Available online at www.sciencedirect.com

ScienceDirect

Journal of the European Ceramic Society 27 (2007) 873–877

www.elsevier.com/locate/jeurceramsoc

Effect of internal binder on microstructure in compacts made from granules

Satoshi Tanaka*, Chiu Chia-Pin, Zenji Kato, Keizo Uematsu

Department of Material Science and Technology, Nagaoka University of Technology, 1603-1 Kamitomioka, Nagaoka Niigata 940-2188, Japan

Abstract

This paper focuses on the influence of granule characteristics on the microstructure of the compact. Alumina granules were prepared with a poly-acryl acid (PAA) or a poly-vinyl alcohol (PVA) as binders by a spray-drying method. Observation with a liquid immersion method shows a significant difference in the binder distribution. Very uniform and non-uniform distributions were noted for the PAA and PVA binders, respectively. PVA binder segregated at surface and subsurface of the granules. The compression strength and deformation behavior were examined on a single granule with a micro-compression testing machine. The granule with the PAA binder has a low yield stress. In the forming process, the relative density of the compact body started to increase at low pressure. Homogeneous internal structures were noted in the green compact at all pressures examined. The granule with PVA binder showed higher yield stress. The internal structure of the compact was inhomogeneous, and large interstices were often observed between granules in the green compact also.

Keywords: Pressing; Optical microscopy; Al_2O_3; Structural applications

1. Introduction

The organic binder affects the properties of ceramics made through the powder compaction process, since it governs the mechanical property of granule, controlling the compaction behavior and the resultant structures of green bodies.[1–8] The characteristics of binder must be carefully controlled, but may change easily in many systems, such as PVA. The granules with PVA are hard under glass transition temperature (∼25 °C) and become soft in high relative humidity over 80% and temperature above 20 °C.[9] Hard elastic granules tend to form large flaws in green compacts as well as in sintered ceramics. Soft granules are favorable for uniform structures in green and sintered bodies.[10–15] The binder also affects the structure through their distribution in the granules. PVA binder tends to segregates on the surface of granules, leaving large processing defects in the compact after de-binder.[6–8] A new binder is needed to make powder compacts with uniform structure.

A poly-acrylic acid system (PAA) binder is examined in this study (Fig. 1(b)). This system behaves as a dispersant in the slurry also. Added a large quantity, PAA can play as a binder between particles.[16] The molecules can adsorb on the surfaces of oxide and bridge them together. The glass transition temperature can be changed for wide range from −20 to 30 °C through the co-polymerization of acrylic acid and methacrylic acid, etc.[17] It is one of the thermoplastic resins used for injection molding. With PAA, the high affinity to the oxide surface may eliminate the segregation phenomenon also.

This paper reports the characteristics of the granule and green body made from alumina granules containing PAA or PVA binder. Characterization tool called the immersion liquid microscopy[3–5] is applied to examine the binder distribution as well as the internal structure of granules. The deformation characteristics of granules and homogeneity of the green body will be also reported.

2. Experimental

The raw materials were industrial commercial alumina (Al-160SG, Showadenko K.K., Japan) and poly-acrylic acid system (AQ, Lion, Japan) as a dispersant and binder. The average particle size of alumina powder is 0.6 μm by supplier. They were mixed with distilled water in a ball mill to prepare slurries of binder contents 2.5 mass%, which was the most suitable condition to disperse powders well in the slurry. A slurry was also

---

* Corresponding author. Tel.: +81 258 47 9337; fax: +81 258 47 9300.
E-mail address: stanaka@chem.nagaokaut.ac.jp (S. Tanaka).

0955-2219/$ – see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2006.04.038

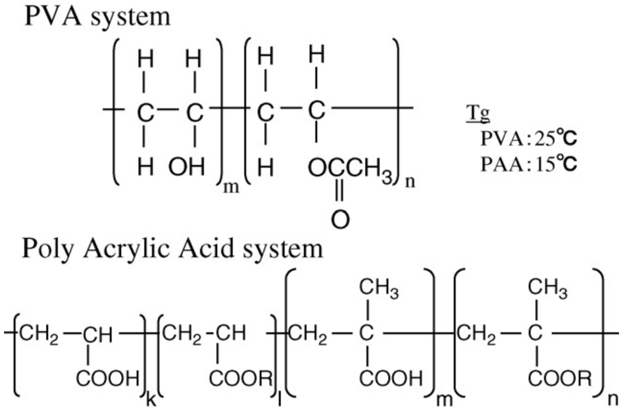

Fig. 1. The structure of each binder system.

prepared with poly-vinyl alcohol (PVA105, Kurarays, Japan) binder 0.5 mass% and PAA dispersant (D305 Chukyo-yushi Co., Japan) 0.5 mass% as a reference. A spray drier (SD-13, Mitsui-Mining Co., Japan) was used to prepare the granules.

