

Binder Distribution in Spray-Dried Alumina Agglomerates

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Abstract

Organic binders, especially those which are water-soluble, tend to migrate with the solvent flow which occurs during the spray-drying process of ceramic suspensions. The adsorption isotherm of PVA on the surface of alumina particles shows a rather low affinity of the polymer when compared to that of the ammonium polymethacrylate. Only 6% of the added PVA (3wt% on a dry weight basis of alumina) was adsorbed onto the alumina surface, and the main fraction of 'free', non-adsorbed, binder was able to migrate during drying. Images of the distribution of the polyvinyl alcohol in the alumina agglomerates and in the green compacts indicate an inhomogeneous distribution of the binder. The PVA segregates to the surface of the granules and leads to the formation of a polymer-rich layer. The thickness of this layer, which contains about 50% of the binder introduced, was estimated to be a few percent of the granule radius. © 1998 Elsevier Science Limited. All rights reserved

1 Introduction

It is well known that, during the process of drying suspensions, the soluble species or fine particles tend to migrate with the solvent to the surface. Capes¹ has studied the redistribution of sodium chloride in sand agglomerates and has concluded there is an important segregation to the vicinity of the surface. More recently, Hidber² has investigated segregation of polyvinyl alcohol (PVA) during the drying of alumina samples prepared by centrifugation of an alumina suspension. The binder, homogeneously distributed through the whole sample before the drying process, segregated in a drastic manner within the sample during drying in

an oven at 60°C. Such results agreed with those obtained by Zhang,³ who, in addition, indicated that the tendency of this polymer to segregate increased with its concentration in the suspension.

Thus, we can reasonably expect that during spray-drying of a ceramic suspension, a segregation of the water-soluble binder occurs and that an inhomogeneous distribution of organic additives in the granules takes place. To the best of our knowledge, no paper, until now, has dealt with the distribution of binder in spray-dried granules or in a green compact prepared by dry-pressing. In order to understand the main contributions of the binder to the properties of the green compact, the distribution of the organic phase in the agglomerates must first be known. The aim of this paper is to clarify the distribution of PVA in spray-dried agglomerates, to discuss it in relation to the adsorption characteristics of the binder onto alumina, and finally to propose an estimation of the thickness of the binder-rich layer at the surface of the granules.

2 Experimental

An α -alumina powder (P152SB, Péchiney, France) with a specific surface area of 3 m² g⁻¹ and an average particle size of 1.3 μ m was used in this work. An aqueous suspension containing 60 wt% of alumina was spray-dried in a pilot plant equipment. The formulation of the suspension included 0.2 wt% of ammonium polymethacrylate (PMAA-NH₄⁺, M_w = 10 000, Darvan C, Vanderbilt, UK) as dispersant and 3 wt% of polyvinyl alcohol (PVA 4-88, M_w = 31 000, degree of hydrolysis = 88 mol%, Hoechst, Germany) as binder on the dry weight basis of alumina. The mean size of spray-dried granules was about 200 μ m. Disk-shaped samples (diameter = 30 mm, thickness \approx 5 mm) were die-pressed from this spray-dried powder.

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In order to obtain more accurate results concerning the adsorption behavior of the dispersant (PMAA-NH₄⁺) and of the binder (PVA) onto the surface of alumina particles, an other alumina powder (P172SB, P echiney, France) possessing a larger specific surface area (10 m² g⁻¹) and conversely a smaller particle size of 0.3  m was used. This alumina possesses features, such as surface chemistry and impurities, similar to those of the P152SB alumina. As a consequence we have assumed that the results of adsorption could be transposed from the P172SB to the P152SB alumina. The adsorption of PMAA-NH₄⁺ was evaluated by a rest gravimetric technique. Suspensions containing 20 wt% Al₂O₃ (P172SB) were prepared with various amounts of PMAA-NH₄⁺ at pH   8–9. The suspensions were put onto a gentle mechanical shaker during 72 h to reach equilibrium, and then centrifuged at 2000 rpm for 60 min. A given fraction of the supernatant was dried in an oven for 3 days at 50 C then at 120 C for 1 h, a temperature selected to avoid thermal degradation of the dispersant. The residue was then heated at 600 C for 5 h. The weight difference before and after calcination allows an estimate the concentration of non-adsorbed polyelectrolyte in the suspension, and finally the amount adsorbed on the surface of alumina particles.

The adsorption of PVA on the surface of P172SB alumina particles, once dispersed with 0.2 wt% of PMAA-NH₄⁺ was also evaluated by the same method.

