

Competitive Adsorption of Dispersant and Binder on Alumina and Its Effect on the Electrokinetic Behavior in Aqueous Media

Ungyu Paik

Department of Ceramic Science and Engineering, Changwon National University
Changwon, Kyungnam 641-773, Korea

(Received October 21, 1998)

In wet powder processing of alumina, a number of organic molecules such as dispersant and binder are used to produce the flow behavior and properties requisite for shape forming. In this study, interparticle forces of alumina particles suspended in aqueous media were controlled by suspension pH, poly (methacrylic acid) (PMAA, used as dispersant) and poly (vinyl alcohol) (PVA, used as binder). The combined adsorption isotherms of the dispersant and binder additives on alumina were determined by total organic carbon analyzer, while the adsorption of dispersant was differentiated from binder in the mixed additive system by ultraviolet spectroscopy. The electrokinetic behavior of alumina suspensions were then correlated with the adsorption characteristics of dispersant and binder onto alumina particles. It was found that the isoelectric (pH_{iep}) of alumina shifted from $\text{pH } 8.9 \pm 0.1$ to acidic pH as PMAA concentration increased, while PVA adsorption did not affect the pH_{iep} but caused a decrease in the near surface potential.

Key words : Alumina, Dispersant, Binder, Adsorption isotherm, Interparticle forces

I. Introduction

Characterization of electrokinetic behaviors of alumina particles suspended in aqueous media is important in developing an optimum ceramic powder processing condition.^{1,2)} It is obvious that a large number of unit operations and chemical additives are involved as very fine ceramic particles are processed in aqueous environment. Various chemical additives are used to produce the flow behavior and suspension properties requisite for shape forming. Most often, anionic and nonionic molecules are used to the ceramic suspensions to achieve a number of functions. Anionic molecules such as polyacrylates are added to provide electrostatic interaction-based stability to the ceramic suspension.^{3,4)} The charge developed at the solid/liquid interface gives rise to the formation of a diffuse electrical double-layer surrounding each particle. The interaction of these double-layers provides a repulsive force between two approaching particles, and, if sufficiently large, will prevent agglomeration from two approaching particles.

Nonionic molecules such as poly (vinyl alcohol) (PVA) and cellulose are used as binder to provide green strength for handling.^{5,6)} The binder phase affects not only green strength, but also the stability of the ceramic suspension. Suspension processing has been widely used in ceramic forming processes such as spray drying, slip casting, tape casting and gel casting, etc. In general, multiple organic additives are used to satisfy the desired suspension properties required for each processing opera-

tion and to control resulting green-body characteristics. The majority of research efforts in suspension processing have been focused on the isolated interactions between a single organic component and the particle surface.^{7,8)} However, the complex interactions among organic components arising in suspensions containing multiple organic additives are expected to play a significant role in various suspension processing steps through their affect on dispersion stability, rheological properties, drying, and binder burn-out. In the present study, attempts are made to describe the results of surface-chemical and physical measurements to clarify the interactions between dispersant and binder in the aqueous alumina suspension system.

II. Experimental Procedure

High purity alumina (AKP-50, Sumitomo Co., Japan) was used in the present investigation. The mean particle size of alumina determined by x-ray sedimentation (Sedigraph 5100, Micromeritics, Norcross, GA) was $0.30 \pm 0.05 \mu\text{m}$, and the specific surface area measured by BET nitrogen-gas adsorption (Autosorb-1, Quantachrome, Syosset, NY) was $9.9 \pm 0.1 \text{ m}^2\text{g}^{-1}$. Poly (methacrylic acid) (Daxad-34, Mw=8000-10,000, Hampshire Chemical, Lexington, MA) was used as the dispersant and poly (vinyl alcohol) (Mw=25,000, 98 mole% hydrolyzed, Polysciences, Warrington, PA) was used as the binder. All suspensions were prepared in deionized water and pH adjustments were made by using analytical grade 1.0 N HCl or

NH_4OH . The deagglomeration procedure consisted of ultrasonic treatment of suspensions using a cup horn providing the suspension temperature constant and then suspensions were aged for 12 hours at room temperature.

