Journal of the European Ceramic Society 22 (2002) 625–628
www.elsevier.com/locate/jeurceramsoc

Dextrin plasticizers for aqueous colloidal processing of alumina

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Received 14 September 2000; received in revised form 12 April 2001; accepted 20 May 2001

Abstract

Rheological experiments were conducted to investigate the applicability of dextrins as plasticizers for the aqueous, colloidal processing of alumina ceramics. Upon the addition of 1–10 wt.% of dextrins, aqueous suspensions of 20 vol.% α-alumina exhibited a transition from strongly-flocculated, pseudoplastic behavior to a low-viscosity, Newtonian-like state. We evaluated rheological properties as a function of a range of polysaccharide molecular weights between 900 and 63 000 Daltons. Dextrins of molecular weight between 6450 and 15,000 Daltons were the most effective from the standpoint of cost and rheological performance.

Keywords: Al_2O_3; Dextrius; Plasticizers; Rheology; Suspensions

1. Introduction

This study focuses on the development of aqueous, environmentally-benign feedstocks to replace organic plasticizers and binders that are commonly utilized in ceramic manufacturing for injection molding, gelcasting, tape casting, or slip casting. There are serious safety and environmental concerns with the evaporation and debinding of these organics, which traditionally include alcohols, ketones, polyethylene wax, vinyl additives, and others.[1–3] In addition, the diffusion of these organic binders and plasticizers 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 200 °C and above) are typically needed to complete pyrolysis. Higher rates of heating produce internal stresses that commonly cause cracks and shape distortion.[4] Another concern with traditional, organic additives is that not all of the decomposition products of pyrolysis are removed by evaporation and gaseous diffusion; carbonaceous residues can be left behind which contaminate microstructures. Water-soluble additives are needed that can replace these organic chemicals and evaporate safely without causing cracks, shape distortion, or microstructure contamination in sintered parts. These new additives should also meet the following three requirements: (i) they should enable slurry consolidation to the high powder-packing densities that are needed to minimize shrinkage and warpage during drying, debinding, and sintering, (ii) they should produce a high degree of plasticity during plastic molding and shape-forming operations, and (iii) they should be capable of producing strong, crack-free green bodies at very low concentrations to promote clean pyrolysis.

Our previous studies indicate that maltodextrins are promising additives that meet the above demands.[5–7] In this paper, we focus on the application of dextrins. Maltodextrins are water-soluble, commonly available food ingredients that are made by enzyme-catalyzed hydrolysis of starch. More common on the market are dextrins, which are products of acid-catalyzed hydrolysis and/or thermolysis (dextrinization) of granular starch.[8] Dextrinization is a facile, well-recognized process that is easy to control in order to generate specific dextrins having a controlled and variable molecular weight. Hydrochloric acid (0.05–0.15%) is the most common acid catalyst. Thermolysis requires a temperature as high as 170–220 °C. Time of dextrinization which may extend from minutes to several hours is one of key parameters providing the required degree of transformation of starch.[8,9]

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[1] Ames Laboratory is operated by Iowa State University under the contract number W-7405-eng-82 with the U.S. Department of Energy.

0955-2219/02/$ - see front matter
PII: S0955-2219(01)00337-5

Maltodextrins and dextrins are D-glucose polymers of different molecular weight. They are composed of from five to several thousand D-glucose units. Dextrins are branched polysaccharides that have predominantly higher molecular weight fractions than maltodextrins, which are mainly linear molecules. Both dextrins and maltodextrins are composed of D-glucose units connected by (1–4) glucosidic linkages in the case of linear, and (1–4) as well as (1–6) glucosidic linkages in the case of branched saccharides. Maltodextrins are available from enzymatic hydrolysis of starch. α-Amylase, β-amylase, glucoamylase, and/or pullulanase can be suitable for this kind of conversion.[10] Dextrins have a lower pH than maltodextrins. Their low pH could influence sorption and interparticle electrostatic interactions in aqueous suspensions of ceramic powder. For the above reasons, we considered dextrins as interesting, alternative additives that could be useful for the aqueous processing of technical ceramics. In the current study, we also evaluated over which range of molecular weights and concentrations dextrins are capable of satisfying the above demand of being a viscosity reducer at low concentrations.

