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Temperature dependence of dynamic moduli of alumina suspensions and alumina powder compacts

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Abstract

The complex moduli of 10–30 vol% aqueous suspensions of alumina particles of median size of 310 nm were measured at 1 Hz of applied frequency in a temperature range of -100 to 100 °C at a heating rate of 1 °C/min. The storage modulus of distilled water as a reference material showed a drastic decrease at 0 °C, where a phase transition occurred from solid ice to liquid water. The loss tangent of water showed a sharp peak associated with the phase transition at 0 °C. In 10 vol% alumina suspensions at pH 3, 5 and 7, more additional peaks of storage modulus and loss tangent appeared at $7-51$ °C. The peaks at 30–51 °C represent the phase transition of colloidal suspension from a dispersed state to a flocculated state. When the alumina content of the suspension was increased to 30 vol%, little change of storage modulus and loss tangent were measured in the wide temperature range of -100 to 100 °C, reflecting little change of dense packing structure of alumina particles after the melt of solid ice with increasing temperature. A similar dependence of storage modulus and loss tangent on heating temperature was measured in the calcined alumina porous compact infiltrated with water in the open pores.

Keywords: A. Slip casting; A. Suspensions; C. Thermal properties; D. Al_2O_3

1. Introduction

Colloidal processing has been well recognized as a powder processing to improve physicochemical properties of advanced ceramics through the microstructural control of green and sintered bodies. This processing involves the dispersion of starting particles in a liquid medium and subsequent consolidation using a gypsum mold, pressure filtration or doctor blade method. The dispersion of colloidal particles has been understood by the DLVO theory representing the interaction energy between charged particles [1,2].

Pressure filtration has some advantages to consolidate densely colloidal particles in a short time [3–5]. We have studied the pressure filtration of nanometer-sized ceramic particles (20–800 nm diameter) in a wide pressure range up to 19 MPa and proposed a new filtration theory for a flocculated suspension [6–9]. When a high pressure was applied to a dispersed suspension, a phase transition from dispersed to flocculated particles occurred. Recently the filtration behavior of a flocculated suspension of 150 nm alumina particles was analyzed based on viscoelastic models [10]. The viscoelastic properties of a flocculated suspension were well fitted by the Voigt model. The flocculated suspension behaved like a liquid at a low particle concentration. The influence of solid element of the Voigt model became stronger with decreasing suspension height (increasing solid content of the flocculated suspension).

Otsubo and Watanabe [11] measured strain dependence of dynamic viscoelastic properties of aqueous suspensions containing silica particles of 15 nm diameter, polyacrlyamide and glycerin. The breakdown process of the flocculated network of silica particles through polymer bridging was analyzed by the measurement of storage modulus. Garrido and Califano [12] studied the effect of polyelectrolyte on viscoelastic behavior of highly concentrated suspensions of alumina–zirconia mixed particles. The well dispersed suspensions exhibited a predominantly viscous response, which changed to a slight elastic behavior at a

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critical solid content. The elastic contribution increased with increasing concentration of free polyelectrolyte in a solution. On the other hand, the heterocoagulated suspensions with an insufficient amount of dispersant showed a predominantly elastic behavior. Belza et al. [13] investigated the effects of electric field strength and temperature on viscoelastic properties of electrorheological suspensions of urea-modified silica nanoparticles. They suggest that the increase of storage modulus with temperature reflects the formation of a higher rigid structure due to the increased particle polarization in agreement with the increased permittivity. As mentioned above, the measurement of storage modulus of a ceramic suspension is significantly useful to interpret the suspension structure. The purpose of this paper is to understand the viscoelastic properties of alumina suspensions with heating temperature by the measurement of complex moduli. The measured results were compared with the elastic properties of calcined alumina compacts.

