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Thermogelling polysaccharides for aqueous gelcasting—part II: influence of gelling additives on rheological properties and gelcasting of alumina

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Abstract

In the present work the influence of the addition of aqueous solutions of agar, agarose and carrageenan on the rheological properties of alumina slurries is studied. Precursor binder solutions were prepared to concentrations between 1.5 and 4 wt.% in water by heating at 92 °C. Alumina suspensions were prepared at a solid loading of 50 vol.% and heated to 60 °C. At this temperature different amounts of the starting precursor solutions of each gelling binder were added so that the final concentrations of binder were 0.25, 0.5 and 0.75 wt.% referred to dry solids. For concentrations of the precursor solution $\leqslant 2$ wt.%, the viscosity of the slurry tends to decrease when the total amount of gel increases, while for concentrations of the precursor solution $\geqslant 3$ wt.% viscosity increases with the amount of gel. This defines a yield concentration of precursor solution where the suspension properties change. Gelcasting performance is a function of slurry viscosity, gelling behaviour and time, and body deformation during drying. In general, carrageenan leads to higher shape distortion in the body. Better shape retention is achieved with precursor solutions with $\geqslant 3$ wt.% additive and total content of gel of $\geqslant 0.5$ wt.%. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Al_2O_3; Forming; Gelcasting; Rheology

1. Introduction

The technological impact of near-net shaping techniques based on aqueous slurries has been discussed elsewhere.[1–3] The main advantages of these procedures refer to the low cost of the production cycle and the possibility to minimise the machining step. Aqueous suspensions can be easily gelcast or injection moulded using thermogelling binders. In the first part of this series[4] the rheological properties, the gelling behaviour and the effect of other processing parameters (pH, shearing, temperature cycles) have been studied for aqueous solutions of three gelling binders (agar, agarose, and carrageenan). It has also been shown[5] that it is necessary to fully dissolve the binder powders by heating at temperatures between 60 and 90 °C before they are added to the ceramic slurry to improve the gelling properties, avoiding the presence of undissolved agglomerates. In this way, ceramic bodies with higher microstructural uniformity and density are obtained.

The aqueous solutions of these additives form a gel network on cooling whose strength depends on the type and concentration of the polysaccharide.[6–10] When the binder solution is added water is also incorporated to the suspension, thus decreasing the solid loading. This leads to longer drying times, larger shrinkage and lower particle packing in the green bodies. Then, concentrated solutions should be used to reduce excess of water.

In general, previous works on aqueous gelcasting have focused on the optimum conditions to obtain manageable suspensions by considering the effect of the total binder concentration. However, the way in which the additive is incorporated into the slurry has not yet been studied. Therefore, in order to optimise the incorporation of the gelling agent into the slurry either the concentration in the precursor solution or the total quantity of gel added to the suspension should be carefully controlled as both determine the viscosity and

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hence, are necessary to select the more favourable conditions for shaping.

In this work the influence of the gelling binder on the rheological properties of alumina suspensions is studied by changing both the concentration of the precursor solution and the final concentration of gel. The slips were gelcast on steel moulds and the distortion of the shape on drying was observed in order to select suitable conditions for gelcasting.

2. Experimental

As ceramic material, a high purity Al_2O_3 powder (Condea HPA05, USA) with a mean particle size of 0.35 µm and a surface area of 9.5 m^2/g was used. Ceramic suspensions were always prepared to a solid loading of 50 vol.% (80 wt.%) dispersing with an ammonium salt of a polyacrilic acid (Duramax D3005, Rohm and Haas, USA). Homogenisation was carried out by first mechanical mixing and further ball milling for 6 h using alumina balls and jar.[11] The alumina slurries were rheologically characterised at room conditions and as a function of temperature.

The gelling additives were agar (Grand Agar), agarose (Dl LE), and carrageenan (Secogel TC), all supplied by Hispanagar S.A. (Burgos, Spain). Precursor solutions were prepared by mixing the powders with deionised water to total concentrations of 1.5, 2, 3 and 4 wt.%, and dissolved by heating at 92 °C. These solutions were added in different quantities to the alumina slurries maintaining the temperature of both the ceramic suspension and the gelling solution at 60–70 °C. The total concentrations of active gelling matter added to the slurries were 0.25, 0.5 and 0.75 wt.% on the basis of dry solids. The same procedures were followed for the three gelling binders. Table 1 shows the final concentration of solids of the suspensions with different concentration of gelling binder as a function of the concentration of the precursor solution. As can be seen, the starting solid loading of 80 wt.% decreases with increasing binder addition.