Finally, we should mention that there are several, previous publications on the use of different polysaccharides for ceramic processing.[11–17]

2. Experimental procedure

All experiments were performed with commercially available, α-Al_2O_3 powder, having an equiaxed particle shape, an average particle size of 0.4 μm, and a specific surface area of 8.5 m^2 / gram (A16-SG, Alcoa Corporation, Bauxite, Arkansas USA). Maltodextrins were obtained from the Grain Processing Corporation (Muscatine, Iowa, USA) and had the tradenames Maltrin 040, 100 and 200, depending on the molecular weight (Table 1). Dextrins were purchased from Sigma Chemical Company (St. Louis, Missouri, USA, Table 1).

Stock solutions of deionized water, containing 0.01 M NaCl, and either 0, 1, 3, 5 or 10 wt.% of a given polysaccharide were prepared. These solutions were subsequently used to make suspensions containing 20 vol.% alumina. All suspensions were placed in sealed, plastic bottles and agitated on a shaker for 24 h. The pH of each suspension was measured.

A double-gap Searle type rheometer (RheoStress RS 75, Gebrueder Haake GmbH, Karlsruhe, Germany) was used to determine rheological properties of all suspensions at 20 °C. Each suspension was subjected to an increasing strain rate starting at 0 s^{-1} and increasing to 500 s^{-1}. The strain rate was subsequently reduced to 0 s^{-1}. Upon pouring a given specimen 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. Results were fitted to the Herschel–Bulkley model[18]:

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

where τ is the shear stress, τ_o is the yield stress, K is the consistency coefficient, $\dot{\gamma}$ is the strain rate, and n is the flow behavior index. This model is convenient for analysis of rheological behavior over a wide range of fluids that are either Newtonian ($n = 1$), shear-thinning ($0 < n < 1$), or shear-thickening ($1 < n$).

Table 1
Average molecular weights[a] of polysaccharides and pH of their 1 wt.% aqueous solutions

Polysaccharide	Average molecular weight (Daltons)	pH of 1 wt.% aq. solutions
Maltodextrins		
Maltrin 200	900	4.7
Maltrin 100	1800	4.9
Maltrin 040	3600	5.2
Dextrins		
D1 (potato)	6650±150	3.4
D2 (corn)	6450±150	3.8
D3 (corn)	15 000	4.4
D4 (corn)	63 000	4.0

[a] Average molecular weights were determined by the manufacturer using gel permeation chromatography.

3. Results and discussion

In Table 1, we note that, as expected, aqueous solutions of dextrins are more acidic than aqueous solutions of maltodextrins. Therefore, upon the addition of dextrins to aqueous alumina suspensions, the pH of these suspensions could be lowered. However, as shown in Table 2, the addition of all polysaccharides in this study did not significantly reduce the alumina suspension pH. For example, depending on the polysaccharide, the pH was reduced by only 0.3–0.6 pH units after the addition of the highest dose of a given polysaccharide (Table 2).