The adsorption amount of PMAA and PVA onto alumina particle surfaces was determined by the solution depletion method using a total organic carbon (TOC) analyzer (DC-80, Rosemount Analytical, Santa Clara, CA). The PMAA adsorption was then differentiated from the total organic fraction using ultraviolet absorption spectroscopy (U-3000, Hitachi, Japan). To characterize the electrokinetic behavior of alumina particles suspended in various aqueous media conditions, an electroacoustic technique (ESA-8000, Matec Applied Sciences, Hopkinton, MA) was used. The measured electrokinetic sonic amplitude (ESA) is the pressure amplitude generated by the colloid per unit electric field strength, and is directly proportional to the dynamic electrophoretic mobility, $\mu(\omega)$, which in turn is a function of the particle zeta (shear-plane) potential:⁹⁾

$$\text{ESA} = c \Phi \Delta \rho \mu(\omega) G_r$$

where c is the speed of sound, $\Delta \rho$ is the density difference

between the particles and suspending medium, Φ is the volume fraction of solids and G_r is a form factor related to the geometric and acoustic characteristics of the electrode system.

III. Results and Discussion

In colloidal powder processing, the coincidental interaction of dispersants and binders at the solid-liquid interface creates a more complex situation, relative to the presence of a single additive. This will impact on the dispersion or aggregation of ceramic particles suspended in aqueous media. Fig. 1 schematically depicts the various surface chemistry states which are possible in the presence of model anionic and nonionic organic molecules. Fig. 1(a) represents the non-interactive state in which no significant adsorption occurs from either species. In this case, particle charge is determined solely by reactions of surface groups with the aqueous media. Fig. 1(b) and 1(c) depict the selective adsorption of anionic and nonionic species, respectively. Competition and displacement between nonionic and anionic organic molecules is illustrated

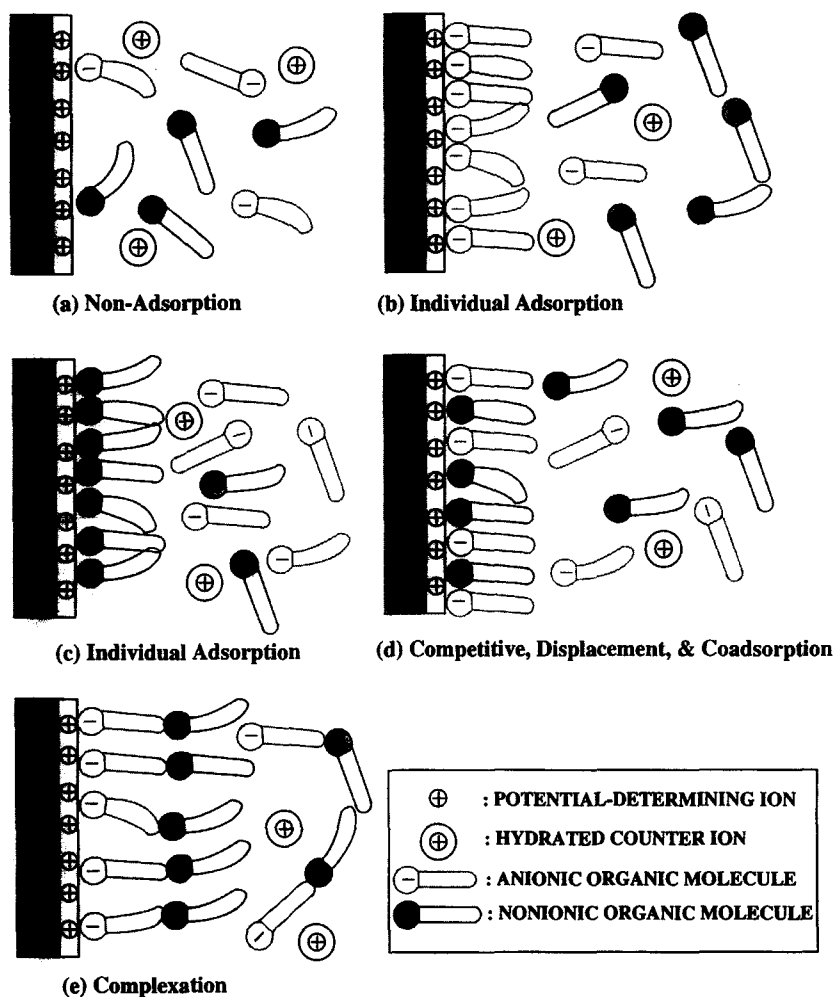


Fig. 1. Schematic illustration of possible interactions involving model organic compounds at the charged solid-solution interface.

