

Young's Modulus of Dry-pressed Ceramics: The Effect of the Binder

S. Baklouti,^{a*} T. Chartier,^b C. Gault^b and J. F. Baumard^b

^aLaboratoire de Chimie Industrielle, E.N.I. de Sfax, BP W, 3038 Sfax, Tunisia

^bLMCTS, ESA CNRS 6015, ENSCI, 47 Avenue A. Thomas, 87065 Limoges Cedex, France

(Received 17 September 1998; accepted 26 October 1998)

Abstract

Measurements of Young's modulus of green compacts prepared from spray-dried alumina powders containing two binders: polyvinyl alcohol or polyethylene glycol are reported. The variations of Young's modulus with forming pressure are compared to those of mechanical strength and discussed in terms of glass transition temperature (T_g). When the T_g of the polymer is lower than the pressing temperature (case of PEG and moisture-plasticized PVA), the variation of the Young's modulus is related to the evolution of the binder film covering the surface of primary particles inside the granules. Microcracking of the brittle external polymer-rich layer of granules seems to be responsible for a different evolution of Young's modulus of green compact in the case of a binder with a T_g higher than the forming temperature (dry PVA). © 1999 Elsevier Science Limited. All rights reserved

Keywords: Al₂O₃, microstructure: prefiring, pressing, Young's modulus, shaping.

1 Introduction

Compaction of spray-dried ceramic powders is largely used in processing of ceramic parts. The spherical granules with a typical diameter of 100–200 μm , obtained by spray-drying, confer a good flowability necessary to achieve reproducible (i) filling of the mould, (ii) compaction behaviour during pressing and, (iii) microstructure of the pressed green body. A hydrosoluble organic polymeric binder is generally added to the ceramic suspension before spray-drying in order to improve the strength of the granules and of the green products

during (ejection from die) and after (handling and machining) the forming step.^{1–3} It has been previously reported that a polymer-rich layer forms at the surface of the granules during drying in the spray-drier.² It has been suggested that the properties of this polymeric shell surrounding the granules is responsible for the mechanical strength of the green parts which results from a compromise between adhesive properties of the layers, which are reinforced by interdiffusion when the T_g of the binder is below the pressing temperature, and the tensile strength of these layers.

The aim of this study is to investigate the variations of Young's modulus of pressed samples versus forming pressure for spray-dried powders with different organic compositions and to compare with the variations of strength in order to establish relations between the binder distribution in the granules and the mechanical properties of pressed samples.

2 Experimental

2.1 Starting materials and spray-drying of granules

The ceramic powder used in this study is an α -alumina (P152SB, P echiney, France). The surface area and the mean particle size were respectively 3 m² g⁻¹ and 1.3 μm . Aqueous suspensions containing 60 wt% alumina were prepared using 0.16 wt% of ammonium polymethacrylate salt (PMAA-NH₄⁺, M_w = 10 000, Darvan C, Vanderbilt, UK) as a dispersant and partially hydrolysed (88 mol%) polyvinyl alcohol (PVA 4-88, M_w = 31 000, Mowiol, Hoechst, D) or polyethylene glycol (PEG 20 M, M_w = 20 000, Union carbide, USA) as a binder. The amounts of binder added are 3 wt% for PEG and 1 or 3 wt% for PVA (dry weight basis of alumina). The slurries were then spray-dried in a pilot plant equipment. The mean size of spray-dried granules was about 200 μm . Spray-drying condi-

*To whom correspondence should be addressed.

tions (flow rate and temperature of the inlet air) were adjusted to get a residual moisture content of 0.6 wt% and of 0.25 wt% with respect to alumina for powders containing 3 and 1 wt% binder, respectively. Powders containing PVA and PEG with 0.6 wt% moisture will be denoted PVA3-M (3 wt% PVA-Moisture) and PEG3-M, respectively. The powder containing 1 wt% PVA with 0.25 wt% moisture will be denoted PVA1-M. A part of PVA3-M powder, was subsequently dried at 100°C for 2 h in an oven to get moisture-free agglomerates (and then moisture-free PVA binder). This powder will be denoted PVA3-D (3 wt% PVA-Dry).