Without polysaccharide, alumina suspensions are strongly flocculated, exhibiting shear-thinning behavior as shown in Fig. 1. We note three significant observations in Fig. 1: (i) the lowest, 1% admixture of 3600 Dalton maltodextrin significantly decreases the shear stress at a given strain rate relative to the control specimen without maltodextrin; (ii) this 1% addition brings the suspension to very low pseudoplastic condition, based on the near linearity of the stress–strain rate plot in Fig. 1; and (iii) increasing the concentration of maltodextrin maintains this property of a suspension, and it only slightly reduces the shear stress at a given strain rate. With the exception of dextrin D4, the remaining polysaccharides in this study exhibited essentially the

Table 2
Herschel–Bulkley parameters for aqueous suspensions of alumina powder containing polysaccharides

Polysaccharide	Concentration (wt.%) / pH	Yield stress τ_0 (Pa)	Consistency coefficient K (Pa.s^n)	Flow behavior index, n
None	0 / 9.1	1.54[a]	8.12	0.230
M100	1 / 9.0	2.16	0.053	0.664
M100	3 / 9.0	0.55	0.004	0.956
M100	5 / 8.9	0.58	0.003	1.024
M100	10 / 8.8	1.40	0.008	0.950
M200	1 / 9.0	3.10	0.371	0.533
M200	3 / 9.0	2.47	0.007	1.046
M200	5 / 9.0	0.99	0.005	0.988
M200	10 / 8.9	1.73	0.016	0.875
M040	1 / 9.0	2.14	0.008	1.045
M040	3 / 9.0	0.03	0.005	0.934
M040	5 / 8.9	0.05	0.004	0.969
M040	10 / 8.7	0.56	0.005	1.013
D1	1 / 9.0	6.23	0.001	1.057
D1	3 / 8.9	0.62	0.004	0.963
D1	5 / 8.8	0.68	0.003	1.068
D1	10 / 8.5	0.63	0.017	0.786
D2	1 / 9.0	3.14	0.002	1.175
D2	3 / 8.9	0.12	0.008	0.874
D2	5 / 8.7	0.11	0.003	0.965
D2	10 / 8.3	0.16	0.008	0.902
D3	1 / 9.0	3.23	0.004	1.035
D3	3 / 8.9	0.30	0.003	1.002
D3	5 / 8.8	0.06	0.009	0.847
D3	10 / 8.6	0.17	0.023	0.796
D4	1 / 9.0	0	5.136	0.210
D4	3 / 8.9	0	4.301	0.236
D4	5 / 8.8	2.83	0.329	0.431
D4	10 / 8.5	7.73	0.040	0.790

[a] As with all Herschel–Bulkely parameters in this table, the value of 1.54 Pa for this yield stress was determined by computer fitting the measurements of shear stress as a function of strain rate. As shown near the origin in Fig. 1, the slope of the shear stress–strain rate curve is high.

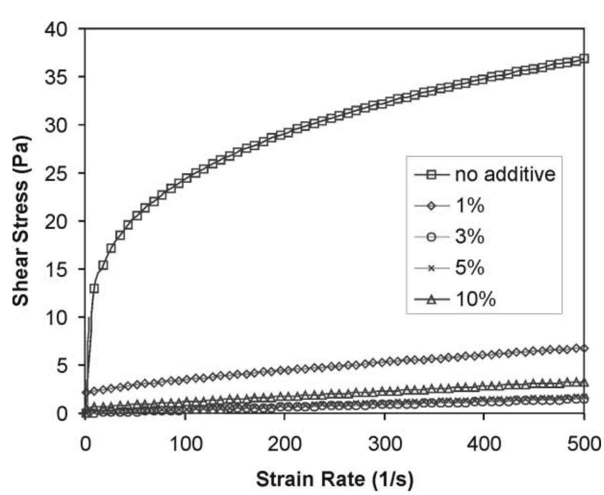

Fig. 1. Aqueous suspensions of 20 vol.% alumina exhibit a transition from strongly-flocculated, pseudoplastic behavior to a Newtonian-like state upon the addition of various concentrations of 3600 Dalton maltodextrin.

same trends (i to iii above) as maltodextrin in Fig. 1. This behavior is exhibited by the Herschel–Bulkley parameters in Table 2.

