

The Effect of Binders on the Strength and Young's Modulus of Dry Pressed Alumina

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Abstract

The strength of green samples prepared from spray-dried powders of alumina is investigated versus forming pressure. The binders used are polyethylene glycol and polyvinyl alcohol (3 wt% with respect to alumina). The variation of strength is discussed in terms of, (i) the binder distribution in granules and in the pressed compacts, (ii) the glass transition temperature of the polymer and (iii) the adhesive properties of the external part of spray-dried granules. A transition from intra- to intergranule fracture mode is observed when the glass transition temperature of the binder increases. Finally, the results of a preliminary investigation concerning the variation of the Young's modulus versus forming pressure are also presented and discussed. © 1998 Elsevier Science Limited.

1 Introduction

Large scale manufacturing of ceramics requires simple, reproducible and economic processes, one of which is forming by uniaxial die pressing. The details of this unit operation have been described in many publications^{1,2} to which the reader is referred for further information. The feed material must satisfy some stringent requirements. First the powder should be free-flowing, in order to get reproducible characteristics of the powder bed in the mould before, during, and after pressing. Generally speaking, the mean grain size of powders for advanced ceramics lies in the micrometer range, sometimes less, so that these powders must be agglomerated before dry pressing to reach the desired flowability. The spherical morphology and the smooth surface of spray-dried granules confer on them unique characteristics for pressing.^{3–5}

The mean size of agglomerates obtained by this process is typically 100–200 μm .

Although the spray-dried granules should deform or break easily during compaction, in order to eliminate coarse porosity under small or moderate pressures, they should be strong enough not to damage during powder transportation and handling. This is the reason why a soluble organic polymeric binder is most often added to the ceramic suspension before spray-drying.⁶ Not only does this organic binder enhance the strength of agglomerates, as shown in earlier studies,^{7,8} but it also improves the mechanical properties of green products during and after the forming operation.⁹ For instance, ejection of pieces from the die as well as subsequent handling or machining of ceramic green parts require minimum mechanical strength to maintain their integrity. Although many binders have been proposed in the scientific and technical literature,^{10,11} the most common of them is probably polyvinyl alcohol (PVA). Because the glass transition temperature of PVA is higher than the usual pressing temperature,¹² in the vicinity of room temperature, pure, dry PVA makes spray-dried agglomerates hard and brittle. Thus the glass transition temperature of this binder is generally lowered by addition of plasticizers, for instance polyethylene glycol. A similar role is played by residual water, which is also known to soften the agglomerates spray-dried with PVA.⁵

Although a lot of work has been published in literature concerning the influence of binders on the densification behaviour of powders during compaction,^{6,9,13–15} and, to a little extent, on the mechanical strength of green bodies, very limited knowledge is available on the exact mechanisms through which a binder proves efficient.^{16,17} It is more or less expected to play the role of a soft adhesive, not only with respect to grains contained in a spray-dried granule, but also between deformed granules in a green ceramic part once it has been subjected to forming pressure. The purpose of the

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present paper is to elucidate some of these aspects. The variation of strength and of Young's modulus of pressed samples have been investigated versus forming pressure for several spray-dried powders, which differ by the composition of the binder phase.

2 Experimental

Aqueous suspensions containing alumina (Péchiney P152SB, France, specific surface area = $3 \text{ m}^2 \text{ g}^{-1}$) and polyvinyl alcohol (PVA 4-88, $M_w = 31\,000$, Hoechst, Germany) or modified polyethylene glycol (PEG 20M, $M_w = 20\,000$, Union Carbide, USA) were spray-dried in a pilot-plant equipment. The quantity of binder added amounts to 3 wt% on a dry wt basis of alumina. Spray-drying conditions (flow rate and temperature of drying) were stabilized in the spray-dryer to obtain a residual moisture content of 0.6 wt% with respect to alumina. The mean size of spray-dried granules was about $200 \mu\text{m}$. These powders containing PVA and PEG will be named PVA-W (PVA-Wet) and PEG-W, respectively. According to thermal gravimetric analysis, a part of the powder containing PVA was subsequently dried at 100°C for 2 h in an oven to obtain moisture-free agglomerates. This powder will be named PVA-D (PVA-Dry). Characteristics of such powders are summarized in Table 1.