2. Experimental procedure

2.1. Viscoelastic properties of alumina suspensions

A high purity alpha-alumina powder with isoelectric point pH 8.6 (Al_2O_3 purity $>$ 99.99 mass%, median size 310 nm, specific surface area 10.2 m^2/g, Sumitomo Chemical Co., Ltd., Tokyo, Japan) was dispersed in double distilled water to make 10, 20 and 30 vol% solid suspensions at pH 3, 5 and 7. The particle size distribution in a dilute alumina suspension at pH 3.5 was measured by centrifugal particle size analyzer (CAPA-700, Horiba Ltd., Kyoto, Japan) and the particle sizes at cumulative 10%, 50% and 90% were 210, 310 and 580 nm, respectively. After the suspensions were stirred for 12 h, dynamic viscoelastic properties (storage modulus and loss tangent) of alumina suspensions were measured with a dynamic mechanical analyzer (DMA 8000, Perkin Elmer, MA, U.S.A.). A small amount of alumina suspension was put into a stainless steel container (30 mm length, 15 mm width, 2 mm thickness). This container was clamped in a dynamic mechanical analyzer to measure the dynamic viscoelastic properties by single cantilever configuration method (0.05 mm dynamic displacement, 1 Hz applied frequency). The stainless steel container including alumina suspension was cooled at -100 °C using liquid nitrogen. The viscoelastic measurement was carried out in the temperature range from -100 to 100 °C at a heating rate of 1 °C/min.

2.2. Elastic properties of alumina compacts

Aqueous 20 vol% alumina suspensions at pH 3 were consolidated by pressure filtration at a constant pressure of 1 MPa using a glass filter of 20 μm pore diameter and three sheets of a membrane filter of 0.1 μm pore diameter, which were attached to the bottom of the piston (Tensilon RTC-1350A, A&D Co., Ltd, Tokyo, Japan) [4,7,10]. The consolidated alumina compacts of 20 mm diameter were taken out of the cylinder and dried at 100 °C in air for 24 h. The dried compacts were heated at 700 °C in air for 1 h. The calcined compacts contained 36.4% open pores and 3.84% closed pores. The sizes of alumina compact for the measurement of dynamic viscoelastic properties were 9.1 mm length, 5.6 mm width and 7.0 mm height. The elastic properties under compression mode were measured for dried compact and wet compact including distilled water in the open pores, in the temperature range from -100 to 100 °C at a heating rate of 1 °C/min and at 1 Hz of applied frequency.

3. Results and discussion

3.1. Viscoelastic properties of alumina suspensions

The zeta potential of the alumina particles in a 0.01 MNH_4NO_3 solution was 50.2, 25.1 and 19.7 mV at pH 3.0, 5.0 and 7.0, respectively, and the isoelectric point was pH 8.6 [14]. The rheological properties and packing density of the alumina suspensions were greatly influenced by the surface potential of the charged particles. In our previous experiment [14], the apparent viscosity decreased when the surface potential of positively charged particles was increased at a low pH. The increased repulsive energy between charged alumina particles leads to the high packing density during the filtration of alumina suspension in gypsum mold. According to our recent study [8], the critical surface potential of submicrometer-sized particles causing a colloidal phase transition (dispersed particles → flocculated particles) is calculated to be 18.2 mV for 100 nm diameter and 12.8 mV for 500 nm diameter at 1 atm. That is, the surface potential of alumina particles with a particle size distribution of 150–700 nm at pH 3.0 (50.2 mV) and pH 5.0 (25.1 mV) was higher than the critical surface potential. However, the surface potential at pH 7.0 (19.7 mV) was comparable to the critical surface potential for the phase transition, increasing the probability of flocculation of colloidal alumina particles due to their thermal energy.

Fig. 1 shows the influence of suspension pH on (A) storage modulus and (B) loss tangent of 10 vol% alumina suspensions. The data of blank test represent the elastic properties of stainless steel container as a function of heating temperature. The storage modulus decreased slightly at a high temperature and loss tangent was less than 0.01. On the other hand, the storage modulus of the container with distilled water was high below 0 °C and dropped suddenly at 0 °C, where the loss tangent showed a sharp peak. This change of storage modulus and loss tangent is attributed to the phase transition from solid ice to liquid water at 0 °C. The temperature dependence of storage modulus and loss tangent of 10 vol% alumina suspensions was similar to that of distilled water.

The steep drop of storage modulus and the sharp peak of loss tangent at 0 °C are basically explained by the phase

