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Rheology of alumina–nanoparticle suspensions: effects of lower saccharides and sugar alcohols

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Abstract

We empirically correlated the rheology of aqueous suspensions of ultrafine (40 nm diameter) γ-alumina powder with the concentration and structure of the following sugars and sugar alcohols: maltodextrin, sorbitol, maltitol, D-fructose, D-glucose and sucrose. It is shown that several monosaccharides, especially pentoses and sugar alcohols, significantly improve fluidity of aqueous suspensions and high-density pastes of alumina powder. In hexoses, the orientation of the 4-hydroxyl group plays a key role in controlling alumina-suspension rheology. The green strength and the sintering densification of slip cast alumina pellets were not affected by the addition of 5 wt.% of either arabinose, xylose, mannitol, or maltitol. © 2002 Published by Elsevier Science Ltd.

Keywords: Al_2O_3; Nanoparticles; Rheology; Suspensions; Saccharides

1. Introduction

Nanomaterials present one of the most promising and challenging fields of science and technology at the onset of the 21st century.[1–4] The tendency of nanometric-sized ceramic particles to agglomerate during powder production is a major obstacle towards the realization of new markets for these materials, because powder agglomeration prevents near-net-shaping of reliable (i.e. crack-free, high-density) green bodies.[5,6]

Several researchers addressed this problem by conducting rheological and surface-chemical studies to help understand the role of solution-chemistry parameters on colloidal surface-forces in ceramic suspensions. Reviews of this literature were recently published.[5–8] The majority of this previous research focuses on mediating the agglomeration of micrometer-sized ceramic-powder through the development of short-range, interparticle repulsion forces by one of three methods: hydration repulsion, electrosteric stabilization, or steric hindrance.

Several authors report the use of oligo and polysaccharides for ceramic shape-forming applications.[8–24] One of the more interesting aspects of these studies is that rather small concentrations (~ 1–3 wt.%) of several different oligo- and poly-saccharides (e.g. dextrins, dextrans, maltodextrins) significantly reduce the viscosity and significantly enhance consolidation of aqueous suspensions of micron-sized ceramic particles.[8–15] Electrokinetic and sorption studies on aqueous suspensions of micron-sized alumina with maltodextrin recently showed that this behaviour is caused by reduction of interparticle attraction through sorbate mediated steric hindrance.[8] The fact that many different oligo and polysaccharides in aqueous media have a strong tendency to adsorb to alumina by hydrogen bonding is also well known from chromatography studies in the carbohydrate chemistry literature.[25,26]

However, in this study, we show that oligo- and poly-saccharides fail as aqueous suspension plasticizers when nanometric-sized alumina powder is substituted for micrometric-sized alumina powder. This prompted us to evaluate the rheological behavior of aqueous suspensions

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of nanometric-sized alumina powder with monosaccharides, disaccharides, and sugar alcohols.

2. Experimental

All experiments were conducted with deionized water and 99.5% gamma alumina having average particle size of 27 to 56 nm (Nanotek alumina powder, Nanophase Technologies Corporation, Burr Ridge, IL). Sorbitol, maltitol, D-fructose, D-glucose and sucrose were obtained by the Sigma Corporation (St Louis, MI). Analytical grade ammonium chloride was purchased from Fisher Scientific Corporation (Fair Lawn, NJ). Maltodextrin (0.9 kDa) was supplied by the Grain Processing Corporation. (Muscatine, IA).

Aqueous solutions of 0.01 M ammonium chloride were prepared. Sugars or sugar alcohols were subsequently added at each of the following concentrations: 0 (control), 1, 3; and 5 wt.%. Two types of specimens were produced: suspensions and pastes. In the former case, alumina powder (30 vol.%; true density = 3.6 g/cm^3) was subsequently added to each solution above. Each suspension was sealed in a Nalgene plastic bottle and agitated for 24 h at 25 °C. The pH was subsequently measured and observed to be 5.7 in all cases. Viscous pastes were produced by blending alumina powder (10 g) with one of 3.0; 3.5; 4.0; and 4.5 ml of 1 wt.% aqueous solution of each sugar and sugar alcohol listed above. Pastes were homogenized by hand-stirring in a glass beaker.

