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Alginate as a Ceramic Processing Aid

**Nancy B. Pellerin,[1] G. L. Graff,[2] David R. Treadwell,[2]
James T. Staley,[1,3] and Ilhan A. Aksay[2]**

Alginic acid obtained from Macrocystis pyrifera *(kelp) has been used in a novel way to produce stable suspensions of* α-Al_2O_3 *ceramic particles for use in producing a high (>40%) packing density in the unfired ceramic material. Native alginate was effective in producing low-viscosity, stable suspensions up to 20 vol% of solids; however, the higher viscosity of the polymer solution interfered with the preparation of higher-solids loading suspensions. The hydrolysis products of alginic acid, polymannuronic acid- and polyguluronic acid-rich fractions, were effective in producing stable suspensions up to 30 and 40 vol%, respectively. The higher charge density of polyguluronic acid appears to be responsible for its more effective role as a dispersant.*

KEY WORDS: ceramic processing; dispersants; alumina; alginate; Macrocystic pyrifera.

INTRODUCTION

Recent progress in the field of ceramics has focused on the development of highly dense, homogeneous materials for new applications such as ceramic engine components and superconductive composites (Ulrich, 1990). For these applications, nonclay materials such as alumina (Al_2O_3) are synthesized in very small (submicron) sizes. Submicron particle systems yield finer-grained products after sintering provided that they can first be compacted to a high-density state with a uniform pore size distribution. However, a long-standing problem is that

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[1] Department of Microbiology and Advanced Materials Technology Center, Washington Technology Centers, University of Washington, Seattle, Washington 98195.

[2] Department of Materials Science and Engineering and Advanced Materials Technology Center, Washington Technology Centers, University of Washington, Seattle, Washington 98195.

[3] To whom correspondence should be addressed at Department of Microbiology, SC-42, University of Washington, Seattle, Washington 98195.

these submicron-sized particles are highly attracted to each other due to van der Waals forces, causing aggregations which effectively increase the particle size and leave undesired voids in the finished product (Aksay, 1984). The prime requirement for preparation of a high density in the compact is that particles be completely dispersed in the solvent system and exhibit no agglomeration (Calvert *et al.*, 1986).

One method to overcome agglomeration and achieve dispersion is to use a polyelectrolyte to coat the particles, which creates a net repulsive force between them due to electrosteric interactions (Cesarano and Aksay, 1988; Cesarano *et al.*, 1988). The synthetic polymer, poly(methacrylic acid) (PMAA) has been commonly used to disperse alumina in aqueous suspensions. This polymer causes a decrease in the interparticle attraction as reflected by a decrease in viscosity of the suspension and, thus, in an increase in the packing density of the wet cake (Cesarano and Aksay, 1988; Cesarano *et al.*, 1988). However, PMAA and its monomer, acrylic acid, are toxic and corrosive (Merck and Co., 1989).

In this paper we report the use of a naturally occurring, polymer that can produce well-dispersed colloidal suspensions of submicron-sized alumina particles. We have demonstrated that alginate obtained from the marine alga, *Macrocystis pyrifera* (kelp), has dispersing capabilities comparable to those of PMAA. Furthermore, it is neither toxic nor corrosive.

Alginate is a copolymer of the isomers D-mannuronic (M) and L-guluronic (G) acids. The biosynthesis is thought to involve the initial formation of polymannuronic acid, followed by the epimerization of D-mannurosyl residues to L-gulurosyl residues (Grasdalen *et al.*, 1979). The two uronides are distributed along the chain in blocks of three types, polymannuronic acid (poly M), polyguluronic acid (poly G), and poly-mannuronic-guluronic acid (poly MG) (Grasdalen *et al.*, 1979; Haug *et al.*, 1966, 1974; Larsen *et al.*, 1970). A similar polymer is produced extracellularly by some bacteria, including *Azotobacter vinelandii* (Pindar and Bucke, 1975) and various *Pseudomonas species* (Linker and Jones, 1966). Alginate-producing, mucoid variants of *P. aeruginosa* have been obtained from patients suffering from respiratory infections accompanying cystic fibrosis (Govan, 1976). It is thought that the production of polymer by the bacterium confers protection from antibiotics.