The gelling behaviour was studied through rheological measurements using a rheometer Haake, RS50 (Germany) under control rate conditions. A double cone geometry was used (DC60/2°, Haake, with 60 mm in diameter and 2° cone angle). This measuring system has a covering plate that prevents evaporation and helps to maintain the temperature of the suspension. The evolution of viscosity with temperature was studied at a constant shear rate of 100 s^{-1}.

Table 1
Variation of solid content of the alumina suspension after different binder additions

Total concentration of binder (wt%)	Concentration of the precursor solution (wt.%)			
	1,5%	2%	3%	4%
	Final solid content (wt%)			
0,25 %	70,6	72,7	74,8	76,2
0,5 %	63,3	66,7	70,7	72,7
0,75 %	57,2	61,5	66,6	69,5

The differently prepared alumina suspensions were gelcast in steel moulds (dimensions 60×10×10 mm^3) which were cooled by flowing tap water. Typical gelation times were found to be 5–20 s. After that time, the cast bars were removed from the moulds and left in air for drying for 48 h. The changes of dimensions and shape of the dried samples were evaluated.

3. Results and discussion

It has been shown[5] that alumina suspensions remain stable up to temperatures of 60–65 °C, but higher temperatures promote evaporation of water and destabilisation. The gelling efficiency increases when the binders are dissolved, which requires the solutions to be prepared at around 90 °C for agaroids. For this reason the suspension of the ceramic powder and the solution of the binder must be prepared independently and mixed at 60–70 °C.

The evolution of viscosity on cooling has been studied in the range of temperatures between 60 and 25 °C for all the conditions shown in Table 1 for the three gelling binders. To illustrate the gelling behaviour of the slurries Fig. 1 shows the viscosity on cooling of the alumina slurry without binder and with 2 wt.% solution of agarose made up to a total content of 0.5 wt.%. For comparison purposes the curve of the 2 wt.% solution of agarose is also plotted. The alumina slurry without binders shows a linear trend where viscosity slightly increases on cooling as expected from the change of

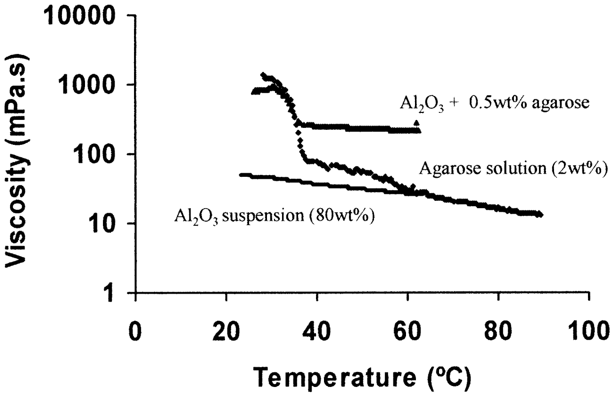

Fig. 1. Evolution of viscosity on cooling of a 2 wt.% solution of agarose, a 80 wt.% suspension of alumina, and a suspension of alumina containing 2 wt.% solution of agarose up to a total concentration of 0.5 wt.% (final solid loading, 66.7 wt.%).

viscosity of water with temperature. The solution of agarose shows that viscosity linearly increases on cooling to reach the gelling temperature, where the slope sharply increases. In the case of the alumina slurry that contains the gelling agent the viscosity remains nearly constant up to the gelling temperature.

The viscosity gap occurring on gelation is directly dependent on the rheological properties of the binders, and their relative concentrations. Fig. 2 compares the cooling behaviour of slurries containing total contents of agarose of 0.25, 0.5 and 0.75 wt.% prepared by adding different volumes of a 2 wt.% solution. The solid content strongly decreases from the starting 80 wt.% down to 62 wt.%, as increasing amounts of water are added. For this reason, viscosity decreases for increasing additions of gel above the T_g, while the maximum gel viscosity seems to increase with increasing gel content, i.e. the gel strength increases.

Similar plots can be drawn for the different concentrations of agar and carrageenan solutions. The main aspect controlling the rheology is the nature of the gelling binder. For the sake of comparison Fig. 3 shows the rheological behaviour on cooling of alumina slurries containing 0.5 wt.% of each gelling additive prepared from 2 wt.% solutions. In this case, the total quantity of binder is the same, as well as the solid and liquid contents, so the observed differences are directly related to the binder properties. The viscosity is always lower for agarose, as it was expected, because agarose is obtained by purifying agar and it has lower concentrations of salts, mainly sulphates. Although the three additives exhibit a high gelling efficiency the lower viscosity of the suspensions with agarose above the T_g makes them easier to handle prior to gelation.