Rheological properties were measured on all samples at 25 °C (RheoStress RS 75, Gebrueder Haake GmbH, Karlsruhe, Germany). Suspensions were evaluated in a double-gap-couette system and were subjected to an increasing shear rate from 5 to 500 s^{-1}. Pastes were evaluated with a serrated parallel-plate system. Mineral oil was applied to the air-exposed edges of the pastes to minimize drying. Each paste underwent stress-controlled (100 Pa) creep for 300 s, followed by stress relaxation for 300 s. Immediately thereafter, each paste underwent oscillatory testing, wherein the stress was cycled between zero and 100 Pa and the frequency was swept from 0.1 to 10 Hz over 300 s. All suspensions and pastes were evaluated in duplicate.

Suspensions were slip cast onto a flat surface of a plaster mold. Cylindrical pellets were formed by firmly placing a flat sheet of acrylic (5.4 mm thick) onto this plaster mold and then pouring suspension into an array of circular holes (14.3 mm diameter) previously drilled through the acrylic sheet. Pellets were dried at 70 °C for 24 h. Pellets were sintered in air for 3 h at one of the following maximum temperatures: 600, 750, 960 and 1500 °C. Upon cooling, 10 pellets of a given composition and sintering temperature were evaluated by water immersion and the Archimedes principle. The main purpose of the sintering experiments was to determine if a given lower saccharide or sugar alcohol additive influences sintering densification.

Cylindrical pellets were formed by hand-pressing pastes into the holes of the same acrylic fixture as described above for slip casting. In this case, the pellets were hand-pressed when the acrylic fixture was placed on the flat surface of the plaster mold. Such pellets underwent drying and sintering as described above.

Tensile strengths of the pellets were measured by the diametric compression method[27]. We performed five such measurements on specimens of each type. The main purpose of these experiments was to determine if the addition of a given lower saccharide or sugar alcohol influences green strength.

3. Results and discussion

Rheological measurements of suspensions were fitted to the Herschel–Bulkley model:[28]

$$\tau = \tau_0 + K(\dot{\gamma})^n \tag{1}$$

In this model, τ_0 is the shear stress, τ_0 is the yield stress, K is the consistency coefficient, $\dot{\gamma}$ is the strain rate, and n is the flow behaviour index. Table 1 summarizes the effects of the additive type and concentration on the rheological properties of 30 vol.% alumina suspensions.

With no additive, we observed shear thinning behaviour ($n = 0.4$) and substantial values of both the yield stress (13.1 Pa) and consistency coefficient (5 Pa s^n) (Table 1). Earlier, we noted that, with aqueous suspensions of micron-sized alumina particles, the addition of maltodextrins significantly improved flow behaviour.[8] However, we did not observe this same effect upon the addition of maltodextrin to aqueous suspensions of nanometric-sized gamma alumina particles. Instead, suspensions became highly viscous and intractable (Table 1). The exact reason for this behaviour is not clearly understood, however, we can suggest that bridging flocculation may play a role given that oligo and polysaccharides are known to adsorb to alumina in aqueous media.[25,26] This prompted us to evaluate lower-molecular-weight plasticizers such as the monosaccharides, disaccharides, and sugar alcohols in Table 1.

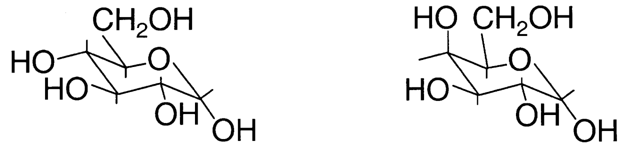
Most of the lower molecular weight additives in Table 1 significantly improved rheological behaviour with respect to suspensions containing no additive. D-glucose and maltose did not improve rheological parameters, with respect to suspensions containing no additive. The remaining low-molecular-weight additives, however, produced yield stresses near zero and consistency coefficients well below unity.