According to literature data, the glass transition temperature (T_g) of the dry polymers are 79 and -60°C for PVA and PEG, respectively.⁴ These glass transition temperatures of PVA and PEG are respectively located above and below room temperature at which pressing was performed. We have to take into account the fact that water acts as a plasticizer for the PVA binder. If we consider the moisture only adsorbed in the organic phase, a 0.6 wt% moisture corresponds to 20 wt% water in the PVA and the T_g of this moisture-plasticized PVA should be somewhat slightly below room temperature.⁵

2.2 Pressing

A hydraulic press was used to prepare samples to perform Young's modulus measurements ($50 \times 4 \times 4 \text{ mm}^3$). The used speed was 4 mm mn^{-1} until the desired pressure was reached. The pressure was released immediately and the sample was ejected.

2.3 Characterisation

Just after pressing, a low frequency (60 kHz) pulse-echo method working in a longitudinal 'long bar' mode was used to determine the Young's modulus.⁶ In this 'long bar' configuration, for which the cross-sectional dimension is small compared to wavelength λ , the ultrasonic compressional wave propagates with a phase velocity V_L given by:

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

where E is the Young's modulus and ρ the density of the tested sample.

This technique has two main advantages, (i) the attenuation of the low frequency ultrasonic wave is sufficiently low to allow propagation in highly heterogeneous media like green materials and (ii) the Young's modulus is obtained from only one measurement of the ultrasonic velocity from eqn (1).

The parallelepipedic sample is glued on the end of a wave guide, made of a tungsten wire, with a phenyl salicylate cement (Salol) which allows

ultrasonic propagation. The ultrasonic velocity in the sample is determined with an adequate electronic equipment.⁶ From the measurement of the round-trip time t between two echos corresponding to the propagation in the sample of length L , the velocity is obtained from:

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

The mechanical strength of green samples is estimated on disk-shaped samples; just after pressing, by the so-called 'Brazilian test'.⁷ Using a testing machine, the load F is applied radially at a speed rate of 0.5 mm min^{-1} until the specimen fractured. The strength of samples was calculated through the formula:

$$\sigma = 2F_{\max}/\pi De \quad (3)$$

F_{\max} being the load at fracture, D and e denoting the diameter and the thickness of the sample, respectively.

3 Results

The variation of the Young's modulus of green compacts prepared from PEG3-M and PVA3-M powders versus forming pressure (Fig. 1) exhibits the same evolution that of the mechanical strength of pressed samples prepared from the same powders (Fig. 2). At low forming pressures, the Young's modulus increases rapidly, and approximately linearly, until it reaches a plateau for similar pressures as do the variations of the strength. The pressures at which the transitions are observed are about 70 and 100 MPa for PEG3-M and PVA3-M powders, respectively, and correspond to the complete elimination of the intergranular porosity (according to Hg porosimetry¹) as shown in Fig. 3 in the example of the PVA3-M powder.

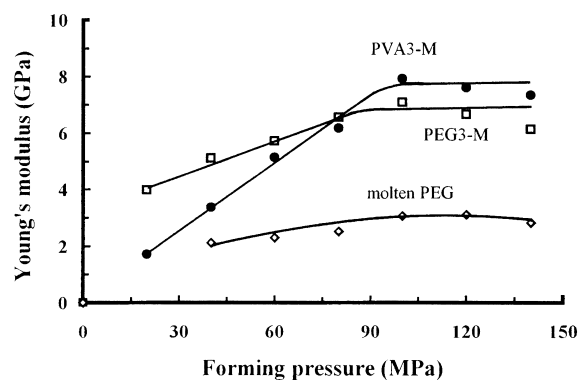


Fig. 1. Variations of the Young's modulus of samples prepared from PVA3-M and PEG3-M powders with the forming pressure. Measurements were also done on samples containing PEG at 80°C, beyond the melting point of the polymer.