The liquid immersion technique was applied to examine the internal structure of the granules. In this examination, the granules were immersed in methylene iodide to make them transparent, and the internal structure was observed with an optical microscope in transmission mode (OPTIPHOT, Nikon, Japan). Scanning electron microscope (JSM-5310L, JEOL, Japan) was used to examine the morphology and structure of granules in detail.

Commercial micro-compaction equipment (MCTE-500, Shimadzu, Japan) was used to examine the compaction behavior of individual granules. To equilibrate with the moisture, the granules were placed in an ambient atmosphere for a day. The granule with a diameter around 50 μm was selected under a microscope for examination. Temperatures were controlled at 16 °C for the granules containing PAA binder, and at 25 °C for the PVA systems. The tensile strength of the granule S_t was determined with the equation proposed by Hiramatsu et al.[18]

$$S_t = \frac{2.8P_f}{\pi D^2} \tag{1}$$

where P_f is the applied load at fracture and D is the average diameter of the granule.

The spray-dried granules were uniaxially pressed in a die with the double action by a universal mechanical testing machine (Autograph AG1, Shimadzu, Japan) at crosshead speed 1.0 mm/min. Temperatures were controlled at 16 °C for granules containing PAA binder system, and at 28 °C for the PVA systems. The test at 20 °C was also carried out for both granules. The compaction curve was constructed from the load–displacement curve recorded automatically for each granule. The relative density (R.D.) of the compact was determined during compression test using a following equation:

$$\text{R.D.} = \frac{100w}{Ah\rho} \tag{2}$$

where w is the weight of filled granules, A the base area of the compact (cross-section area of the pressing punch), h the height of the compact in the die and ρ is the theoretical density of alumina: 3.987×10^3 kg/m^3.

3. Results

Fig. 2 shows the SEM micrographs of granules prepared in this study. All the granules appear to have spherical shapes with a dimple. The absolute densities of granules were 1.6 kg/m^3 for the PAA binder system and 1.9 kg/m^3 for the PVA binder system, respectively.

Fig. 3 shows the liquid immersion photomicrographs of the as-spray-dried granules. The granules heat-treated at 500 °C are shown in Fig. 3(c and d). Their internal structure is quite uniform and has a dimple in the center, but the rim. The rim of the granules containing PVA system appears darker than other region of the granules (Fig. 3(b)). This dark layer at the circumferential region of granules corresponds to the segregated PVA binder.[6–8] It appears darker since the binder scatters light more than alumina, due to large mismatching of the refractive indices. The dark region disappeared after they were heated at high temperature for binder removal. The PAA binder appears to distribute very homogeneously in granules. No structure change was noted before and after the binder removal (Fig. 3(a and c)). If the figure reflects the granules from different depth into an immersion liquid, it must be marked in discussion.

Fig. 4 shows typical stress–strain curves in the compaction test of a single granule in a humid atmosphere for PAA system

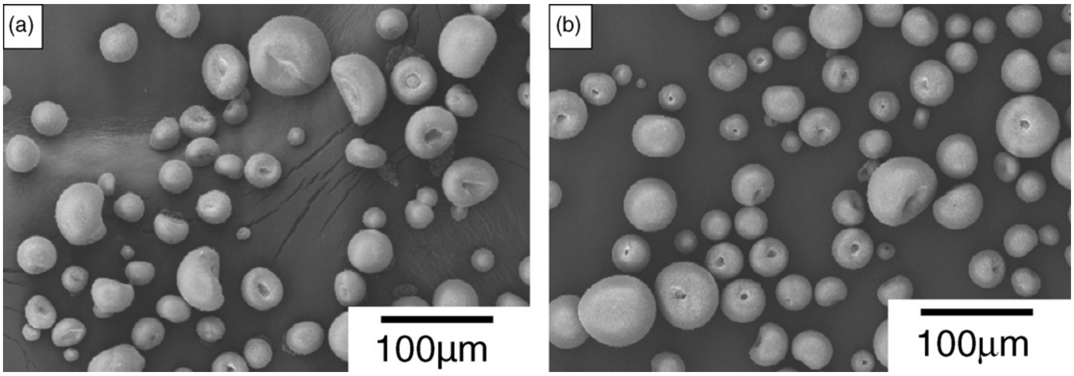

Fig. 2. Schematic of granule containing binder: (a) PAA system and (b) PVA system.