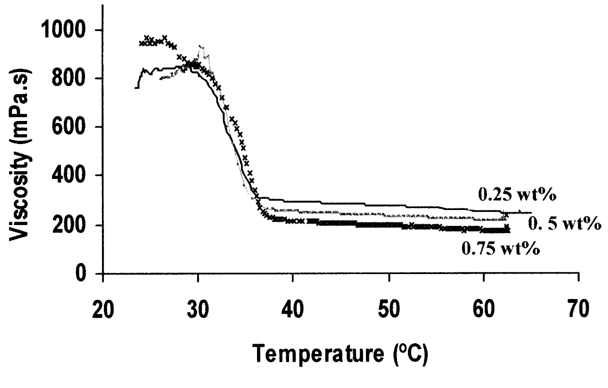

Fig. 2. Evolution of viscosity on cooling of a 80 wt.% suspension of alumina to which different amounts of 2 wt.% solution of agarose were added up to total concentrations of 0.25, 0.5, and 0.75 wt.% (final solid loadings, 72.7, 66.7, and 61.5 wt.%).

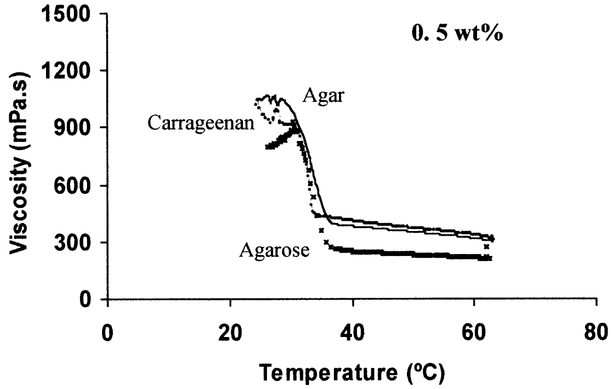

Fig. 3. Evolution of viscosity on cooling of a 80 wt.% suspension of alumina to which 2 wt.% solutions of agar, agarose, and carrageenan, were added up to a total concentration of 0.5 wt.% (final solid loading, 72.7 wt.% in all cases).

The homogeneity of the mixtures of ceramic slurry and gelling solution is essential for obtaining dense, defect-free green bodies. To avoid gelation these mixtures must be maintained at around 60 °C. Viscosity values at this temperature would give a good idea about stability, homogeneity and processability of the casting suspension. Fig. 4 plots the viscosity values of alumina slips containing different concentrations of agar added from solutions having also different concentrations. Similar plots are shown in Figs. 5 and 6 for agarose and carrageenan. All the values were obtained from the viscosity/temperature curves at 60 °C on cooling and a shear rate of 100 s^{-1}.

For agaroids two different trends can be distinguished. When the precursor solution is prepared to a concentration $\leqslant 2$ wt.% the viscosity decreases with increasing concentration of active matter. This is in agreement with the strong reduction in the solid content of the final suspensions, as can be seen in Table 1. However, for precursor solutions with $\geqslant 3$ wt.% of active gelling matter the viscosity tends to increase with increasing contents of binder in the suspension. In these series the solid loading also decreases but in a slightly lower extent. Hence, the evolution of viscosity must be now related to the rheological behaviour of the polymer

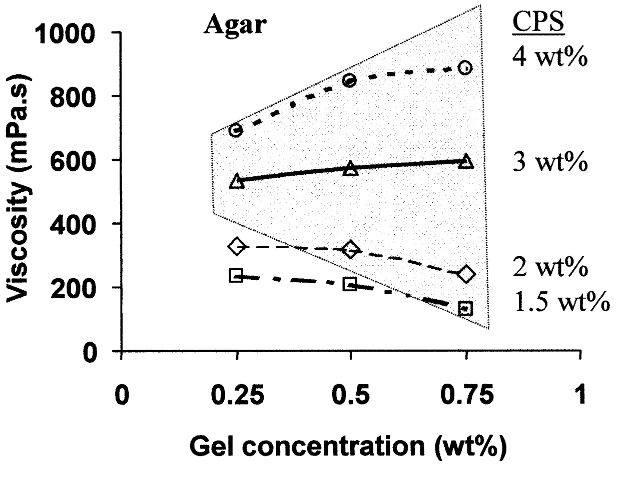

Fig. 4. Viscosity at 100 s^{-1} and 60 °C of alumina suspensions with total additions of agar of 0.25, 0.5, and 0.75 wt.%, prepared from precursor solutions with concentrations of 1.5, 2, 3, and 4 wt.%.

