ACIDIC BIOPOLYMERS AS DISPERSANTS FOR CERAMIC PROCESSING

N. PELLERIN,* J. T. STALEY,* T. REN,* G. L. GRAFF, D. R. TREADWELL, and I. A. AKSAY

Department of Microbiology,* and Department of Materials Science and Engineering; and Advanced Materials Technology Center, Washington Technology Center, University of Washington, Seattle, WA 98195

Some acidic biopolymers serve as dispersants for colloidal processing of ceramics. One biopolymer we tested was alginate, a heteropolysaccharide containing two carboxylic sugar acids, D-mannuronic and D-guluronic. Kelp alginate was a suitable dispersant, provided that its viscosity was reduced by partial acid hydrolysis. Low molecular weight polymers rich in guluronic acid proved to be better dispersants than those rich in mannuronic acid, perhaps due to their greater charge density caused by their buckled molecular configuration. In situ *processing of ceramic materials was tested by growing the alginate-producing bacterium,* Azotobacter vinelandii, *in the presence of alumina particles. Growth occurred at 15 vol% alumina in medium. Alumina particles which were exposed to such treatment showed a high packing density comparable to that with purified polymer. We also tested polypeptide polymers of the dicarboxylic amino acids, glutamate and aspartate, which also served as excellent dispersants for small alumina particles.*

INTRODUCTION

Colloidal processing of submicron-size ceramic powders is impeded by interparticle attractions from van der Waals forces which cause aggregations that effectively increase the particle size and leave undesired voids in the finished product.[1] To achieve high density in a green compact it is desirable to disperse particles in a liquid medium to prevent the formation of strong agglomerates.[2-4]

Polyelectrolytes have been used in aqueous solvents to overcome agglomeration and achieve dispersion by coating the particles. In such a system, the pH is adjusted so that the polyelectrolyte and particles have opposite charges.[2] Further, the cake densities and viscosities of such systems are dependent not only on the solids loading of the suspension but also upon the concentration of polymer relative to the solids. Too little polymer results in incomplete coating of the particles and an agglomerated suspension. Excess polymer in the system causes depletion flocculation and loss of stability.[3]

We have investigated the use of several naturally occurring polyelectrolytes as dispersants for high purity, submicron-size Al_2O_3 powders. Naturally occurring polymers are nontoxic and biodegradable and, therefore, do not the present problems of handling and disposal that may be encountered with some of their synthetic counterparts. Since it has been known for many

Mat. Res. Soc. Symp. Proc. Vol. 218. ©1991 Materials Research Society

years that the activity of microorganisms is responsible for the beneficial effects of aging of clays for ceramic processing,[5,6,7,8] we directed our attention to polymers formed by bacteria and algae.

One polymer we investigated was dextran, formed by the bacterial genera *Leuconostoc* and *Streptococci*. While dextran was not effective as a dispersant, its derivative, dextran sulfate was.[9] This indicated that a charged group was needed to interact with the surface charge of the particle in order to stabilize the dispersion. Unfortunately, however, the added sulfate ion is not removed by the sintering of dextran sulfate. Therefore, we sought polymers containing acidic groups such as carboxylic acids that are volatilized during processing. Alginate, an acidic polysaccharide, was next selected for examination as a dispersant for alumina. Alginate is a heteropolymer composed of mannuronic and guluronic acids and is obtained from the marine alga, *Macrocystis pyrifera* (kelp). It is also produced by the bacterium *Azotobacter vinelandii*.

A second group of organic polymers was also investigated. In particular, polypeptides containing a second acidic group in addition to the carboxyl involved in the peptide bond were studied. These include poly-glutamic acid which is produced naturally by the bacterium, *Bacillus licheniformis*, and poly-aspartic acid.

MATERIALS AND METHODS

The ceramic used in this study was a high purity (99.99%) Al_2O_3, with an average particle size of 0.4 μm as determined by x-ray sedigraph (AKP-30, Sumitomo Chemical America, Inc., New York, N.Y.).

