

## CERAMIC PROCESSING USING INORGANIC POLYMERS

JOHN J. LANNUTTI,\* CHRISTOPHER H. SCHILLING\*\*, AND ILHAN A. AKSAY\*

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

\*\*Pacific Northwest Laboratory, + Richland, WA 99352

### ABSTRACT

Inorganic polymers are used in the formation of green compacts via sedimentation of colloidal alumina suspended in chloroform. Polymers containing highly polar components tend to produce constant density profiles of greater than 55% density, while those containing nonpolar, reactive components produce profiles with a large gradient in packing density. Density profiles describing the sedimentation behavior versus time and the final dried density of the compacts are generated via the use of gamma-ray densitometry. These polymers have the potential not only to increase green compact density but also to reduce weight losses due to "burnout" and subsequent sintering requirements by pyrolyzing to a ceramic phase.

### INTRODUCTION

Polymer additives are important in nearly all types of ceramic processing [1]. However, they can create problems during burnout such as void formation from gaseous decomposition products, unwanted carbon-based residues, and the generally slow heating rates required to pyrolyze the polymer.

The present study addresses the use of inorganic polymer additives which may transform to useful ceramic upon pyrolysis. Our goal is to develop inorganic additives that give high green density compacts with high ceramic yield. Ideally, introduced oxide should act to increase the effective density of the green compact by occupying the interparticle pore spaces. If the polymer "backbone" remains in the body, less weight loss will be experienced during burnout, decreasing the possibility of void formation.

The effects of four different polymers on sedimentation were analyzed in this study. Three have oxide-forming capabilities, and one can form direct chemical bonds to the powder surface. A fully organic polymer is included for comparison. Experiments were performed in order to evaluate the effect of varying alumina water and/or hydroxyl concentrations on compaction behavior during sedimentation. Further studies seek to gauge the effect of polymer molecular

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weight and the presence of highly polar groups in the polymer on the time evolution of density profiles.

## EXPERIMENTAL

The polymers used in this study were: (1) Hydrosiloxanes (Figure 1): This polymer<sup>a</sup> consists of an inorganic -Si-O-Si- backbone and protons along the polymer chain. Figure 1a shows the mechanism of direct chemical attachment to the particle surface which this particular polymer can undergo [2]. A variety of molecular weights were used in this investigation; (2) Polyacryloxypropylsiloxane (PAS) (Figure 2): This polymer<sup>a</sup> is similar to the hydrosiloxanes in that it also consists of an -Si-O-Si- backbone, but it possesses acryloxypropyl groups containing highly polar carbonyls along its length; (3) "Mullite-former" (MF) (Figure 3): A polymeric material shown to be capable of forming 100% mullite [3] after pyrolysis. This was synthesized from the reaction of aluminum triisopropoxide acetoacetic chelate and diphenyl silane diol.<sup>b</sup> The compound has not yet been fully characterized; and (4) Fluorinated Polyester (FPE) (Figure 4): A fluorinated polyester<sup>c</sup> is used that has the inexact structure [4] shown (note the presence of highly polar -C=O and -F groups).

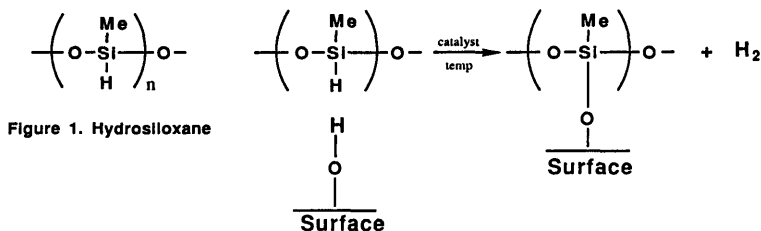
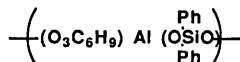
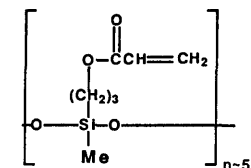


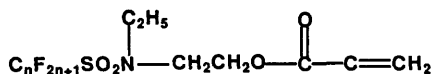
Figure 1a. Chemical attachment of hydrosiloxanes to a surface.



a Huls America, Bristol, PA.

b Alfa Chemicals, Danvers, MA.

c 3M Corporation, Minneapolis, MN.

