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MOLDING TECHNICAL CERAMICS WITH POLYSACCHARIDES

Abstract

Technical ceramics represent a large, international market dominated by electronic applications, such as insulators, substrates, integrated circuit packages, capacitors, and magnets. Typical manufacturing operations involve blending ceramic powder with organic liquids (e.g., polyethylene wax, organic solvents) to form a slurry that is molded into a three-dimensional shape before it is dried and kiln-fired. There are serious problems with the pyrolysis of these organics prior to kiln firing: (i) slow and costly heating (e.g., 200 °C for one week) is required to avoid the formation of cracks and gas bubbles, (ii) toxic fumes are emitted, and (iii) residual carbon contaminates the final microstructure. Aqueous suspending media are needed to eliminate these organic carrier liquids and evaporate safely without causing cracks, shape distortion, and microstructure contamination in sintered parts. Our experiments indicate that various dextrans and maltodextrans are useful to achieve this goal because of their natural tendency to sorb to oxide powders in aqueous suspensions. Small concentrations of these starch hydrolysis products (< 5 wt%) significantly improve molding paste rheology and enable clean pyrolysis with minimal carbon contamination of microstructures. In addition, these polysaccharides form strong, interparticle bonds after water evaporation, which enables processing of strong, crack-free ceramics before they are kiln-fired. In this paper, we begin by discussing background information on surface chemical aspects of controlling the rheology of ceramic molding slurries. Experiments involving sedimentation, filtration, extrusion, rheology, and surface chemical analysis are then presented which illustrate the practical potential of maltodextrans and dextrans as rheological modifiers in ceramic manufacturing.

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Introduction

Technical ceramics: market overview

In the past two decades, significant advances have been made in the synthesis of technical ceramic powders, which have an unprecedented degree of control over particle size, shape, and chemistry (Segal 1989 and 1996). In 1994, the market value of technical ceramic powder for electronic applications was estimated at 613 million U.S. dollars. By the year 2000, the market value of ceramic powders used in electronic applications is estimated to reach 977 million U.S. dollars as a result of 8.1 percent average annual growth (Abraham 1996).

Oxide ceramics have as much as 97% of the market for electronic ceramics. Aluminum oxide has the largest market for substrate materials that are utilized in making insulators and integrated circuits. Ceramic ferrite powders are used for making permanent and soft magnetic materials and constitute the second largest market. Ceramic titanates are the basis for electronic capacitors as well as piezoelectric components and constitute the third largest market (Abraham 1996).

Technical ceramic powders are also utilized in structural applications such as wear-resistant parts, mechanical seals, sliding bearings, cutting tool inserts, and surgical implants. Oxides, silicon carbide, and silicon nitride are three of the most common technical ceramics for structural applications. The market for technical ceramic powder for structural applications is smaller than that of electronic ceramics and was estimated at 45 million U.S. dollars in 1994 (Abraham 1996).

Plastic molding of ceramics: why polysaccharides?

Technical ceramics are typically produced by a sequential process of (i) mixing ceramic powder with an organic liquid carrier (e.g. alcohols, ketones, polyethylene wax, vinyl additives) to form a moldable slurry, (ii) forming the slurry into a three-dimensional shape (e.g., by injection molding or plastic shaping), (iii) thermal treatment to evaporate or pyrolyze the liquid carrier, and (iv) kiln firing. Large concentrations (up to 60 to 70 vol%) of the organic carrier liquid are typically needed to maintain plasticity during shape-forming. A transition to brittle, dilatant behavior occurs at lower concentrations of organic liquid (Pujari 1989; Franks and Lange 1996). Aside from the associated environmental hazards, another concern is that the diffusion of hydrocarbon liquids during heating and the gases produced during pyrolysis cause unwanted cracks and shape distortion in pre-sintered parts. Relatively long heat treatments (e.g., up to one week at $\approx 200^\circ\text{C}$) are typically needed to complete pyrolysis; more rapid heating produces internal stresses that can cause cracks and shape distortion (Stangle and Aksay 1990). In addition, evaporation and gaseous diffusion typically

remove not all of the decomposition products of pyrolysis; carbonaceous residues are frequently left behind which contaminate microstructures.

Aqueous suspending media are needed to eliminate these organic carrier liquids and evaporate safely without causing cracks, shape distortion, and microstructure contamination in sintered parts. Several industrial firms and academic researchers are currently working towards this goal. Much of this research entails fundamental studies of the surface chemical origins of the rheology of ceramic powder suspensions. In the paragraphs below, we shall review important aspects of these studies to help build an understanding of the advantages of dextrans and maltodextrins in formulating molding pastes for the ceramic industry.