Two items of equipment were used for pressing the samples. First, disk-shaped specimens (dia. = 25 mm, thickness $\approx 5 \text{ mm}$) were prepared in a laboratory steel die with a standard mechanical testing machine. The speed used was 4 mm min^{-1} until the desired pressure has been reached. The pressure was then immediately released and the samples ejected. An hydraulic press was also used to prepare larger samples ($100 \times 20 \times 4 \text{ mm}^3$) from which bars ($50 \times 4 \times 4 \text{ mm}^3$) were cut to perform measurements of the Young's modulus.

The mechanical strength of pressed green samples was estimated by the diametral compression method so-called 'Brazilian test'.¹⁸ Just after pressing, the disk-shaped samples were inserted in the testing machine, and the load F applied radially at a speed rate of 0.5 mm min^{-1} until the specimen

fractured. The strength of samples was calculated using the following expression:

$$\sigma = 2 F_{\max} / \pi D e \quad (1)$$

where F_{\max} is the load applied at fracture, D and e are the diameter and the thickness of the sample, respectively.

A low frequency (60 kHz) pulse-echo method working in a longitudinal 'long bar' mode was used to determine the Young's modulus.¹⁹ The 'long bar' condition means that the cross-sectional dimension is small compared to wavelength λ . The ultrasonic compressional wave propagates with a phase velocity V_L given by:

$$V_L = (E/\rho)^{1/2} \quad (2)$$

where E is the Young's modulus and ρ is the density of the pressed sample. The device uses a wave guide made of a tungsten wire (length 1 m, dia. 1 mm). The parallelepipedic sample is glued on the end of the wave guide with a phenyl salicilate cement which allows ultrasonic propagation. The ultrasonic velocity in the sample is determined with an adequate electronic equipment.¹⁹ From the measurement of the round-trip time t between two echos corresponding to the propagation in the sample, the velocity is obtained from:

$$V_L = 2 L / t \quad (3)$$

where L is the length of the specimen.

3 Results and Discussion

The case of 'soft' binders will be considered first. The glass transition temperatures of dry PEG are in the range of -67 to -27°C ,²⁰ thus much lower than room temperature, so that the spray-dried agglomerates of PEG-W powder deform easily during the compaction process. In the case of PVA-W powder, a residual moisture content of 0.6 wt% corresponds to a 20 wt% water content in the binder if moisture is considered absorbed only in the organic phase. According to several authors,⁵ the Tg of this binder should be located in the vicinity of room temperature, possibly slightly below. The strength of compacts prepared from PEG-W and PVA-W powders is plotted versus forming pressure in Fig. 1, where the data is also compared to the strength of compacts prepared from the original alumina powder, thus containing no organic

Table 1. Composition (wt%) of spray-dried powders used in the present work

	PEG-W	PVA-W	PVA-D
Alumina	96.5	96.5	97.0
Binder	PEG	PVA	PVA
Binder content	2.9	2.9	3.0
Moisture content	0.6	0.6	0

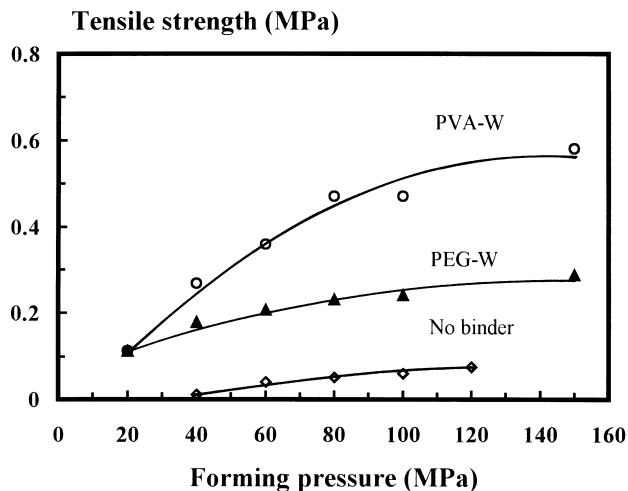


Fig. 1. The variation of strength for samples prepared from PEG-W and PVA-W powders, and from alumina (P152 SB) with no additive versus forming pressure.