A closer look at Table 1 shows that 5 wt.% of the monosaccharides, L-arabinose, D-xylose and D-fructose exhibit the most superior, plasticizing effect. Table 1 also shows that 5% of the sugar alcohols (mannitol, maltitol, sorbitol, and xylitol) perform similarly. D-glucose, D-galactose, and D-fructose are isomeric hexoses (they all possess the same six-membered ring structure). As shown in Fig. 1, they differ from one another with respect to the orientation of the hydroxyl groups in space. Among them, only D-glucose performs poorly in rheological tests. This is evidence that the conformation of the sugar plasticizer plays a role in controlling rheology. This is also supported by comparison of the rheological data for sucrose and maltose, both of which are disaccharides (Fig. 2). Sucrose performs well, and maltose performs poorly. Sugar alcohols, similarly as saccharides with pyranose structures (D-glucose, D-galactose, D-sorbitol, and maltose), have primary and secondary hydroxyl groups. One may see that the difference in the orientation of the 4-hydroxyl group in hexoses influences the fluidity of alumina–nanoparticle suspensions. D-glucose and maltose, both with equatorial 4-hyroxyl groups, perform poorly, whereas D-galactose, with an axial 4-hydroxyl group, performs well. Sucrose, which also has an equatorial 4-hydroxyl group, performs well, but this good performance may result from involvement of the fructosyl moiety in sorption to the surfaces of alumina nanoparticles. The fructosyl moiety in sucrose is bound to the glucosyl moiety by the glycosidic bond, which is axially oriented with respect to the fructofuranose ring (Fig. 1). In contrast to saccharides with pyranose structures, sugar alcohols are linear, flexible molecules (Fig. 3). It could be possible that these flexible molecules

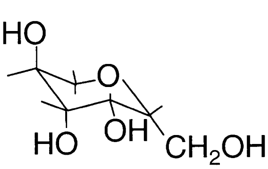
Table 1
Effect of the type and concentration of saccharide and sugar alcohol on the rheology of aqueous suspensions of nanometric alumina powder

Additive	Concentration (wt%)	Yield stress τ_0 (Pa)	Consistency coefficient K (Pa.s^n)	Flow behaviour index n
None	0	13.1	5.00	0.40
D-mannitol	1	0.4	1.20	0.49
	3	0.0	0.69	0.54
	5	0.0	0.46	0.58
Xylitol	5	0.0	0.49	0.56
D-sorbitol	5	0.0	0.47	0.57
Maltitol	5	0.0	0.43	0.58
Arabinose	1	0.0	0.83	0.50
	3	0.0	0.56	0.55
	5	0.0	0.42	0.58
Xylose	1	0.0	0.78	0.52
	3	0.0	0.52	0.57
	5	0.0	0.47	0.57
D-Galactose	5	0.0	0.71	0.53
D-Fructose	5	0.0	0.41	0.58
D-Glucose	5	12.7	6.44	0.37
Sucrose	1	0.0	0.64	0.55
	3	0.0	0.69	0.54
	5	0.0	0.67	0.55
Maltose	5	13.8	3.24	0.43
Maltodextrin 250	5	[a]	[a]	[a]

[a] Suspensions were intractable.

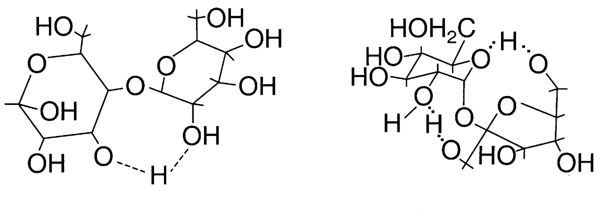


α-D-Glucose α-D-Galactose



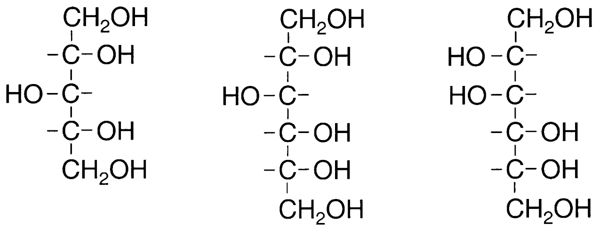
β-D-Fructopyranose

Fig. 1. Structures of α-D-glucose, α-D-galactose, and β-D-fructopyranose.

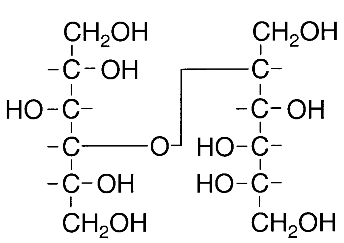


Maltose Sucrose

Fig. 2. Structures of sucrose and one of the two structures of crystalline maltose. Sucrose possesses one hydrogen bond between the CH_2OH group of one glucose unit and the 4-hydroxyl group of the second glucose unit.