MATERIALS AND METHODS

Materials and Chemicals

The ceramic used in this study was a high-purity (99.99%) α-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).

The polymer was a low-viscosity kelp alginate (75,000 to 100,000 MW;

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. The guluronic acid fraction was obtained by lowering the pH to 2.4 and collecting the precipitate; the mannuronic acid fraction was precipitated by further lowering the pH to 1.3 (J. M. Beale, personal communication).

Reagent-grade HCl and NaOH were used for pH adjustments. Distilled water was used throughout. Mannuronic acid lactone was obtained from Sigma Chemical Company.

Sedimentation Experiments

Sedimentation columns were prepared with 2 vol% α-Al_2O_3 in aqueous solutions of polymer. The suspensions were sonicated for 5 min, then mixed on a magnetic stirrer for 0.5 h, 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 polystyrene tube (Falcon 2095, Becton Dickinson, Cockeysville, Md.) and left undisturbed for several weeks. Final sediment volumes were measured to ±0.1 ml. The wet sediment density was calculated as (theoretical volume/final volume) × 100.

Viscosity Measurements

Suspensions for viscosity measurements were prepared with 30 to 40 vol% α-Al_2O_3 in 0.5% (dwb) aqueous solution of polymer (pH 5 or 8) and mixed as above. Measurements were obtained by the method of Cesarano and Aksay (1988) using a digital viscometer (Model RVTD, Brookfield Engineering Laboratories, Inc., Stoughton, Mass.). Viscosities of polymer solutions were measured using parallel plates on a Rheometrics fluid spectrometer (Model 8400, Rheometrics Inc., Piscataway, N.J.).

Determination of Degree of Polymerization of Alginate Oligomers

Samples of the poly M- and poly G-rich fractions and unhydrolyzed alginic acid were each mixed with 1 ml of D_2O and dissolved by adding a few drops of 5% NaOD in D_2O dissolved in D_2O. The pD of the solutions was adjusted to slightly acidic with 1% DCl in D_2O. Na_2EDTA was added to complex any Ca^{2+} present. The ^1H NMR spectra of the samples were recorded on a Varian VXR 300 spectrometer at 300 MHz and analyzed by the method of Grasdalen *et al.*, (1979; Grasdalen, 1983). The chemical shifts are reported as parts per million downfield of internal 3-trimethylsilyl-1-propanesulfonic acid-2,2,3,3-d_4 sodium salt. The ratios of mannuronate to guluronate were determined from the integrals of the anomeric protons: M at 4.64δ and G at 5.02δ. The degrees of

Table I. MR Data for Determination of Uronide Residue Composition and Degree of Polymerization (DP) of Hydrolyzed Alginate Fractions[a]

Sample	Polymer wt (mg)	Na_2EDTA wt (mg)	Final pD	% G	DP
Poly M	10.2	2.2	5.0	10	18
Poly G	9.0	2.0	5.3	83	>24

[a] Transients collected: 128.

polymerization of the poly M- and poly G-rich fractions were estimated by the ratio of the sum of the integrals of these two peaks to that of the reducing-end protons at 5.20δ (see Table I). The linewidths of the unhydrolyzed alginic acid were too great to yield useful information.

RESULTS AND DISCUSSION

Effect of pH on the Particle Packing Density

Several factors must be considered when working with polyelectrolytes in aqueous solutions. First, the dissociation behavior of the polymer is greatly affected by the solution pH. The dissociation of a weak acid group on the polyelectrolyte depends on the overall degree of dissociation, since dissociation of a proton from an already ionized polyacid is hampered by the negative potential of such a polyacid (Hesselink, 1983). Thus the pK_a varies for every acid site and increases as each successive site dissociates. Second, 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) occurring at about pH 8.7 (Cesarano *et al.*, 1988). These factors result in suspensions that are extremely pH sensitive.

