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# Synergy of polysaccharide mixtures in gelcasting of alumina

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**Abstract**

The synergetic effect of mixtures of agar and galactomannan on their gelling ability was exploited to consolidate concentrated aqueous alumina suspensions by gelcasting. Aqueous polysaccharide solutions were prepared at 60°C and added to stabilised and highly concentrated alumina suspensions maintained at the same temperature. These ceramic/polymer slurries were then poured into non-porous moulds, and direct consolidation was accomplished by cooling. Rheological characterisation was used to study the influence of alumina particles on gel network and to determine the optimal processing conditions for gelcasting. Relatively low amounts of polymers ($\approx$ 1 wt%) were sufficient for consolidation, thereby avoiding the binder burnout step. High green density was achieved by this method due to the bimodal character of the starting alumina powder. However, the presence of relatively coarse particles in the starting powder exerted a deleterious effect on densification and requires the use of an external driving force to full densify the samples. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* $Al_2O_3$; Gelcasting; Microstructure-pre-firing; Rheology; Shaping; Suspensions

## 1. Introduction

Ceramic processing can be accomplished by a number of different techniques with different degrees of success in terms of reliability. In recent years it has been demonstrated that colloidal methods, i.e. methods of controlling and manipulating the forces between the particles within a liquid, have many advantages over dry processing.[1–4] Wet processing routes (slip casting, pressure casting, etc) provide the possibility of breaking up agglomerates by milling or ultrasonic treatment or by removing them and other flaw sources from the slurry by filtration, or sedimentation. In this way optimal particle packing and homogeneous green microstructures can be obtained. However, for thick pieces, traditional slip casting in plaster moulds has serious limitations in terms of maximum achievable thickness. Density gradients, heterogeneous distribution of soluble species such as binder molecules or inorganic ions,[5] and particle segregation phenomena represent the main defect sources in the slip casting of ceramics.[6] Although improvements are possible by applying pressure during the slip casting operation,[7,8] some difficulties still persist when solid complex shapes with varying thickness have to be formed. The green body consolidates first in the thinner parts, which hinder the passage of the slip to feed the thicker ones. On the other hand, injection moulding has versatility and capability of providing shape-complexity but possesses several shortcomings, mostly related with binder removal, that limit its use to the production of small and thin parts.[9]

To overcome these limitations, several concepts for transforming fluid slurries, filling non-porous moulds, into rigid bodies, without liquid removal, have been developed recently. These new forming processes include: (i) direct coagulation casting (DCC),[10] which is based on enzyme catalysed reactions to change the pH or the ionic strength; (ii) hydrolysis assisted solidification (HAS),[11] using thermally activated and/or accelerated hydrolysis of added aluminium nitride; (iii) starch consolidation,[12,13] based on gelling ability of starches in water on heating; (iv) freezing of the suspension (Quick Set),[14] (v) gelcasting, that uses in-situ polymerisation of monomers[15,16] or the methylcellulose gelation[17] that occur on heating, or the gelation of other polysaccharides on cooling[18,19] to create a three-dimensional network.

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Although all these new forming techniques have the potential to maintain in the green bodies the high degree of homogeneity achieved in the slurry, they also have some specific weaknesses. For example, the cost and toxicity of reagents in gelcasting, the relatively low wet-body strength in DCC and HAS, dimensional variations and solvent segregation on setting in freezing forming, and the low gel strength derived from polysaccharides. The formation of pores due to the burn out of starch granules in starch consolidation is not desired when full dense materials are required, but offers an interesting opportunity to design porous microstructures.[12,13]

Despite giving relatively low strength gels, polysaccharides as consolidating agents are attractive because they are safe, low cost and easily accessible polymer materials, and the processes in which they take part are entirely in aqueous media. Rives[17] utilised the reversible inverse thermal gelation of methylcellulose that occurs on heating to consolidate metal powders by injection moulding. Fanelli et al.[18] also proposed a new aqueous injection moulding process for ceramic powders based on the gelation of agar on cooling. Based on the same principle, Bendeich and Walls[19] used gellan gum to gelcast SiAlON ceramics.