Low viscosity kelp alginate (75,000-100,000 molecular weight) was obtained from Sigma Chemical Company (St. Louis, Mo.). Low molecular weight fractions were prepared by hydrolysis in 0.1 N HCl under reflux for 4 h. The solution was centrifuged, after which the pellet was dissolved using NaOH. A guluronic acid-rich fraction (poly G) was obtained by lowering the pH to 2.4 and collecting the precipitate; a mannuronic acid-rich fraction (poly M) was precipitated by further lowering the pH to 1.3.[10] Reagent grade HCl and NaOH were used for pH adjustments. Distilled water was used throughout. Other chemicals were obtained from Sigma Chemical Company.

Sedimentation columns were prepared with 2 vol% alumina particles in aqueous solutions of polymer. The suspensions were sonicated for 5 min, mixed on a magnetic stirrer for 30 min, and the pH adjusted to the experimental value before bringing the final volume to 10 ml. The suspension was decanted into a conical bottom, graduated tube and left undisturbed for several weeks. Final cake volumes were measured to +/− 0.1 ml. The wet density was calculated as [final volume/theoretical volume] × 100.

Suspensions for viscosity measurements were prepared with 30-40 vol% alumina powder in an aqueous solution of polymer and mixed as above. Measurements were obtained by the method of Cesarano and Aksay[3] using a Digital Viscometer, Model RVTD, (Brookfield Engineering Laboratories, Inc., Stoughton, Mass.). The viscosities of the polymer solutions were

measured using parallel plates on a Rheometrics Fluid Spectrometer, Model 8400 (Rheometrics Inc., Piscataway, N.J.).

The poly M and poly G fractions were analyzed by the method of Grasdalen[11,12] using 1H NMR spectra obtained on a Varian VXR 300 spectrometer at 300 MHz.

Azotobacter vinelandii NCIB 8789 (National Collection of Industrial Bacteria, Aberdeen, Scotland) was maintained on Larsen's broth[13] medium in cyst stage culture. Cells were counted by standard plate counting techniques.

Alginate was assayed by the *meta*-hydroxydiphenyl-sulfuric acid method.[14] Because sucrose interferes with the assay, it was replaced by mannitol in the Larsen's medium.[13] The polymer was harvested from culture supernatants by alcohol precipitation[15] after which it was dissolved in distilled water and dialyzed overnight.

The amount of polymer adsorbed to the particles was measured by preparing a 5 vol% alumina suspension containing a known amount of polymer. After ultrasonication for 2 min, the pH of the suspension was adjusted to around 8. The suspension was centrifuged to pellet the particles and the polymer remaining in solution was assayed.

RESULTS AND DISCUSSION

Algal Alginate as a Dispersant

Aqueous suspensions of alumina in polyacids are sensitive to changes in pH. The surface charge of the alumina particles varies from highly positive at low pH to negative at high pH with the zero point of charge (zpc) being around pH 8.7.[2] Further, the degree of ionization of the polymer is pH dependent. In order to determine the optimum pH range for the alginate/alumina system, we prepared 2 vol% suspensions at various pHs and measured the density of the resulting cakes. Maximum sediment densities were obtained near pH 8-9 where the polymer is fully dissociated and the surface of the alumina has a slight positive charge.

Wet sediment densities of 2 vol% alumina suspensions showed a dependence on polymer concentration relative to powder concentration (Table I). Too much or too little polymer resulted in flocculated suspensions with low-density cakes. The maximum packing density was obtained at a polymer concentration of 0.5% dry weight basis (dwb) alumina. This indicates full surface coverage of the particles at this concentration. Above the saturation adsorption level there was a decrease in cake density, most likely due to excess polymer resulting in gel formation which prevents close packing in the wet cake.

The viscosity of a highly concentrated suspension (30 vol% alumina) showed thixotropic behavior. There are two possible explanations for the increase in viscosity at a low rate of mixing: (i) the polymer may be forming a gel structure which is disturbed by more vigorous mixing or (ii) the suspension may be unstable. A 40 vol% suspension displayed less hysteresis, but the viscosities were approximately 10-fold higher than the 30 vol% suspension. An equivalent solution of polymer alone, without the particles, had a viscosity of 431 mPa·s, strongly suggesting that the polymer itself was forming a gel.