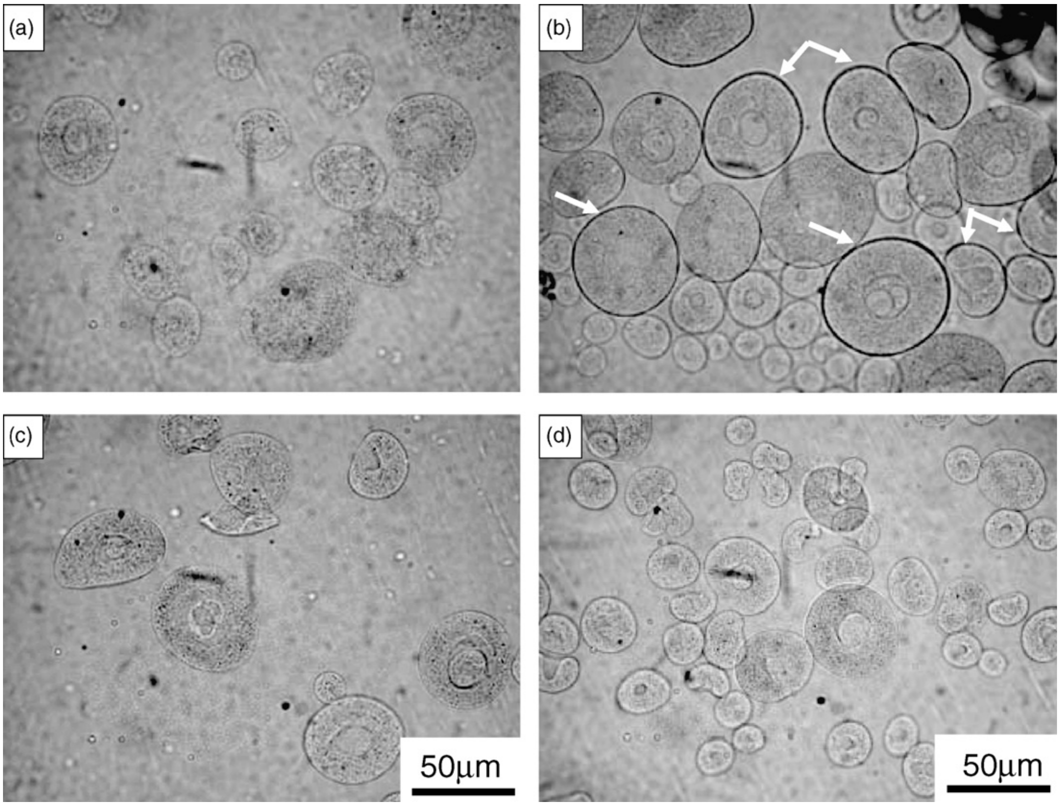

Fig. 3. Granules containing binder: (a and c) PAA system, (b and d) PVA system, (a and b) before de-binder treatment and (c and d) after de-binder treatment.

(16 °C, 80% relative humidity) and PVA system (25 °C, 80% RH). These test temperatures are slightly higher than the glass transition temperatures of the respective binders. With increasing applied stress, the granule deformed suddenly at the strain approximately 3–5%, and thereafter deformed rapidly. This sudden change corresponds to the fracture of the granules, showing the strength of granules about 0.1 and 0.45 MPa for PAA system and PVA system, respectively.

Fig. 5 shows the typical compaction curves for die pressing of these granules. The compaction curves vary with the types of granules. The relative density of the compact increased gradually with increasing stress in both granule systems. Changes of slope appear at two places, about 1 and 10 MPa for the curve of PVA granules. The first change corresponds to the starting point of granule deformation, and the second change the starting point of particles rearrangement within the granule in the compact