The gel strength at room temperature depends on the amount and nature of polysaccharides in solution. However, from a ceramic processing point of view, the amount of polysaccharides should be kept as low as possible because of the inherent increase in slip viscosity, shrinkage of the formed bodies, and drawbacks related to burn out of organics. Therefore, to increase the performance of polysaccharides as consolidator agents in ceramic processing, investigations need to be addressed towards increasing the gel strength by playing with their nature. This approach has been followed in other fields. In fact, mixtures of polysaccharides are often used as binders in paint, texture-enhancing food additives, or matrices for controlled drug release. Their key property is the ability to form three-dimensional networks. In particular, when agarose is mixed with locust bean gum (galactomannan), a synergistic effect is usually experienced (i.e. mixtures of the two polysaccharides leads to much stronger gels than those formed from each polysaccharide alone), which leads to a more effective and economical use of these polymers.[20] In a previous report,[21] the synergetic effect given by mixing agar and galactomannan was evidenced by viscosimetric measurements on diluted suspensions of submicrometer alumina particles. Besides the higher gel strength achieved at low temperature, this mixture of polysaccharides also enabled to obtain a more stable temperature-dependence of the gel, compared to agar alone. Furthermore, this mixture of polysaccharides did not affect the fluidity of the slurries or the filling of non-porous moulds at high temperature.

The present work aims to exploit the synergetic effect of mixtures of agar and galactomannan to improve the gelling ability of concentrated alumina suspensions for direct consolidation by gelcasting. The influence of solid loading and amount of polysaccharides on the various processing stages (slip preparation, consolidation and sintering) are evaluated.

## 2. Chemistry of polysaccharides

Agar is a gelling seaweed hydrocolloid that is composed by a heterogeneous complex mixture of related polysaccharides: agarose and agaropectin. These polymers have a common backbone chain, the disaccharide repeating unit agarobiose: →3)-β-D-galactopyranosyl-(1→4)-3,6-anhydro-α-L-galactopyranose (1→, that may be esterified with sulphate. The amount of sulphate allows the differentiation between agarose and agaropectin. Agarose, the polysaccharide responsible for gelation, is a linear polymer with a mean degree of sulphate esterification of one in every 10 galactosyl residues. Agaropectin, instead, has a higher degree of sulphate than agarose, and has pyruvic acid bound to D-galactosyl residues in ketil form.[22,23] At temperatures higher than 40°C agarose exists as a random coil and, when cooled, it forms strong gels, due to the adoption of an ordered double-helix state.[23] Agar solutions present a significant hysteresis effect in respect to its thermally reversible changes from gel to solution phase as they set to firm gels at 30–40°C and, to be melted, need to be heated up to about 85–95°C.[23]

The main component of locust bean gum is galactomannan, a polysaccharide constituted by a backbone of β-(1→4)-linked D-mannosyl residues with single α-D-galactosyl residues attached to the *O*-6 of certain D-mannosyl residues. Galactomannans have the ability to interact with other gelling polysaccharides to give firmer, less brittle and more elastic gels.[24,25] In particular, galactomannans with low galactose content interact with polymers such as agarose, giving rise to an ordered binding between the ribbon-like galactomannan chains and the double helical regions of agarose.[24,26–28]

To take advantage of the characteristic hysteresis of agar and, at the same time, to increase the strength of the gel at room temperature, a binary mixture containing agar and galactomannan was used in the present work.

## 3. Experimental procedure

### 3.1. Materials and reagents

Two commercial and easily available polysaccharide powders were used: agar (Fluka, Mr 3000–9000) and locust bean gum, i.e. the galactomannan extracted from seeds of *Ceratonia siliqua* (Sigma, USA). A previous study[21] revealed that the best compromise between gel strength at room temperature and suitable fluidity at the starting temperature (60°C) was obtained from mixtures agar/galactomannan = 80/20. Since high solid loading of the suspensions is a key requirement to direct consolidate ceramic slurries, an alumina with very high particle packing ability was used (CT530 SG, Alcoa, USA). This alumina powder is characterised by a bimodal particle size distribution with particle size ratio and weight proportion between coarse and fine particles close to that ideally predicted by Furnas to achieve high packing density.[29] To disperse the alumina powder, an anionic polyelectrolyte dispersant (Dolapix CE64, Zschimmer and Schwarz, Germany) was used.