As shown in Table 2, the reduced fluidity of dextrin D4, at concentrations of 5 and 10 wt.%, results from a so-called pasting process that occurs when the aqueous solubility limit of this dextrin is exceeded. In this case a part of dextrins is not fully dissolved and forms a paste. Under such conditions proportion of water and dextrins is suitable for the formation of a special gel-like network, which can raise the viscosity of the system. Pasting of high-molecular-weight dextrins and starch, under basic conditions, is well known in the polysaccharide literature.[19]

The most beneficial formulations producing highly fluid behavior are those with a low yield stress, a low consistency coefficient, and a high flow behavior index. Most of the polysaccharide-containing formulations in Table 2 meet this criterion. The most fluid behavior is provided by maltodextrins and dextrins that are applied at concentrations between 3 and 5 wt.%. However, dextrin D4, added at the lowest, 1% concentration, also produced very fluid behavior. Based on a comparison of Herschel–Bulkely parameters at 3 and 5%, we would like to make the point that dextrins appear to be better additives than maltodextrins. Hence we can conclude that the most desirable molecular weight is between 6450 and 15,000 Daltons (dextrins D2 and D3). Polysaccharides of lower molecular weight only slightly reduce the suspension fluidity, whereas polysaccharides of higher molecular-weight significantly worsen flow behavior. Polysaccharides of molecular weight below 6450 Da when adsorbed on the alumina particles do not produce steric hindrance between the particles strong enough to prevent their attraction by van der Waals forces. Contrary to them high molecular weight, over 15,000 Da, polysaccharides in the amount introduced to the suspension of alumina form colloidal solutions.[8] It might be also likely that long-chain high molecular weight dextrins adsorb on the surfaces of two or more alumina particles causing so-called bridging flocculation and, in consequence, increase in the viscosity of the alumina suspension.

We should point out that the polysaccharide–alumina formulations we have studied are very fluid, and it is important to take precautions that the rheometer is sensitive enough to measure rheological properties reliably. We took this precaution by utilizing a rheometer with a double-gap, Searle type, one that maximizes the surface area of contact between the spindle and a given suspension. Our results in this paper for maltodextrins are consistent with those measured in a previous study with a less sensitive measurement system (utilizing a single-gap, Searle type, with lower surface area of contact between the spindle and suspension).[7]

We should also mention that, in a previous paper, we measured rheological behavior of aqueous alumina suspensions as a function of the molecular-weight of polysaccharides ranging from maltodextrins (900–3,600 Daltons) to soluble starch (above 2,000,000 Daltons).[7] The series of polysaccharides in that study did not contain molecular weights between 3600 and 9500 Daltons and also between 9500 and 69,000 Daltons. In the current study, we focused our experiments on these molecular-weight ranges by evaluating dextrins from 6450 through 15,000–63,000 Daltons.

Finally, we would like to emphasize that dextrins are inexpensive, commercially available products of dextrinization of starch. Water and CO_2 are the major products of thermal decomposition of dextrins. Other volatile products (lower hydrocarbons, alcohols, aldehydes, ketones, and carboxylic acids as well as furan-2-aldehyde) resulting from thermolysis and pyrolysis of dextrins mainly under oxygen deficient conditions constitute a few percent (below 10%) of the initial weight of dextrin.[8] At these low concentrations, all of the above volatile products present no harm to the environment. In the food processing industry, such volatile products are purposefully generated by caramelization of saccharides to enrich the flavor and aroma of foodstuffs. Caramel is a common ingredient of foodstuffs.[20]

4. Conclusions

Dextrins of molecular weight 6450–15,000 Daltons are suitable plasticizers for aqueous, colloidal processing of alumina. They can compete with maltodextrins from the standpoint of cost and rheological performance. Polysaccharides below 6450 Daltons perform slightly worse from the standpoint of improving rheological characteristics of suspensions, whereas, polysaccharides above 15,000 Daltons performed significantly worse in this regard.

Acknowledgements

The authors wish to thank the Office of Basic Energy Sciences at the US Department of Energy supporting this research.

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