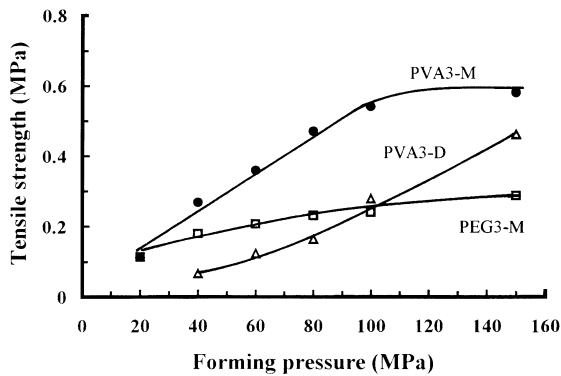


Fig. 2. Variations of strength with forming pressure for samples prepared from PVA3-M, PEG3-M and PVA3-D powders.

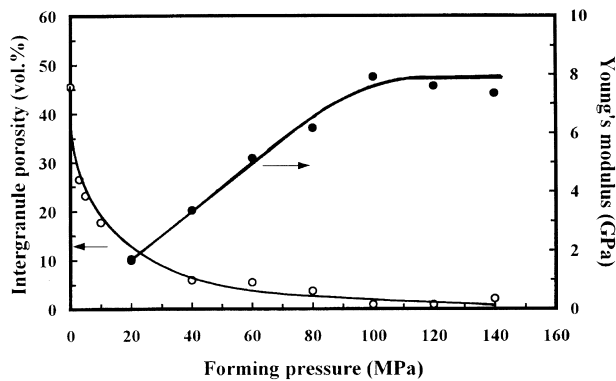


Fig. 3. Variations of the intergranule porosity and of the Young's modulus with forming pressure for samples prepared from PVA3-M powder.

However, at a pressure higher than 100 MPa, the Young's modulus does not differ to a large extent for PEG and moisture-plasticized PVA samples with values of 6–7 and 8 GPa, respectively, while the mechanical strength was larger by almost a factor two for samples prepared from PVA3-M powder.

The effect of the binder on the mechanical strength is obvious with an increase by a factor 4,³ but its influence on Young's modulus is not known. It was not possible to obtain long bars, suitable for Young's modulus measurements, by pressing binder-free powders due to insufficient strength. Then, the importance of the organic binder was evidenced through two ways:

1. by increasing the temperature of the samples, prepared from PEG3-M powder, beyond the melting point of the polymer ($\approx 70^\circ\text{C}$ ⁴). Although the liquid likely still contributes to the stiffness of the compact, through capillary forces,⁸ one observes that the Young's modulus drops by more than 50% of its original value (Fig. 1). Furthermore, if the PEG binder was removed from the PEG3-M pressed samples by thermal treatment, the Young

modulus decreased down to a very low value close to 0 GPa.

2. by studying the evolution of the Young's modulus for samples prepared from powder containing only 1 wt% PVA with respect to alumina (PVA1-M). The Young's modulus decreases markedly when the amount of the binder decreases (Fig. 4).

Then one can conclude that the presence of binder in a spray-dried ceramic powder, not only influences the densities of the green compact,¹ and improves their mechanical strength³ but also increases their Young's modulus.

4 Discussion

As illustrated in Figs 1 and 4, the presence of organic binder in a spray-dried powder increases markedly the Young's modulus of green compact.

Using the model of Ravichadran,⁹ Baklouti showed the low contribution of the external polymer-rich layer of granules to the Young's modulus values compared to its effect on mechanical strength.¹⁰ Thus, the Young's modulus of pressed samples mainly depends on the amount and on the nature of the binder present within the granules.