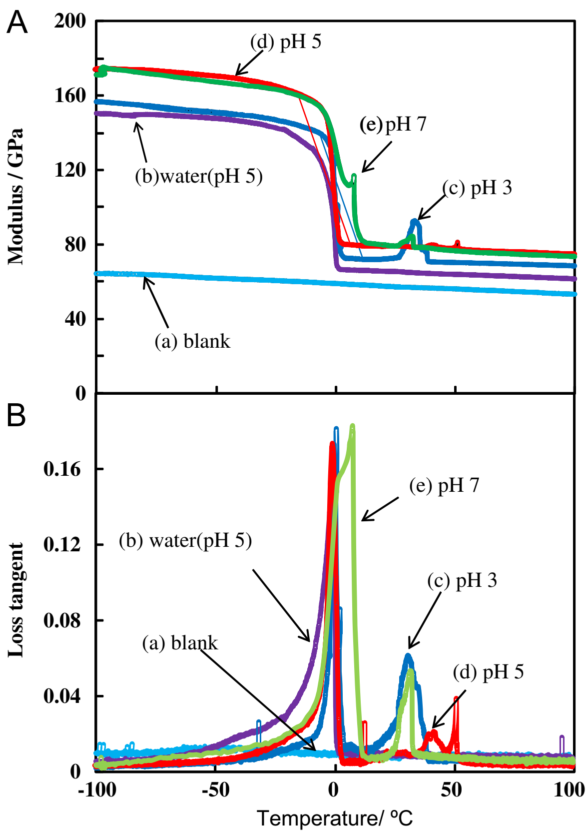

Fig. 1. Influence of suspension pH on (A) storage modulus and (B) loss tangent of 10 vol% alumina suspensions. The data of blank test represent the elastic properties of stainless steel container.

transition of solution in an alumina suspension. Furthermore, additional small peaks were measured at 7–51 °C in the storage modulus and loss tangent, depending on suspension pH. These types of peaks were not observed in distilled water. In a colloidal suspension, the dispersed particles collide to form flocculated particles. The molar fraction (α) of dispersed particles to the total colloidal particles (dispersed and flocculated particles) depends on settling time, surface potential of particle, particle size and concentration of electrolyte. In the suspension with a lower zeta potential at pH 7.0, the relatively wide peaks of loss tangent and the corresponding two step change in storage modulus were measured at 0–7 °C of heating temperature. This result may be associated with the melting of (1) the solid ice of free bulk solution (at 0 °C) distributed between dispersed particles and (2) the solid ice of solution trapped in flocculated particle clusters (at 7 °C). A similar shift to a higher temperature was also measured in the pyrolysis of organic compound (tetrapropylammonium bromide) trapped in ZSM-5 zeolite in air [15]. The H_2O molecules strongly bonded in the narrow spaces among flocculated alumina particles below 0 °C need a higher temperature to melt. Furthermore, the peaks measured at 30–51 °C in Fig. 1(A) and (B) in the alumina suspensions at pH 3, 5 and 7 indicate the change in the structure of colloidal suspension with heating. This result is discussed in the next section.

3.2. Phase transition of colloidal suspension with heating

The peaks of storage modulus and corresponding loss tangent at higher temperature (30–51 °C) represent the phase transition of colloidal suspension from a dispersed state to a flocculated state. The collision rate between dispersed particles to form flocculated particles is accelerated at a high temperature because the diffusion coefficient of dispersed particles increases at a high temperature and the viscosity of solution decreases with increasing temperature [16]. The chemical potential of dispersed (μ_d) and flocculated particles (μ_g) in a colloidal suspension is expressed by the following equations [6,9]:

$$d\boldsymbol{\mu}_d = \overline{V}_d dP - \overline{S}_d dT \quad (1)$$

$$d\boldsymbol{\mu}_g = \overline{V}_g dP - \overline{S}_g dT \quad (2)$$

where $\overline{V}$ and $\overline{S}$ are the partial molar volume and partial molar entropy of particles in a suspension, respectively, and $\boldsymbol{P}$ is the applied pressure and $\boldsymbol{T}$ the temperature. Integration of Eqs. (1) and (2) at a constant pressure ($d\boldsymbol{P}=0$) yields Eqs. (3) and (4), respectively, under the constant $\overline{S}$ value:

$$\boldsymbol{\mu}_d = \mu_{d0} - \overline{S}_d(T - T_0) \quad (3)$$

$$\mu_g = \mu_{g0} - \overline{S}_g(T - T_0) \quad (4)$$

The μ_{d0} and μ_{g0} represent the chemical potential of particles at a temperature of T_0 (=298 K). The phase transition temperature (T_c) is solved under the condition $\mu_d = \mu_g$ at $T = T_c$ for Eqs. (3) and (4).

$$T_c = T_0 + \frac{\boldsymbol{\mu}_{g0} - \boldsymbol{\mu}_{d0}}{\overline{S}_d - \overline{S}_g} = T_0 + \frac{\Delta\boldsymbol{\mu}_0}{\Delta\overline{S}} \quad (5)$$

