

## The effect of an amino acid of low molecular weight on consolidation of nanoparticle suspensions

Shinichi Baba, Yoshihiro Hirata\*, Naoki Matsunaga and Soichiro Sameshima

Department of Chemistry, Biotechnology, and Chemical Engineering, Kagoshima University, Kagoshima 890-0065, Japan

The applied pressure and suspension height during consolidation of an aqueous suspension containing SiC (30 nm diameter, 5 vol% solid) or Al<sub>2</sub>O<sub>3</sub> particles (150 nm diameter, 7 vol% solid) with and without phenylalanine (molecular weight 165) or polyacrylic ammonium (PAA, molecular weight 10,000) were continuously recorded using a developed pressure filtration apparatus at a constant crosshead speed. The dispersed SiC and Al<sub>2</sub>O<sub>3</sub> particles at pH 7 and 3, respectively, changed to flocculated particles at an applied pressure of 0.24-0.63 MPa. The packing density of flocculated SiC and Al<sub>2</sub>O<sub>3</sub> particles increased by the addition of dissociated PAA and phenylalanine. Since phenylalanine has two charged groups (-NH<sub>3</sub><sup>+</sup>, -COO<sup>-</sup>) in one molecule, this dispersant can be used for surfaces of both positively and negatively charged particles.

**Key words:** Nanoparticles, Colloidal processing, Phenylalanine, Polyacrylic ammonium, Phase transition.

### Introduction

Pressure filtration can reduce the consolidation time of a colloidal suspension when compared with the filtration method using a gypsum mold because of a higher compressive pressure. The capillary tube suction pressure of a gypsum mold is 50-100 kPa, but the applied pressure of pressure filtration can be as high as 80 MPa when stainless steel equipment is used [1]. In previous papers [2-8], we analyzed the consolidation behavior of aqueous suspensions of nanoparticles in a size range of 20 to 800 nm with and without a polyelectrolyte dispersant using a newly-developed pressure filtration apparatus at a constant crosshead speed or at a constant pressure of a piston. Addition of a small amount of polyacrylic ammonium (PAA) to 20-800 nm particles changed the consolidation behavior and increased the resultant packing density because of the steric or electrosteric stabilization effect of PAA [4, 7-9]. However, little information has been reported on the adsorption and the influence of a low molecular dispersant on the consolidation of nanoparticles. In our previous papers [10-12], we studied the interaction between submicrometre-sized colloidal particles and amino acid with both carboxyl and amino groups in one molecule. The addition of phenylalanine (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CHNH<sub>3</sub><sup>+</sup>COO<sup>-</sup>, molecular weight 165.2) with equal numbers of COO<sup>-</sup> and NH<sub>3</sub><sup>+</sup> groups to negatively charged 800 nm SiC particles at pH 7 caused (1) an increase of the zeta potential to a negative value (0.05-5 mass% against

SiC), (2) little change of the apparent viscosity and (3) adsorption of phenylalanine on SiC surfaces (0.1-0.2 mg/m<sup>2</sup>) [13]. The adsorbed and free phenylalanine in the SiC suspension suppressed the colloidal phase transition from a dispersed to a flocculated state at an applied pressure. A high packing density (64-65%) after calcination in an Ar atmosphere at 1000 °C was achieved by the addition of a small amount of phenylalanine (0.05-0.5 mass%). Based on the above results, this paper reports the influence of phenylalanine on (1) the filtration of 30 nm SiC and 150 nm Al<sub>2</sub>O<sub>3</sub> particles at a constant crosshead speed of a piston and (2) the packing density after calcination at 700-1000 °C in air or an Ar atmosphere. The above results were coupled with the data for 800 nm SiC particles to discuss the relation between the sizes of the dispersant and particles in colloidal pressure filtration.

### Experimental Procedure

A plasma CVD-processed β-SiC powder (SiC B) supplied by Sumitomo Osaka Cement Co., Ltd., Tokyo, has the following characteristics: chemical composition-SiC 95.26 mass%, SiO<sub>2</sub> 0.97 mass%, C 3.76 mass%, median particle size 30 nm, true density 3.10 g/cm<sup>3</sup>, specific surface area 50.4 m<sup>2</sup>/g and isoelectric point pH 2.95. The following α-alumina powder supplied by Sumitomo Chemical Co., Ltd., was also used: Al<sub>2</sub>O<sub>3</sub> > 99.99 mass%, median particle size 150 nm, true density 3.99 g/cm<sup>3</sup>, specific surface area 10.5 m<sup>2</sup>/g and isoelectric point pH 8.7. As-received SiC B and alumina powders were dispersed at pH 7 (5 vol% solid) and pH 3 (7 vol% solid), respectively, in aqueous solutions containing phenylalanine (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CHNH<sub>3</sub><sup>+</sup>COO<sup>-</sup>, molecular weight 165.2) of 0.05-15 mass% against colloidal particles