strated in Fig. 1(d). Finally, Fig. 1(e) depicts one possible configuration in which complexation between nonionic and anionic organic molecules may take place to result in bilayer formation.

The interaction of dispersant and binder additives will be examined first individually and then collectively to understand the nature of this complex system.

1. Adsorption of PMAA

Fig. 2 shows that the electrokinetic behavior of alumina suspensions prepared with PMAA is strongly dependent on suspension pH and polymer concentration. The as-received alumina powder has a native isoelectric point (pH_{iep}) near pH 8.9. Below this pH, particles carry a net positive charge. However, with the addition of PMAA, the pH_{iep} of alumina shifted toward acidic pH, resulting in an increasingly negative surface at lower pH values. When the particles are saturated with ionized PMAA chains, the shear-plane potential exhibits a negative polarity at pH values in excess of about pH 2.7, with a nearly constant potential above pH 6. This has the effect of broadening the available pH range for processing, and permits access to a wider range of possible slurry processing conditions. As a result of the dissociation of carboxylic acid groups, PMAA ionizes with increasing pH to form a negatively charged organic molecule. PMAA chains form a compact polymeric coil in acidic pH, at low degrees of ionization, while in alkaline pH the highly ionized PMAA chains assume a stretched conformation.¹⁰

Table 1 shows the saturated adsorption of PMAA on

alumina at suspension pH values of 4.0 ± 0.1 , 6.0 ± 0.1 , and 9.0 ± 0.1 . Adsorption of PMAA at pH 9 is minimal, but the uptake increases significantly with decreasing suspension pH. Fully ionized PMAA at pH 9, exhibits small interaction with the alumina surface. Below the pH_{iep} , however, electrostatic forces become favorable for strong interaction between the anionic PMAA and positively charged alumina surface. It is apparent that the adsorption of PMAA on alumina is primarily driven by electrostatic interactions, although hydrogen bonding may play an auxiliary role. At pH 6, where alumina carries positive charge, the adsorption of anionic PMAA on the particles increased and became saturated near 0.6 mgm^{-2} . At pH 4, the PMAA chains carry only a small residual charge,¹⁰ but exhibit a substantial increase in the adsorption amount. This is due to a precipitation process driven by instabilities, in which the hydrophobic PMAA chains simply clump together and adhere to the alumina surface.

2. Adsorption of PVA

Fig. 3 shows the electrokinetic behavior of alumina prepared with PVA as a function of suspension pH. The shear-plane potential of alumina is largely unaffected with the addition of PVA. Therefore, adsorption of PVA on alumina is driven by either hydrogen bonding or hydrophobic interaction. However, a significant decreasing surface potential of alumina with the increasing PVA concentration was observed. This effect is attributed to disruption of the shear-plane due to the presence of uncharged PVA chains at the alumina surface-solution interface,¹¹ and is essentially a physical phenomenon. This is further supported by the adsorption data for PVA (see Table 1), which clearly shows decreased adsorption in the acidic range where alumina particles are highly positively charged. This is because reduced affinity resulting from a "salting out" effect due to the electrostatic field near the highly charged surface.¹⁰

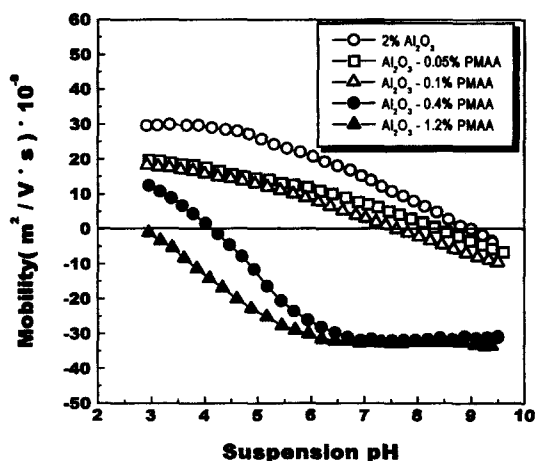


Fig. 2. Electrokinetic titration curves for alumina suspensions as a function of PMAA concentration and suspension pH.