Fig. 2 shows the schematic relation for Eqs.(3)–(5). The μ_d, μ_g and the difference of $\mu_d - \mu_g$ decrease with increasing temperature and the μ_d value becomes equal to the μ_g value at the temperature (T_c) of the intersection of both the lines. As seen in Fig. 2, $\overline{S}_d$ (slope of the μ_d line) is larger than $\overline{S}_g$ and T_c depends on the ratio of $\Delta\mu_0/\Delta\overline{S}_g$, where $\Delta\mu_0 = \mu_{d0} - \mu_{g0}$ and $\Delta\overline{S} = \overline{S}_d - \overline{S}_g$. The dispersed particles have a tendency to change to flocculated particles at $T < T_c$ and the flocculated particles formed at $T = T_c$ have a tendency to change to dispersed particles at $T > T_c$, depending on the phase transition rate. The activity of dispersed particles (a_d), which controls the μ_d value, is expressed by Henry's law and equal to the product of the molar fraction (α) of dispersed particles in a suspension containing both dispersed and flocculated particles and the activity coefficient (γ°) expressed as C_0/C_{max} (C_0: total volume fraction of dispersed and flocculated particles, C_{max}: maximum packing density of particles) [8,9,17]. For a random closed packing model, C_{max} is 0.637. The γ° value is 1 for $C_0 = C_{max}$. That is, a_d is defined as a ratio of volume of dispersed particles (C_d) to the maximum volume packed, $a_d = C_0\alpha/C_{max} = C_d/C_{max}$. The activity of flocculated particles (a_g) follows Raoult's law and is

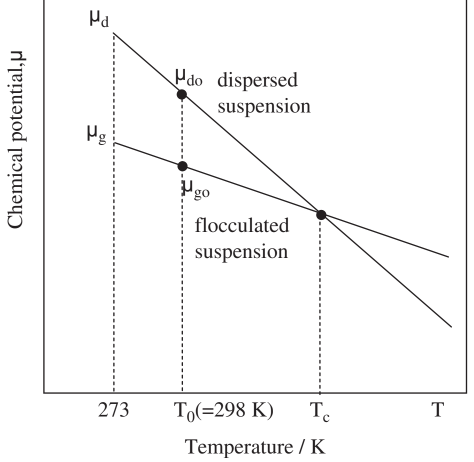

Fig. 2. Schematic relation of chemical potential and temperature for dispersed and flocculated alumina suspensions.

expressed as $(1-\alpha)$ using the Gibbs-Duhem equation. The difference of chemical potential ($\Delta\mu_0$) of both the particles at $T=T_0$ is expressed by Eq.(6),

$$\Delta\mu_0 = \mu_{\mathrm{d}}^{\bullet} + \mathrm{R}T_0\ln\left(\frac{C_0\alpha}{C_{\max}}\right) - \left[\mu_{\mathrm{g}}^{\bullet} + \mathrm{R}T_0\ \ln(1-\alpha)\right]$$

$$= (\mu_{\mathrm{d}}^{\bullet}\text{-}\mu_{\mathrm{g}}^{\bullet}) + \mathrm{R}T_0\ln\left(\frac{C_0}{C_{\max}}\right) + \mathrm{R}T_0\ \ln\left(\frac{\alpha}{1\text{-}\alpha}\right) \qquad (6)$$

where $\mu_d^\bullet$ and $\mu_g^\bullet$ values represent the chemical potential of dispersed particles for $\alpha=1$ and $\gamma^\circ=1$ and flocculated particles for $\alpha=0$, respectively. The $\Delta\mu_0$ increases with increasing C_0 and α values. That is, the T_c values shift to a higher temperature for a suspension with a high solid concentration of well dispersed particles. The above discussion was compared with the experimentally measured T_c values in Fig. 1(A) and (B). As seen in Fig. 1(A), no significant difference of T_c (≈ 31 °C) was observed in the alumina suspensions at pH 3 and 7, suggesting a small influence of α value in Eq. (6) on $\Delta\mu_0$ value. The T_c value in the suspension at pH 5 was measured at a higher temperature (41 °C). This result is not well understood at this moment. When the suspensions are heated, the included solution evaporates into steam, resulting in the increased concentration of alumina particles. This effect of evaporation of solution may increase the C_0 value in Eq. (6) and shift the T_c value in Eq. (5) to a higher temperature. Recently our group has measured the influence of heating temperature on shear stress of 20 vol% alumina suspension (pH 3.0) at 192 s^{-1} of shear rate [18]. Little change of shear stress was measured for 1 h at 28–40 °C, indicating a small change of alumina concentration during the measurement of rheology. However, a rapid increase of shear stress within 10 min was measured at 60–80 °C, indicating a high evaporation rate of the solution. The T_c values measured in a high temperature range >60 °C include the additional effect of evaporation of solution to C_0 value in Eq. (6).