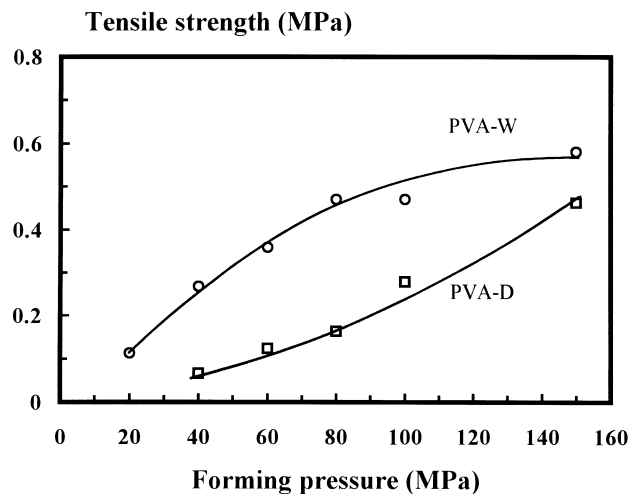


Fig. 2. The variation of strength for samples prepared from PVA-W and PVA-D powders versus forming pressure.

additive. The effect of the binder is obvious with an increase of the strength by a factor of four. Thus, the strength conferred by other mechanisms, such as van der Waals forces between the ceramic particles, modelled for instance by the J.K.R. theory²¹ or interpreted by mechanical interlocking,²² will be neglected in the present analysis. The strength of compacts increases more or less linearly with the forming pressure to reach a region where the evolution is less pronounced, and looks like a plateau. Let us note at this stage that the pressure at which the plateau is observed corresponds to the pressure at which the intergranular porosity disappears, according to Hg porosimetry measurements described in a former work on the compaction of the same powders.⁷

We turn now to the case of compacts prepared from PVA-D powder, which had been dried to get moisture-free agglomerates, and to make the binder hard and brittle. The glass transition temperature of dry PVA is equal to $+79^{\circ}\text{C}$.¹² The variation of strength of pressed samples is quite different from the case of PEG-W and PVA-W powders (Fig. 2). The strength remains small at low forming pressure, but increases rapidly in the domain where a plateau was previously observed for PEG-W and PVA-W powders. One can then conclude that the properties of the binder play a major role on the relative densities of green pressed samples,⁷ but also greatly influence their mechanical properties.

Keeping in mind that the binder must confer cohesion both to granules after spray-drying, and to ceramics parts once pressed, the distribution of the organic phase in the agglomerates must be ascertained before any interpretation of the variations depicted in Figs 1 and 2 could be given. The determination of this distribution is not an easy

matter from a practical point of view, but nevertheless a suggesting image can be obtained by optical microscopy on samples containing polyvinyl alcohol and treated at 300°C for 20 min. The pyrolysis of PVA starts by 200°C in air, leading to brown coloured species issued from polymer degradation, which help to trace the distribution of the organic phase either in the agglomerates or in the compacts. An example of picture obtained is given in Fig. 3.