In order to determine the optimum pH range for the alginate/alumina system, we prepared a series of sedimentation tests under different pH conditions. At low pH (2.8) the suspension was flocculated, with a cake density of less than 10% of the theoretical packing density, similar to the cake formed when no suspending agent was used (Fig. 1). This result was expected since at low pH the polyuronic acid would be essentially nondissociated, with very few ionized groups on the polymer to interact with the alumina surface. The increase in cake densities with rising pH reflects an increasing number of ionized COO^- sites on the polymer. Interestingly, maximum sediment densities were obtained near pH 8–9 where the polymer is fully dissociated, and the surface of the alumina particles has a slight positive charge. This condition provides the maximum electrostatic contribution from the polymer while providing a driving force

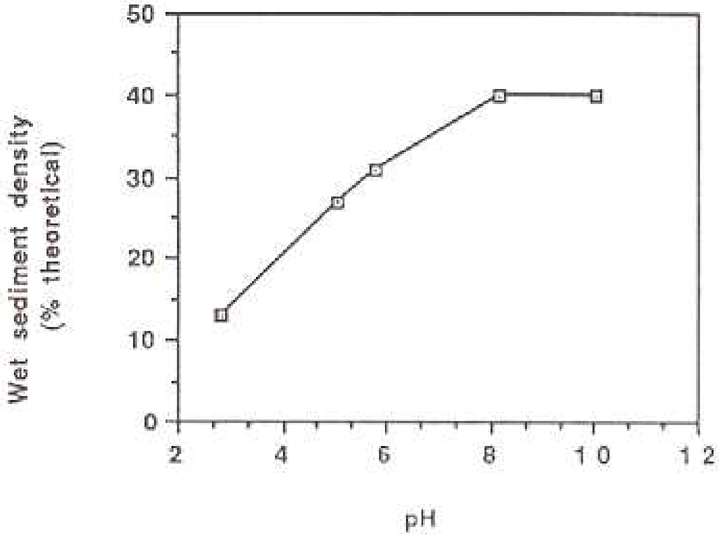

Fig. 1. Wet sediment densities of 2 vol% suspensions of alumina in alginate (0.5% dwb alumina) prepared at various pH levels

for high-affinity adsorption of the negatively charged polymer on the positive surface of the particle.

Effect of Polymer Concentration

To determine the optimum concentration of polymer required to disperse the alumina powder, a series of sedimentation tests was performed at a fixed pH of 8.5. Dilute (2 vol%) suspensions were prepared with various concentrations of polymer relative to the dry weight of the particles (dwb). Figure 2 shows the wet sediment densities obtained in these suspensions after several weeks of settling. In the absence of polymer, the suspension was unstable, with particles spontaneously agglomerating into poorly packed, ramified structures with packing densities of approximately 10% of the theoretical value. The addition of 0.1% polymer had no observable effect, but with slight increases in polymer concentration, the sediment densities increased dramatically. At a polymer concentration of 0.5% (dwb), the sediment cakes reached a maximum density of greater than 40% theoretical (density). This indicates that the added polyelectrolyte is acting to stabilize the particles in suspension by creating a barrier against spontaneous flocculation of the individual particles. This facilitates particle packing upon consolidation in the sediment, resulting in the higher densities observed.

Cesarano *et al.* (1988) reported wet sediment densities of approximately

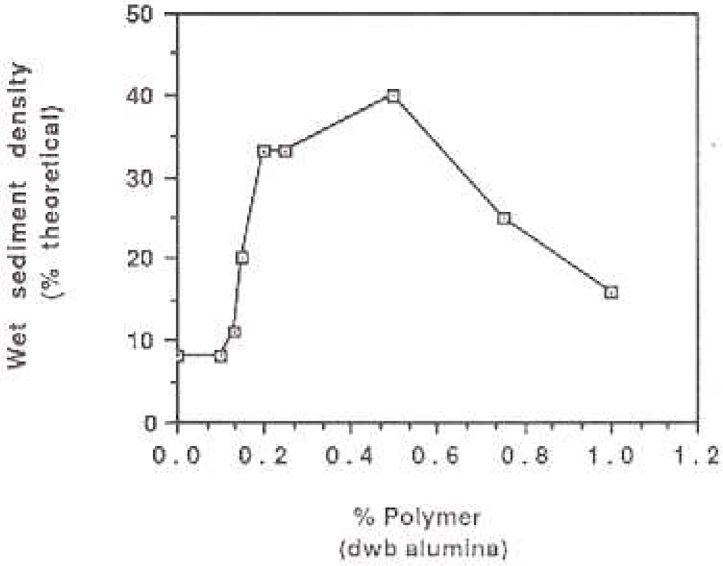

Fig. 2. Wet sediment densities of 2 vol% suspensions of alumina prepared with various concentrations of alginate (dwb alumina). The pH of the suspensions was adjusted to 8.5–8.6.