### 3.2. Slip preparation and characterisation

Aqueous polysaccharide solutions were prepared by adding 0.5, 1 and 1.5 wt% (based on liquid volume fraction) of the polymeric powders to warm water up to complete dissolution. Contemporary, a stock aqueous alumina suspension was prepared at 70 vol% solid loading by ball milling. Aliquots of this stock alumina suspension were added to the polysaccharide solutions at 60°C. The total solid loading of the alumina + polysaccharide suspensions was set at 40, 50 and 60 vol% by adding the required amounts of polysaccharide solution + water. The recipes for 100 ml of the final prepared suspensions are reported in Table 1. The resulting suspensions were kept under stirring and temperature-controlled conditions (IKA Labortechnik, Germany) at 60°C for further 2 h.

Rheological measurements were conducted (i) on polysaccharide solutions at 0.5, 1 and 2 wt% concentrations, and (ii) with alumina + 1 wt% of polysaccharides at 20, 30 and 40 vol% solid loading. A rotational CS rheometer (AR1000, TA Instruments, UK) equipped with cone and plate configuration (∅ = 4 cm, gap = 58 μm) in stainless steel was used. To minimise water evaporation, a solvent trap was used and the environment surrounding the sample was saturated with water.

Preliminary tests were run to determine the correct stress/strain range in which the oscillatory tests would be performed, i.e. the range where response of the sample was in the linear viscoelastic region. Then, temperature sweep measurements were conducted on fresh solutions and/or suspensions from 60 to 20°C (1°C/min), at a frequency of 0.5 Hz and a constant strain of ≈ 1%. Since the structure of the gel produced by such polysaccharides is not reversible,[23] i.e. when broken down they did not recover their initial structure, no pre-shear was imposed and special care was taken to reproducibly prepare the samples. To evaluate the consistency of the polysaccharide solutions and suspensions, mechanical spectra were carried out at 20°C, after temperature sweep experiments, within the frequency range 0.05–50 Hz at constant strain of ≈ 3%.

### 3.3. Preparation and characterisation of the consolidated and sintered body

For material evaluations (density and linear shrinkage), three cylinders were formed (∅ = 23 mm, thickness ≈ 8 mm) for each amount of added polysaccharides. The alumina + polysaccharide suspensions were poured into non-porous mould, previously warmed at 60°C to avoid inhomogeneous temperature distribution within the body. Then, gelation of the suspensions was allowed to by natural cooling down. At this stage, moulds were covered to minimise water evaporation and to prevent segregation phenomenon that may produce uneven shrinkage. After consolidation, the coverings were removed to allow a further shrinkage and facilitate demoulding. For comparison, three further cylinders were also formed by unidirectional slip casting by pouring the alumina suspensions (without polysaccharides), at the three solid loading tested, into plastic rings placed on a plaster mould.

The so-obtained greens were further dried in an oven at 60°C overnight and pre-sintered at 500°C for 1 h at 5°C/min to enable density measurements after burn out of the organic matter present. The pre-sintered bodies

Table 1

Recipes for the preparation of the suspensions with polysaccaridew from 100 ml of the stock alumina slip

| | | | Amount of polysaccharide mixture (wt% based on the available water) | | |
|---|---|---|---|---|---|
| | | Slip casting (g) | 0.5% (g) | 1% (g) | 1.5% (g) |
| 40 vol% | $Al_2O_3$ | 159.2 | 159.2 | 159.2 | 159.2 |
| | $H_2O$ | 60 | 60 | 60 | 60 |
| | Psacch. | – | 0.3 | 0.6 | 0.9 |
| 50 vol% | $Al_2O_3$ | 199.0 | 199.0 | 199.0 | 199.0 |
| | $H_2O$ | 50 | 50 | 50 | 50 |
| | Psacch. | – | 0.25 | 0.5 | 0.75 |
| 60 vol% | $Al_2O_3$ | 238.8 | 238.8 | 238.8 | 238.8 |
| | $H_2O$ | 40 | 40 | 40 | 40 |
| | Psacch. | – | 0.2 | 0.4 | 0.6 |

were then sintered in a Super-Kanthal furnace at 1600°C. The sintering schedule adopted was: 10°C/min from 20 to 1580°C and 5°C/min up to the sintering temperature, holding at this temperature for 2 h and free cooling down.