In order to confirm the main contribution of the concentration of binder located within the granule to the Young's modulus, smallest alumina (P152SB) granules were spray-dried using a laboratory equipment (Büchi 190). These granules of about 20 μm mean size contained 3 wt% PVA with respect to alumina and almost the same moisture (~ 0.7 wt%) as PVA3-M powder. Then, we can expect a parallel evolution of the Young's modulus, versus forming pressure, of samples prepared from the two sizes of granules because the relative amount of binder segregated during drying is likely similar in both cases even if the thickness of the external polymeric layer is greatly reduced in

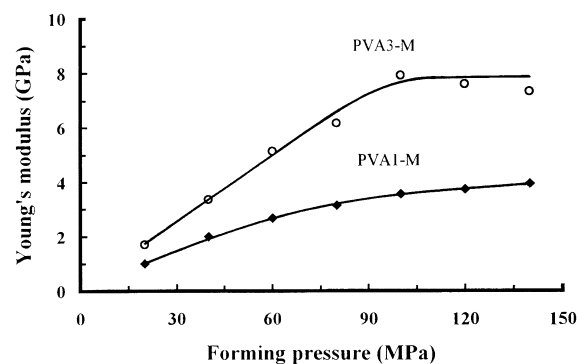


Fig. 4. Variations of the Young's modulus with forming pressure for samples prepared from PVA3-M and PVA1-M powders.

the case of 20 μm diameter granules.² That is in agreement with Fig. 5. The more rapid increase of the Young's modulus, at low forming pressure, for the smallest granules is attributed to the larger moisture (0.7 wt%) contained in this powder.

According to the minor contribution to the Young's modulus of the binder segregated around the granules, we will only consider, in the following discussion, the granules constituted of primary alumina particles covered by a polymeric shell. Models proposed in the literature to calculate the Young's modulus of two phase material^{11–13} can not be applied here, because the pressed samples are composed of three phases, i.e. alumina powder, organic binder and porosity (intragranular). On the other hand the binder and the porosity have opposite effects on Young's modulus. The Young's modulus increases when the binder content increases or when the porosity decreases. It is then not possible to estimate the Young's modulus of pressed samples using Voigt and Reuss or Hashrin–Shtrikman limits.¹³

Figure 3 shows that the increase of the Young's modulus of pressed samples prepared from the PVA3-M powder with forming pressure becomes significant when the intergranule porosity has almost disappeared, i.e. when the pressure exceeds about 20 MPa. This suggests that the variation of the Young's modulus during pressing can be correlated with the evolution of the organic bridges between the alumina particles with increasing forming pressure. On the assumption of a cubic assembly of isodiametric alumina particles, covered by a polymeric shell, constituting the granules,¹⁴ the evaluation of the Young's modulus of the pressed compact may be based on Kendall studies.¹⁵ During pressing, the total surface of the polymeric bridges increases by crushing progressively the binder layer between alumina particles

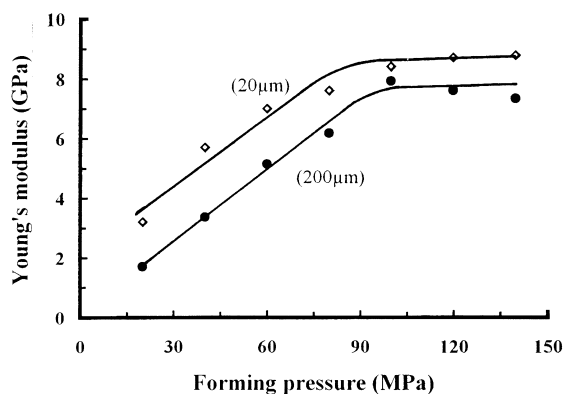


Fig. 5. Effect of the mean size of spray-dried granules on the evolution of Young's modulus of pressed samples from powders containing 3 wt% PVA and almost the same residual moisture. The spray-dried powder prepared using the laboratory equipment (20 μm) and the pilot plant (200 μm) have a moisture content of 0.7 and 0.6 wt%, respectively.

(Fig. 6). We can likely expect an impression, in the polymer, by the grain, proportional to the applied stress. The pressure necessary to totally 'crush' the layer of the binder between two spherical alumina particles and then to reach the contact between particles can be estimated on the basis of the hardness of the binder. According to Van Krevelen,⁴ hardness H of a polymer is related to its Young's modulus E_{pol} through the following expression:

$$H \approx 10(E_{\text{pol}})^{3/4} \quad (3)$$

where H and E_{pol} are expressed in MPa and GPa, respectively.