3 Results and Discussion

3.1 The adsorption of PMAA-NH₄⁺

The amount of adsorbed PMAA-NH₄⁺ on the surface of P172SB alumina particles increases rapidly near the origin until it reaches a plateau at 0.35 mg m⁻², suggesting a high affinity of the polyelectrolyte for the alumina surface (Fig. 1). This adsorption isotherm of PMAA-NH₄⁺ is similar to that obtained by Cesarano *et al.*⁵ for a different alumina (AKP30, Sumitomo, Japan) in the same range of pH. At the adsorption plateau, very close values (0.37 mg m⁻² for Cesarano *et al.*,⁵ 0.35 mg m⁻² in the present work) were reached.

The knowledge of the adsorption isotherm of PMAA-NH₄⁺ allowed a choice of the optimum amount of dispersant in a further study concerning the adsorption of PVA on dispersed alumina particles. According to the results displayed in Fig. 1, the concentration of free PMAA-NH₄⁺ in the suspension is negligible if the amount introduced is below 0.2 wt% on a dry weight basis of alumina.

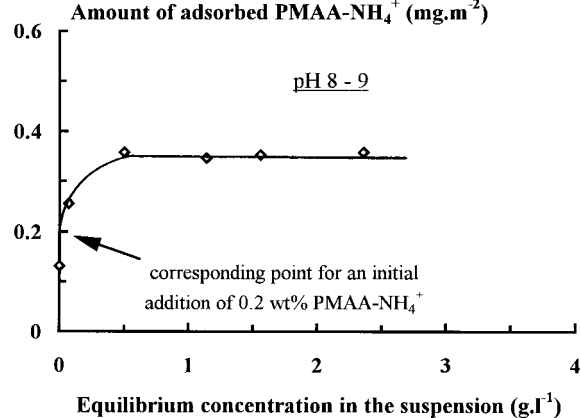


Fig. 1. Adsorption isotherm of PMAA-NH₄⁺ on alumina particles (P172SB).

3.2 The adsorption of PVA

The adsorption isotherm of PVA on P172SB alumina particles is typical of a low affinity type (Fig. 2). The amount of adsorbed PVA increases more or less linearly with the concentration of the binder in solution for initial concentrations ranging from 0 to 4 wt% with respect to alumina.

In a recent paper, Hidber studied the adsorption of PVA on an alumina powder dispersed with citric acid at pH 4–10.² He has shown that the presence of PVA did not change the adsorption characteristics of citric acid. The mechanisms responsible for the stabilization of suspensions of alumina, using either citric acid or PMAA-NH₄⁺ as dispersant, present some similarity. The citric acid is an organic polyacid, like polyacrylic acid, and the groups responsible for both adsorption on the surface of alumina and for electrostatic stabilization of alumina are the carboxylic groups COO⁻, as in the case of PMAA-NH₄⁺.

These results reported by Hidber,² as well as the low-affinity revealed by the adsorption isotherm of PVA onto alumina, suggest that the PVA does not

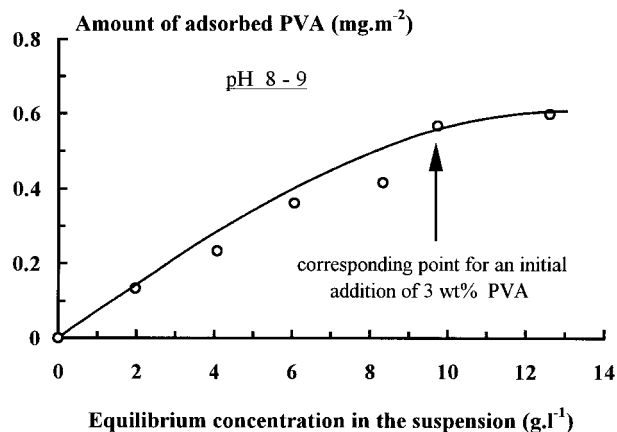


Fig. 2. Adsorption isotherm of PVA on alumina particles (P172SB), once dispersed with 0.2 wt% of PMAA-NH₄⁺ on a dry weight basis of alumina.

desorb the acrylic dispersant, and that the non-adsorbed amount of PMAA-NH₄⁺ can be considered as negligible, for the concentration introduced (i.e. 0.2 wt%), even in the presence of the binder.

The maximum quantity of PVA adsorbed amounts to 0.6 mg m⁻² after an initial addition of 3 wt% (Fig. 2). On the linear part of the adsorption isotherm, only about 20 % of the binder introduced is adsorbed. This value was in agreement with the result obtained by Hidber,² who reported that 14% of the PVA introduced was adsorbed on an alumina powder (HRA10, Martinswerk, Germany) with a similar specific surface area (10 m²g⁻¹), dispersed by citric acid, at a pH value ranging from 5 to 8.5.