Table I. Wet sediment densities of 2 vol% suspensions of alumina in kelp alginate [MW 75,000-100,000; degree of polymerization (Dp) 380-515].		
Concentration of polymer (dwb alumina)	Wet sediment density (% theoretical)	
0	8	Flocculated
0.1	9	Flocculated
0.125	11	Flocculated
0.15	20	Slightly flocculated
0.20	33	Dispersed
0.25	33	Dispersed
0.50	40	Dispersed
0.75	25	Flocculated
1.0	16	Flocculated

In order to reduce the viscosity of the native polymer, we partially hydrolyzed it, yielding two fractions: one mannuronic acid-rich (poly M, molecular weight, ~ 2,400); the other guluronic acid-rich (poly G, molecular weight, > 5,000). The poly G fraction proved to be 100-fold less viscous than the native alginate. Sedimentation tests of 2 vol% suspensions and viscosities of high solids loaded suspensions revealed that the poly G fraction was superior to either the native alginate or the poly M fraction as a dispersant (Table II).

Table II. Viscosities of concentrated suspensions of alumina in poly G, poly M, or native alginate fractions at a shear rate of 9.2 s^{-1}.			
Fraction	30 vol%	40 vol%	50 vol%
Poly G	< 20 mPa·s	35 mPa·s	110 mPa·s Slightly flocculated
Poly M	95	465	Too viscous to be prepared
Alginate	*140-445	*2460-3720	Too viscous to be prepared

*Unstable

The reason for these differences probably lies in the conformation of the oligomers in solution. NMR studies[11] reveal that the two adopt different chain forms when in solution such that the bulky carboxyl group is in the equatorial position. This would lead to a flat, ribbonlike conformation in polymannuronic acid sequences. In contrast, polyguluronic acid would adopt a buckled conformation, giving an arrangement whereby the oxygen atoms on adjoining residues are in close proximity, leading to a localized increase in charge density.[16] The high charge density is likely the reason why polyguluronic acid is a more effective dispersant than polymannuronic acid.

Bacterial Alginate as a Dispersant

We have also investigated whether bacterial alginate can be produced in an *in situ* process in which the alumina particles are incubated with *Azotobacter vinelandii* while polymer is being synthesized. It might be of commercial interest to know if such an *in situ* process is feasible. We have found that *Azotobacter vinelandii* are able in grow in 5, 10, and 15 vol% suspensions of alumina in Larsen's medium. Over a four-day period the bacteria produced sufficient polymer to effectively treat the particles. Cake densities were enhanced 49% and 58% over that of the untreated controls in the 5 and 10 vol% suspensions. Further, the viscosities of these suspensions were reduced 4-fold (from 480 to 120 mPa·s) at a shear rate of 9.3 s^{-1} and 100-fold (from 6000 to 100 mPa·s) at a shear rate of 9.3 s^{-1} respectively, over that of the controls. We suspect that the poorer packing density and higher viscosity of the 5 vol% suspension was due to excess polymer in the suspension.

Adsorption studies, in which we mixed the particles with a polymer solution and determined the amount of polymer remaining in solution after adsorption, have shown that 1 g of particles adsorbs 3.23 mg of bacterial alginate at pH 8.

In order to simplify the system, we investigated the possibility of producing the polymer in a nongrowing bacterial population. For this purpose cells were first grown on Larsen's medium and then resuspended in nitrogen and sulfur-limited salt solutions. By limiting these nutrients but still providing a carbon source for the production of the polymer, we hoped to maximize polymer production per cell. Three solutions were used: solution 1, which contained a carbon source only; solution 2, which contained a carbon source and phosphate buffer; and solution 3, which contained a carbon source, phosphate buffer, and sodium acetate (additional carbon source). Pre-grown *Azotobacter vinelandii* cells were inoculated in the solutions to a cell density of 2.8×10^5. Growth did not occur in solutions 1 and 2; polymer production was only 5.9 μg/ml in solution 1, but 30.5 μg/ml or 100 μg/1000 cells was achieved in solution 2. In solution 3, growth occurred to a final density of 5.0×10^6, and polymer production per 1000 cells was the same as in solution 2.