Table 1. Estimated Plateau Adsorption Values (mg/m^2) for PMAA and PVA on Alumina as a Function of pH

pH	PMAA	PVA
4.0	1.32	0.10
6.0	0.57	0.19
9.0	0.25	0.20

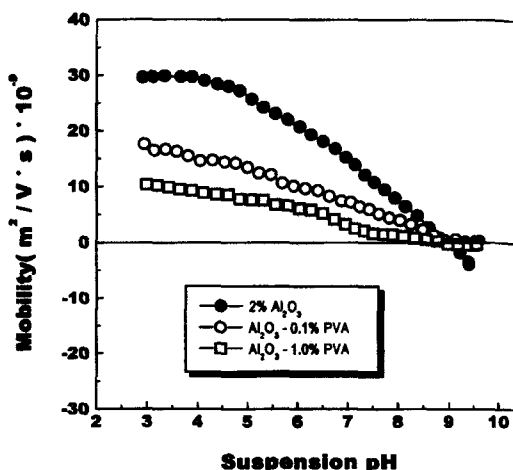


Fig. 3. Electrokinetic titration curves for alumina as a function of PVA concentration and suspension pH.

3. Competitive adsorption and coadsorption of PMAA-PVA

Fig. 4 shows the adsorption behavior of PVA onto alumina surface in the presence of PMAA at two suspension pH values and two concentrations of PMAA (mass fractions 0.4% and 1.2%). For the measurement of adsorption, alumina suspension prepared with PMAA and PVA were centrifuged at 18,000 rpm (41,700 m²/s) and the clear supernatant solution was then withdrawn to determine the concentration of the supernatant (defined as "residual concentration"). The amount of PMAA and PMAA+PVA is represented by open and filled symbols, respectively; the amount of PVA adsorption on alumina in the presence of PMAA is then defined by the difference listed in Table 2. At pH 4.0 and a mass fraction of 0.4%, the PMAA concentration represents roughly 1/3 of surface saturation amount based on an estimate of the plateau adsorption level in Table 1 for 1.2% PMAA (1.3 mgm⁻²). In these experiments, at a constant PMAA concentration, the level of PVA was gradually added from 0% to 1.0%.

The data in Fig. 4 clearly demonstrate that adsorption of PMAA on alumina is not affected by the subsequent

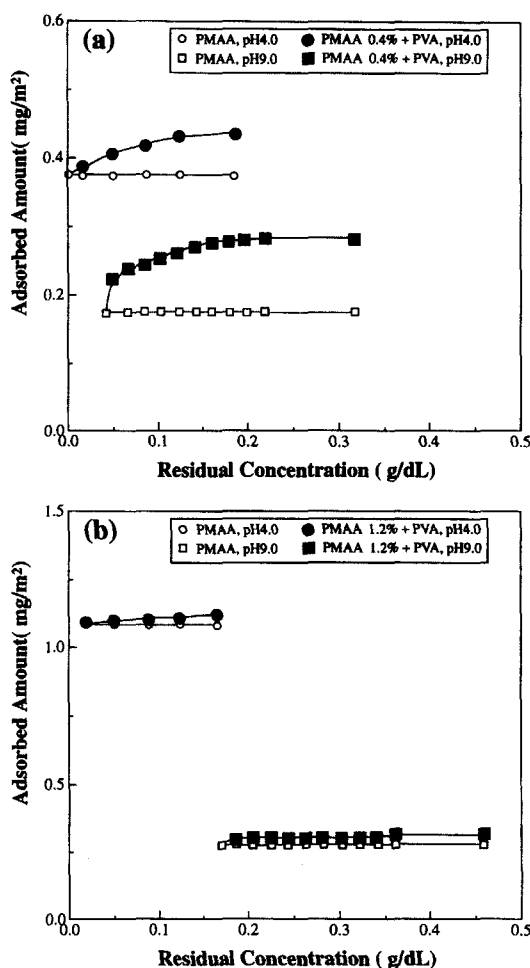


Fig. 4. Adsorption isotherms of PVA on alumina in the presence of (a) 0.4% PMAA and (b) 1.2% PMAA.