3.3. *Influence of alumina concentration on viscoelastic properties*

Fig. 3 shows the influence of solid content on storage modulus and loss tangent of alumina suspensions at pH 3. The 10 and 20 vol% suspensions showed a sudden change of storage modulus and loss tangent at 0 °C associated with the phase transition of included solution. Furthermore, additional peaks of storage modulus and loss tangent were measured at 31 and 57 °C in 10 and 20 vol% suspensions, respectively. However, the storage modulus and loss tangent of 30 vol% alumina suspension were not sensitive to the heating temperature. The shift of the peak temperature in Fig. 3(A) and (B) to a higher temperature with increasing alumina content (10→20 vol%) is explained by the increase of $\Delta\mu_0$ in Eq. (6), resulting in the increased T_c in Eq. (5). However, little change of suspension structure occurred with heating in the 30 vol% alumina suspension. The distance (H) between two particles (diameter D) in a random close packing

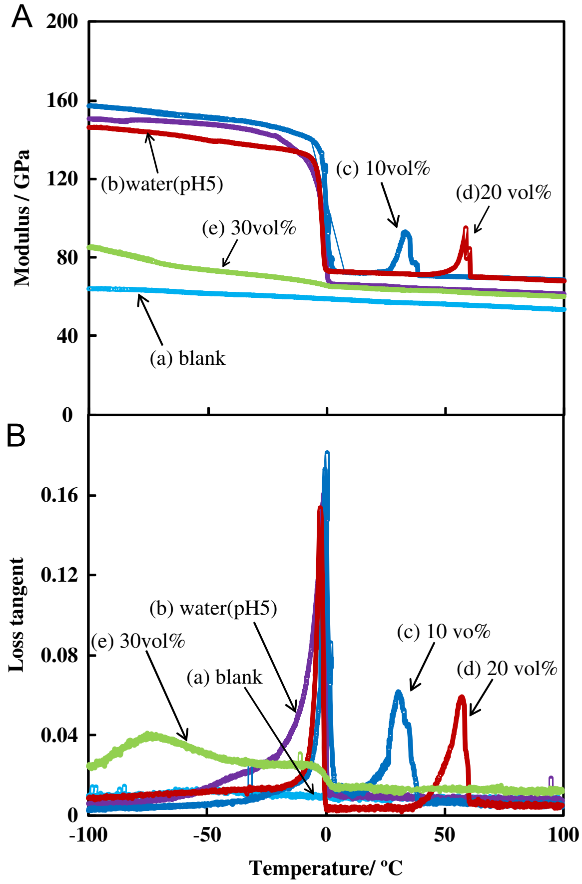

Fig. 3. Influence of alumina concentration on (A) storage modulus and (B) loss tangent of alumina suspensions at pH 3.0.

structure is expressed by Eq. (7) [4]

$$\frac{H}{D}=\left(\frac{1}{3\,\pi\,C_0}+\frac{5}{6}\right)^{1/2}-1 \qquad (7)$$

where C_0 is the solid content of suspension. Fig. 4 shows the H/D ratio as a function of solid content of alumina suspension. The increased solid content decreases drastically the H/D ratio, accelerating the touching of dispersed particles. The H/D ratio approaches 0 at 63.7 vol% solid. Little change of suspension structure may occur when the dispersed particles touch. The H/D ratio is calculated to be 0.168 and 0.090 for 20 and 30 vol% suspensions, respectively. The above calculation indicates that it is difficult to change the position of dispersed particles to form flocculated particle clusters when the H/D ratio becomes smaller than 0.1.