\*Corresponding author:  
Tel : +81 99-285-8325  
Fax: +81 99-257-4742  
E-mail: hirata@apc.kagoshima-u.ac.jp

(0.0475–5.01 mg/m<sup>2</sup>). Polyacrylic ammonium (PAA, (CH<sub>2</sub>-CHCOONH<sub>4</sub>)<sub>n</sub>, molecular weight 10000) of 0.36–9.2 mass% was also mixed with colloidal particles (0.35–3.04 mg/m<sup>2</sup>). The saturated amount of phenylalanine adsorbed on 800 nm SiC particles (named SiC A) was 0.1–0.2 mg/m<sup>2</sup> at pH 7 in our previous experiment [13]. SiC A powder (*α*-SiC) supplied by Yakushima Electric Industry Co., Ltd., Kagoshima, Japan, has the following characteristics: chemical composition-SiC 98.90 mass%, SiO<sub>2</sub> 0.66 mass%, Al 0.004 mass%, Fe 0.013 mass%, free C 0.37 mass%, median particle size 800 nm, true density 3.23 g/cm<sup>3</sup> and specific surface area 13.4 m<sup>2</sup>/g, and isoelectric point pH 3.5. The solution pH was adjusted with 1.0 M-HCl and 1.0 M-NH<sub>4</sub>OH solutions.

The above SiC and Al<sub>2</sub>O<sub>3</sub> suspensions were stirred for 24 h at room temperature. The zeta potential of SiC A, B and alumina particles was measured at a constant ionic strength of 0.001 M-NH<sub>4</sub>NO<sub>3</sub> (Rank Mark II, Rank Brothers Ltd, Cambridge, UK). The colloidal suspension in a closed cylinder was filtered through a glass filter of 20 μm pore diameter and three sheets of a membrane filter of 0.1 μm pore diameter. These filters were attached to the bottom of the piston (polymeric resin) moving at a crosshead speed of 0.2 mm/minute. When the suspension in a closed cylinder was compressed by the piston, the filtrate flowed into and through the pore channels formed in the upper piston. The applied load and the height of the piston were continuously recorded (Tensilon RTC, A & D Co. Ltd., Tokyo, Japan). The consolidated SiC and Al<sub>2</sub>O<sub>3</sub> compacts were taken out of the cylinder and dried at 100 °C in air for 24 h. The dried SiC and Al<sub>2</sub>O<sub>3</sub> compacts were heated at 1000 °C in an Ar atmosphere and at 700 °C in air for 1 h, respectively, to give an enough strength for the measurement of bulk density by the Archimedes method using kerosene.

## Results and Discussion

### Zeta potential of colloidal SiC and Al<sub>2</sub>O<sub>3</sub> particles

Fig. 1 shows the zeta potential of SiC A, B and alumina particles in a 0.001 M-NH<sub>4</sub>NO<sub>3</sub> solution as a function of suspension pH. The isoelectric points were pH 3.5 for SiC A, 2.95 for SiC B and 8.7 for alumina, respectively. The surfaces of SiC particles were coated by a thin SiO<sub>2</sub> film [14]. At a pH below the isoelectric point, the number of positively charged SiOH<sub>2</sub><sup>+</sup> sites becomes greater than that of negatively charged SiO<sup>-</sup> sites. The opposite case occurs at a pH above the isoelectric point. Similarly, the number of positively charged AlOH<sub>2</sub><sup>+</sup> sites becomes greater than that of negatively charged AlO<sup>-</sup> sites at a pH below the isoelectric point. Phenylalanine (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CHNH<sub>2</sub>COOH) is charged positively below pH 2.61 (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CHNH<sub>3</sub><sup>+</sup>COOH) and has both charged groups of NH<sub>3</sub><sup>+</sup> and COO<sup>-</sup> in the pH range of 2.61 to 9.18 (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CHNH<sub>3</sub><sup>+</sup>COO<sup>-</sup>) [12]. In a high pH range above 9.18, phenylalanine is charged negatively

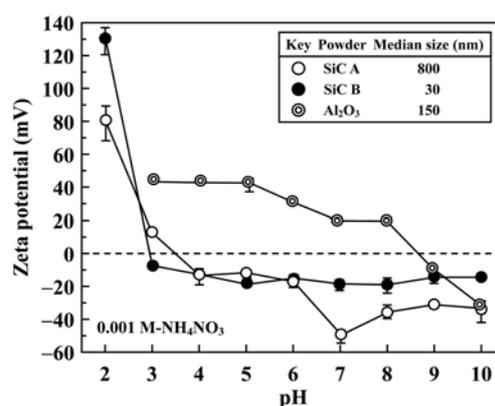


Fig. 1. Zeta potential of SiC A (800 nm SiC), B (30 nm SiC) and alumina (150 nm) in a 0.001 M-NH<sub>4</sub>NO<sub>3</sub> solution as a function of suspension pH.