During spray-drying, the granules develop non uniform distribution of the binder when water evaporates. The water soluble binder tends to concentrate at the surface of the granules, forming a shell containing ceramic particles embedded in a porous polymeric matrix. A crude estimation of the shell thickness ε can be obtained as follows. According to a preliminary work on polymer adsorption on alumina powders,²³ the amount of PVA binder adsorbed onto the powder surface in the suspension before spray-drying amounts

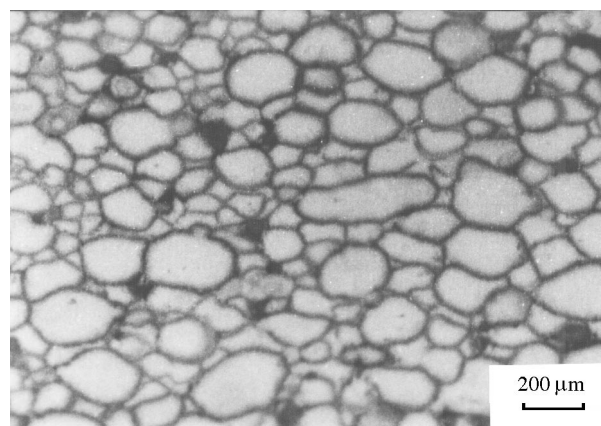


Fig. 3. An image of the binder distribution as revealed by optical microscopy on a sample containing PVA and treated at 300°C in air for 20 min.

probably to about 0.5 mg m^{-2} , e.g. about 1.5 mg per gram of the alumina used in the present work (0.15 wt\% only). If we assume that, during spray-drying, all the 'free' binder molecules in the solvent migrate to the surface of droplets from which water vapour escapes, most of the binder then concentrates near the surface of granules. The thickness of a pure polymer shell in the present conditions would then be given by:

$$\varepsilon \approx 0.01 R \rho_a / \rho_b \quad (4)$$

where R is the radius of the granule (typically $100 \mu\text{m}$), and ρ_a and ρ_b denote the density of alumina (3.98 g cm^{-3}) and of the polymer (1.26 g cm^{-3}), respectively.²⁴ Then one gets $\varepsilon \approx 3 \mu\text{m}$. This value should be corrected at least by a factor 2 because the shell also contains ceramic particles, the packing density of which is expected to be not too far from 0.5 .²⁴ Then the order of magnitude of the binder-rich shell would be about $6 \mu\text{m}$. Such a value is even probably underestimated, because the shell in question is porous, as revealed by standard SEM examinations on the granule surfaces. Nevertheless this simple calculation provides an useful value which is confirmed by the thickness of dark zones on Fig. 3.

Any interpretation of the results concerning the mechanical properties of green compacts must rely on this binder distribution, because one expects cohesion to be conferred by the adhesive properties of the shells in question. In a first, very qualitative approach, one can consider that the strength of compacts increases with the contact surface between granules, when the agglomerates deform progressively against each other under the action of external pressure. The mechanical strength reaches a plateau when the macroporosity disappears, e.g. when the surface of contact between granules reaches its maximum value.

Further information can be obtained from the inspection of fracture surfaces obtained on samples made with the three powders. Samples prepared from PEG-W powder fracture through granules while those from PVA-D powder fracture between granules (Fig. 4). Samples prepared from PVA-W powder present an intermediate behaviour, since the surface fracture is located mostly between granules in the domain where the strength increases linearly versus forming pressure, but tends to proceed through the granules once the plateau has been reached. Then, the mechanical properties observed probably result from a compromise between the adhesive properties of the outer shells and the strength of these shells. In a first approximation, we assume that the inner part of the