Experience indicates that the simple addition of deionized water to ceramic powder results in essentially the same problem mentioned above: a dramatic reduction of slurry plasticity if the water concentration is beneath a critical value. As a result, molding becomes impossible because insufficient water tends to produce a stiff, brittle consistency. Experience indicates that this critical water concentration is usually much smaller for aqueous, clay suspensions as opposed to aqueous suspensions of oxide ceramics. Therefore, shapes that are molded from oxides are often too porous, which results in cracks, warpage, and excessive shrinkage during drying and kiln firing. In contrast, clay-based ceramics are much easier to manufacture at smaller concentrations of water, which in turn makes them less susceptible to warpage and cracks during drying. Unfortunately, clay-based ceramics are unsuitable for most consumer products that are made of technical ceramics, because they do not possess the high performance electrical, magnetic, and mechanical properties that are required.

The remarkable difference in rheology between oxides and clay minerals can be attributed to a large extent to inherent differences in particle morphology, the nature of the surface charge, and the adsorption of structured water molecules on clay surfaces (van Olphen 1977; Pashley and Israelachvili 1984; Lawrence 1978). The stacked-platelet morphology of clays, along with a superposition of long range, interparticle van der Waals (attractive) and short range, interparticle hydration (repulsive) forces, are thought to contribute to the high degree of plasticity of clays. In contrast, nonclay, technical ceramic powders do not generally have this same shape and surface-repulsion characteristic that aid particle rearrangement in clay-based systems.

Several researchers have recently shown that the key to improving the plasticity of concentrated suspensions of nonclay ceramic powders is to develop a weakly-flocculated state by coating powders with a substance producing a „clay-like” superposition of interparticle, long-range attraction and short-range repulsive forces. Two general methods are reported: (i) the hydration-layer approach (Velamakanni et al. 1990 and 1994; Chang et al. 1991 and 1994 a and b; Luther et al. 1994; Franks et al. 1995; Franks and Lange 1996) and (ii) adsorbate-mediated steric-hindrance (i.e., the creation

of a steric adlayer that inhibits complete mutual approach of individual particles). Before presenting our research, we shall briefly mention previous studies on rheological effects of adsorbate-mediated steric hindrance, studies that have led to the current interest in the use of polysaccharides for ceramic molding.

Yin et al. (1988) first introduced the method of weak-flocculation by adsorbate-mediated, steric-hindrance and reported the formation of high-density, low-viscosity suspensions with polymethacrylates adsorbed on alumina powders suspended in heptane or paraffin oil. Schilling (1992) and Bergström et al. (1992) subsequently reported significant improvements in the packing densities of centrifuged suspensions in which short-range, steric-repulsion forces were established by the adsorption of fatty acids to alumina powders suspended in decalin. Kramer and Lange (1994) performed similar experiments with alcohols adsorbed on silicon nitride powders suspended in an organic solvent.

More recent studies focused on developing aqueous analogs to the method of weak-flocculation by adsorbate-mediated steric-hindrance, analogs producing highly-concentrated and highly-plastic suspensions of oxide powders without the practical concerns of the organic solvents used in the studies mentioned above. For example, Leong et al. (1993) reported significant reductions in the viscosities of aqueous suspensions of concentrated zirconia by establishing short-range, steric repulsion through the adsorption of anionic molecules (sulfate, various phosphates) and simple, organic-acid anions (lactate, malate, and citrate). Luther et al. (1995) reported similar results by the use of ammonium citrate additives in aqueous alumina suspensions. Although focused on interparticle dispersion and not weak flocculation per se, there are also excellent reports on the use of sorbed-polyelectrolytes in the preparation of highly concentrated and dispersed, aqueous alumina suspensions (Shanefield 1995; Hidber et al. 1996). In addition, Chan and Lin (1995) reported significant reductions in viscosity by the adsorption of steric acid onto alumina powder surfaces in paraffin/polypropylene suspensions.

More recently, Schilling and co-workers (Schilling et al. 1995; Goel et al. 1996) reported significant improvements in the consolidation and rheology of aqueous, filter-pressed suspensions of submicron alumina powder, weakly-flocculated suspensions that were prepared with maltodextrin. It was reported that these suspensions exhibited a high degree of „clay-like” plasticity based on measurements of equibiaxial extensional rheometry. Schilling et al. (1998a) then performed surface chemical experiments to analyze the mechanism of enhanced fluidity caused by one, model polysaccharide: a commercially available maltodextrin having an average molecular weight of 3,600 Daltons. It was concluded that this mechanism primarily entails reduction of interparticle attraction by adsorbate mediated steric hindrance rather than double-layer, interparticle repulsion. Another benefit of this maltodextrin is that, during drying, it acts as

a binder to strengthen ceramic bodies (Schilling et al. 1998 b). We will highlight some of the results of these earlier studies in the paragraphs below. In addition, we will present new experimental data on the effects of polysaccharide molecular weight and concentration on suspension rheology and the strength of dried ceramics.