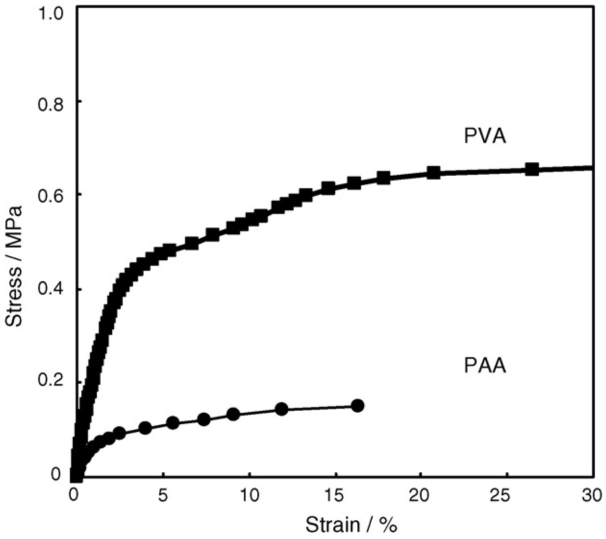

Fig. 4. Stress–strain curves of compaction test of single granule.

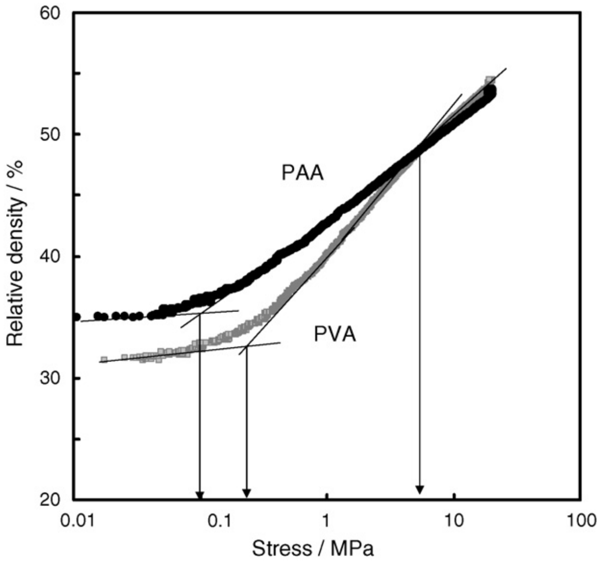

Fig. 5. Compaction diagram of die-pressing using granules.

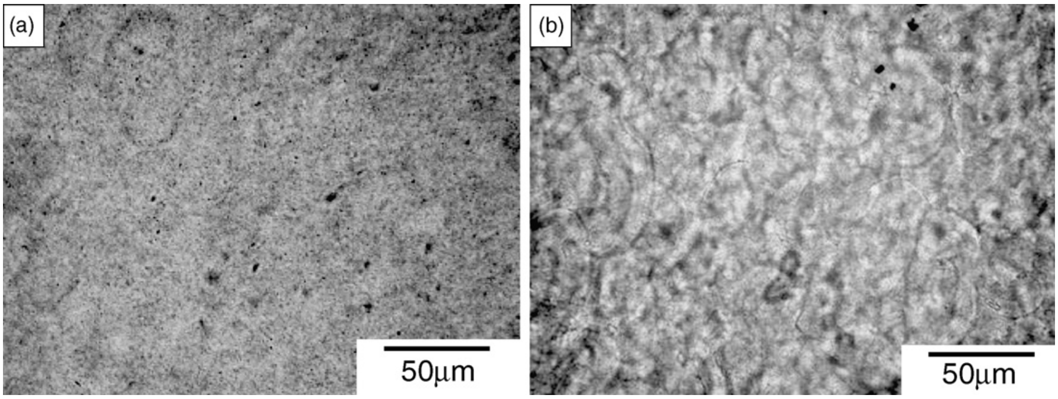

Fig. 6. Internal structure of the green body pressed (a) at 17 °C and 80% RH in PAA system and (b) at 28 °C, 80% RH in PVA system.