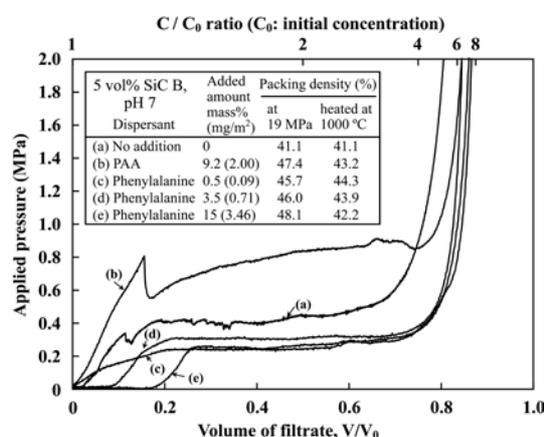


Fig. 2. Relation between the normalized volume of filtrate ( $V_0$ : volume of initial SiC suspension) and pressure applied at a crosshead speed of 0.2 mm/minute for 5 vol% SiC B suspensions.

(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CHNH<sub>2</sub>COO<sup>-</sup>). When the SiC suspension is prepared at pH 7, two types of interaction occur between phenylalanine and SiC surfaces: (1) NH<sub>3</sub><sup>+</sup> group ... SiO<sup>-</sup> site, (2) COO<sup>-</sup> group ... SiOH<sub>2</sub><sup>+</sup> site. Similarly two types of interaction occur between phenylalanine and Al<sub>2</sub>O<sub>3</sub> surfaces at pH 3: (1) NH<sub>3</sub><sup>+</sup> group ... AlO<sup>-</sup> site, (2) COO<sup>-</sup> group ... AlOH<sub>2</sub><sup>+</sup> site. The amount of adsorbed phenylalanine was measured to be 0.1–0.2 mg/m<sup>2</sup>-SiC A particles at pH 7 [13]. Similarly, the saturated amounts of polyacrylic acid adsorbed on SiC surface at pH 7 and on alumina surface at pH 3 were measured to be 0.29 mg/m<sup>2</sup> and 0.23 mg/m<sup>2</sup>, respectively [15, 16].

### Pressure filtration of colloidal suspensions with PAA and phenylalanine

Figs. 2 and 3 show the applied pressure for SiC B and alumina suspensions at a crosshead speed of 0.2 mm/minute as a function of normalized volume of filtrate. According to the filtration theory of well-dispersed particles [5, 6], the applied pressure increases proportionally with the volume of filtrate. However, an almost plateau region of applied pressure was measured after the initial increases of pressure. This is due to the

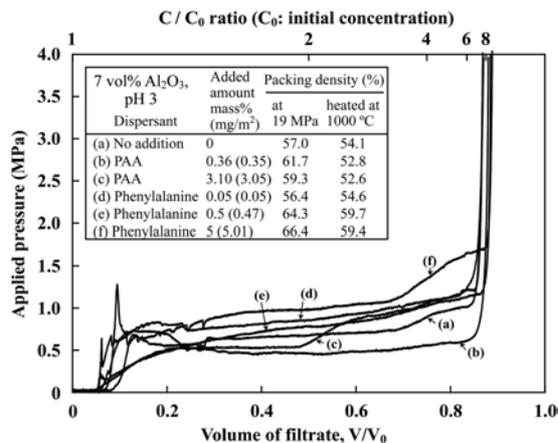


Fig. 3. Relation between the normalized volume of filtrate ( $V_0$ : volume of initial  $\text{Al}_2\text{O}_3$  suspension) and pressure applied at a crosshead speed of 0.2 mm/minute for 7 vol%  $\text{Al}_2\text{O}_3$  suspensions.

phase transition from a dispersed to flocculated suspension at a critical pressure [5, 6]. A filtration theory for a flocculated suspension is also proposed in our previous papers [5-7]. The consolidation of flocculated SiC B particles resulted in a 41.1% packing density at an applied pressure of 19 MPa. After heating at 1000 °C, no change was measured for the packing density. The addition of PAA and phenylalanine to a SiC B suspension increased the packing density to 45.7-48.1%. After heating at 1000 °C, the packing density decreased to 42.2-44.3% because of the relaxation of the dispersant after elimination of applied pressure. As seen in Fig. 3, the addition of phenylalanine was also effective in increasing the packing density of  $\text{Al}_2\text{O}_3$  particles when compared with no addition of dispersant. Fig. 4 summarizes the packing density of SiC and alumina compacts after calcination. It is apparent that the packing density of colloidal particles without a dispersant decreases when the particle size becomes small [4]. The addition of negatively charged PAA at pH 7 and phenylalanine with  $\text{COO}^-$  and  $\text{NH}_3^+$  groups enhanced the packing density of SiC and alumina particles in the range of 30 to 800 nm. However, neutral PAA at pH 3 gave little influence on the packing density of alumina particles. The zeta potential of SiC A particles at pH 7 shifted to more negative values (-34.0 to -42.9 mV) when 0.05-5 mass% PAA or phenylalanine was added to SiC particles [17]. The electrosteric stabilization of colloidal particles by PAA and phenylalanine is still effective to form dense packing after the phase transition of colloidal suspension at a given applied pressure.