Finally, we should mention that there are a few publications on the use of different polysaccharides for ceramic processing (Sarkar and Greminger 1983, Fanelli et al. 1989; Shanefield 1995; Dmitriev et al. 1990; Bonomi et al. 1989; Mach et al. 1988; Panda et al. 1988). In fact, a broad range of polysaccharides are commonly utilized as additives for aqueous suspensions of colloidal, oxide powders in other applications including papermaking, mineral separation, and treatment of chemical waste (Tomasik and Schilling 1998 a and b).

Experimental procedure

Suspensions were prepared with deionized water and α -Al₂O₃ powder having an equiaxed particle shape, an average particle size of 0.4 μm , and a specific surface area of 8.5 m² per gram (A-16 SG, Alcoa Corporation, Bauxite, Arkansas, U.S.A.). Kaolin suspensions were prepared with deionized water and Pioneer Airfloated Clay (Dry Branch Kaolin Company, Dry Branch, Georgia, U.S.A.), having an average particle size of 1.0–1.2 microns according to the supplier. The majority of the experiments below were conducted using a single, commercially-available maltodextrin, which we shall refer to as maltodextrin 040 (Maltrin 040, Grain Processing Corp., Muscatine, Iowa, U.S.A., average molecular weight 3,600 g/mole; average degree of polymerization 22.1). Chromatography measurements by the manufacturer revealed the following composition of maltodextrin 040: (i) 85% maltodextrins having a degree-of-polymerization greater than 10 and (ii) a 15% concentration of shorter chain maltodextrins, oligo- and monosaccharides. The manufacturer also reported that the dextrose equivalent value of maltodextrin 040 was 5.

Commercially-available maltodextrins and dextrans having a range of average molecular weights from 900 to 63,000 Daltons were used in the rheology experiments below (Table 1). Maltodextrin 100 and 200 were provided by the Grain Processing Corporation as described above. Four different dextrans, D1, D2, D3, and D4, were provided by Sigma Chemical Company of St. Louis, Missouri, U.S.A. The average molecular weight of these polysaccharides is listed in Table 1 and is based on chromatography measurements reported by each manufacturer. Dextrans, pullulan (Sigma Chemical Company, St. Louis, Missouri, U.S.A.), and soluble starch (Difco Corporation, Detroit, Michigan, U.S.A.) were used in the mechanical properties experiments below.

Suspensions were prepared by simply adding alumina powder to an aqueous solution of a given polysaccharide. In some instances, the solutions contained 0.01 M

NaCl. Each suspension was then sonicated for approximately two minutes using a sonifier with a 0.25 inch horn (CV17 Vibracell, Sonics and Materials Inc., Danbury Connecticut, U.S.A.). The sonicator was operated at between 60 to 80% of the maximum power output of 600 W. Suspensions were then poured into sealed, plastic bottles and placed on a shaker for 24 hours.

Table 1

Average molecular weights of polysaccharides

Specimen	Average Molecular Weight (Daltons)
Maltodextrin 200	900
Maltodextrin 100	1800
Maltodextrin 040	3600
Dextrin D1 (potato)	6650
Dextrin D2 (corn)	6450
Dextrin D3 (corn)	15,000
Dextrin D4 (corn)	63,000

Sedimentation, filtration, and extrusion

Gravity sedimentation experiments were performed to analyze the effects of the maltodextrin 040 concentration on the degree of consolidation (Schilling et al. 1998a). Each suspension was prepared with an initial volume fraction of alumina of $\phi_0 = 0.15$ and a zero total concentration of NaCl. One hundred milliliters of a given suspension were added to a 100 ml graduated cylinder (Pyrex glass), and the sediment height was recorded as a function of time. Each graduated cylinder was sealed to minimize evaporation.

We also compared the filtration behavior of the following suspensions: (i) alumina with 0.03 grams of maltodextrin 040 per gram of Al_2O_3 , (ii) flocculated alumina near the isoelectric point without maltodextrin and (iii) kaolin without maltodextrin. Each suspension was prepared with a solids volume fraction of $\phi_0 = 0.2$ and a zero total concentration of NaCl. In case (ii) above, NH_4OH was added to suspensions to raise the pH to 8.6. In case (iii) above, kaolin powder was simply added to deionized water and then stirred for 2 hours before filtration (Schilling et al. 1998a).