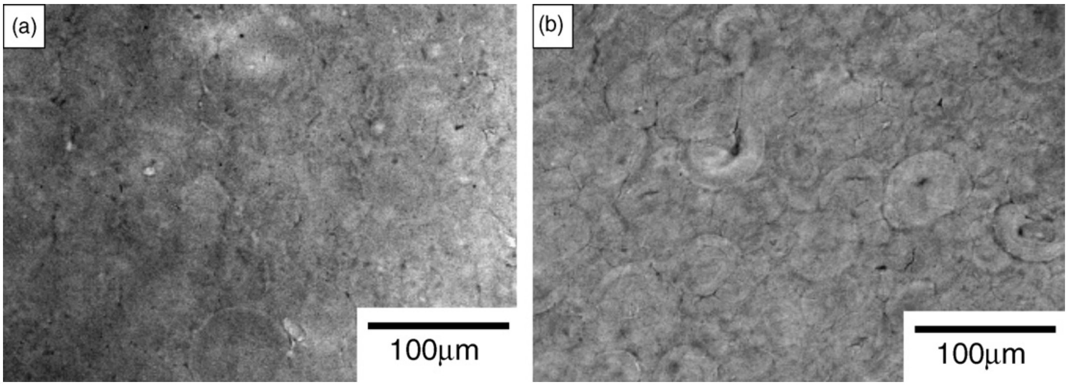

Fig. 7. Internal structure of the green body pressed at 20 °C and 70% RH (a) PAA system (b) PVA system.

body.[13] The curve of PAA granules shows only one change in the slope at 1 MPa.

Fig. 6 shows the microstructure of the green body examined with the immersion liquid technique. The structure depended on the characteristics of the granules. Homogeneous microstructure is noted in the green body made from granules with PAA binder. The shapes of granules are clearly noted in the green body made from granules with PVA binder.

Fig. 7 shows the microstructure of the green bodies, which were prepared at 20 °C and 70% RH atmosphere with the granules of PVA and PAA binders. Clearly, the glass transition temperature of binders affects the microstructure. The traces of granules are observed easily in the body made from granules with PVA system. The granules with PVA binder are hard at this condition, since it is below the glass transition temperature of PVA.

4. Discussion

The distribution of binder governs characteristics of the granules and thus the green body. The homogeneous structure is achieved for the granules with PAA binder (Fig. 3). The PAA binder appears to distribute uniformly in the granule, whereas, PVA tends to segregate at the surface and the subsurface of the granules (Fig. 3(a and b)). Several granules out of focus appear the same with diffuse dark rims in Fig. 3(b and d). The granules with PAA binder deformed easily during compression tests (Figs. 4 and 5). No region of low density is observed after the de-binder (Figs. 6 and 7). This result is significantly different noted for the granules with PVA binder.

The differences in the binder distribution and the structure of compact can be ascribed to the adsorption of binder molecule on the alumina particles. It is well known that the PAA molecules ionize to R-COO$^-$, and H$^+$ in the aqueous slurry. Ionized R-COO$^-$ absorbs on the positively charged sites on the surface of alumina particle, through the Coulomb attraction, making the surface negatively charged. The charged surface creates a repulsive force to disperse the particles and stabilizes the slurry. The adsorbed PAA ions are fixed between particles and do not move during spray drying. They are uniformly distributed in the granules and behave as a binder. The PVA binder ionizes slightly and absorbs only weakly on the particles. The PAA molecule added as a dispersant in the slurry absorbs preferentially to PVA molecule on the particles,[19] forming free PVA. The free PVA binder can migrate to the drying surface with the evaporation of water during spray drying, causing the surface segregation of PVA binder. Segregated binder is commonly noted on the granule surface in our past studies, and its origin is ascribed to the flow of water containing PVA in the spray-drying process.[8] The segregated binder hinders the densification under the compaction stress and forms the region of low packing density in the green body.

The binder and their distribution affect the strength and deformation behavior of the granules (Figs. 4 and 5). The granules with PAA binder system showed the onset of density increase at much lower pressure than those with PVA in die pressing. The second change of the slope is noted in the compaction curve for the PVA system, but not for the PAA system. In PAA system, the rearrangements of the particles within the granules take place simultaneously with the net deformation of the granules during increment of stress.

5. Conclusion

The influence of the granule characteristics was examined on the microstructure of granule compact. Alumina granules were prepared with a poly-acryl acid (PAA) or a poly-vinyl alcohol (PVA) as binders by a spray-drying method. The conclusions are obtained as follows:

(1) Liquid immersion method shows a significant difference in the binder distribution. Very uniform and non-uniform distributions were noted for the PAA and PVA binders, respectively. PVA binder segregated at surface and subsurface of the granules.
(2) The compression strength and deformation behavior were examined on a single granule with a micro-compression testing machine. The granule with the PAA binder has a low yield stress. In the forming process, the relative density of the compact body started to increase at low pressure. Homogeneous internal structures were noted in the green compact at all pressures examined. The granule with PVA binder showed higher yield stress. The internal structure of the compact was inhomogeneous, and large interstices were often observed between granules in the green compact also.