Relative densities and linear shrinkage of the bodies after consolidation, pre-sintering and sintering were determined either by measuring the diameter and thickness of the compacts or by using the Archimedes immersion technique in Hg. For the pre-sintered and sintered bodies, the relative density was calculated based on the theoretical density of alumina (3.98 g/cm$^3$), whereas for the green bodies the amount and the density of polysaccharides present (1.2 g/cm$^3$) was taken into account to adjust the theoretical density. Before density and shrinkage measurements, the bodies were dried in an oven at 120°C for 24 h.

## 4. Results and discussion

### 4.1. Characterisation of the suspensions

The evolutions of $G'$, $G''$ from the temperature at which the solutions/suspensions were prepared (60°C) down to 20°C are showed in Fig. 1(a) and (b), respectively. Obviously, in the high temperature range results should be regarded with care because all the analysed systems exhibit a relatively high fluidity and are outside of the linear viscoelastic region. As the temperature decreases a network structure starts to be formed allowing to extract information about the gelling behaviour.

The gelling behaviour observed is rather typical of the polysaccharide solutions (Fig. 1, dotted lines). Both, the gelling temperature (i.e. the temperature at which $G'$ sharply grows) and the elastic modulus, increase as the concentration of polysaccharide solutions increases. Furthermore, both parameters ($G'$, $G''$) show similar dependence on the temperature and concentration of polysaccharides. However, the loss modulus ($G''$) tends to be lower than the corresponding storage modulus ($G'$), except for temperatures ⩾45°C where the viscous character of the solutions predominates over the elastic one.

Fig. 1(a) and (b) also reveal that addition of alumina modifies the gelling behaviour of pure polysaccharide solutions (continuous lines). Namely, the gelling temperature and the storage/loss modulus increase when increasing the alumina volume fraction. It can be noticed that in this case $G'$ is always higher than $G''$ along all temperature range tested, indicating that the elastic character of the suspensions is dominating over the viscous one. The difference between $G'$ and $G''$ being relatively small at 60°C, increases by 1–2 orders of magnitude as the temperature decreases.

In order to characterise the composite network structure of alumina +1 wt% polysaccharide suspensions, mechanical spectra were carried out at 20°C (Fig. 2) after temperature sweep experiment. Due to the great differences in magnitude between $G'$ and $G''$, the dynamic analysis were restricted to the elastic component. In fact, under these conditions, the value of $G''$ is no longer reliable, since it depends on the instrumental

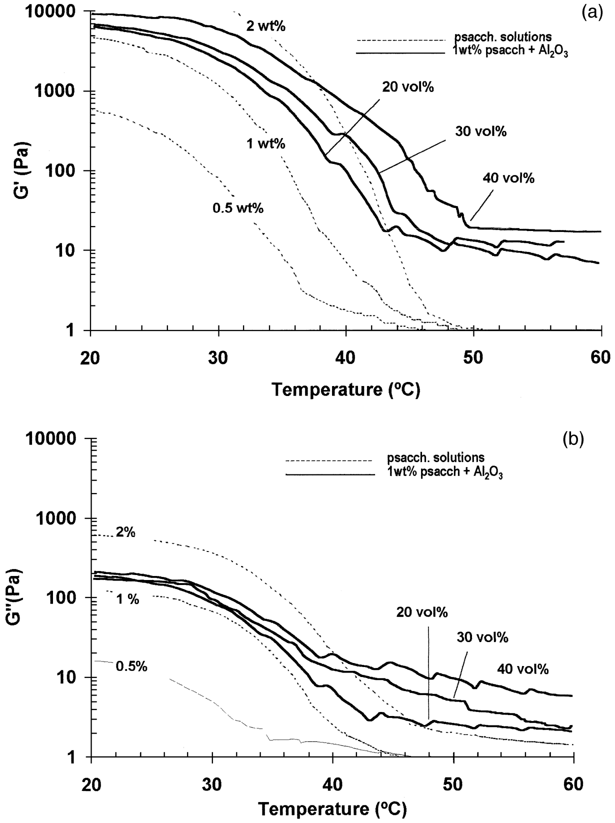

Fig. 1. Temperature sweep of polysaccharide solutions at 0.5, 1 and 2 wt% concentrations (····) and alumina suspensions at 20, 30 and 40 vol% solid loading in the presence of 1 wt% polysaccharides (——): (a) $G' = f(T)$; (b) $G'' = f(T)$.