Each suspension was poured into a filter-press that was precision machined from an acrylic tube (5.08 cm inside diameter) fitted with filter paper membranes and a porous, polyethylene piston. The applied pressure remained constant, and the movement of the piston was monitored as a function of time. In each filtration experiment, a single, liquid-saturated cake was removed from the filter press after the piston stopped

moving, and its green density was immediately analyzed by an oil-immersion technique based on the Archimedes principle (Schilling et al. 1995; Goel et al. 1996). Three specimens of each composition were filter-pressed and evaluated by this procedure in order to confirm repeatability of the packing-density measurements.

Liquid-saturated filter-cakes were examined by extrusion measurements and Benbow analysis (Schilling et al. 1998a; Benbow et al. 1987 and 1989). We performed these experiments with a stainless steel, piston extruder having a barrel diameter, D_o , of 12.7 mm. Square-entry dies of circular crosssection were used with die-land diameters, D , of 1 and 2 mm and die-land lengths, L , of 10 and 15.8 mm. L/D ratios of 5:1, 7.9:1, 10:1, and 15.8:1 were obtained.

The extruder was manually filled with a given filter cake and placed in mechanical testing machine, which operated in the compression mode and subjected the piston to a constant axial velocity. Extrusion data were fitted to the Benbow equation, which describes the relationship between the piston velocity and the pressure drop, both in the die-entry region and in the die land (Benbow et al. 1987 and 1989):

$$P_{tot} = \frac{4F}{\pi D^2} = P_{de} + P_{dl} = 2 \ln \frac{D_o}{D} [\tau_b + k_b V^n] + 4 \frac{L}{D} [\tau_f + k_f V^m]$$

In this expression, P_{tot} is the total extrusion pressure, P_{de} is the pressure drop in the die entry region, P_{dl} is the pressure drop in the die land, V is the velocity, τ is the yield strength, k is a constant, the subscripts b and f refer to the body and the die-land slip film, respectively, and n and m are the shear-thinning exponents for the body and film, respectively. In all experiments, we used the Benbow assumption that $m = n = 1.0$ (Benbow et al. 1989).

Rheology studies

Experiments were performed to determine the effects of the polysaccharide concentration and molecular weight on rheological properties (Sikora et al. 1998). Stock solutions of deionized water, 0.01 M NaCl, and varying concentrations of a given polysaccharide were initially prepared. A weighed amount of alumina powder ($\phi_o = 0.2$) was then added to each solution, followed by 24 hours of shaking in sealed, plastic containers.

Rheological measurements were performed at room temperature with a computer-controlled rheometer (RheoStress RS 75, Gebrüder Haake GmbH, Karlsruhe, Germany) having a double-gap cylinder (DG 41; DIN 54453). Each specimen was subjected to an increasing shear rate starting at 1 s^{-1} and ending at 500 s^{-1} . The shear rate was subsequently swept back to 1 s^{-1} . This process of sweeping the shear rate up and down was subsequently repeated on the each specimen two more times in order to ver-

ify repeatability. In addition, we verified repeatability by performing rheological measurements on two additional specimens of each composition. A total of 87, separate specimens were analyzed in the rheometer.

Rheological measurements were expressed in terms of the shear stress τ as a function of the shear rate $\dot{\gamma}$. These measurements were fitted to the Herschel-Bulkley model $\tau = \tau_0 + K \dot{\gamma}^n$ using a computer (Steffe, 1996). In this expression, τ_0 is the yield stress, K is the consistency coefficient, and n is the flow behavior index. This model is convenient, because it describes the rheological behavior of a broad range of fluids that are either Newtonian ($n = 1$), shear-thinning ($0 < n < 1$), or shear-thickening ($1 < n$). A computer was used to statistically analyze the parameters τ_0 , K , and n for as a function of the polysaccharide concentration and molecular weight (Sikora et al. 1998).

