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The rheology of alumina suspensions: influence of polysaccharides

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Abstract

We empirically correlated the rheology of aqueous suspensions of submicron alumina powder with the concentration, structure, and molecular weight of various polysaccharides that were added to these suspensions. We focus on the question of how to increase the alumina concentration to the highest level possible and still maintain a sufficient degree of plasticity to enable shape forming by plastic molding. We showed that, without polysaccharide, 30 vol.% alumina suspensions are thixotropic. These suspensions exhibited highly fluid, Bingham-plastic-like behavior upon the addition of maltodextrins and dextrans having low molecular weight. Branching of polysaccharide additives is not beneficial for the rheology of 30 vol.% alumina suspensions and 52-vol.%-alumina-filter-cakes. We observed that maltodextrins and potato dextrin (6.6 kDa) enabled filtration of plastic masses of alumina that were easily ram pressed. These materials dried into a strong, crack-free condition that could be handled without breaking. © 2002 Published by Elsevier Science Ltd.

Keywords: Al_2O_3; Plastic forming; Rheology; Saccharides; Suspensions

1. Introduction

A general goal of materials scientists is to develop a strategy for making environmentally benign (i.e. aqueous), high-density ceramic pastes which are moldable, which debind cleanly, and which are useful in forming a broad range of technical ceramics. Several studies have addressed the general problem of achieving clay-like plasticity in nonclay ceramic slurries and consolidated bodies.[1–12] Unlike clay, the simple addition of water to nonclay ceramic powder does not produce adequate moldability at sufficiently-high packing-densities for practical, manufacturing applications. As a result, these papers have explored the impact of two, general approaches to achieving highly dense, moldable pastes: the hydration-layer method and sorbate-mediated steric-hindrance. In several instances, the latter method employs nonaqueous formulations, which are costly, toxic, and therefore rather impractical for large-scale, environmentally benign manufacturing.

In contrast, water-soluble polysaccharides are environmentally benign and have been considered for a variety of ceramic shape-forming applications. For example, several authors reported the use of polysaccharides for the molding of aqueous suspensions of oxide powder,[13–19] and as homogenizers,[20] plasticizers[21], and compaction aids[22] for cement pastes. Schilling et al. reported acetalation (crosslinking) of maltodextrin binders for gelling aqueous suspensions of colloidal alumina.[23] The gelling properties of agar and agarose have been used to develop binders for aqueous injection molding of ceramics.[24–27]

Recently, we presented a series of papers on the application of oligo-and polysaccharides as plasticizers for aqueous suspensions of submicron alumina powder.[2,23,28–34] In that series of papers, we reported, among other topics, effects of polysaccharide concentration and molecular weight on the rheology of dilute suspensions containing only 20 vol.% alumina. In this paper, we introduce two new factors: (i) a lower concentration of water in suspensions, and (ii) a lower concentration of an expanded range of polysaccharide molecular weights. The purpose of the present investi-

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gation is to answer two questions: (i) how can we increase the concentration of alumina powder to the highest level possible and still maintain moldability, and (ii) how do changes in the concentration, structure, and molecular weight of the as-received polysaccharide effect the rheological properties of concentrated alumina pastes.

We performed a series of rheological experiments to answer the above questions. In addition, we performed ram pressing, a common forming method that is traditionally used only for clay-systems. Using polysaccharide plasticizers, we ram pressed dense alumina suspensions that subsequently dried and sintered without cracking. In this manner, we demonstrated the practical significance of polysaccharide plasticizers for aqueous, environmentally benign, plastic molding of nonclay ceramics. Finally, we investigated properties of green- and sintered bodies made from these moldable alumina pastes.

2. Experimental

Alumina powder (α-Al_2O_3 of equiaxial particle shape, average particle size of 0.4–0.5 μm, and specific surface area of 8.5 m^2/g) was the product of Alcoa Corporation, Bauxite, Arkansas USA. Kaolin powder (Pioneer Airfloated Clay of average particle size 1.0 to 1.2 μm) was produced by the Dry Branch Kaolin Company (Dry Branch, Georgia, USA). Three different maltodextrins were obtained from the Grain Processing Corporation (Muscatine, IA, USA), and they respectively had average molecular weights of 900, 1800, and 3600 Daltons. Potato dextrin and three different dextrans were obtained from the Sigma Corporation (St Louis, MO, USA), and they respectively had average molecular weights of 6650, 9500, 69,000, and 2,000,000 Daltons. Pullulan, having an average molecular weight of 72,500 Daltons was also purchased from Sigma Corp. Pregelatinized cornstarch and granular tapioca-starch were obtained from the Department of Food Science and Human Nutrition at Iowa State University.