Thus, it is possible to limit the number of cells in the system, while increasing the level of production of polymer per cell. Our calculations show that in solution 2 and with an alumina particle diameter of 0.4 μm, 3×10^7 cells of *A. vinelandii* are sufficient to coat 1 g of particles or a single cell can coat 232,000 alumina particles.

We also determined whether the bacterial cells could be removed from the *in situ* system after the particles became coated. After cultivation for 6 d in an alumina suspension, the culture was centrifuged, yielding a pellet of the ceramic particles overlain by a pellet of bacterial cells. The cells were scraped off and the particle pellet was resuspended in distilled water. After washing in this manner five times, the bacterial numbers were reduced from 5.6×10^7 per gram particles to 85 cells per gram particles, indicating that the bacterial cells do not strongly adhere to the particles. In contrast to the cells, over 99% of the polymer remained bound to the particles when coated particles were subjected to the same washing regime.

These results indicate that *Azotobacter vinelandii* can be used as a source of polymer which acts as an effective dispersant for small-size alumina particles. Furthermore, we have demon-

strated that the bacterium may be used in an *in situ* process whereby the bacterial culture produces alginate while incubating in an alumina suspension, obviating the need to extract the polymer from the culture before mixing it with the particles.

Acidic Polypeptides as Dispersants

Sedimentation tests using 2 vol% suspensions of alumina in various concentrations of polyamino acids indicate that they also are effective as dispersants for small size powders. The polymers thus far tested are poly-D-glutamic acid, poly-L-glutamic acid, poly-(α, β)-DL-aspartic acid, and poly-L-aspartic acid. We have attained wet cake densities of over 50% of the theoretical density volume in simple sedimentation columns using only gravity to compact the cakes. No differences were noted in the cake densities obtained with D and L isomers of the same polyamine.

ACKNOWLEDGEMENT

This work was supported by the Air Force Office of Scientific Research under Grant No. AFOSR-88-0135.

REFERENCES

1. I. A. Aksay, in ***Advances in Ceramics, Vol. 9, Forming of Ceramics*** edited by J. A. Mengels and G. L. Messing (American Ceramic Society, Columbus, Ohio, 1984), p. 94.
2. J. Cesarano III, I. A. Aksay, and A. Bleier, *J. Am. Ceram. Soc.*, **71**, 250 (1988).
3. J. Cesarano III and I. A. Aksay, *J. Am. Ceram. Soc.*, **71**, 1062 (1988).
4. T. K. Yin, I. A. Aksay, and B. E. Eichinger, in ***Ceramic Powder Science II, Ceram. Trans.***, Vol. 1, edited by G. L. Messing, E. R. Fuller, Jr., and H. Hausner (American Ceramic Society, Westerville, Ohio, 1988), p. 654.
5. D. P. Glick, *J. Am. Ceram. Soc.*, **19**, 169 (1936).
6. D. R. Baker and D. P. Glick, *J. Am. Ceram. Soc.*, **19**, 209 (1936).
7. D. P. Glick, *J. Am. Ceram. Soc.*, **19**, 240 (1936).
8. H. Spurrier, *J. Am. Ceram. Soc.*, **4**, 113 (1921).
9. G. L. Graff, unpublished.
10. J. M. Beale, personal communication.
11. H. Grasdalen, *Carbohy. Res.*, **118**, 255 (1983).
12. H. Grasdalen, B. Larsen, and O. Smidsrod, *Carbohy. Res.*, **68**, 23 (1979).
13. G. Skjak-Braek, H. Grasdalen, and B. Larsen, *Carbohy. Res.*, **154**, 239 (1986).
14. J. Montreuil, ***Carbohydrate Analysis - A Practical Approach***, (IRL Press, Limited, Oxford, England, 1986), p. 175.
15. T. R. Jarman, L. Deavin, S. Slocombe, and P. C. Righelato, *J. Gen. Microbiol.*, **107**, 59 (1978).
16. D. A. Rees, *Biochem. J.*, **126**, 257 (1972).