50% theoretical (density) for the poly(methacrylic acid)-Na (PMAA)-stabilized alumina suspensions. The lower packing densities (40%) observed with the alginate could be due to several effects. First, the higher molecular weight of the alginate (100,000) compared to the PMAA (15,000) would tend to create a thicker adsorbed polymer layer on each individual alumina particle (Hesselink, 1983). The increased volume occupied by the adsorbed polymer would increase the interparticle separation distance and could easily account for a 10% decrease in final sediment density. Second, the difference in charge density between the two polyelectrolytes might explain the lower packing densities. Fully dissociated PMAA has a charged COO$^-$ site for each ethyl group along the polymer backbone. In comparison, the alginate contains a single carboxylic acid for each hexose unit. These differences in structure result in approximately twice (1.84 times) the charge density for PMAA compared to alginate, given identical molecular weight polymer segments. This lower electrostatic repulsion may result in alginate suspensions that are mildly agglomerated, with lower particle packing densities.

Figure 2 further shows a distinct maximum in sediment density at a polymer concentration of 0.5% (dwb), with a decrease in packing density at higher concentrations. This indicates that full surface coverage of the alumina particles by the alginate occurs at approximately 0.5% (dwb). The decrease in packing densities above the saturation adsorption limit is most likely due to excess polymer in solution causing depletion flocculation of the particles (Cesarano and Aksay, 1988). It is also possible that the excess alginate in solution is forming a soft gel which prevents close packing of the particles during sedimentation.

Viscosities of Highly Concentrated Suspensions

To understand better the role of the alginate in controlling particle–particle interactions, we measured the viscosities of concentrated alumina suspensions prepared with the polymer. The viscosity of the suspension can give information as to the effectiveness of the polymer in stabilizing the suspension.

For our experiments we measured the viscosity of the suspension as the mixing speed was decreased from 93 to 0.47 s^{-1} for 5 min and then increased. Figure 3 shows the thixotropic loop obtained for a 30 vol% suspension of particles in alginate solution. After 5 min at a low rate of mixing, the viscosity nearly doubled, but as the rate of mixing was increased the viscosity again decreased.

Of the possible explanations for the increase in viscosity at a low rate of mixing, two are that (i) the polymer may be forming a gel structure which is disturbed by more vigorous mixing or (ii) the suspension may be unstable, i.e.,

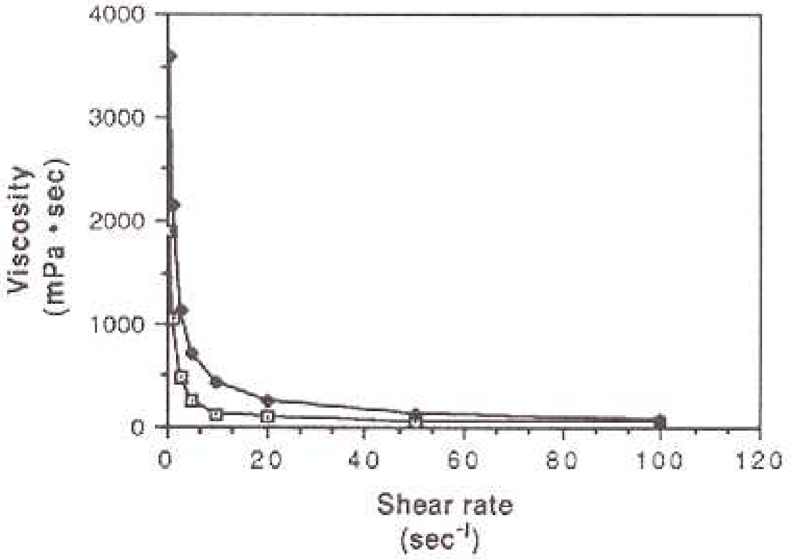

Fig. 3. Viscosity curve obtained from a 30 vol% suspension of alumina in 0.5% dwb alginate. Open squares represent values obtained during increasing shear rate. Filled squares represent values obtained during decreasing shear rates.

the particles may be flocculating (agglomerating) to form a network structure in the suspension due to insufficient stabilization.