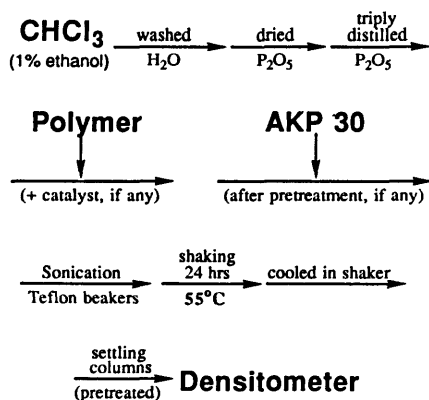


**Figure 4. Fluorinated polyester (FEP).**

The following techniques were used to characterize the effects of the various inorganic polymers on net particle/particle motion:

1. Gamma-ray Densitometry (GRD) was used for non-destructive analysis of density [5-7] as a function of time and position during the consolidation of green compacts. This technique uses the Beer-Lambert Law to describe the absorption of gamma rays by ceramic compacts as a function of particle packing density. GRD allows the monitoring of time- and position-dependent sedimentation behavior in much more detail than by visual estimation of sediment heights alone.
2. Near IR (NIR) uses shorter wavelength IR (0.7 to 3  $\mu\text{m}$ ) to create third and fourth overtones for molecular detection and identification [8-10].
3. Nuclear Magnetic Resonance (NMR) was used in the detection and quantification of -OH [11] and other groups [12] on the surface of oxide powders.

## **Processing**



**Figure 5. Processing route used in the treatment of alumina particles.**

The processing route used to treat the alumina powders is pictured in Figure 5. The polymers, dispensed under Ar in a glove box, were added to the dried  $\text{CHCl}_3$  [13] (at a concentration of  $4 \times 10^{18}$  chains/ $\mu\text{m}$ ) with any needed catalyst. Four volume % alumina<sup>f</sup> (with an average particle size of 0.41  $\mu\text{m}$ ) was then added to the solution followed by 10 min of sonication over a heat source. The parent solution level was adjusted before addition to fluorinated polyester (FEP) centrifuge tubes. These tubes were then placed in a shaker arm, heated to 55°C and agitated for 24 h before pouring the solution into Pyrex sedimentation tubes that were pretreated with  $(\text{CH}_3)_3\text{SiCl}$  to decrease wall effects [14].

## RESULTS AND DISCUSSION

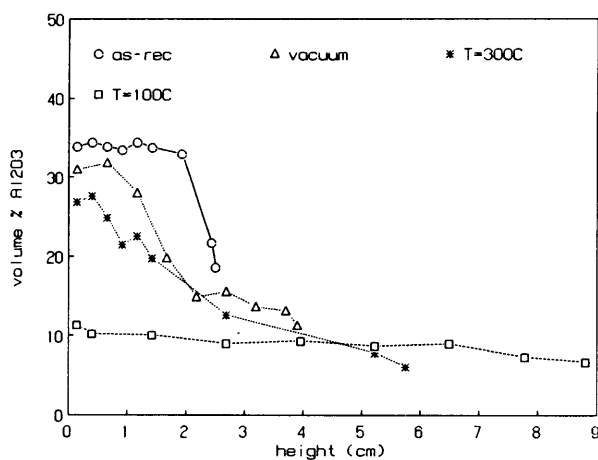
Suspensions were first prepared from as-received powder, powder treated in a vacuum, and powders heated to 100° and 300°C, respectively, in argon. The GRD results obtained from stable sediments are shown in Figure 6. The as-received and vacuum-treated powders formed spherical agglomerates of 2-3 mm in size, while the 100°C treated powder suspension agglomerates exhibited a flake-type morphology. The 300°C treated powder suspension had no discernible characteristics. These results seem to show that at least part of the barrier to forming high density green compacts in chloroform could possibly be due to adhesive surface-induced phase-separation of water (which is immiscible in chloroform); this type of phase-separation has been shown to occur between two surfaces when they are still well separated [15].

Figure 7 shows that there was no significant effect from attaching different molecular weight hydrosiloxanes (given here as the approximate number of monomeric units/chain) on the sedimentation profiles of as-received powder. Preliminary adsorption studies suggest that this behavior is not a function of the molecular weight of the additive but more a function of the amount adsorbed. The polymer chains compete with each other for adsorption sites on the powder surface, and each unit in any size polymer chain that reacts with the powder surface will occupy an identical amount of space. If these chemisorbed polymers adsorb strongly to the surface and nearly all the bonding sites of any size chain are involved in surface interactions, then only the area of powder surface/polymer chain will increase with molecular weight, not the overall thickness of the polymer layer. The higher molecular weight polymers will occupy more surface area and limit the apparent adsorption; this is responsible for the apparent poor adsorption of the higher molecular weights in comparison to the lower molecular weights. Thus it may be that a similar layer of adsorbed polymer is produced on the surface of each particle regardless of molecular weight, giving rise to similar sedimentation behavior.