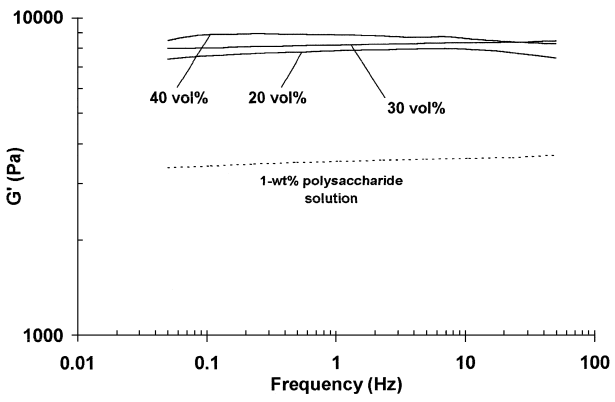

Fig. 2. Mechanical spectra at 20°C of 1 wt% polysaccharide solution (····), and alumina suspensions at 20, 30 and 40 vol% solid loading in the presence of 1 wt% polysaccharides (——).

resolution of the lag phase between sinusoidal stress and strain. Fig. 2 shows that all curves run almost parallel to the *x*-axis, a characteristic behaviour of strong gels.[30] Furthermore, addition of alumina leads to an increase of $G'$ with increasing solids loading over all frequency range tested. This increase in $G'$ can be attributed to particle network formation and agglomeration due to attractive surface forces and/or particle–polymer interactions. It is well known that particle suspensions usually exhibit viscoelastic behaviour. For a given set of experimental conditions, the elastic component increases with increasing solids loading.[31]

On the other hand, the presence of alumina particles would cause local disruptions of the gel structure and at the same time, reduce the freedom of polymeric chains for searching for an ordered binding. The affinity to form the gel network among polymer chains would be stronger than that between particles and polymers. This explains why the 2 wt% polysaccharide solution exhibits higher G than, for example, the suspension containing 40 vol% solids for $T < 38°\text{C}$. However, for long chains as those occurring in agarose-guar gum gels,[28] the possibility for each chain to adsorb onto the surface of different particles leading to bridging flocculation should be considered.[32] In fact, the hydrophilic polysaccharide chains can adsorb onto the alumina surface competing with water molecules as occurs in chromatographic partition techniques that use alumina as stationary phase.[33,34] Some competition for the surface sites might also occur between the polysaccharide chains and the polyelectrolyte used as dispersant.

### *4.2. Characterisation of the consolidated, pre-sintered and sintered bodies*

Table 2 shows the linear shrinkage and relative density of the consolidated bodies after drying and after pre-sintering. First of all, it can be noticed that relatively high green density could be achieved. This can be attributed to the high packing ability of the starting alumina powder.[29] Furthermore, both the shrinkage and relative density values are similar for consolidated (after drying) and pre-sintered bodies, likely due to the low amounts of added polysaccharides. The achievement of such a close dimensional control and shape stability during pre-sintering represents an important advantage of this direct consolidation technique when compared with the classical powder injection moulding.

Table 2 also reveals a close relationship between shrinkage after drying and after pre-sintering, relative density and solid loading. Green density increases and the shrinkage decreases with increasing solid loading, in analogy to similar results obtained by slip casting.[35–37] An increasing number of particles in suspension leads to their closer mutual approach and hinders particle segregation phenomena[6] and thus, to a higher density. Moreover, relative density decreases and the linear shrinkage increases with increasing amounts of added polysaccharides. Although, apparently contradictory, these results can be understood as follows. The higher shrinkage suffered by the sample containing increasing concentration of polysaccharides, might be attributed to the more accentuated gel structure formed, creating a finer porous network. The finer pores would exert a higher capillary suction, which implies the development of larger stresses during drying. On the other hand, the same starting suspensions are more viscous and air bubbles are likely to be entrapped. Furthermore, the volume fraction of alumina (the denser component) somewhat decreases with increasing amount of polysaccharides (Table 1). All these factors can account for increase of linear shrinkage and the concomitant decrease of green density.