Table 2. Estimated Plateau Adsorption Values (mg/m²) for PVA on Alumina as a Function of pH and PMAA Concentration

pH	PMAA Concentration (%)		
	0.0	0.4	1.2
4.0	0.10	0.06	0.03
9.0	0.20	0.11	0.04

addition of PVA, indicating the absence of a competitive adsorption process as depicted in Fig. 1(d). The addition of PVA results in coadsorption onto alumina at 1/3 level of PMAA surface coverage. From this result, the adsorption of PVA onto PMAA-adsorbed alumina must involve at least one of the following processes: (1) a conformational change by adsorbed PMAA chains which frees up surface adsorption sites for PVA, (2) complexation between PMAA and PVA at the interface as schematically depicted in Fig. 1(e), or (3) a constant fraction of available surface sites on alumina which are not blocked by PMAA adsorption and results in coadsorption of PVA onto alumina surface. However, as the alumina surface is saturated with PMAA, no significant amount of PVA adsorption was observed,

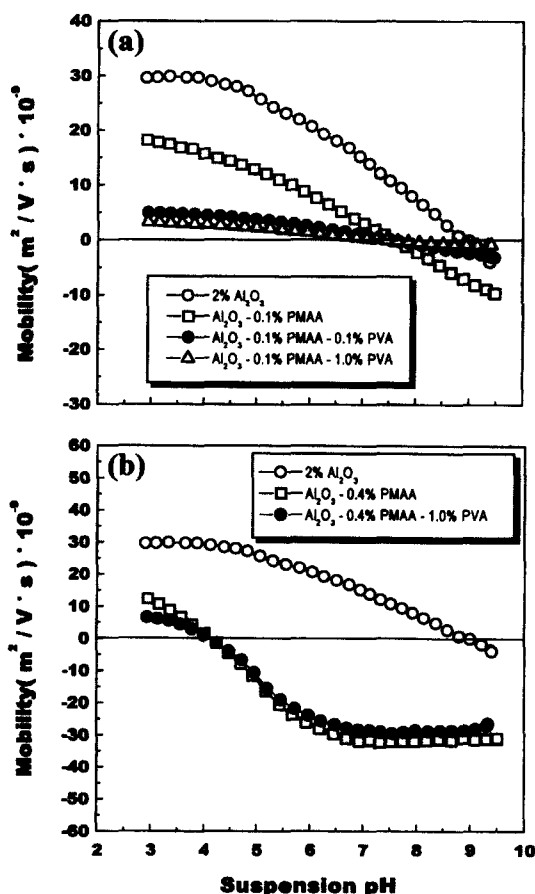


Fig. 5. Electrokinetic titration curves for alumina prepared with PVA in the presence of three mass fractions of PMAA: (a) 0.1% and (b) 0.4%.

which indicates that there is no available sites for further PVA adsorption on alumina surfaces which are blocked by PMAA.

The effect of PVA adsorption on the electrokinetic behavior of alumina suspensions as a function of both PVA and PMAA concentration is illustrated in Fig. 5. It is clear that the pH_{zpc} is not modified by the presence of PVA, in agreement with adsorption results shown in Fig. 4 which indicate that PMAA is not displaced by PVA. In other words, the surface charge characteristics of alumina are determined entirely by the interaction between ionizable surface sites and the carboxyl groups of PMAA. The reduction of mobility values on either side of the pH_{zpc} in the presence of PVA can be interpreted as a physical phenomenon, as previously described, in which PVA chains in the interfacial region cause an outward shift of the shear-plane thereby lowering the measured potential.