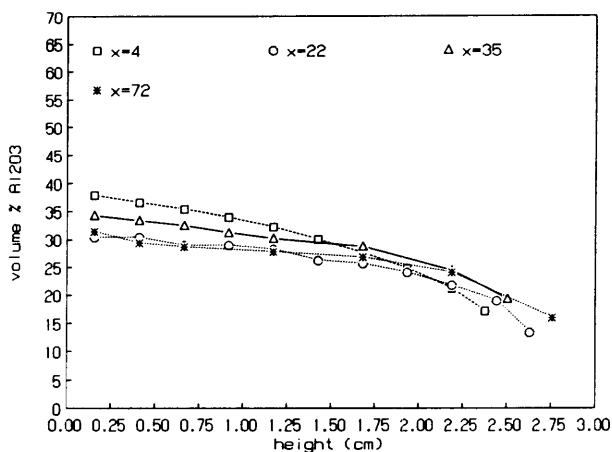
The corresponding density profiles (versus time) for the PAS system are seen in Figure 8. A more dense region less than 2 cm high has built up after 72 h; this region has a relatively dispersed (less than 5% dense) region above it which extends to 15 cm. This figure indicates that, after a certain time, compaction seems to occur mostly at the interface between the compact and the more dispersed region.

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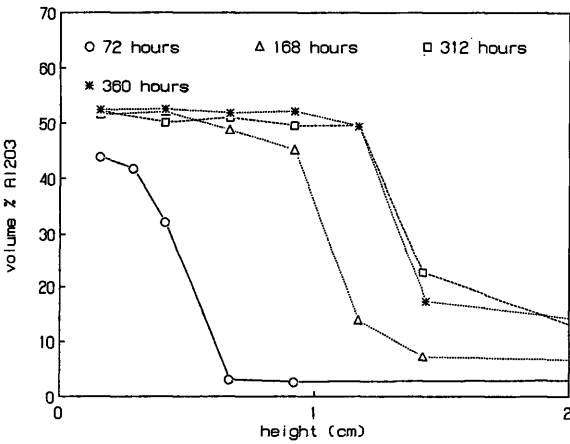
<sup>f</sup> AKP-30, Sumitomo Corp., San Francisco, CA.



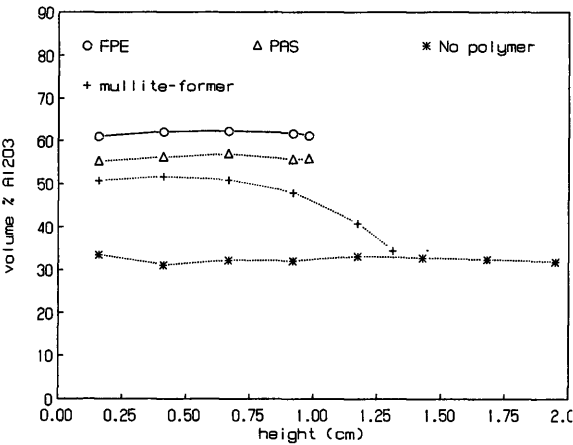
**Figure 6.** Density profiles as a function of powder surface pretreatment. Agglomerate morphology in this solvent varied markedly with powder pretreatment.



**Figure 7.** Density profiles as a function of hydrosiloxane molecular weight. All these polymers were chemically attached to the surface. Observed variances are negligible.



**Figure 8.** PAS density profiles versus time. Only a portion of the data is shown here; at 72 h the observed sediment extended to over 15 cm in height.



**Figure 9.** Comparison of net dried density profiles for the non-attached systems investigated.

The dried compact profile for PAS is shown in Figure 9. By comparing this profile to that of the final "wet" profile (Figure 8, 360 h), we see that the bulk of the compact experiences only a few percent compaction upon drying, while the upper less dense region has collapsed into a small fraction of its former height.

Figure 9 compares the PAS dried density to that produced by FPE, the mullite-former, and a compact prepared from as-received powder. Note that the additives containing highly polar groups give rise to fairly constant density profiles, while the mullite-former exhibits a "tail" of decreasing density. This behavior was also observed in the presence of hydrosiloxanes and a clear explanation for this behavior is not provided presently.