In the case of PVA ($E_{\text{pol}} \approx 2.6 \text{ GPa}^{10}$), eqn (3) gives $H \approx 110 \text{ MPa}$. With PEG ($E_{\text{pol}} \approx 1.7 \text{ GPa}^{10}$), eqn (3) gives $H \approx 80 \text{ MPa}$. These values of hardness correspond approximately to the pressure necessary to totally 'crush' the layer of the binder between two spherical alumina particles and are similar to the pressure values at which Young's modulus plateaus are observed in Fig. 1. The surface of the bridge, formed between two grains, increases linearly with forming pressure until the grains come in contact (Fig. 6).¹⁰ Above this transition pressure, the contact surface and the Young's modulus remain constant. This interpretation allows one to understand the linear increase of the Young's modulus at low forming pressures until it reaches a plateau and the fact that the plateau of pressed samples containing PEG binder was reached at lower pressure than in the case of higher Young's modulus PVA binder. We can conclude that the plateau will be reached more rapidly when the Young's modulus of the polymer is low.

It is interesting now to consider the similarity of the variations of mechanical strength and Young's modulus, with forming pressure, of green compacts prepared with PEG3-M and PVA3-M powders (Figs 1 and 2). The mechanical strength σ_r of a brittle material (e.g. green compact) has been expressed by Griffith:¹⁶

$$\sigma_r = \sqrt{2} \cdot [R/\pi a]^{1/2} \cdot E^{1/2} \quad (4)$$

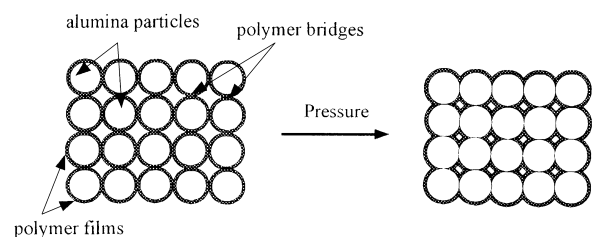


Fig. 6. The polymeric bridge surface, between two particles, increases by crushing progressively the binder layer until the grains come in contact. Above this pressure, the Young's modulus remains constant.

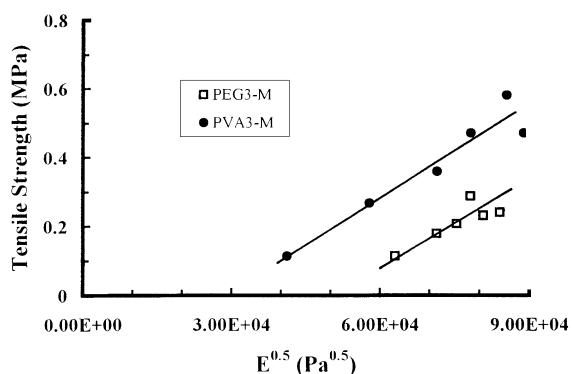


Fig. 7. Variations of the strength versus the Young's modulus for samples prepared from PVA3-M and PEG3-M powders.

where R is the fracture energy of the green compact and a the critical defect size.

Suggested by the expression (4), the evolution of the strength was plotted versus the square root of the Young's modulus in Fig. 7. The proportionality between σ_r and $E^{1/2}$ indicated by eqn (4) was respected but the fitted lines did not extrapolate to the origin point. Then, the ratio (R/a) can not be considered as a constant. However, an estimation of the fracture energy R from the slope of the lines, which are roughly parallel, gives $R \approx 375a$. If we consider that the critical defect size is almost the granules size, i.e. $200 \mu\text{m}$, for the powders spray-dried in the pilot equipment, we obtain $R \approx 75 \text{ mJ m}^{-2}$.

According to the literature,⁴ the fracture energy of polymers is generally in the range of $30\text{--}40 \text{ mJ m}^{-2}$. Without plastic or viscoplastic deformations, the creation of two new surfaces during cracking requires an energy comprised between 60 and 80 mJ m^{-2} . Taking into account that the surface of the polymer bridges between alumina particles only represents a small fraction of the fracture surface, these results suggest that fracture of green compacts involves plastic binder deformation, as mentioned by Muller¹⁷ on silica samples prepared by agglomeration of the powder with polyvinylpyrrolidone.