According to Fig. 1, the amount of PMAA-NH₄⁺ (0.2 wt%) needed to obtain a good dispersion of the suspension is too low to ensure the total coverage of the surface of alumina particles. Then a fraction of this surface remains available for adsorption of the binder. The PVA adsorption decreases when dispersant concentration² increases because less sites are available for binder adsorption. Consequently, in a ceramic slurry for spray-drying, a large fraction of PVA added (about 80 wt%) remains free in the solution, and is able to migrate to the agglomerate surface where the solvent evaporates, during spray-drying. Furthermore during this process, the droplets are subjected to heat. Then with a view to a comprehensive study of adsorption, the temperature would also need to be taken into account because it is expected to influence the adsorption behavior of PVA. In particular, Zhang has shown that the amount adsorbed decreases when temperature was increased.³

The specific surface area of the alumina (P152SB) used to prepare spray-dried powders is approximately three times smaller than that of the P172SB powder studied (10 m²g⁻¹). Then the amount of PVA adsorbed on the P152SB alumina is likely reduced in the same ratio, i.e. 6% of the PVA introduced. Such a low amount is not clearly able to prevent from migration of the binder during spray-drying.

3.3 The migration of PVA during spray-drying

Determination of the binder distribution (PVA) within the spray-dried granules and in the green compacts is not an easy matter from a practical point of view. Especially, modern analytical techniques, such as Raman and IR spectroscopy, prove to have very limited efficiency on samples which are porous, friable and also insulating from an electrical point of view. Nevertheless, a suggesting image can be obtained by optical microscopy on a green sample prepared from the spray-dried

P152SB alumina powder and heat treated at 300°C in air for 20 min. The pyrolysis of the PVA starts at 200°C in air (Fig. 3), and leads to brown-colored species issued from polymer degradation, which help to trace the distribution of the organic phase either in the agglomerates or in the compact [Fig. 4(a)]. This picture clearly showed the formation of a binder 'shell' all around the granules which deformed during compaction. According to SEM observations, the ceramic particles did not seem to be densely packed at the surface of the granules and the observed binder distribution cannot be attributed to capillary migration of eventual molten PVA. Figure 4(b) shows the surface of a pressed sample in contact with the punch after heat treatment, it is obvious that the imposed deformation of this shell during the compaction process leads to its fracture and binder depleted areas, compared to the outer part of the granule, appear as white splotches on Fig. 4(b).

During spray-drying, the granules develop a non uniform distribution of the binder when water evaporates. The water soluble binder ('free' binder molecules) migrate by a combined process:³ transport of PVA by the solvent to the surface during the constant-rate period of the drying process, and diffusion of the polymer in the opposite direction due to a developing concentration gradient. As the solvent evaporates at the surface, however, the non volatile binder remains and forms a surface layer.³⁻⁶ This 'shell' contains ceramic particles embedded in a porous polymeric matrix. A crude estimation of the shell thickness ϵ can be obtained according to the two following assumptions.

First, we assume that the shrinkage of spherical droplets of dispersed slurry proceeds uniformly during drying leading to spherical granules. Secondly, we assume that all the binder added (3 wt%) migrates to the surface of the granules and form a continuous shell of pure polymer. The following relation can then be used:

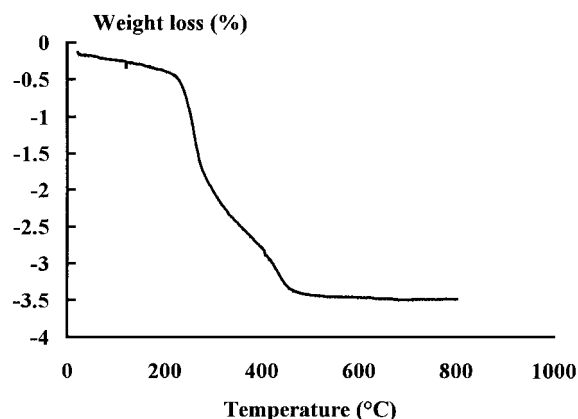
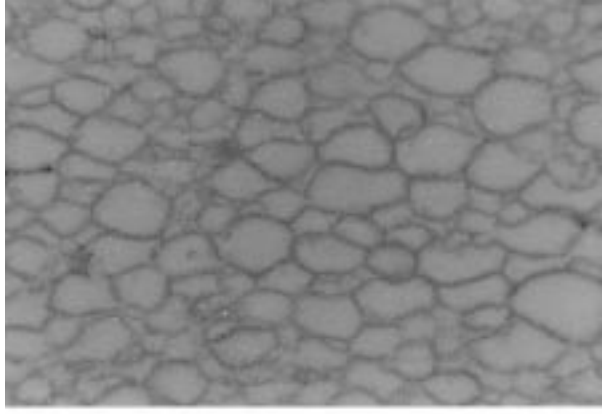
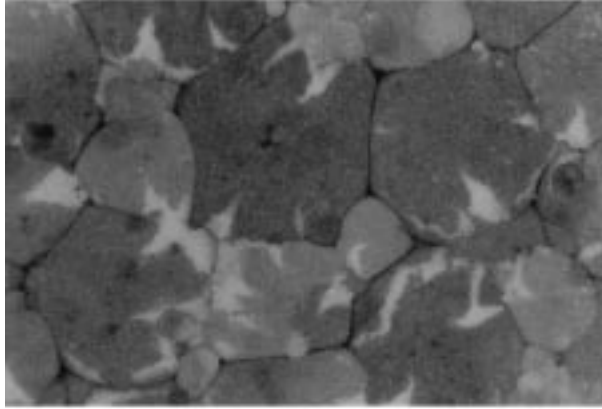


Fig. 3. TGA of the spray-dried P152SB powder, containing 3 wt% PVA and 0.6 wt% H₂O on a dry weight basis of alumina.



(a)



(b)

Fig. 4. An optical microscopy image of the binder (PVA) distribution on a P152SB sample containing PVA and treated at 300 °C in air for 20 min. (a) The sample was fractured and a flat surface obtained with a razor blade; (b) the surface of a pressed sample in contact with the punch after heat treatment.

$$0.03 = \frac{4\pi R^2 \varepsilon \rho_b}{\frac{4}{3}\pi R^3 \rho_c} \quad (1)$$

where R is the radius of the granule, typically 100 μm in this study, and, ρ_b and ρ_c are the density of the binder [1.26 g cm^{-3} (Ref. 7)] and of the core of the granule [2.11 g cm^{-3} (Ref. 8)], respectively. The thickness of the shell, under the present conditions, would then be given by:

$$\varepsilon \approx 1.5 \times 10^{-2} R \quad (2)$$

However, some correcting factors have to be taken into account in the calculation of this value of the thickness. On one hand, the shell contains ceramic particles.⁴ If one assumes that the packing density of ceramic particles is constant from the center to the surface of the granule, as well as in the shell itself, i.e. about 0.5,⁸ the thickness calculated from eqn (2) should be multiplied at least by a factor 2. On an other hand, all the ‘free’ binder does not migrate to the surface to form the ‘shell’.

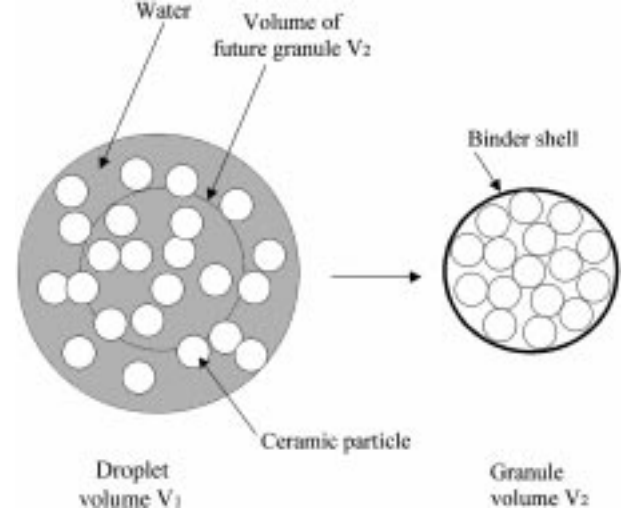


Fig. 5. Schematics of the evolution of a spherical droplet of dispersed slurry during drying.

Two different assumptions were made to get reasonable estimations of the proportion of binder contained in the core of the granules. First, the amount of binder adsorbed on the surface of particles was neglected. Secondly, the volume V_1 of a spherical droplet was considered to decrease, during drying, until it reaches a fixed volume V_2 corresponding to the volume of the final spherical granule (Fig. 5), and the amount of binder initially contained in this volume V_2 was supposed to be maintained. Therefore, the binder initially contained in the volume $(V_1 - V_2)$ was considered to be distributed on the surface of the granule, giving rise to the shell.