Surface chemical analysis

In an earlier study, we performed sorption and acoustophoresis measurements to study whether the enhanced rheological behavior of maltodextrin-alumina suspensions was attributed to adsorbate-mediated steric hindrance, electrostatic, interparticle repulsion, or both (Schilling et al. 1998a). Sorption isotherms measurements entailed centrifugation of aqueous suspensions prepared with varying concentrations of maltodextrin 040. Maltodextrin concentrations in centrifuged supernatants were measured spectrophotometrically by the addition of 1 ml of 5% phenol and 5 ml of concentrated sulfuric acid to 1 ml of the maltodextrin solution to form hydroxymethyl furfural, which strongly adsorbed at 488 nm (Dubois et al. 1956). The Smoluchowski zeta potentials of several suspensions were calculated using measurements of the electrokinetic sonic amplitude as a function of frequency (AcoustosizerTM, Matec Applied Sciences Corp., Hopkinton, Massachusetts, U.S.A.). Suspension preparation entailed use of procedures where we varied the maltodextrin 040 concentration and the pH by the dropwise addition of reagent grade HCl or NH₄OH. All suspensions were prepared at 0.01 M NaCl and $\phi = 0.2$.

Mechanical properties

Experiments were performed to determine the effects of the polysaccharide molecular weight and concentration on the tensile strength of molded alumina specimens. These specimens were prepared using suspensions containing $\phi_0 = 0.2$ alumina, 0.01 M NaCl, and varying concentrations of a single type of polysaccharide. Several types of polysaccharide were investigated, including soluble starch, pullulan, dextrans, and maltodextrins. Each slurry underwent 24 hours of shaking in a sealed, plastic bottle. Slip-casting was subsequently used to prepare disc-shaped specimens (diameter ~ 1.3 cm and thickness ~ 0.25 cm) for mechanical strength measurements. Slip casting is

a common, ceramic molding process that entails pouring a suspension onto gypsum mold (Aksay and Schilling 1984). Capillary suction of the gypsum serves to consolidate the suspensions by filtration (gypsum contains fine pores that are much smaller than the alumina powder). Each cast specimen was dried by storing at room temperature for one week prior to mechanical testing. The tensile strength of each specimen was measured by the diametric compression method (Bortzmeyer 1992). At least 5 measurements of tensile strength were performed on specimens of each type.

Experimental results

Sedimentation, filtration, and extrusion

Significant increases in sediment density resulted after adding small amounts of maltodextrin 040 to suspensions of alumina powder ($\phi_0 = 0.15$) and deionized water (Table 2). The simple addition of alumina powder to deionized water without maltodextrin resulted in a strongly flocculated condition and the formation of a low-density sediment ($\phi = 0.18$). The alumina volume fraction sharply increased from $\phi = 0.25$ to 0.47 as the maltodextrin concentration increased from 0.01 to 0.06 grams of maltodextrin 040 per gram of Al_2O_3 .

Volume-averaged densities of liquid-saturated filter-cakes are shown as a function of the consolidation pressure in Table 3. Suspensions of strongly-flocculated alumina near the isoelectric point without maltodextrin (pH 8.6) exhibited the lowest, alumina volume-fraction of $\phi = 0.49$ when consolidated at a pressure of only 0.54 MPa. A much higher pressure of 3.5 MPa was needed to raise the alumina volume-fraction of this same slurry system to $\phi = 0.57$. In contrast, kaolin cakes exhibited a solid-volume-fraction of $\phi = 0.6$ when consolidated at a pressure of only 0.54 MPa. At the same, low consolidation pressure of 0.54 MPa, maltodextrin-alumina cakes exhibited a slightly lower, alumina volume-fraction of $\phi = 0.57$.

Table 2

Alumina sediment densities ($\phi_0 = 0.15$)

Maltodextrin 040 Concentration (g/g Al_2O_3)	Volume Fraction Alumina ϕ
0	0.18
0.01	0.25
0.03	0.43
0.06	0.47
0.09	0.40

Table 3

Filter-cake properties ($\phi_0 = 0.2$)

Suspension type	Solids volume fraction, ϕ	Consolidation pressure, MPa
Al ₂ O ₃ , pH 8.6	0.49	0.54
Al ₂ O ₃ , pH 8.6	0.57	3.5
0.03 g maltodextrin / g Al ₂ O ₃	0.57	0.54
Kaolin	0.60	0.54

As shown in Table 4, strongly-flocculated alumina suspensions without maltodextrin at pH 8.6 displayed the most „clay-like” extrusion at an alumina volume-fraction of $\phi = 0.49$: they exhibited yield stresses and velocity factors that were similar to those of the kaolin suspensions (Table 4). Raising the alumina concentration of the pH 8.6 suspensions to $\phi = 0.57$ produced specimens that were too stiff to be extruded. Alumina specimens that were prepared with 0.03 grams of maltodextrin 040 per gram of Al₂O₃ (at the same alumina concentration of $\phi = 0.57$) were easily extruded, although they exhibited higher yield stresses than all of the other systems in Table 4. In addition, the alumina specimens containing maltodextrin had yield stresses and velocity factors that were several times higher than the corresponding values for kaolin.