Strictly qualitative observations of these suspensions indicated differences in their relative sedimentation behavior. Some suspensions required several weeks before a stable sediment was formed, had a poorly defined sediment/supernatant interface, and tended to have a visible concentration of fines in the supernatant. Other suspensions formed a stable sediment in less than 48 h, had a sharply defined sediment/supernatant interface, and had no fines visible in the supernatant. If we characterize the first group as being more dispersed than the second, we can rank this "dispersity" as PAS > FPE > mullite-former > no additive. This observation, when combined with the dry density data, is at odds with studies involving aqueous-forming techniques, which suggests that the more dispersed system will form higher density compacts [16]. Although the FPE system did not display as much dispersed behavior as the PAS system, it produced a denser compact.

Finally, although it was found that NIR is not sensitive enough to monitor -OH concentration on the powder surface, it can be used to accurately monitor dilute concentrations of polymer remaining in solution after adsorption by the powder surface. Further studies with this technique will be used to gauge the amount of polymer adsorbed onto the surface of the powder.

The NMR spectra of these powders consist of two components, a broad chemisorbed (strongly bonded) -OH component and a narrow physisorbed (mobile) component. After adsorption of hydrosiloxanes to the surface, the chemisorbed -OH's appear to be unaffected while the concentration of the physisorbed -OH's is decreased. This behavior supports the idea that polymer-surface bonding is taking place under these conditions. Also detectable are the methyl protons of the polymer lying on the surface of the powder. This data may be quantifiable and could provide numerical information on the spatial distribution of -OH and -CH<sub>3</sub> on the powder surface [11]. Coupling this data with NIR data is expected to provide an accurate picture of polymer/surface interactions in these systems.

## CONCLUSIONS

Inorganic polymer additives can modify particle/particle interactions and thus the overall powder compaction behavior in these nonaqueous systems. We have found evidence suggesting the identity of the desired components of inorganic polymers which can produce both high green densities and ceramic yield.

The addition of almost any polymeric material to a particle surface in chloroform changes these interactions, at least partially, via "screening" of adhesive forces between water molecules adsorbed on different particles. The changes these additives induce on the density profiles produced by gross particle motion can be efficiently monitored by GRD. Polymers containing highly polar components tend to produce constant density profiles of greater than 55% density, while those with nonpolar, reactive components produce profiles with a large gradient in packing density.

## ACKNOWLEDGMENTS

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## REFERENCES

1. J. S. Reed, in Ceramic Transactions, Vol. I, Ceramic Powder Science II, edited by G. L. Messing, E. R. Fuller, and H. Hausner, (American Ceramic Society, Westerville, OH, 1988), p. 601.
2. Silicon Compounds, Petrarch Systems (1987), p. 275.
3. J. J. Lannutti and I. A. Aksay, to be submitted to the *J. Am. Ceram. Soc.*
4. D. G. Gallagher, Ph.D. Thesis, University of Washington, Seattle (1988).
5. C. H. Schilling, G. L. Graff, W. D. Samuels, and I. A. Aksay, in Atomic and Molecular Processing of Electronic and Ceramic Materials: Preparation, Characterization, and Properties, edited by I. A. Aksay, G. L. McVay, T. G. Stoebe, and J. F. Wager (Mater. Res. Soc. Symp. Proc., Pittsburgh, PA 1987), pp. 239-51.
6. L. Stroosnijder and J. G. De Swart, *Soil Science* 118, 61 (1974).
7. D. L. Nofziger and D. Swartzendruber, *J. Appl. Phys.* 45, 5443 (1974).
8. D. M. Mayes and J. B. Callis, *Appl. Spect.* 43, 27 (1989).
9. L. G. Weyer, *Appl. Spect. Rev.* 21, 1 (1985).
10. O. H. Wheeler, *Chem. Rev.* 59, 629 (1959).
11. L. B. Schreiber and R. W. Vaughan, *J. Catal.* 40, 226 (1975).
12. G. J. Exarhos, K. F. Ferris, D. M. Friedrich, and W. D. Samuels, *J. Am. Ceram. Soc.* 71, C-406 (1988).
13. D. D. Perrin and W. L. F. Armarego, Purification of Laboratory Chemicals, 3rd ed., (Pergamon Press, New York, 1988), p. 121.
14. J. V. Dawkins and G. Taylor, *Polymer* 20, 599 (1979).
15. H. K. Christenson, R. G. Horn, and J. N. Israelachvili, *J. Colloid Interface Sci.* 88, 79 (1982); H. K. Christenson, *ibid.* 104, 234 (1985).
16. T. Yeh and M. D. Sacks, *J. Am. Ceram. Soc.* 71, 841 (1988).