Moreover, there exists the possibility for such polysaccharides to form polymer bridges by adsorption on adjacent alumina particles. The surface aluminium ions act as Lewis acid sites attracting electrons from other neighbour atoms. On the other hand, agar and galactomannan possess many hydroxyl groups along their chain. In particular, the oxygen ion possesses an extra pair of electrons, which tend to be donated. Hence, the interaction of alumina powders with polysaccharides can be viewed as a Lewis acid-base reaction occurring at the surface of the powders. Therefore, these high molecular weight polysaccharides may act as flocculating agents (bridging flocculation).[32] The bridges formed

Table 2
Density and linear shrinkage of the green bodies after drying and after pre-sintering

| | | Linear shrinkage (%) | | | | Relative density (%TD) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Slip casting | 0.5% | 1% | 1.5% | Slip casting | 0.5% | 1% | 1.5% |
| 40 vol% | Green | 0.4 | 3.9 | 3.9 | 6.1 | 73.1 | 61.3 | 58.8 | 58.0 |
| | pre-sintered | 0.4 | 3.9 | 3.9 | 6.1 | 73.6 | 61.1 | 58.8 | 57.3 |
| 50 vol% | Green | | 0.9 | 2.2 | 2.6 | | 68.3 | 63.8 | 62.8 |
| | pre-sintered | | 0.9 | 2.2 | 2.6 | | 68.3 | 63.6 | 62.1 |
| 60 vol% | Green | 0 | 0.4 | 0.9 | 1.3 | 76.4 | 71.7 | 70.6 | 69.3 |
| | pre-sintered | 0 | 0.4 | 0.9 | 1.3 | 76.6 | 70.9 | 70.6 | 69.3 |

Table 3
Density and linear shrinkage of the bodies on sintering

| | Linear shrinkage (%) | | | | Sintered density (%TD) | | | |
|---|---|---|---|---|---|---|---|---|
| | Slip casting | 0.5% | 1% | 1.5% | Slip casting | 0.5% | 1% | 1.5% |
| 40 vol% | 7.9 | 13.5 | 15.0 | 17.0 | 95.0 | 83.2 | 81.9 | 81.2 |
| 50 vol% | | 10.4 | 11.2 | 12.2 | | 91.5 | 85.9 | 88.9 |
| 60 vol% | 7.5 | 10.4 | 9.6 | 10.0 | 95.7 | 92.2 | 91.2 | 88.9 |

among alumina particles do not allow close particle packing, further accounting for the observed decrease of the green density in the presence of polysaccharides.

Shrinkage on densification and relative density of sintered bodies are reported in Table 3. It can be observed that the achieved sintered density values are rather low. This can be attributed to the presence of relatively coarse particles in the starting alumina powder. Table 3 shows that shrinkage and sintered density follow the same trend observed for the greens, indicating that particle packing influences the densification behaviour. Gelcasting always gives lower density compared with the slip casting, but the differences diminish with increasing solid loading. These results further support the hypothesis of the occurrence of bridging flocculation in the presence of polysaccharides. On the other hand, they show that optimal processing conditions require the use of high solid loading suspensions. A bimodal powder is helpful in the preparation of such suspensions but the coarser particles exert a deleterious effect on densification and require the use of an external driving force. For instance, full densification of the samples 40 vol%–1.5 wt% and 60 vol%–1 wt% was achieved by hot pressing (20 MPa) the bodies at 1550 and 1500°C, respectively.

## 5. Conclusions

The results presented in this work show that exploiting the synergetic effect of mixtures of agar and galactomannan could form gels strong enough for shaping alumina bodies by gelcasting. The process requires relatively low amounts of polymers ($\approx$ 1 wt%, based on liquid volume fraction), thereby avoiding the binder burnout step. Relatively high green density could be achieved by this method due to the bimodal character of the starting. However, the presence of relatively coarse particles exerted a deleterious effect on densification and requires the use of an external driving force to full densify the samples.