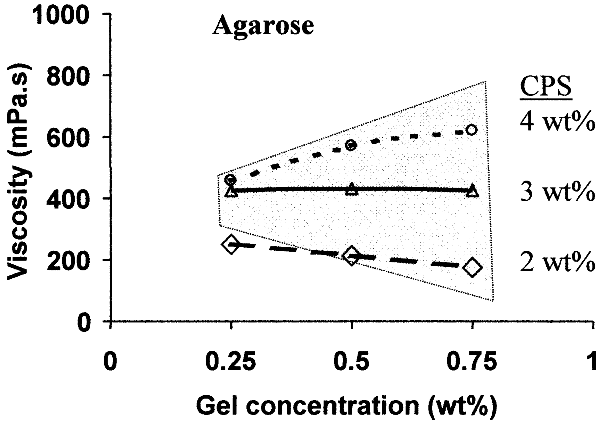

Fig. 5. Viscosity at 100 s^{-1} and 60 °C of alumina suspensions with total additions of agarose of 0.25, 0.5, and 0.75 wt.%, prepared from precursor solutions with concentrations of 2, 3, and 4 wt.%.

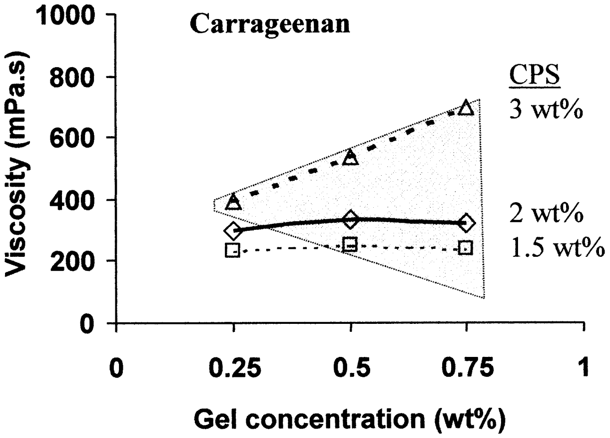

Fig. 6. Viscosity at 100 s^{-1} and 60 °C of alumina suspensions with total additions of carrageenan of 0.25, 0.5, and 0.75 wt.%, prepared from precursor solutions with concentrations of 1.5, 2, and 3 wt.%.

solution itself, where viscosity strongly increases with concentration. This demonstrates that small changes in the preparation of the casting suspension have a noticeable effect on the viscosity of the mixtures. This influences all further processing steps, including the gelling capability and the green properties of the casts.

On the other hand, carrageenan-containing slurries show a similar trend. However, the viscosity of suspensions does not appreciably change with gelling matter when this is introduced from solutions with ⩽2 wt.%, while for more concentrated solutions the viscosity increases with the concentration of gel to a higher extent than agaroids. It seems that there is a yield concentration where the behaviour changes.

The suitable conditions for gelcasting depend on both the rheological behaviour of the suspensions and the control of dimensions and shape of the obtained samples. In Fig. 7 a picture of some as-cast bars is shown. It can be observed that larger deformation was obtained

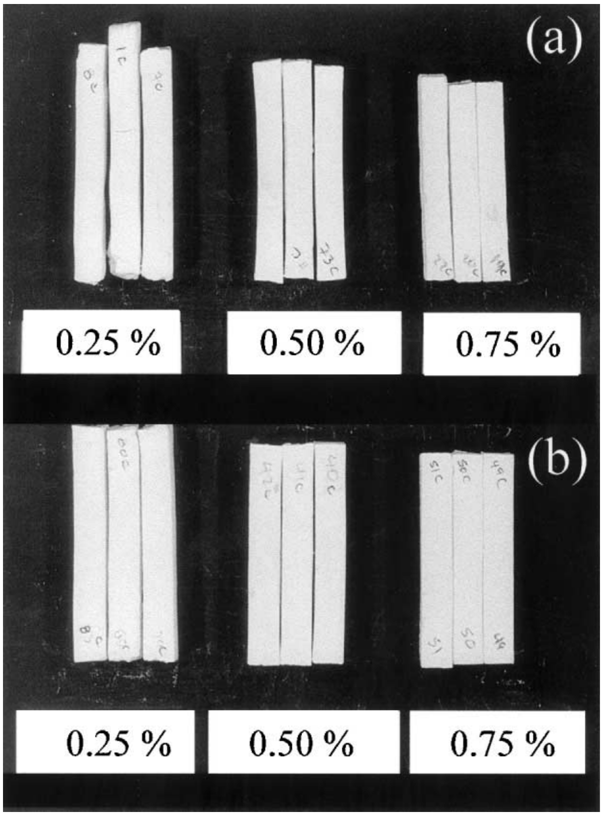

Fig. 7. Picture of as-cast bars obtained with carrageenan illustrating the effect of increasing concentration of precursor solution and the final content of gel on the shape. Precursor concentrations of 2 wt.% (a) lead to some deformation of the bars with a total gel content ⩽0.5 wt.%. For precursor solutions of 3 wt.% (b) samples do not deform.