Suspensions were prepared of deionized water (120 ml), sodium chloride (0.120 g), and alumina powder. Two doses of alumina powder were used in order to produce two sets of suspensions having concentrations of 20 vol.% (156 g) and 30 vol.% (200 g) of alumina. To each suspension we added predetermined doses of one of the above polysaccharides. Control samples were also prepared without any polysaccharide. All suspensions were placed in sealed, plastic bottles and agitated on a shaker for 24 h.

A single-gap couette-rheometer (RheoStress RS 75, Gebrueder Haake GmbH, Karlsruhe, Germany) was subsequently used to determine rheological properties of all suspensions at 20 °C. A predetermined volume of each suspension was analyzed by increasing the strain rate from 0 to 500 s^{-1}. Upon pouring a given suspension into the rheometer, measurements were triplicated. For each composition, we subsequently emptied the rheometer and performed a second set of measurements on a duplicate specimen. Again, these measurements were run in triplicate.

Suspensions were also consolidated by filter-pressing. The filter press was constructed of a 3.81-cm-inside-diameter teflon-tube that was fitted with filter-paper membranes allowing drainage through both the piston and the base. During filtration, we monitored the piston displacement, and full consolidation was achieved after 24 h of filtration of each suspension. The following doses of polysaccharides were used in filter-pressing alumina suspensions: (i) 1.5 and 3.0 wt.% in the case of 20 vol.% alumina suspensions, and (ii) 1.28 wt.% in 30 vol.% alumina suspensions. Suspensions of 20 vol.% kaolin without any organic additives were also filter-pressed using the procedure below.

Filtration of 30 vol.% alumina suspensions occurred at a constant pressure of 468 kPa. Immediately after filter pressing, a resulting cake was pressed out of the filter press and had the shape of a cylinder measuring 3.81 cm diameter by several centimeters in length. A wire knife was subsequently used to cut a series of six discs from the end of a given cylinder, each disc measuring 3.81 cm diameter × 1 cm tall. These discs subsequently underwent drying at 70 °C for 48 h, followed by sintering in air. The sintering process entailed heating at 10 °C/min to a maximum temperature, which was maintained for 2 h, followed by cooling to room temperature. Half of these discs were sintered to a maximum temperature 960 °C, and the remaining half was sintered to a maximum temperature of 1550 °C. Density measurements were subsequently performed on the sintered discs using the Archimedes principle.

Using a wire knife, the remaining portion of each filter-pressed cylinder was cut in half into two batches, which we will hereafter refer to as "as-filtered (AF)" and "as-filtered and kneaded (AFK)". The AF batch was gently separated by hand into small pieces and then gently hand-molded into roughly spherical shapes, each one approximately 2 cm in diameter. We should emphasize that this was a gentle, hand-molding process that persisted for no longer than 30 s on a given specimen. In contrast, the AFK batch, which was separated by hand into small pieces, was rigorously hand-kneaded for approximately 3 to 5 min. These rigorously-kneaded specimens were subsequently hand-molded into roughly spherical shapes, each one approximately 2 cm in diameter. All of the AF and AFK specimens subsequently underwent drying, sintering, and Archimedes-density measurements using the above procedures. None of the AF and AFK specimens underwent rheological measurements.

Equal volumetric portions of the above 30 vol.% alumina suspensions were centrifuged at 4000 rpm for 1 h (Beckman Corp., Fullerton, CA, USA, GS-15 with swinging rotor). The centrifugation tubes were flat-bottomed acrylic tubes measuring 2.54 cm inside diameter ×10 cm tall. The distance from the rotation axis to the bottom of the centrifugation tube was 13.17 cm. After centrifugation, the supernates were decanted from each specimen. Before removing the cakes from the centrifugation tubes, the specimens were dried at 70 °C for 48 h. These cakes subsequently underwent sintering and Archimedes-density measurements using the above procedures.