Since polysaccharides are low cost, non-toxic and easily accessible polymer materials, and that the processes in which they take part are entirely in aqueous media, the exploitation of the synergetic effect of their mixtures for direct consolidation of ceramic materials appears attractive. Investigations of other polysaccharide systems are now under way.

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## References

1. Lange, F. F., Powder processing science and technology for Increased reliability. *J. Am. Ceram. Soc*., 1989, **72**, 3–15.
2. Gauckler, L. J., Processing and properties of advanced ceramics. In *High-Tech Ceramics: Viewpoints and Perspectives*, ed. G. Kostorz. Academic Press, 1989, pp. 59–105.
3. Huisman, W., Graule, T. and Gauckler, L. J., Alumina of high reliability by centrifugal casting. *J. Eur. Ceram. Soc*., 1996, **15**, 811–821.
4. Seidel, J., Claussen, N. and Rödel, J., Reliability of alumina. 2: effect of processing. *J. Eur. Ceram. Soc*., 1997, **17**, 727–733.
5. Reed, J. S., *Introduction to the Principles of Ceramic Processing*. John Wiley and Sons, New York, 1988.
6. Ferreira, J. M. F., Role of the clogging effect in the slip casting process. *J. Eur. Ceram. Soc*., 1998, **18**, 1161–1169.
7. Moreno, R., Salomoni, A. and Stamenkovic, I., Influence of slip rheology on pressure casting of alumina. *J. Eur. Ceram. Soc*., 1998, **17**, 327–331.
8. Ferreira, J. M. F. and Diz, H. M. M., Effect of driving force on pressure slip casting of silicon carbide bodies. *J. Eur. Ceram. Soc*., 1998, **18**, 1171–1175.
9. Evans, J. R. G., Injection moulding. In *Materials Science and Technology — Processing of Ceramics*, Vol. 17A, ed. R. J. Brook. VCH, Weinheim, 1996 (Chapter 8).
10. Graule, T. J., Baaber, F. H. and Gauckler, J. L., Shaping of ceramic green compact direct from suspensions by enzyme catalyzed reactions. *cfi/Ber. DKG*, 1994, **71**, 317–323.
11. Kosmac, T., Novak, S. and Sajko, M., Hydrolysis-assisted solidification (HAS): a new setting concept for ceramic net-shaping. *J. Eur. Ceram. Soc*., 1998, **17**, 427–432.
12. Lyckfeldt, O. and Ferreira, J. M. F., Processing of porous ceramics by "starch consolidation". *J. Eur. Ceram. Soc*., 1998, **18**, 131–140.