Table 4

Extrusion summary

Specimen type	Solids volume fraction, ϕ	Benbow parameters			
		τ_b (MPa)	k_b (MPa·s·m ⁻¹)	τ_f (MPa)	k_f (MPa·s·m ⁻¹)
Kaolin	0.60	0.42	3.7	0.03	0.69
Al ₂ O ₃ , pH 8.6	0.49	0.34	2.8	0.05	1.0
Al ₂ O ₃ , pH 8.6	0.57	*	*	*	*
Al ₂ O ₃ + 0.03 grams maltodextrin/gram Al ₂ O ₃	0.57	1.72	16.4	0.13	4.26

* These samples were too stiff to be extruded.

Rheology studies

In the absence of polysaccharide, alumina suspensions near the isoelectric point commonly exhibited pseudoplastic behaviour (Figure 1). Herschel-Bulkley parameters for these suspensions are: $0.2 < \tau_0 < 3$ Pa, $6.1 < K < 10.18$ Pa·s^{*n*}, and $0.18 < n < 0.25$. The addition of nearly all of the polysaccharides in this study dramatically suppresses this pseudoplastic behaviour. Small amounts (a few weight per cent) of these polysac-

charides typically produce a major reduction in the flow stress along with a transition from pseudoplastic to Newtonian-like behaviour. For example, Figure 1 illustrates this trend for a suspension containing 0.03 grams of maltodextrin 040 per gram of alumina. In this case, Herschel-Bulkley parameters are as follows: $0.01 < \tau_0 < 0.03$ Pa, $0.004 < K < 0.005$ Pa.sⁿ, and $0.89 < n < 0.95$.

As shown in Figure 2, the consistency coefficient K rapidly decreased upon the addition of each of the polysaccharides in this study. For example, all of the polysaccharides except D4 exhibit a sharp reduction in K as the solution concentration increased from 0 to 0.01 gram of polysaccharide per gram of alumina. For these specimens, $K \sim 0$ for all of the higher concentrations of polysaccharide. In contrast, the addition of the polysaccharide with the largest molecular weight (D4) produces more of a gradual decrease in K as the polysaccharide concentration increases. In this case, K approaches zero only when the concentration of D4 exceeds 0.05 g/g alumina.

Surface chemical analysis

Let us define c_o as the maltodextrin 040 concentration of a given, stock solution without adding $\phi_o = 0.2$ alumina powder, c_a as the equilibrium concentration of maltodextrin 040 sorbed to alumina after adding $\phi_o = 0.2$ alumina to the stock solution, and c_f as the equilibrium concentration of free maltodextrin 040 in solution after adding $\phi_o = 0.2$ alumina to the stock solution. We showed in an earlier publication that maximum sorption is achieved at a minimum c_o of 0.02 grams of maltodextrin 040 per gram of alumina (Schilling et al. 1998). Under these conditions when $c_o = 0.02$ grams of maltodextrin 040 per gram of alumina, approximately 50% of c_o sorbs to alumina, whereas the other 50% remains in solution.

At pH 10 and $c_o = 0.01$ grams of maltodextrin 040 per gram of alumina, acoustophoresis indicated a Smoluchowski zeta potential of -7.6 mV (Table 5). At the same pH of 10, a larger c_o of 0.03 grams of maltodextrin 040 per gram of alumina increased the zeta potential to -3.6 mV. At a lower pH of 7, we observed a Smoluchowski zeta potential of +8.7 mV without maltodextrin. Also at pH 7, c_o of 0.01 grams of maltodextrin 040 per gram of alumina resulted in a Smoluchowski zeta potential of +2.5 mV. Also at pH 7, a larger c_o of 0.03 grams of maltodextrin 040 per gram of alumina reduced the Smoluchowski zeta potential to +1 mV.

Since we previously observed maltodextrin sorption to alumina, it is not surprising that acoustophoresis revealed a decreasing surface charge at pH 10 upon raising c_o from 0.01 to 0.03 grams of maltodextrin 040 per gram of alumina. We should mention that a pH of 9.7 was routinely observed in alumina – maltodextrin 040 slurries that were used in all the sedimentation, filtration, and rheology experiments above. Acoustophoresis revealed a relatively small zeta potential of -3.6 mV under similar conditions (pH 10, $\phi = 0.2$, 0.01 M NaCl, $c_o = 0.03$ grams of maltodextrin 040 per gram of

alumina). This small potential suggests that electrostatic, interparticle repulsion is not a primary mechanism for the increased consolidation and fluidity upon adding maltodextrin to alumina. Instead, sorption data suggest that sorbate-mediated steric hindrance appears to play a major role in this regard.