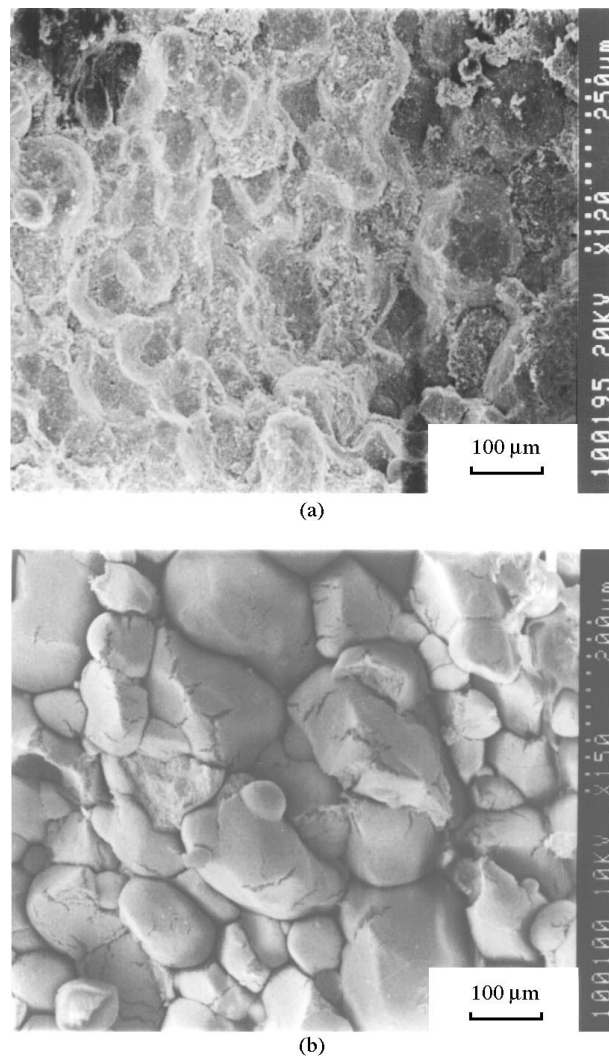


Fig. 4. SEM micrographs of fracture surfaces of samples prepared from (a) PEG-W powder, and (b) PVA-D powder, pressed at 80 MPa .

agglomerates, where the concentration of binder is much smaller, does not contribute to the strength of the compacts. When the glass transition temperature of the binder is well below the pressing temperature, the chain mobility is large enough to allow interdiffusion of polymer shells, a phenomenon which contributes to full efficiency of adhesion between granules. But the mechanical properties of the granule assembly are then limited by the low amount (about 50% of the initial binder content) of poor strength polymer inside the granules. This is the reason why the fracture propagates through the granules themselves, which constitute the lower strength phase assembly. On the other hand, the interdiffusion between polymer layers becomes negligible in the case of dry PVA, so that the fracture proceeds between the shells in contact. The situation encountered for PVA-W powder, containing PVA plasticized by water, is intermediate, since the glass transition of the binder lies probably in the vicinity of room temperature.

It is instructive at the present stage to calculate the strain of the shell during compaction. According to the work of Artz²⁵ on the compaction of plastic, spherical, metallic powders, the mean coordination number of particles increases from about 6 in the powder bed to about 12–14 in the fully dense pressed material. In a first approximation, one can consider that the spheres, here the spray-dried granules, progressively deform to Kelvin polyhedra which share 14 faces with their nearest neighbours once the intergranular porosity has disappeared. Then neglecting the variation of the intragranular porosity, the surface of the granule expands by about 10%. If we refer to the general trends of the stress-strain curve of a polymeric material,¹² the ductile character of the polymer allows the surface expansion required when the pressing temperature is well below the glass transition temperature. On the other hand, when the pressing temperature is smaller than T_g , the brittleness of the polymer is responsible for the granule microcracking which is clearly visible on Fig. 4(b) in the case of dry PVA.

All these ideas are qualitatively confirmed by the variation of the Young's modulus on the green compacts. In the present paper, we shall consider measurements made by the ultrasonic technique described above where the direction investigated is perpendicular to the pressing direction. The variation of Young's modulus E versus forming pressure (Figs 5 and 6) parallels the variations depicted previously in Figs 1 and 2. For samples pressed from PEG-W powder, E increases rapidly to reach a plateau at a forming pressure of 40–60 MPa, as does the variation of strength depicted in Fig. 1. Large bars, suitable for Young's modulus measurements, were not obtained by pressing binder-free powder due to insufficient strength. Then, the