Then, the proportion of the binder contained in the shell of the granules was calculated for three suspensions containing 40, 60 and 80 wt% of alumina, respectively (Table 1).

The amount of binder located on the surface of the granule increases when the concentration of alumina in the suspension decreases. For a 60 wt% solid loading, almost 50 wt% of the introduced

Table 1. An estimation of the binder proportion distributed between the surface and the volume of the granule

Weight of alumina(g)	40	60	80
Weight of water	60	40	20
Volume of alumina (cm^3) (density $\approx 4 \text{g cm}^{-3}$)	10	15	20
Volume of the spherical droplet (V_1) (cm^3)	70	55	40
Volume of the spherical granule (V_2) (cm^3)	19	28.6	38
Amount of binder contained in the shell (% of the initial binder content) $= 100(V_1 - V_2)/V_1$	72.8	48	5

The initial volume of the spherical droplet of dispersed slurry containing 3 wt% of binder, on a dry weight basis of alumina, was arbitrary taken corresponding to an initial alumina + water mass equal to 100 g. The density of the spherical dry granule was taken equal to 2.1 g cm^{-3} .

binder would be able to migrate to the surface of the granule. One expects that this second factor compensates the first one. Then, the estimated thickness is $\varepsilon = 1.5 \mu\text{m}$ for a granule diameter of $200 \mu\text{m}$.

Such a value is probably underestimated, because the shell was porous, as revealed by SEM examinations on the granule surfaces.⁴ Whereas the estimation of the thickness ε of the binder-rich shell, from the coloured region observed on micrograph Fig. 4, is not rigorously correct because the granules were randomly cut, a rough approximation of the shell thickness is approximately $3 \mu\text{m}$ in our study conditions.

According to eqn (2), the thickness of the polymeric shell is also a linear function of the granule size.

4 Conclusion

The low specific surface area of the P152SB alumina (and even higher specific surface area P172SB one) only allows the adsorption of a limited amount of binder on the particle surfaces in the suspension. The non-adsorbed binder in the solvent migrates to the surface of droplets during spray-drying process and forms a polymer-rich shell at the surface of granules. This shell contains about 50% of the binder introduced. Its thickness is a linear function of the granule radius and was estimated to be several percent of the granule radius.

This heterogeneous distribution of the binder in spray dried granules affects the mechanical properties of the pressed samples.⁹

References

1. Capes, C. E., In *Agglomerate Bonding, Particle Size Enlargement*, ed. J. C. Williams and T. Allen. Elsevier Scientific, Amsterdam, 1980, pp. 43–49.
2. Hidber, P. C., Graule, T. J. and Gauckler, L. J., Competitive adsorption of citric acid and poly(vinyl alcohol) onto alumina and its influence on the binder migration during drying. *J. Am. Ceram. Soc.*, 1995, **78**(7), 1775–1780.
3. Zhang, Y., Kawasaki, M., Ando, K., Kato, Z., Uchida, N. and Uematsu, K., Surface segregation of PVA during drying of PVA–water– Al_2O_3 slurry. *J. Ceram. Soc. Japan*, 1992, **100**(8), 1070–1073.
4. Baklouti, S., Pressage de poudres d'alumine atomisées: influence des liants organiques sur l'aptitude au pressage. Ph.D. thesis, Limoges, France, 1996.
5. Cesareno III, J., Aksay, I. A. and Bleier, A., Stability of aqueous $\alpha\text{-Al}_2\text{O}_3$ Suspensions with poly(methacrylic acid) polyelectrolyte. *J. Am. Ceram. Soc.*, 1988, **71**(4), 250–255.
6. Lukasiwicz, S. J., Spray-drying ceramic powders. *J. Am. Ceram. Soc.*, 1989, **72**(4), 617–624.
7. Brandrup, J., and Immergut, E. H., (Eds) *Polymer Handbook*, 3rd ed. Wiley-Interscience, New York, 1989.
8. Baklouti, S., Coupelle, P., Chartier T., and Baumard, J. F., Uniaxial pressing of spray-dried alumina agglomerates. In *Ceramic Transactions*, Vol. 51, Ceramic Processing Science and Technology, ed. H. Hausner, G. L. Messing and S. Hirano. The American Ceramic Society, Columbus, OH, 1995 pp. 271–275.
9. Baklouti, S., Chartier, T. and Baumard, J. F., Mechanical properties of dry-pressed ceramic green products: the effect of the binder. *J. Am. Ceram. Soc.*, 1997, **80**(8), 1992–1996.