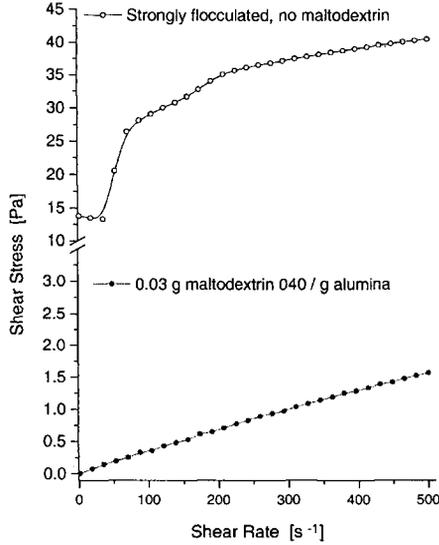


Fig. 1 Aqueous suspensions of 20 vol% alumina exhibit a transition from strongly-flocculated, pseudo-plastic behavior to a Newtonian-like state upon the addition of 0.03 grams of maltodextrin 040 per gram of alumina (Sikora et al. 1998).

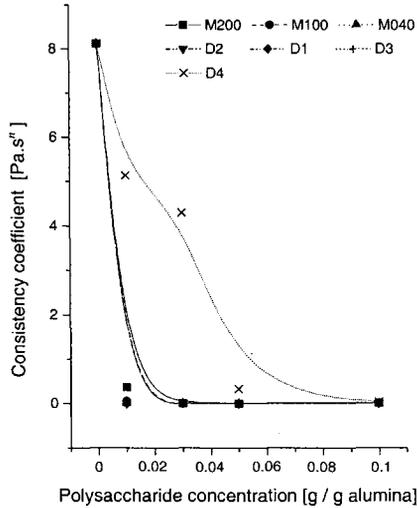


Fig. 2 Increasing the polysaccharide concentration significantly enhanced suspension fluidity, as apparent from the reductions in consistency coefficient. The largest molecular weigh dextrin (D4) was least effective in this regard (Sikora et al. 1998).

Table 5

Acoustophoresis measurements

Maltodextrin concentration (g/g Al ₂ O ₃)	pH	Mean Smoluchowski zeta potential (mV)
0.01	10	-7.6
0.03	10	-3.6
0.01	7	2.5
0.03	7	1.0
0	7	8.7

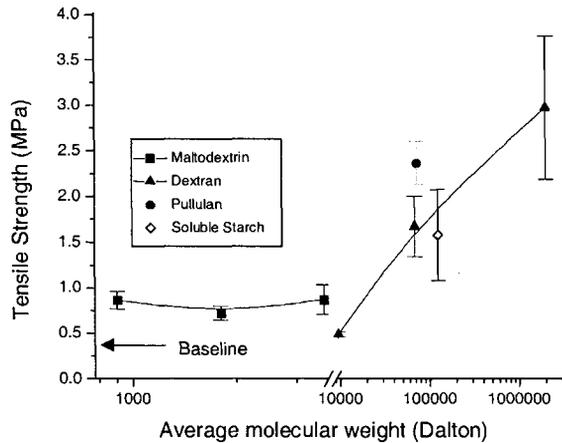


Fig. 3. Tensile strength of slip cast and dried alumina as a function of the polysaccharide molecular weight. Baseline specimens were prepared without polysaccharide and had the lowest strength. All other specimens were prepared with 0.03 grams of a given polysaccharide per gram of alumina.

Mechanical properties

Diametric compression measurements indicated tensile strengths between 0.2 to 0.5 MPa for baseline alumina specimens that were prepared without polysaccharide (Figure 3). The strength increased to approximately 0.75 MPa upon the addition of 0.03 grams of maltodextrin per gram of alumina. Figure 3 illustrates the general trend of increasing the tensile strength upon increasing the molecular weight of the polysaccharide above 10,000 Daltons. Below 10,000 Daltons, the strength does not appear to be influenced by the molecular weight. Specimens containing pullulan and the largest-molecular-weight dextran were approximately 10 times stronger than that of the baseline specimens made without polysaccharide. We should mention that we also observed systematic increases in tensile strength as the concentration of each polysaccharide increased. Finally, we should mention that we had previously reported ultrasonic velocity measurements illustrating that the simple addition of 3 grams of maltodextrin 040 per gram of alumina results in dried filter cakes with high elastic stiffness (13.8

GPa as opposed to 8.2 GPa for specimens prepared without maltodextrin 040) (Schilling et al. 1998b).