### Conclusions

The packing density of SiC and alumina particles of 30-800 nm diameters through pressure filtration at a constant crosshead speed increased with the addition of dissociated PAA and phenylalanine. Since phenylalanine has two charged groups ( $-\text{NH}_3^+$ ,  $-\text{COO}^-$ ) in one molecule, this dispersant can be used for surfaces of

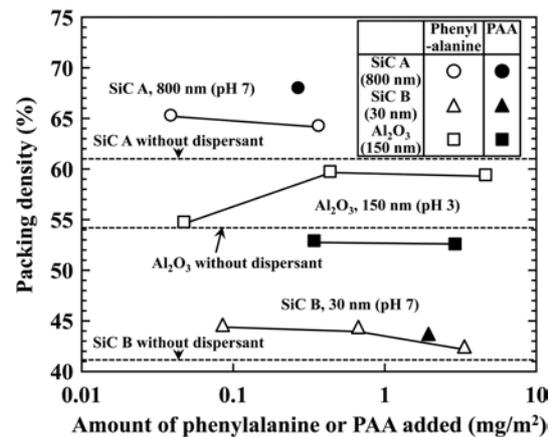


Fig. 4. Influence of phenylalanine and PAA on the packing density of SiC and  $\text{Al}_2\text{O}_3$  particles.

both positively and negatively charged particles.

### References

1. F.F. Lange and K.T. Miller, Am. Ceram. Soc. Bull. 66 [10] (1987) 1498-1504.
2. K. Kishigawa and Y. Hirata, J. Eur. Ceram. Soc. 26 (2006) 217-212.
3. K. Kishigawa and Y. Hirata, J. Ceram. Soc. Japan 114 [3] (2006) 259-264.
4. Y. Hirata, M. Nakamura, M. Miyamoto, Y. Tanaka and X.H. Wang, J. Am. Ceram. Soc. 89 [6] (2006) 1883-1889.
5. Y. Tanaka, Y. Hirata, N. Matsunaga, M. Nakamura, S. Sameshima and T. Yoshidome, J. Ceram. Soc. Japan 115 [11] (2007) 786-791.
6. Y. Hirata, and Y. Tanaka, J. Am. Ceram. Soc. 91 [3] (2008) 819-824.
7. Y. Hirata, H. Uchima, Y. Tanaka and N. Matsunaga, J. Am. Ceram. Soc. 92 [S1] (2009) S57-S62.
8. Y. Hirata, Y. Tanaka, S. Nakagawa and N. Matsunaga, J. Ceram. Process. Res. 10 [3] (2009) 311-318.
9. X.H. Wang and Y. Hirata, Ceram. Inter. 31 (2005) 677-681.
10. M. Chaen and Y. Hirata, Trans. Mater. Res. Soc. Japan 29 [5] (2004) 2379-2382.
11. H. Takahashi, H. Shimazu, Y. Hirata and S. Sameshima, J. Ceram. Process. Res. 5 (2004) [1] 25-29.
12. Y. Hirata, H. Takahashi, H. Shimazu and S. Sameshima, Ceram. Trans., Vol. 152, Colloidal Ceramic Processing of Nano-, Micro-, and Macro-Particulate System, The American Ceramic Society ed. by W.H. Shih, Y. Hirata and W. Carty (2004) 1-10.
13. S. Baba, Y. Hirata, N. Matsunaga and S. Sameshima, Ceram. Trans., Characterization and Control of Interfaces for High Quality Advanced Materials III, John Wiley & Sons Inc, New Jersey, ed. by K. Ewisuk, M. Naito, T. Kakeshita, S. Kirihara, K. Uematsu and H. Abe 219 (2010) 105-110.
14. Y. Hirata, K. Hidaka, H. Matsumura, Y. Fukushige and S. Sameshima, J. Mater. Res. 12 [11] (1997) 3146-3157.
15. Y. Hirata, S. Tabata and J. Ideue, J. Am. Ceram. Soc. 86 [1] (2003) 5-11.
16. Y. Hirata, J. Kamikakimoto, A. Nishimoto and Y. Ishihara, J. Ceram. Soc. Japan 100 [1] (1992) 7-12.
17. N. Matsunaga, A. Yamashita, and Y. Hirata, J. Ceram. Soc. Japan 119 [3] (2011) 161-167.