We next prepared a 40 vol% suspension of particles in alginate solution (Fig. 4). This suspension showed characteristics different from those of the 30 vol% suspension. Here, the viscosity displayed less hysteresis, but at all rates the viscosity was 10-fold higher than that of the 30 vol% suspension. The suspension acted like a soft gel, leading us to suspect that the polymer was contributing to the high viscosity.

When we compared the viscosities of solutions of alginate in water without the particles, we found that of the polymer solution alone in the 30 vol% suspension to be 160 mPa·s and that of the solution in the 40 vol% suspension to be 341 mPa·s. This is strong evidence that the polymer forms a gel in the solution.

Low Molecular Weight Fractions as Dispersants

We next investigated whether lower molecular weight fractions would be effective as dispersants and would avoid the problem of gel formation encountered with the native polymer. Kelp alginate (75,000–100,000 MW) was hydrolyzed in 0.1 *N* HCl for 4 h, after which two fractions were collected by

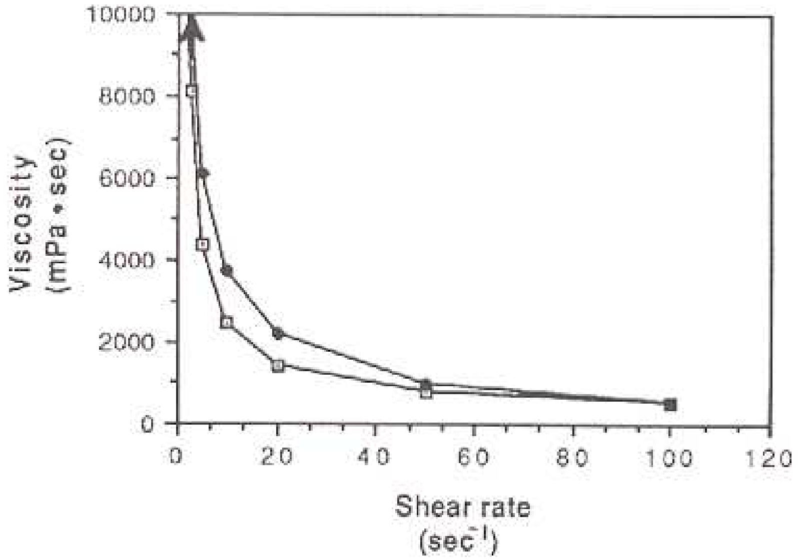

Fig. 4 Viscosity curve obtained from a 40 vol% suspension of alumina in alginate. Open squares represent values obtained during increasing shear rate. Filled squares represent values obtained during decreasing shear rates. The arrow represents an off-graph value of 10,500 mPa·s at the shear rate of 2.5 s^{-1}.

precipitation. Fraction poly G was collected by precipitation at pH 2.4. The degree of polymerization and uronide composition was determined by NMR (Table I). This fraction contained an oligomer with an average degree of polymerization greater than 24 (≥4800 MW) and a ratio of guluronic to mannuronic acid of 6 to 1. The viscosities of solutions of the oligomer in water were reduced approximately 100-fold as compared to the native polymer (Table II).

Fraction poly M, with an average degree of polymerization of about 18 and molecular weight ~3600 (Table I), was precipitated at pH 1.3. It contained more than 10 mannuronate residues to 1 guluronate residue. Viscosity measurements were not performed, but the values would be expected to be similar to or less than that of the poly G fraction since the gel forming capacity of the polymer is directly related to the guluronic acid content (Penman and Sanderson, 1972).

We also included mannuronic acid monomer in this study to determine the effectiveness of a single uronic acid sugar as a dispersant. This was obtained by treating commercially available mannuronic lactone with base (final pH 8.3).

The packing densities obtained with these fractions show clearly that there are differences in their ability to stabilize suspensions (Fig. 5). The poly G fraction was effective over a wider concentration range than the native alginate, and slightly less oligomer was needed to produce an effect equal to the native polymer. The poly M fraction was effective only at a higher concentration (0.4 to 0.5% dwb) of oligomer to particle. The monomer had only a slight effect at very high concentrations (1% dwb) and could not be considered a useful suspension stabilizer.