We conducted a second series of filter-pressing experiments on suspensions containing a lower concentration (20 vol.%) of alumina. The main focus of these experiments was to compare the effects of polysaccharide concentration and molecular weight on the rheological properties of filter cakes. To achieve this comparison, it is important that the alumina concentration is maintained constant in each rheological test specimen, regardless of the organic additive. Especially at high concentrations of alumina, small changes in alumina concentration can produce significant changes in viscous behaviour. Therefore, we first embarked on a series of experiments to determine the pressures needed to filter-press constant-density cakes.

Alumina suspensions (20 vol.%) were individually filter-pressed in order to produce one disc-shaped specimen from a given suspension, each disc measuring 3.81 cm diameter×1 cm tall. Three to four discs were individually filter-pressed from each slurry composition. Immediately after filter-pressing, each disc was gently removed from the filter-press and immersed in mineral oil in order to (i) obtain Archimedes-density measurements and (ii) to prevent water evaporation. The discs were immediately evaluated by equibiaxial extensional rheometry as described below.

Equibiaxial extensional rheometry entailed use of a mechanical testing machine where compressive load as a function platen displacement was continuously monitored with a computer (AccuForce EZ250 from Ametek Corp., Largo, Florida, USA).[35] Compression platen surfaces were lubricated with paraffin oil, and the platen velocity was maintained at 5.0 mm/min in each test.

Ram pressing[36] (Ram Products Inc., Columbus, OH, USA) was performed on two sets of filter-cakes that had compositions exhibiting high degrees of plasticity, based on the rheometry measurements. The main reason for these experiments was to provide a practical demonstration of the usefulness of polysaccharide additives in achieving plastic, moldable masses of alumina. For these

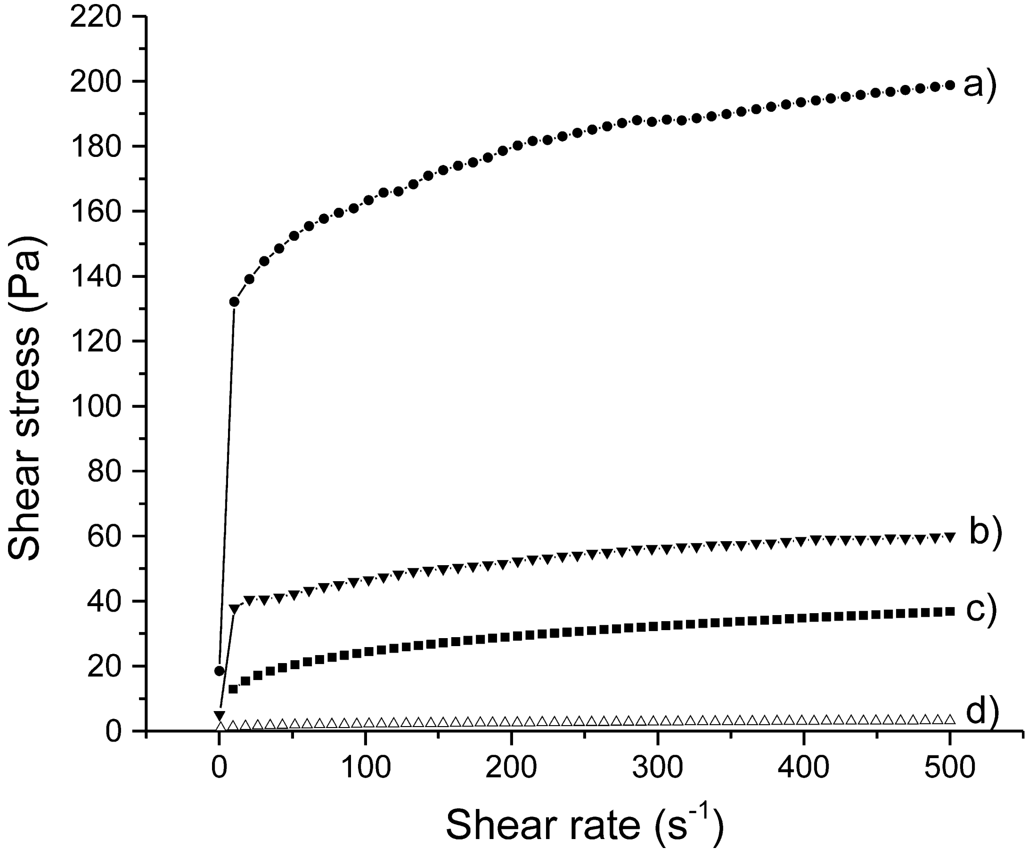

Fig. 1. Rheology of suspensions containing 20 and 30 vol.% alumina, with and without 0.9 kDa maltodextrin: (a) 30 vol.% alumina without additive; (b) 30 vol.% alumina with 0.64 wt.% of 0.9 kDa maltodextrin; (c) 20 vol.% alumina without additive; (d) 20 vol.% alumina with 1.0 wt.% of 0.9 kDa maltodextrin.