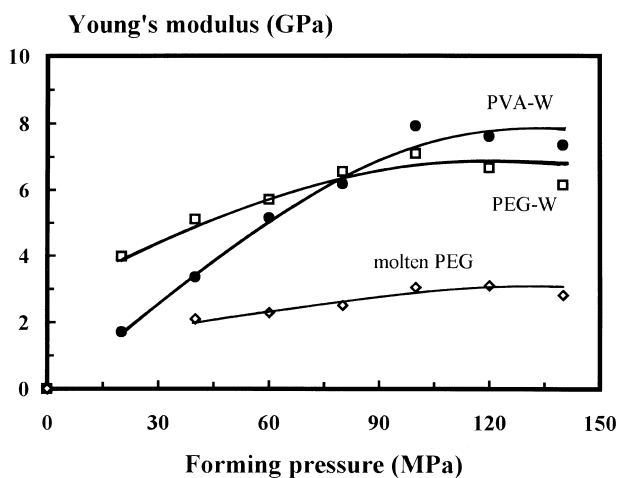


Fig. 5. A plot of the Young's modulus of samples prepared from PEG-W and PVA-W powders versus forming pressure. Measurements were also done on samples containing PEG at 80°C, beyond the melting point of the polymer.

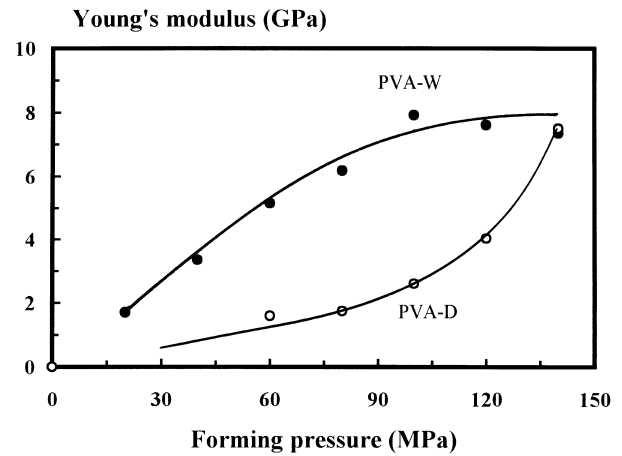


Fig. 6. The variation of the Young's modulus for samples pressed from PVA-W and PVA-D powders.

importance of the organic binder was evidenced by increasing the sample temperature to 70°C beyond the melting point of the polymer (80°C). Although the liquid polymer still contributes to the mechanical properties of the compact, through formation of liquid bridges, one observes that the Young's modulus drops by more than 50% of its original value. Furthermore, if the PEG binder was removed from the PEG-W pressed samples by thermal debinding, the Young's modulus drops to a very low value close to 0 GPa.

The variation for samples prepared from PVA-W powder, with moisture-plasticized PVA, includes a linear variation of Young's modulus versus forming pressure, then a plateau beyond about 100 MPa. It is interesting to note at this stage that the Young's modulus does not differ to a large extent for PEG and moisture-plasticized PVA, while the strength of samples containing PVA was larger by almost a factor two when the forming pressure exceeds 100 MPa (Fig. 1). Finally, the Young's modulus of samples prepared from dry PVA remains small at low forming pressures (Fig. 6), probably because extensive microcracking of the granule shells [Fig. 4(b)] lowers the elastic properties until larger forming pressures help to eliminate microcracks through densification of the whole assembly.

4 Conclusions

While the effect of organic binders on the compaction behaviour of spray-dried powders has been well documented in literature, the present work indicates that the polymers also exert a deep influence on the mechanical properties of pressed specimens. During spray-drying of alumina powders, the binder migrates to the surface of granules where it accumulates to form an organic-rich layer. The properties of the 'diphase' alumina/polymer

layers are then probably responsible for the compaction behaviour as well as the mechanical strength of the assembly. The strength results from a compromise between adhesive properties of the layers, which are reinforced by interdiffusion when the T_g of the binder is depressed below the pressing temperature, and the tensile strength of these layers which is expected to decrease for increasing contents of plasticizer. Intra- or intergranule fracture surfaces are observed depending on the limiting mechanism. Results obtained in the present work suggest that the variation of strength closely parallels the variation of the Young's modulus versus forming pressure, so that the elastic properties would be of major concern to investigate the mechanical properties of green samples prepared by dry-pressing.

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