IV. Conclusions

The electrokinetic properties of the alumina-PMAA-PVA system are largely determined by specific interactions of PMAA with alumina surface. PVA has little impact on the electrokinetics, other than a small-to-moderate decrease in dynamic mobility, probably as a result of its physical disruption of the particle shear-plane shown in Fig. 1-(d). In contrast, PMAA expands the stable pH range for alumina from above pH 9 to below pH 5; in the absence of PMAA, alumina is only stable below pH 4 or above pH 9. Coadsorption of PVA on alumina in the presence of PMAA occurs at 1/3 level of PMAA surface coverage, but no further adsorption of PVA on alumina saturated with PMAA. This indicates that adsorption of anionic molecules on alumina surfaces bonded by electrostatic attractive forces competed over the nonionic molecules.

Acknowledgment

This work was supported by the Korea Science and Engineering Foundation(KOSEF) under contract No. 971-0801-001-2.

References

1. D. W. Fuerstenau, R. Herrera-Urbina and J. S. Hanson, "Adsorption of Processing Additives and the Dispersion of Ceramic Powders"; pp. 323-51, in Ceramic Tran-

- sactions, Vol. 1, Ceramic Powder Science. Edited by G. L. Messing, E. R. Fuller Jr. and H. Hausner. American Ceramic Society, Westerville, OH, 1988.
2. A. Roosen and H. Hausner, "Techniques for Agglomeration Control During Wet-Chemical Powder Synthesis," *Adv. Ceram. Mater.*, **3**(2), 131-137 (1988).
3. J. C. Cesarano III, I. A. Aksay and A. Bleier, "Stability of Aqueous- Al_2O_3 Suspensions with Poly (methacrylic acid) Polyelectrolyte," *J. Am. Ceram. Soc.*, **71**(4), 250-255 (1988).
4. V. A. Hackley, "Colloidal Processing of Silicon Nitride with Poly (acrylic acid). I. Adsorption and Electrostatic Interactions," *J. Am. Ceram. Soc.*, **80**(9), 2315-2325 (1997).
5. C. S. Khadikar and M. D. Sacks, "Effect of Poly (vinyl alcohol) on the Properties of Model Silica Suspensions"; pp. 397-409, in Ceramic Transactions, Vol. 1, Ceramic Powder Science. Edited by G. L. Messing, E. R. Fuller Jr., and H. Hausner. American Ceramic Society, Westerville, OH, 1988.
6. G. Y. Onoda Jr., "The Rheology of Organic Binder Solutions"; pp. 235-51, in Ceramic Processing Before Firing. Edited by G. Y. Onoda and L. L. Hench. Wiley-Interscience, New York, 1978.
7. P. C. Hidber, T. J. Graule, and L. J. Gauckler, "Competitive Adsorption of Citric Acid and Poly (vinyl alcohol) onto Alumina and Its Influence on the Binder Migration during Drying," *J. Am. Ceram. Soc.*, **78**(7), 1775-1780 (1995).
8. A. W. M. de Laat and G. L. T. van den Heuvel, "Competitive and Displacement Adsorption of Polyvinyl Alcohol and the Ammonium Salt of a Polyacrylic Acid on $BaTiO_3$," *Colloids Surf.*, **70**, 179-187 (1993).
9. R. W. O'Brien, Electro-Acoustic Effects in a Dilute Suspension of Spherical Particles, *J. Fluid Mech.*, **190**, 71-86 (1988).
10. A. R. Mathieson and J. V. McLaren, "Potentiometric Study of the Conformational Transition in Poly (acrylic Acid)," *J. Polym. Sci. Part A: Polym. Chem.*, **3**, 2555-2565 (1965).
11. D. J. Hemker, K. Char, H. T. Oyama, A. P. Gast and C. W. Frank, "Macromolecular Complex Formation and Polymer Adsorption on Colloidal Particles in Aqueous Solution," Chapt. 13, pp. 263-84, in Polymers in Aqueous Media, Performance Through Association, Edited by J. E. Glass, American Chemical Society, Washington, D.C., 1989.
12. V. A. Hackley, U. Paik, B. Kim and S. G. Malghan, "Aqueous Processing of Sintered Reaction-Bonded Silicon Nitride. I. Dispersion Properties of Silicon Powder," *J. Am. Ceram. Soc.*, **80**(7), 1781-1788 (1997).