specimens, 20 vol.% alumina suspensions were filter-pressed with a constant pressure of 0.83 MPa. In this case, a larger-sized filter press was utilized, having an inside diameter of 5.08 cm. Each of the resulting cakes was removed from the filter press and had the shape of a cylinder measuring 5.08 cm diameter by several centimeters in length. Each cylinder was rigorously hand-kneaded for approximately 3 min before ram pressing. Ram pressing entailed use of porous, gypsum molds that were provided by Ram Products Inc.

Table 1
Rheological characteristics of 30 vol.% alumina suspensions containing polysaccharides[a]

Additive	τ_{50}	τ_{300}	τ_{500}	η_{50}	η_{500}
No polysaccharide	155	185	200	3	0.4
Maltodextrin 0.9 kDa	43	56	60	0.7	0.15
Maltodextrin 1.8 kDa	48	72	84	0.9	0.2
Maltodextrin 3.6 kDa	71	117	120	1.4	0.25
Dextran 9.5 kDa	100	122	128	1.9	0.25
Dextran 69 kDa	36	60	56	0.7	0.15
Dextran 2000 kDa	100	20	250	0.1	0.5
Pullulan 72.5 kDa	21	27	37	0.3	0.1
Pregelatinized starch 125 kDa	950	1000	1050	17	2.5
Tapioca starch	115	130	140	2.15	0.3

[a] The shear stress (τ_x) at a given shear rate of x^{-1} is in units of Pa, and the dynamic viscosity (η_x) at given shear rate of x^{-1} is in units of Pa s.

3. Results and discussion

Immediately after the addition of a given polysaccharide, blends of 20 or 30 vol.% alumina were pourable. Filter-pressed blends of 52 vol.% alumina primarily exhibited a paste-like consistency and were not pourable.

Earlier, we reported effects of polysaccharide concentration and molecular weight on the rheology of aqueous suspensions of 20 vol.% of the same alumina powder as in this study.[33] In that earlier paper, we evaluated a range of polysaccharide molecular weights between 0.9 kDa maltodextrin to 2000 kDa dextran. In this paper, we introduce two new factors: (1) a lower water concentration in suspensions, and (2) a lower concentration of a wider range of polysaccharides.

In the absence of polysaccharide additive, alumina suspensions exhibited thixotropic behavior, with high values of the shear stress and viscosity (Fig. 1; Table 1). One may see from Fig. 1 that the addition of 0.64 wt.% 0.9 kDa maltodextrin significantly reduces the shear stress