Now, consider the particular case of samples prepared with moisture-free PVA binder (PVA3-D), with a glass transition temperature above pressing room temperature. The evolution of the Young's modulus of the samples prepared from PVA3-D powder, containing dry PVA, is quite different from that observed for PEG3-M and PVA3-M powders (Fig. 8). The Young's modulus remains rather small at low forming pressures then increases rapidly when the pressure exceeds about 100 MPa . This behaviour is similar to that observed for mechanical strength of samples prepared from the same powder (Fig. 2). The fracture surface of a sample prepared from PVA3-D powder and pressed at 80 MPa (Fig. 9) shows an intergranular

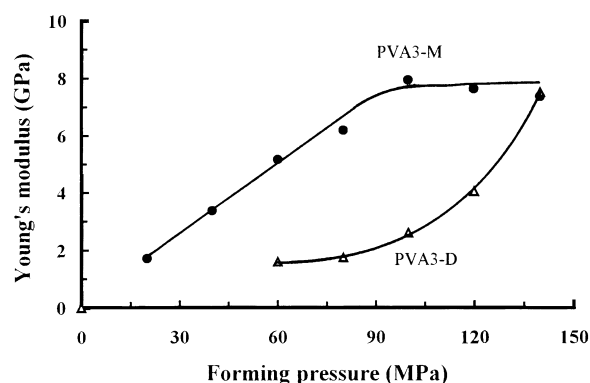


Fig. 8. Effect of the moisture on the variation of the Young's modulus with forming pressure for samples prepared with 3 wt% PVA (PVA3-M and PVA3-D).

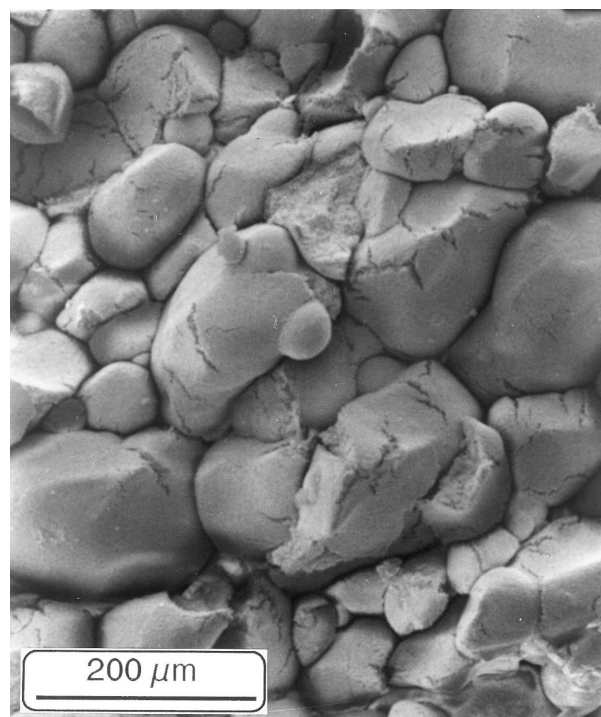


Fig. 9. SEM micrograph of fracture surface of sample pressed at 80 MPa from PVA3-D powder.

propagation with an important microcracking of granules. These microcracks are related to the elongation of the external layer containing a brittle dry PVA polymer, with a glass transition temperature higher than the forming room temperature. The Young's modulus is very sensitive to microcracks¹⁸ and remains low until the forming pressure reaches a high enough value to allow the closure of these microcracks through densification of the whole assembly. Then, the Young's modulus increases rapidly.

5 Conclusion

The variation of the Young's modulus of pressed alumina compacts with forming pressure is similar

to that of mechanical strength. The addition of organic binder in spray-dried ceramic powder increases markedly the Young's modulus of green product.