Conclusions

Aqueous suspensions of submicron alumina powder exhibited striking improvements in consolidation and rheological properties after adding small amounts of various maltodextrins and dextrans. These results provide strong support for the use of these additives in technical ceramic manufacturing.

High-density sediments (47 vol%) and high-density filter-cakes (57 vol%) were produced at low filtration-pressures (0.54 MPa). In contrast, alumina filter-cakes that were flocculated at the isoelectric point without maltodextrin required an order-of-magnitude greater filtration pressure to achieve the same 57 vol% density.

Maltodextrin-alumina filter-cakes were easily extrudable with Benbow parameters comparable to but higher than those of kaolin at approximately the same packing density of 57 vol%. Alumina filter-cakes without maltodextrin at the same 57 vol% density were too stiff to be extruded.

Rheometry experiments indicated a strongly-flocculated, Bingham-plastic response upon adding 20 vol% alumina powder to aqueous solutions of 0.01 M NaCl without maltodextrin. In contrast, the addition of 3 wt% of various dextrans and maltodextrins resulted in low viscosities, Newtonian-like behavior, and Bingham yield stresses of approximately zero.

Sorption measurements indicated that maltodextrin sorption to alumina enhances the consolidation and flow behaviour of these specimens. Acoustophoresis data support the hypothesis that sorbate-mediated steric-hindrance, rather than electrostatic, interparticle repulsion, plays a significant role enhancing the consolidation and plastic flow behavior.

The addition of 0.03 grams of a given polysaccharide per gram of alumina significantly increased the tensile strength of slip cast and dried alumina. Specimens containing pullulan and dextran were approximately 10 times stronger than that of the baseline specimens made without polysaccharide.

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FORMOWANIE CERAMIKI TECHNICZNEJ Z UŻYCIEM POLISACHARYDÓW

Streszczenie

Techniczna ceramika stanowi olbrzymi międzynarodowy rynek zbytu zdominowany przez zastosowania elektroniczne. Wyrobami do tego celu są izolatory, pakiety zintegrowanych obwodów, kondensatory i magnesy. Typową operacją w produkcji tego rodzaju wyrobów jest mieszanie proszku ceramicznego z ciekłą substancją organiczną (np. smar polietylenowy, rozpuszczalniki organiczne) w celu uzyskania masy konsystencji plasteliny, której nadaje się trójwymiarowy kształt który następnie się suszy i wypala. Piroliza dodatków organicznych stwarza problemy przed ostatecznym wypalaniem wyrobu. Najpierw trzeba taki wyrób powoli (ok. tygodnia) ogrzewać w 200°C aby uniknąć pęknięć wyrobów i tworzenia się pęcherzyków gazowych. W trakcie tego, związanego z wysokimi kosztami ogrzewania tworzą się trujące wyciepy. Wyrób zostaje przy tym zanieczyszczony mikrokrystalicznymi cząsteczkami węgla. Chcąc uniknąć pęknięć, odkształceń oraz zanieczyszczeń węglowych w wyrobach spiekanych przy równoczesnym wyeliminowaniu dodatków organicznych należy posługiwać się szlamem proszku w zawiesinie wodnej, do którego dodaje się rozpuszczalnych w wodzie dodatków wiążących. Z naszych badań wynika, że do tego celu nadają się różne dekstryny i maltodekstryny, gdyż w roztworze wodnym wykazują one naturalną zdolność do sorbowania się na powierzchni cząsteczek tlenków metali. Niewielki ich dodatek (<5 wag%) znacznie ułatwia proces formowania i zapewnia łatwą pirolizę z minimalnym zanieczyszczeniem drobinami węgla. Ponadto po odparowaniu wody te polisacharydy mocno wiążą ze sobą ziarenka tlenków zapewniając otrzymywanie mocnych, wolnych od pęknięć wyrobów ceramicznych przed ich wypalaniem. Niniejsza praca przedstawia omówienie podstawowych elementów wpływających na reologię wodnych zawiesin proszków ceramicznych w oparciu o chemiczną naturę oddziaływań międzycząsteczkowych. Przedstawiono wyniki badań nad sedymentacją, sączeniem, ekstruzją i chemiczną analizą powierzchni obrazujące praktyczne możliwości zastosowania maltodekstryn i dekstryn jako reologicznych modyfikatorów w produkcji wyrobów ceramicznych. ❧