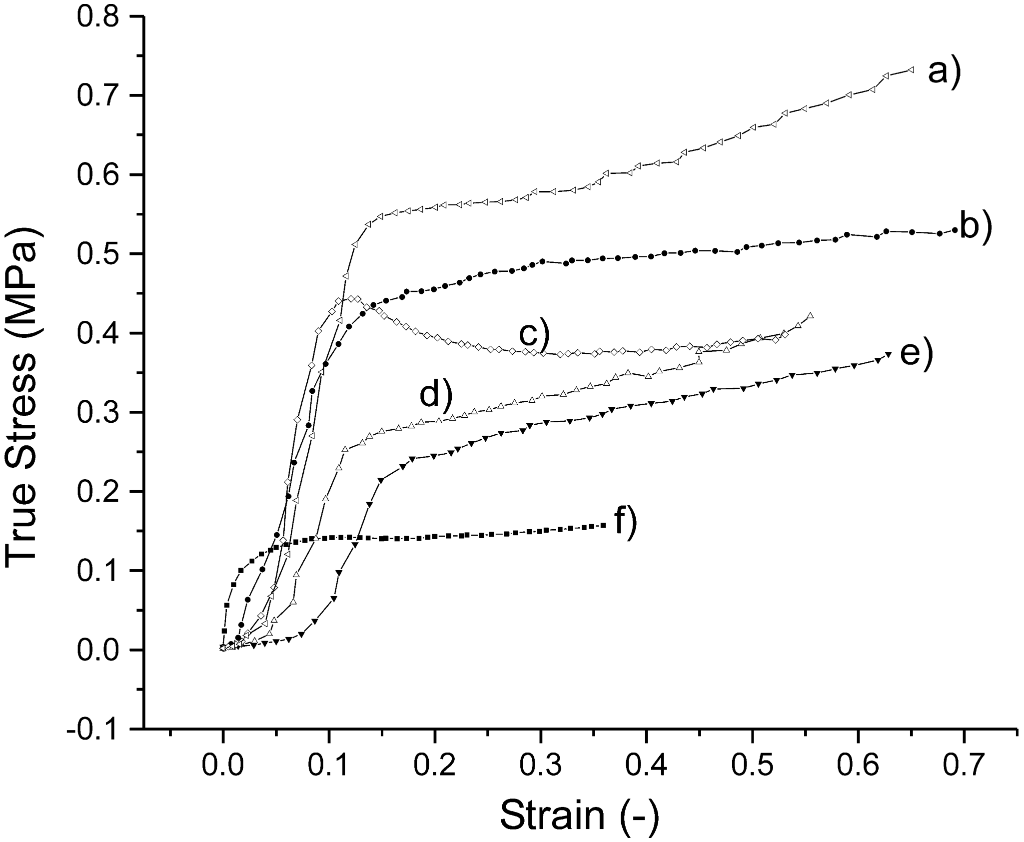

Fig. 2. Example of equibiaxial-extensional-rheometry tests on filter-cakes made of kaolin and alumina. Each filter-cake has a density of 52 vol.% solids: (a) 3.0 wt.% of 3.6 kDa maltodextrin; (b) alumina without additive; (c) 1.5 wt.% of 3.6 kDa maltodextrin; (d) 1.5 wt.% of 0.9 kDa maltodextrin; (e) 3.0 wt.% of 0.9 kDa maltodextrin; (f) kaolin.

at a given strain rate. Also shown in Fig. 1 are results from our previous studies on suspensions with higher concentrations of both water and polysaccharide.[33] In those previous studies, we observed that the addition of all polysaccharides produced a Newtonian-like condition: near-zero yield stresses and linear behaviour at higher strain rates. In contrast, all of the saccharide-containing specimens in the present study exhibited Bingham-plastic-like behaviour, i.e. they exhibited far-from-zero yield-stresses with approximately linear behaviour at higher strain rates. An example of this behaviour is shown in Fig. 1. As shown in Table 1, the polysaccharide molecular weight and structure significantly influenced this Bingham-plastic-like behaviour.

With the exception of pregelatinized corn-starch, all polysaccharides improved fluidity (Table 1). Among them, tapioca starch produced a slight improvement in fluidity, whereas the remaining polysaccharides significantly reduced the flow stress at a given strain rate. In our previous experiments, fluidity was evidently dependent only on the molecular weight of the polysaccharide.[33] In the present study, where we have lower concentrations of both water and polysaccharide, we observed effects of both the polysaccharide molecular weight and structure. In particular, for the group of maltodextrins, lower molecular weights produce more fluid behaviour. Opposite behaviour is exhibited by the group of dextrans (Table 1).

Based on the knowledge of the structure of polysaccharides, we present the following hypothesis for this behavior. Dextrans are randomly branched polyglucopyranosyl polysaccharides carrying up to 95% of their D-glucosyl units in a main chain. In other words, dextrans are essentially linear molecules, with short, random branches. It is known that the degree of branching in dextrans is not necessarily proportional to molecular weight. We speculate that this might explain the lack of a consistent trend of the shear stress with dextran molecular-weight in Table 1. The branching character also makes dextrans readily water-soluble and more bulky.[37] In consequence, dextrans, as water-demanding molecules, may cause incomplete hydration of alumina particles. This explanation is consistent with the observed behaviour of alumina suspensions containing water-soluble pregelatinized-corn-starch, which has a higher degree of branching than dextrans. Pregelatinized starch contains high molecular-weight, linear amylose (20–30 wt.%) and very-high molecular-weight, branched amylopectin (80–70 wt.%). As shown in Table 1, pregelatinized starch, having a lower molecular weight (125 kDa) than the highest dextran (2000 kDa), produced alumina suspensions with extremely low fluidity.