for bars prepared from low concentrated precursor solutions and with low total content of the additive. Consequently, the compositions located within the dark areas in Figs. 4–6 were considered adequate for gelcasting, whereas those located outside of the marked areas were rejected because of the low consistency of the as-gelcast bodies or because they needed longer residence times into the moulds. For the selected compositions, linear shrinkage and weight loss were determined.

The additive solutions themselves have a very large shrinkage after drying, especially when stored in an open atmosphere due to the retained water in the structure of gel, which is later evaporated. Table 2 shows the drying linear shrinkage of selected gelcast alumina bars. Obviously, the shrinkage is lower when the solid content is higher. In the case of samples processed using agar, the shrinkage changes between 21% for a final solid content of 57 wt.% and 5.2% for a content of 76 wt.% solids when precursor solution concentration changes from 1.5 to 4 wt.% However, it can be noted that for different preparation procedures leading to the same final solid loading (e.g. 0.25%/1.5% vs. 0.5%/3% or 0.5%/2% vs. 0.75%/3%) the shrinkage is different. This illustrates the marked effect of the gel network formation

Table 2
Linear shrinkage (%) of alumina gel cast bars obtained from different precursor solutions and concentrations

Total binder concentration (wt.%)	Concentration of the precursor solution (wt.%)									
	Agarose			Agar				Carrageenan		
	2	3	4	1.5	2	3	4	1.5	2	3
0.25	11.0	7.7	8.0	12.8	11.9	6.7	5.2	–	14.3	10.5
0.5	15.0	10.7	10.1	15.5	13.9	9.4	7.3	19.6	16.2	10.8
0.75	18.0	13.0	11.6	21.0	18.0	12.7	9.0	26.2	18.8	13.0

mechanism, where water retention is a key parameter to be taken into account. The drying weight loss changes from 42 to 23% in good agreement with the water content of the suspensions. Similar values of both parameters were obtained for agarose and carrageenan samples, respectively.

These results suggest that there are two related effects in the interaction between water and polysaccharide. The fact that shrinkage depends not only on the total concentration of water but also on the concentration of the precursor solution indicates that there is a structural water related to the gelling process and a major fraction of free water in the medium, responsible for the shrinkage behaviour. As explained above, these polysaccharides are dissolved at around 90 °C and then temperature is reduced to 60–65 °C to facilitate mixing with the ceramic slurry. At this temperature the gel network has not been formed but the random-coiled chains start to develop a simple-helix structure.[7,8] This explanation is supported by the evolution of viscosity with temperature shown in Fig. 1. The agarose solution shows that the slope of the cooling curve (above the T_g) is much higher than that of the ceramic slurries. The concentration of polysaccharide in the precursor solution defines the number of contacts among the chains on cooling. For low concentrations of polysaccharide (<2 wt.%) the large volume of particles in the slurry push apart the polysaccharide coil helices, that remain isolated at the working temperatures (between T_m and T_g). For higher concentrations of polysaccharide the separation distance among coil helices is shorter, thus allowing the formation of helical aggregates. On further cooling the gel network is formed below the T_g, where the helical aggregates interact with each other to form the three-dimensional gel.

4. Conclusions

Agar, agarose and carrageenan have been succesfully used as gelling binders for ceramic suspensions providing a high consistency on cooling. In order to optimise the suitable processing conditions for any particular system (ceramic/additive/water) the total binder concentration in the ceramic slurry has to be controlled, as it determines the total solid loading of the suspension, and hence, its viscosity. However, the concentration of binder in the precursor solution also has a key role in the variation of viscosity. On the other hand, for the same final content of gelling binder, the concentration in the precursor solution has a significant influence on drying shrinkage. The increasing viscosity of the slurries with gelling agents on cooling (above the T_g) can be associated to the formation of coil helices from a random-coil structure. It has been found that for mother solutions with concentrations higher than 2 wt.% there is an interaction of coil helices to form helical aggregates.

Acknowledgements

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