Acknowledgements

This study was partially supported by a grant from Matsuda foundation. We are grateful to Dr. Kakui and Mr. Ishiguro at Lion Corporation for their courtesy and assistance in preparing compact.

References

1. Reed, J. S., *Principle of Ceramics Processing Second Edit*. John Wiley and Sons, Inc., New York, 1995, p. 418–449.
2. Frey, R. G. and Halloran, J. W., Compaction behavior of spray-dried alumina. *J. Am. Ceram. Soc.*, 1984, **67**, 199–203.
3. Uematsu, K., Kim, J.-Y., Miyashita, M., Uchida, N. and Saito, K., Direct observation of internal structure in spray-dried alumina granules. *J. Am. Ceram. Soc.*, 1990, **73**, 2555–2557.
4. Zhang, Y., Uchida, N. and Uematsu, K., Direct observation on non-uniform distribution of PVA binder in alumina green body. *J. Mater. Sci.*, 1995, **30**, 1357–1360.
5. Uematsu, K., Immersion microscopy for detailed characterization of defects in ceramic powders & green bodies. *Powder Technol.*, 1996, **88**, 291–298.
6. Zhang, Y. and Uematsu, K., Binder segregation in the processing of ceramics, mass and charge transport in ceramics. *Ceramics Transactions*, 1996, **71**, 357–373.
7. Zhang, Y., Suga, T., Kawasaki, M., Tang, X.-X., Uchida, N. and Uematsu, K., Effect of poly (vinyl alcohol) adsorption on binder segregation during drying. *J. Am. Ceram. Soc.*, 1996, **79**, 435–440.
8. Zhang, Y., Tang, X.-X., Uchida, N. and Uematsu, K., Binder surface segregation during spray drying of ceramic slurry. *J. Mater. Res.*, 1998, **13**, 1881–1887.
9. Saito, Y., Nyumura, J., Zhang, Y., Tanaka, S., Uchida, N. and Uematsu, K., Kinetics of property change associated with atmospheric humidity changes in alumina powder granules with PVA binder. *J. Eur. Ceram. Soc.*, 2002, **22**, 2835–2840.
10. Brewer, J. A., Moore, R. H. and Reed, J. S., Effect of relative humidity on the compaction of barium titanate and manganese zinc ferrite agglomerates containing polyvinyl alcohol. *Am. Ceram. Soc. Bull.*, 1981, **60**, 212–215.
11. Scott, C. E. and Gilbertson, H. J., Effects of humidity on binder strength in green ceramic compacts. *Am. Ceram. Soc. Bull.*, 1982, **61**, 579–581.
12. Dimilia, R. A. and Reed, R. S., Dependence of compaction on the glass transition temperature of the binder phase. *Am. Ceram. Soc. Bull.*, 1983, **62**, 484–488.
13. Nies, C. W. and Messing, G. L., Effect of glass-transition temperature of polyethylene glycol-plasticized polyvinyl alcohol on granule compaction. *J. Am. Ceram. Soc.*, 1984, **67**, 301–304.
14. Tanaka, H., Sakamoto, A., Nagao, Y., Fukai, S., Uchida, N. and Uematsu, K., Effect of moisture on the structure and fracture strength of ceramics green body. *J. Am. Ceram. Soc.*, 1994, **77**, 3077–3080.
15. Tanaka, H., Sakamoto, A., Nagao, Y., Fukai, S., Zhang, Y., Uchida, N. *et al.*, Effect of moisture content of granules on the properties of green and sintered bodies of alumina ceramics. *J. Ceram. Soc. Jpn.*, 1994, **102**, 397–400.
16. Wu, X. K., Whitman, D. W., Kaufell, W. L., Finch, W. C. and Cumbers, D. I., Acrylic binders for dry-pressing ceramics. *Am. Ceram. Soc. Bull.*, 1997, **76**, 49–52.
17. Kakui T., Additives for ceramic green sheet, Japan Patent 07-033533, 28 June 1993.
18. Hiramatsu, Y., Oka, Y. and Kiyama, H., Determination of the tensile strength of rock by a compression test of an irregular test piece. *J. Miner. Eng. Jpn.*, 1965, **81**, 1024–1030.
19. Nakashima, T., Mizutani, H., Zhang, Y., Uchida, N. and Uematsu, K., Competitive adsorption of PVA and PAA on alumina surface. *Key Eng. Mater.*, 1999, **159–160**, 151–156.