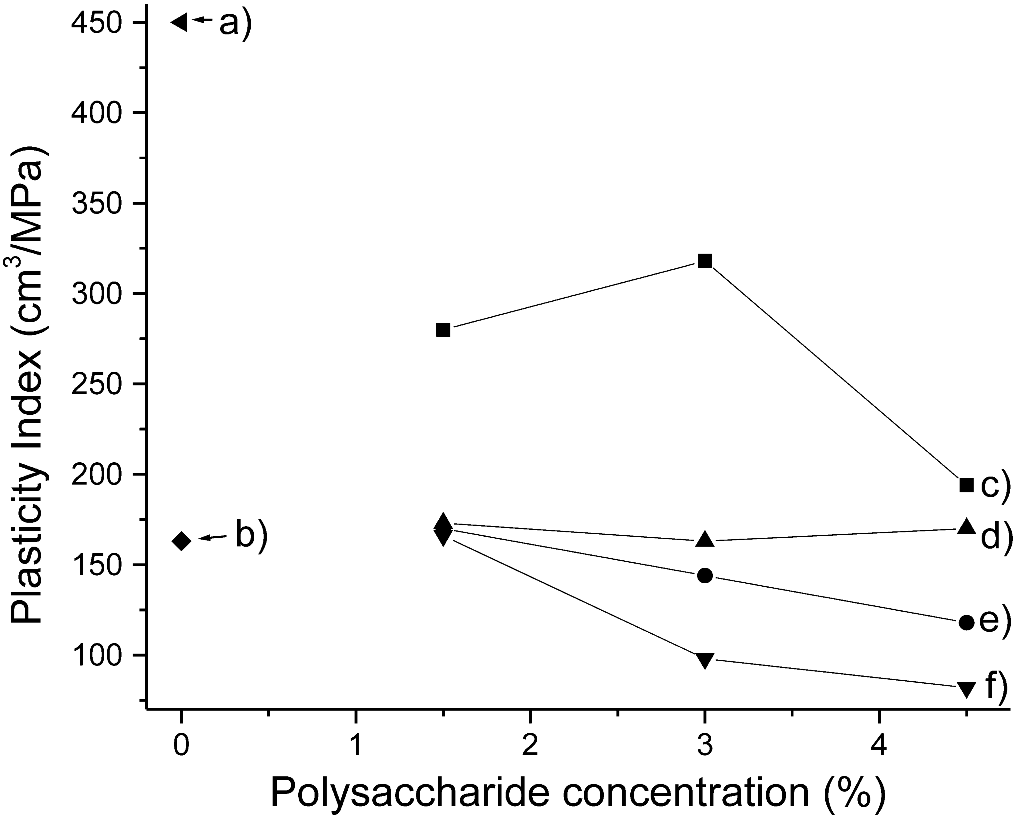

Fig. 3. Effects of polysaccharide molecular weight and concentration on the plasticity of filter-pressed alumina and kaolin. Each filter-cake has a density of 52 vol.% solids: (a) kaolin; (b) alumina without additive; (c) 0.9 kDa maltodextrin; (d) 6.6 kDa dextrin; (e) 3.6 kDa maltodextrin; (f) 72.5 kDa pullulan.

When comparing the structures of amylopectin and dextran, it is well known that amylopectin is more highly branched and has much longer branches. Branches in amylopectin occur at every 8th to 12th glucose unit in the straight chain, and terminal branches contain also 8 to 12 D-glucose units. These arguments point to branching of polysaccharides as an essential and non-beneficial factor reducing the fluidity of aqueous alumina suspensions.

Little is known regarding the structure and dynamics of polysaccharides in aqueous suspensions of concentrated oxide particles. Although chromatography studies in the polysaccharide literature clearly indicate that polysaccharides sorb on alumina,[38,39] little is known regarding the conformation of sorbed polysaccharides or the structure of the solution phase at particle-particle interfaces. In addition, the literature on the structure of maltodextrins in solutions relates to more concentrated solutions without a solid phase in suspension.[41]

Thus far, we are making the point that dextrans and potato dextrin, as water-demanding molecules, may cause incomplete hydration of alumina particles. Among all the filter cakes produced in this study, they all had 52 vol.% alumina, and only two sets of filter-cakes exhibited non-plastic, brittle behaviour: sets containing either 2000 kDa dextran or pregelatinized corn starch (125 kDa). In this manner such polysaccharides could be considered as efficient dryers of suspensions.

