gums (Fig. 9c), in agree-



Fig. 6. Flow curves at 60 °C of the  $Al_2O_3$  suspensions with carrageenan (A+C), with synergistic mixture (2) (A+LBG+XG), and synergistic mixture (4) (A+C+LBG+XG).



Fig. 7. Evolution of viscosity on cooling of the  $Al_2O_3$  suspensions with synergistic mixtures (2) (A+LBG+XG), and (4) (A+C+LBG+XG). (Shear rate: 5 s<sup>-1</sup>).



Fig. 8. Stress-strain curves of alumina samples with: a) carrageenan (A+C); b) mixture (1) (A+C+LBG); c) mixture of gums (2) (A+LBG+XG); and d) mixture (4) (A+C+LBG+XG).

ment with the large variability associated with the microstructural and mechanical properties of these bodies (Table 2). In all cases, the fracture occurs in the middle of the span, confirming the homogeneity of the samples.

For similar processing parameters (final content and concentration of the precursor solution of polysaccharides), the strain to fracture values of the bars containing gums were lower ( $\approx 30\%$ ) (Fig. 8) and apparent Young's modulus values were significantly higher ( $\approx 35\%$ ) (Table 2) than those corresponding to the bars with only carrageenan. Accordingly, large differences existed between the fracture surfaces of the carrageenan samples, in which numerous plastically deformed zones of  $\approx 150 \mu m$  size were observed across the whole surfaces (Fig. 10a), and samples with only gums (Fig. 9 and 10c), which presented mostly brittle fracture. In the samples containing carrageenan and



Fig. 9. Low magnification SEM micrographs of fracture surfaces of alumina green bodies prepared with: (a) carrageenan (A+C); (b) mixture (4) (A+C+LBG+XG); and (c) mixture of gums (2) (A+LBG+XG). The tension surface is located in the lower part of the micrograph.

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Composition	Linear shrinkage (%)	Weight loss (%)	Green density (% TD)	$\sigma$ (MPa)	$E_{\rm a}~({\rm GPa})$
A+C	16±1	$31 \pm 0.5$	$54.5 \pm 0.8$	$3.7 \pm 0.2$	$1.3 \pm 0.2$
A + (LBG + XG)	$5\pm 2$	$29 \pm 4$	$60 \pm 4$	$4.6 \pm 0.7$	$1.8 \pm 1.0$
A + (C + LBG + XG)	$5\pm 2$	$27.0 \pm 0.5$	$56.4 \pm 0.5$	$4.3 \pm 0.5$	$2.0\!\pm\!0.2$

Table 2 Green properties of gelcast Al<sub>2</sub>O<sub>3</sub> bodies

LBG [composition (1)], the equivalent zones were smaller ( $\approx$ 50 µm) and also spread across the whole surfaces. In the samples made from composition (4), the plastically deformed zones were the smallest (< 50 µm) and scarcely observed (Fig. 10b).

These observations indicate that, once the drying process is finished, the effect of the gums is that of stiffening the structure. Moreover, the bend strength values of the samples containing gums are also higher revealing the strengthening effect of the gums. The highest values are found for the samples prepared using only two gums, but these samples presented very high variability due to the defects (Fig. 9c) originated during casting of the high viscosity suspension. These defects will develop during firing and the reliability of the materials will decrease. In this case, the beneficial effect of the gums on green strength is tied to a decrease in the material performance and therefore, the use of two gum mixtures is not recommended. Conversely, the green parts prepared from mixtures of one or two gums with carrageenan (mixtures 1



Fig. 10. SEM micrographs of fracture surfaces of green bodies prepared with: (a) carrageenan (A + C); (b) mixture (4) (A + C + LBG + XG); and (c) mixture of gums (2) (A + LBG + XG). The tension surface is located in the lower part of the micrograph.

and 4) presented larger strengths with low variability and no defects were detected in the fracture surfaces. The samples containing only one gum exhibit some plastic deformation (Fig. 8) which will limit the machineability of the parts. In those containing two gums plastic deformation is very limited, as desired for green machining.

It has been shown before<sup>8</sup> that in samples with C + LBG the value of apparent stress ( $\sigma_a$ ) increases with increasing LBG content up to a ratio 1:1, as well as the value of apparent Young's modulus,  $E_a$ . A further increase is obtained for the mixture with xanthan gum, showing that the double synergistic effect acts by making dry bars more rigid.

All these results confirm that the synergism of carrageenan-LBG, and the double synergism carrageenan-LBG/ LBG-XG, make it possible to obtain stiff green bodies with high green strength while maintaining a relatively high green density. This might have important applications in ceramic processing, specially regarding the manufacturing of complex shaped ceramic parts that can be easily machined in the green state without extensive plastic deformation, as occurs when only carrageenan is added. Green casts were sintered at 1500 °C/2 h in air. Sintered relative density was rather similar for all the additive compositions ( $\sim$ 98%DT), and similar to that obtained by carrageenan gelation without gums. Homogeneous microstructures with some residual porosity located at triple points and inside the larger grains are obtained.

#### 5. Conclusions

Synergistic interaction of different polysaccharides has been successfully applied for manufacturing alumina parts by an aqueous gelcasting process. Locust bean gum interacts synergistically with carrageenan and with xanthan gum increasing the viscosity, gel strength and gel deformability. The viscosity increases with the content of gum.

The isolated gums do not form a rigid gel structure on cooling, but the mixture leads to a sharp increase of viscosity at ~50 °C associated with the synergistic interaction. The synergism between the three polysaccharides is demonstrated by the increase in the shift of viscosity at the  $T_{\rm g}$ .

Gelcasting on cooled moulds needs longer residence times that when carrageenan alone is used, and after demoulding a more elastic gel is formed. However, a stronger and more rigid gel is obtained after drying. The bodies containing carrageenan and both gums have a higher elastic modulus ( $\sim 2$  GPa) and also a higher green strength ( $\sim 4.3$  GPa) associated with low plastic deformation during fracture. The green density of the gelcast bodies is > 55% of theoretical and at 1500 °C/2h sintered bodies with homogeneous microstructures and a relative density of  $\sim 98\%$  of theoretical are obtained.

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