The viscosities of concentrated suspensions prepared with 0.5% (dwb) of the oligomers again show a difference between the fractions (Table III). The poly M fraction stabilized suspensions at a 30 vol% solids loading, while the poly G fraction was capable of stabilizing suspensions with 40 vol% solids. A fluid (< 1 Pa·s) 50 vol% suspension could not be prepared with the poly M

Table II. Viscosities of Native Alginate and Polyguluronic Acid in Water[a]

	Vicosity (mPa·s)	
Sample	30 vol%	40 vol%
Poly G	0.9	4.9
Native alginate	160	341

[a] Solutions were prepared to yield the same final concentrations as were in the 30 and 40 vol% suspensions, but the particles were omitted.

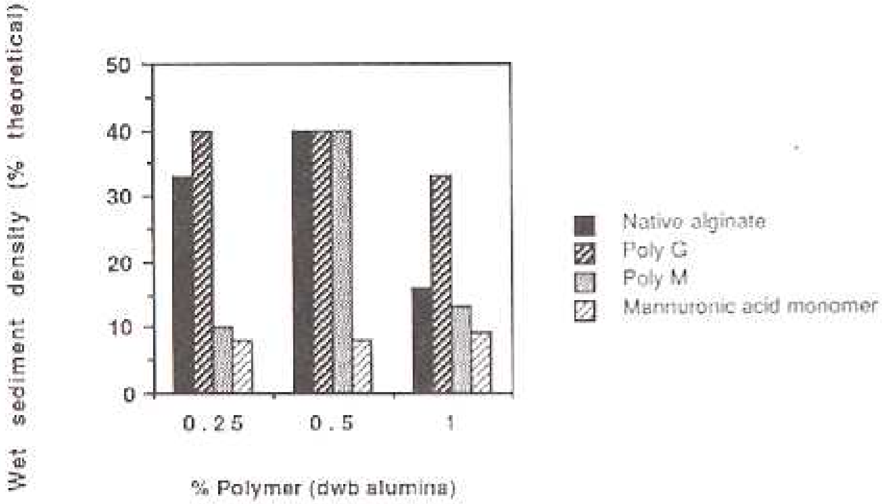

Fig. 5. Wet sediment densities of 2 vol% suspensions of alumina prepared with native alginate, polyguluronic acid (poly G), polymannuronic acid (poly M), or mannuronic acid monomer. The pH of the suspensions was adjusted to 8.3–8.6.

Table III. Viscosities (mPa·s) of Concentrated Suspensions of Alumina in Polymannuronic or Polyguluronic Acid Fractions at a Shear Rate of 9.3 s^{-1}

Fraction	pH	30 vol%	40 vol%	50 vol%
Poly G	8	40	230	470–625 Slightly flocculated
Poly G	5	<20	35	110 Slightly flocculated
Poly M	8	95	465	Too high to be prepared

fraction because of particle agglomeration, yet the poly G fraction yielded a weakly flocculated, low-viscosity suspension at this solids loading.

The reason for these differences may lie in the molecular configuration of the two polymers. Solution studies using NMR (Penman and Sanderson, 1972) provide evidence that the uronic acids adopt different chain forms when in solution, such that the bulky carboxyl group is in the equatorial position. The resultant glycosidic bonds at positions 1 and 4 would be equatorial in β-D-mannuronate but axial in α-L-guluronate. This would lead to a flat, ribbon-like conformation in poly M sequences, whereas poly G would adopt a buckled conformation. The buckled arrangement brings the oxygens on either side of the glycosidic bond in close proximity, leading to a localized increase in charge density (Rees, 1972). This is likely to be the reason that poly G acts as a more effective polyelectrolyte for the stabilization of ceramic particles than poly M.

CONCLUSIONS

We have demonstrated that uronic acid-containing polysaccharides are useful as dispersants in preparing concentrated, aqueous suspensions of ceramic powders. This represents an easily isolated, inexpensive, and nontoxic polymeric additive for potential commercial applications.

In addition, we have shown that oligomeric fractions of the native alginates are equally effective, or superior, as dispersants in colloidal alumina suspensions. Therefore, the undesirable gelling characteristics of the high molecular weight alginates can be eliminated while maintaining the necessary suspension stabilizing properties.

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