Tapioca starch, which has the highest molecular weight among the additives in this study, exists in granular form. In order to act via sorption to alumina particles, it should swell and gelatinize. However, to pass through both these steps, tapioca starch requires a sufficient number of water molecules. The latter might not be available in suspensions of 30 vol.% alumina, based on our recent studies of water-deficient polysaccharide systems.[40–42]

Fig. 2 presents an example of rheological measurements on pastes of alumina and kaolin. Let us first

Table 2
Shrinkage, mass loss, and concentration of alumina specimens after sintering at 960 °C

Sample		Shrinkage (%)	Mass loss (%)	Alumina concentration (vol.%)
No binder	Centrifuged	0.2	0.6	52.3
	Pressed: AF[a]			54.2
	AFK[b]			57.4
0.9 kDa Maltodextrin	Centrifuged	0.7	0.9	52.7
	Pressed: AF			54.3
	AFK			56.5
1.8 kDa Maltodextrin	Centrifuged	0.1	1.0	52.8
	Pressed: AF			53.8
	AFK			56.3
3.6 kDa Maltodextrin	Centrifuged	0.4	0.6	53.3
	Pressed: AF			53.9
9.5 kDa Dextran	Centrifuged	1.6	0.9	52.2
	Pressed: AF			53.6
	AFK			56.0
69 kDa Dextran	Centrifuged	0.3	1.1	52.2
	Pressed: AF			53.6
	AFK			56.7
2000 kDa Dextran	Centrifuged	0.8	1.1	52.7
	Pressed: AF		1.1	54.6
	AFK			55.4
72 kDa Pullulan	Centrifuged	1.2	1.1	52.5
	Pressed: AF			53.7
	AFK			56.7
Pregelatinized starch (125 kDa)	Centrifuged	0.3	1.0	52.5
	Pressed: AF			53.5
	AFK			56.2
Tapioca starch	Pressed: AF			53.7
	AFK			55.7

[a] AF, as-filtered.

[b] AFK, samples that were as-filtered and kneaded.

compare the cases of alumina and kaolin, both without polysaccharide. One may see that kaolin pastes of the same 52 vol.% concentration have higher plasticity. One may also see that the plasticity of alumina pastes improves upon the addition of 0.9 kDa maltodextrin. The concentration of this maltodextrin has a negligible effect on plasticity. In contrast, the addition of higher-molecular-weight (3.6 kDa) maltodextrin effects the plasticity in a concentration-dependent manner: the higher concentration reduces plasticity.

Fig. 3 illustrates a similar trend for the rheology of alumina pastes containing a wider range of polysaccharide molecular weights and concentrations. In Fig. 3, we defined a plasticity index as equal to the volume of a given specimen divided by the work of deformation up to an arbitrary, maximum strain of 0.2: one may see two significant trends in Fig. 3: as the molecular weight of the polysaccharide increases, the plasticity is reduced. Also, as the concentration of polysaccharide increases, the plasticity is generally reduced (except in the case of 0.9 kDa maltodextrin). Apparently, 6.6 kDa potato dextrin does not follow the former trend. However, it should be mentioned, that this polysaccharide, being the only branched molecule in Fig. 3 shows a combined effect of molecular weight and branching. This is consistent with the behaviour of suspensions characterized in Table 1: plasticity is sacrificed with increases in the water demand of the polysaccharide (due to higher molecular weight).

As shown in Table 2, hand-kneading the alumina filter cakes always increased the density by 2 to 4 vol.% alumina (at 960 °C). All samples sinter to near full density at 1550 °C, showing no deleterious effects of the polysaccharide additive. Shrinkages and weight losses, upon sintering to 960 °C, are also negligible in each case. Also shown in Table 2, the densities (at 960 °C) for a given method of consolidation do not depend on the type of polysaccharide additive. In general, centrifuged cakes exhibited slightly lower densities than filter-cakes, and this result is consistent with common knowledge of the stress state in centrifuge cakes. It should be recalled all samples in Table 2 were filter-pressed at the same applied pressure (468 kPa). Nevertheless, the densities of the resulting filter cakes were relatively independent of the suspension composition (53 to 54 vol.% alumina upon sintering to 960 °C).