13. Alves, H. M., Tarí, G., Fonseca, A. T. and Ferreira, J. M. F., Processing of porous cordierite bodies by "starch consolidation". *Mat. Res. Bull.*, 1998, **33**, 1439–1448.
14. Novich, B. E., Sundback, C. A. and Adams, R. W., Quickset™ Injection moulding of high performance ceramics. In *Ceramic Transactions*, Vol. 26. 1992, p. 157.
15. Young, A. C., Omatete, O. O., Janney, M. A. and Menchhofer, P. A., Gelcasting of Alumina. *J. Am. Ceram. Soc.*, 1991, **74**, 612–618.
16. Omatete, O. O., Janney, M. A. and Strehlow, R. A., Gelcasting — a new ceramic forming process. *Am. Ceram. Soc. Bull.*, 1991, **70**, 1641–1649.
17. Rives, R. D., Method of injection moulding powder metal parts. US patent 4113480, 1976.
18. Fanelli, A. J., Silvers, R. D., Frei, W. S., Burlew, J. V. and Marsh, G. B., New aqueous injection moulding process for ceramic powders. *J. Am. Ceram. Soc.*, 1989, **72**, 1833–1836.
19. Bendeich, P. J. and Walls P. A., Aqueous milling and near net shape forming of SiAlON ceramics, Proceedings of the 2nd International Meeting of Pacific RIM Ceramic Societies, Vol. 2, ed. P. Walls, C. Sorrel and A. Ruys. Australian Ceramic Society, Queensland, Australia, 1996, pp. 627–632.
20. Lundin, L. and Hermansson, A.-M., Understanding synergistic polysaccharide networks using electron microscopy and rheology. In *Food Colloids — Proteins, Lipids and Polysaccharides*, Ed. E. Dickinson and B. Bergenstahl. The Royal Society of Chemistry, Cambridge, 1997.
21. Olhero, S. M., Tarí, G., Coimbra, M. A. and Ferreira, J. M. F., Direct consolidation of alumina powders with polysaccharides. Proceedings of 2nd ESAFORM Conference on Material Forming, Guimaróes, Portugal, 13–17 April 1999, pp. 447–450.
22. Percival, E. and McDowell, R. H., Algal walls — composition and biosynthesis. In *Plant carbohydrates II — Extracellular Carbohydrates*, ed. W. Tanner, and F. A. Loewus. Encyclopedia of Plant Physiology, New Series, Vol. 13B. Springer–Verlag, Heidelberg, NY, 1981, pp. 277–316 (Chapter 12).
23. Matsuhashi, T., Agar. In *Food Gels*, ed. P. Harris. Elsevier Applied Food Science Series. Elsevier Applied Science, 1990, pp. 1–51 (Chapter 1).
24. Dea, I. C. M. and Morrison, A., Chemistry and interactions of seed galactomannans. *Adv. Carbohydr. Chem. Biochem*, 1975, **31**, 241–359.
25. Clark, A. H., Dea, I. C. M. and McCleary, B. V., Effect of galactomannan fine structure on their interaction properties. In *Gums and Stabilisers for the Food Industry — 3*, ed. G. O. Phillips, D. Y. Wedlock and P. A. Williams. Elsevier Applied Science, 1986, pp. 429–440.
26. Tako, M. and Nakamura, S., Synergistic Interaction between agarose and D-galacto-D-mannan in aqueous media. *Agric. Biol. Chem.*, 1988, **52**, 1071–1072.
27. Turquois, T., Taravel, F. R. and Rochas, C., Synergy of the agarose–carob galactomannan blend inferred from NMR and rheological studies. *Carbohydr. Res.*, 1993, **238**, 27–38.
28. Garcia, R. B., Boinis, M. and Andrade, C. T., Mechanical and morphological features of agarose-guar gum gels. *Polyner Bulletin*, 1994, **32**, 111–116.
29. Tarí, G., Lyckfeldt, O., Fonseca, A. T. and Ferreira, J. M. F., Influence of particle size distribution on colloidal processing of alumina. *J. Eur. Ceram. Soc.*, 1998, **18**, 249–253.
30. Lapasin, R., *Rheology of Industrial Polysaccharides; Theory and Applications*, Chapman and Hall, 1995, p. 398.
31. Bergstrom, L., Rheology of concentrated suspensions. In *Surface and Colloid Chemistry in Advanced Ceramic Processing*, ed. R. J. Pugh and L. Bergstrüm. Marcel Dekker, 1994, p.193.
32. Shanefield, D. J., *Organic Additives and Ceramic Processing*, 2nd edn. Kluwer Academic Publisher, 1996.
33. Pombeiro, A. J. L. O., Técnicas e Operações Unitárias em Química Industrial. Fundação Calouste Gulbenkian, Lisboa, 1980, p. 524.
34. Hardwood, L. M., Moody, C. S. and Percy, J. M., *Experimental Organic Chemistry — Standard and Microscale*, 2nd edn. Blackwell Science, MA, 1999.
35. Tarí, G., Ferreira, J. M. F. and Lyckfeldt, O., Influence of stabilisation mechanism and solid loading on colloidal processing of alumina. *J. Eur. Ceram. Soc.*, 1998, **18**, 479–486.
36. Tarí, G., Ferreira, J. M.F and Lyckfeldt, O., Influence of solid loading on drying-shrinkage behaviour of slip cast bodies. *J. Eur. Ceram. Soc.*, 1998, **18**, 487–493.
37. Ruys, A. J. and Sorrel, C. C., Slip casting of alumina. *Am. Ceram. Bull.*, 1996, **75**, 66–69.