When the binder is ductile (glass transition temperature lower than forming temperature), the Young's modulus increases rapidly and linearly with forming pressure until it reaches a plateau above a transition pressure. The major contribution of the binder to the Young's modulus is attributed to the binder located inside the granules with a low contribution of the organic-rich shell around the granules. The evolution of the Young's modulus probably results from an increase in the contact surface of the polymer bridges between primary alumina particles considered covered by a binder film. The estimation of the fracture energy of the pressed green compacts suggests that a plastic deformation takes place during failure.

When the glass transition temperature of the binder is higher than the pressing temperature, microcracking of the brittle polymer-rich shells surrounding the granules seems to be responsible for the low values of Young's modulus until the forming pressure become large enough to close these microcracks through densification of the whole assembly. Then, the Young's modulus increases rapidly.

References

1. Baklouti, S., Coupelle, P., Chartier, T. and Baumard, J. F., Compaction behaviour of alumina powders spray-dried with organic binders. *J. Phys. III*, 1996, **6**, 1283–1291.
2. Baklouti, S., Chartier, T. and Baumard, J. F., Binder distribution in spray-dried alumina agglomerates. *Journal of the European Ceramic Society*, 1998, **18**(14), 2117–2121.
3. Baklouti, S., Chartier, T. and Baumard, J. F., Mechanical properties of dry-pressed ceramics: the effect of the binder. *Journal of Am. Ceram. Soc.*, 1997, **80**(8), 1992–1996.
4. Van Krevelen, D. W., *Properties of Polymers*, 3rd edn. Elsevier, Amsterdam, 1990, p. 697.
5. Reed, J. S., *Introduction to the Principles of Ceramic Processing*. John Wiley and Sons, New York, 1988, p. 176.
6. Gault, C., Ultrasonic non destructive evaluation of microstructure changes and degradation of ceramics at high temperature. In *Mat. Res. Symp. Proc.*, Vol 142, ed. J. Holbrook and J. Bussière. 1989, Materials Research Society, pp. 263–274.
7. Bortzmeyer, D., Tensile strength of ceramic powders. *J. Mat. Sci.*, 1992, **27**, 3305–3308.
8. Capes, C. E., Agglomerate bonding. In *Particle Size Enlargement*, Chapter 2. Elsevier Scientific, Amsterdam, 1980, pp. 43–49.
9. Ravichandran, K., Elastic properties of two-phases composites. *J. Am. Ceram. Soc.*, 1994, **77**(5), 1178–1184.
10. Baklouti, S., Pressage de poudres d'alumine atomisées: influence des liants organiques sur l'aptitude au pressage. Ph.D. thesis, Limoges, France, 1996.
11. Anderson, O. L., Determination and some uses of isotropic elastic constants of polycrystalline aggregates using single crystal data. In *Physical Acoustics*, Vol. IIIb, ed. W. P. Mason. Academic Press, New York, 1965, p. 4395.
12. Lees, S. and Davidson, C. L., Ultrasonic measurement of some mineral filled plastics. *IEEE Trans. on Sonics and Ultrason*, 1997, **24**(3), 222–225.
13. Hashin, Z. and Shtrikman, S., Variation approach to the theory of the elastic behaviour of multiphase materials. *J. Mech. Phys. Solids*, 1963, **11**, 127.
14. Onoda Jr, G. Y., Theoretical strength of dried green bodies with organic binders. *Am. Ceram. Soc. Bull.*, 1978, **56**(5-6), 236–239.
15. Kendall, K., McAlford, N. and Birchall, J. D., Elasticity of particles assemblies as a measure of the surface energy of solids. *Proc. Royal Soc. London*, 1987, **A412**, 269–283.
16. Griffith, A. A., *Proc. Royal Soc. London*, 1920, **A221**, 163.
17. Budiansky, B. B. and O'Connell, R. J., Elastic moduli of cracked solid. *International Journal of Solid and Structures*, 1976, **12**, 81–97.
18. Muller, M. A., Seville, J. P. K. and Adams, M. J., A fracture mechanics approach to the breakage of particle agglomerates. *Chem. Eng. Sci.*, 1987, **42**(4), 667–677.