D-Xylitol D-Sorbitol D-Mannitol



Maltitol

Fig. 3. Structures of sugar alcohols.

Table 2
Selected rheological parameters for alumina–additive pastes (data in this table are averages of two runs)[a]

Volume fraction alumina	Complex viscosities (Pa s)		Strain[a]	Creep parameters	
	At 0.1 Hz	At 10 Hz		K_1 (Pa s)	K_2 (Pa)
Water					
0.48	142,330	2147	0.00488	269,870	43,635
0.44	32,220	428	0.01092	166,918	9645
0.41	15,300	184	0.02648	100,259	3201
0.38	9597	123	0.05744	65,411	1747
Sorbitol					
0.48	46,980	782	0.00817	283,528	14,263
0.44	35,585	520	0.01197	156,008	8655
0.41	19,005	229	0.01832	122,224	4012
0.38	6496	84	0.15100	22,619	508
Sucrose					
0.48	99,655	2451	0.00619	314,071	14,314
0.44	39,950	750	0.01285	165,096	6427
0.41	27,050	670	0.02445	108,055	3410
0.38	8937	175	0.08218	41,432	1028

[a] Creep strain at 300 s.

can change their conformation to facilitate sorption to alumina.

Three different types of alumina paste were evaluated: those with water only, those with sucrose and water, and those with sorbitol and water. At 0.1 Hz, the three different pastes exhibited essentially the same complex viscosities at alumina concentrations of 44 vol.% and lower (Table 2). At 48 vol.% alumina, however, the paste containing sorbitol produces the most fluid behaviour, whereas, the paste containing water only is the least fluid. At 10 Hz, we see similar results: at 48% alumina, sorbitol exhibits the most fluid behaviour. One exception, however, is that water and sucrose have very similar complex viscosities at 48% alumina.

We do not fully understand the reasons for this behaviour. We can speculate that the reasons may be associated with the fact that sorbitol is a flexible molecule, and its conformation may adjust to the surfaces of particles. As a result, more hydroxyl groups could be involved in sorption. Contrary to sorbitol, the sucrose molecule is more rigid, because it is composed of two cyclic moieties, which by definition are rigid. In addition, the whole structure may become more rigid as a result of intramolecular hydrogen bonding between these two cyclic moieties. Such bonding is well known in solid sucrose.[29] In aqueous pastes of nanometric alumina powder, however, the structure of sucrose is not fully understood. We can speculate that the small volume of water in a paste may be insufficient to satisfy the hydration demands of both sucrose and alumina powder. Therefore, the former may reside in the paste in the rigid, intramolecular-hydrogen-bonded structure described above. This problem is currently under study by our group.

Using linear regression, creep data in all experiments could be fitted to the Peleg model[30] with r^2 exceeding 0.99:

$$t/J = k_1 + k_2 t \tag{2}$$

In this expression, t is equal to time, J is equal to the shear creep-compliance, and k_1 and k_2 are empirical constants. The second constant, k_2 is a convenient indicator of plastic behaviour (as k_2 decreases, a paste becomes more fluid).

Creep behaviour exhibited similar trends as in the oscillatory tests: again, sorbitol exhibits the most fluid behaviour. As shown in Table 2, k_2 is highest for water at all alumina concentrations. For sorbitol and sucrose, k_2 is approximately the same at all concentrations except at the lowest alumina concentration. In this case, k_2 for sorbitol is half of that for sucrose. Also shown in Table 2, creep strains follow the same trend. In all cases, sorbitol produces the highest creep strain, followed by sucrose and then water.

Table 3
Diametral compression strengths of green bodies made from slip-cast suspensions

Sample	Average stress (MPa)
No additive	0.88±0.30
5 wt.% of arabinose	0.91±0.24
5 wt.% of xylose	0.69±0.28
5 wt.% of mannitol	0.86±0.31
5 wt.% of maltitol	1.08±0.28

Table 3 presents measurements of diametral compression strengths of green pellets. All green bodies exhibited approximately the same strength, regardless of composition and origin. In addition, we did not observe any significant trends in sintering densification of pellets that were prepared from different additives. These data show that 5 wt.% of either arabinose, xylose, mannitol, or maltitol did not impair green body strength or sintering densification.

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