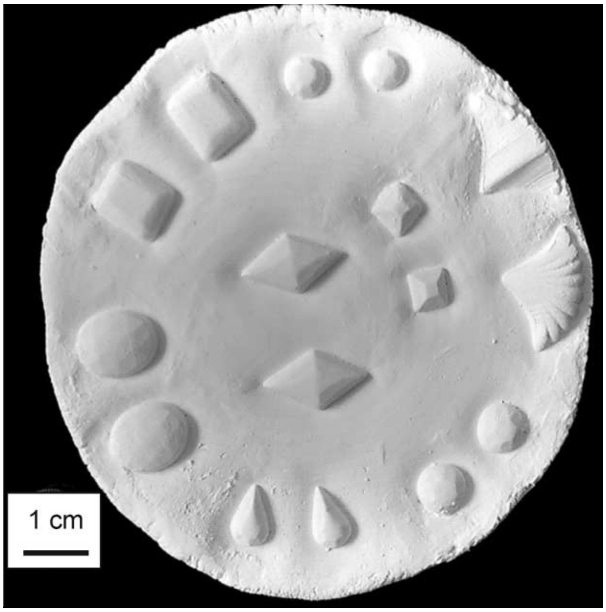

Fig. 4. The green body shown in this figure was ram-pressed using a filter-cake made from an aqueous suspension of alumina with 5.5 wt.% of 0.9 kDa maltodextrin. The shape is 5 mm in thickness and was ram-pressed with a jewelry mold.

Fig. 4 demonstrates an example of the practical usefulness of polysaccharide additives in ram-pressing alumina. We observed that all maltodextrins and 9.5 and 6.6 kDa potato dextrin enabled filtration of plastic masses of alumina that were easily ram pressed. Cakes containing 2000 kDa dextran or pullulan were too stiff to be ram pressed. These results are consistent with the equibiaxial extensional rheometry measurements in Fig. 3.

Ram-pressed green bodies could be dried into a crack-free condition and could be handled without breaking. This is consistent with our previous measurements of the strength of slip-cast alumina bodies made from similar formulations.[32,43] We interpret this strength increase as follows: in aqueous suspension, polysaccharide additive sorbs on the surfaces of each alumina particle, where this polysaccharide exists in hydrated form.[2,30] Pressure filtration and subsequent drying produces a system that is water deficient. During filtration and drying, water exists in different states: (i) it hydrates alumina particles, (ii) it resides as water condensed in capillaries between alumina particles, and (iii) it is also held to polysaccharides. As water is removed, the polysaccharide is brought to a state where it undergoes a phase transition to either an amorphous or crystalline state. Typically, the higher-molecular-weight polysaccharides tend to form amorphous structures rather than crystalline structures. We know such phase transformations occur from saturated (and thus obviously) more viscous solutions. Thus, throughout the course of dehydration, the green body is strengthened. This phenomenon is well-known and widely utilized in the food processing industry.[37] For example, dehydration of solutions of saccharides, oligosaccharides, and polysaccharides is a common procedure used to develop coatings on foodstuff surfaces in order to prevent drying-related food-spoilage. This general approach is also used to coat pharmaceuticals.

4. Conclusions

1. Without polysaccharide, 30 vol.% alumina suspensions are thixotropic. These suspensions exhibited

highly fluid, Bingham-plastic-like behaviour upon the addition of maltodextrins and dextrans having low molecular weight. Suspensions were thixotropic and highly viscous upon adding high-molecular weight dextran (2000 kDa) or pregelatinized corn starch.

2. Rheology is influenced by the polysaccharide molecular-weight and structure. Branching of polysaccharide additives is not beneficial for the rheology of 30 vol.% alumina suspensions and 52-vol.%-alumina-filter-cakes. This is due to the well-known phenomenon of polysaccharide hydration, which increases with the degree of branching. In this manner, high levels of polysaccharide hydration cause drying of filter cakes, depriving them of plasticity.

3. Kneading alumina filter cakes always increased the density by 2 to 4 vol.% alumina upon sintering to 960 °C. All samples sintered to near full density at 1550 °C, showing no deleterious effects of the polysaccharide additive.

4. We observed that all maltodextrins and potato dextrin (6.6 kDa) enabled filtration of plastic masses of alumina that were easily ram pressed. Cakes containing 2000 kDa dextran or pullulan were too stiff to be ram pressed.

5. Ram-pressed green-bodies could be dried into a crack-free condition and could be handled without breaking.

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