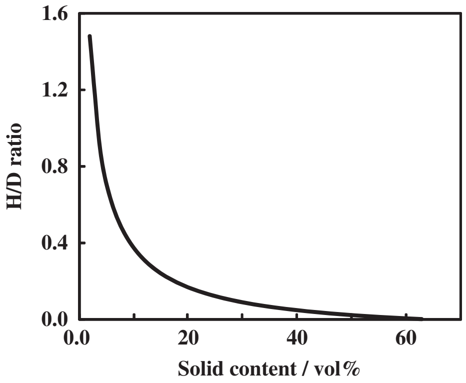

Fig. 4. Ratio of distance (H) between two spherical particles to diameter (D) in a random close packing structure.

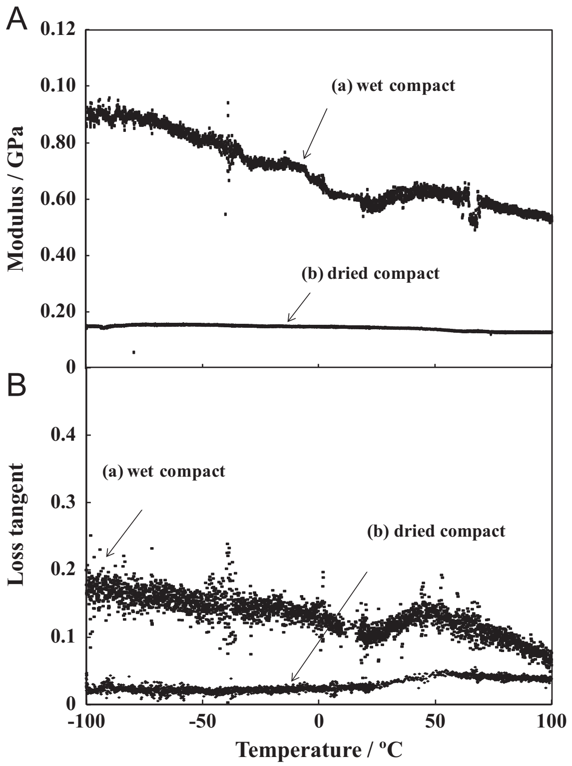

Fig. 5. (A) Storage modulus and (B) loss tangent of dried compact and wet alumina compact including distilled water in open pores (open porosity 36.4%) under compressive mode.

Fig. 5 shows the storage modulus and loss tangent of dried and wet alumina compacts under compressive mode. The temperature dependence of storage modulus and loss tangent of both the compacts was small, and was similar to that of 30 vol% alumina suspension (Fig. 3(e)). That is, the solution included in the concentrated suspension (solid content > 30 vol%) provided little influence on the visoelastic properties in the wide temperature range.

4. Conclusions

The storage modulus of distilled water decreased suddenly at 0 °C, where a phase transition from solid ice to liquid water occurred. The loss tangent of water showed a sharp peak associated with the phase transition at 0 °C. In 10 vol% alumina suspensions at pH 3, 5 and 7, the steep drop of storage modulus was also observed at 0 °C. More additional peaks of storage and loss tangent appeared at 7–51 °C. The peak at 7 °C may be associated with the melting of solid ice of solution trapped in flocculated particle clusters. The peaks at 30–51 °C represent the phase transition of colloidal suspension from a dispersed state to a flocculated state. This phase transition temperature shifts to a higher temperature for a suspension with a high solid concentration of well dispersed particles. When the alumina content of the suspension was increased to 30 vol%, little changes of storage modulus and loss tangent were measured in the wide temperature range of −100 to 100 °C. Since the ratio of distance between two particles to particle diameter is less than 0.1 in a 30 vol% suspension, it is difficult to change the position of dispersed particles to form flocculated particles. In addition, the phase change of solution included in the highly concentrated suspension provides little influence on the viscoelastic properties. A similar dependence of storage modulus and loss tangent on heating temperature was measured in dried and wet alumina porous compacts.

References

[1] J.T.B. Overbeek, in: H.R. Kyuyt (Ed.), Colloid Science I, Elsevier Publishing Company, Amsterdum, 1952, pp. 245–301.

[2] Y. Hirata, Theoretical aspects of colloidal processing, Ceramics International 23 (1997) 93–98.

[3] A. Dietrich, A. Neubraund, Y. Hirata, Filtration behavior of nanoparticle ceria slurries, Journal of the American Ceramic Society 85 (2002) 2719–2724.

[4] Y. Hirata, M. Nakamura, M. Miyamoto, Y. Tanaka, X.H. Wang, Colloidal consolidation of ceramic nanoparticle by pressure filtration, Journal of the American Ceramic Society 89 (2006) 1883–1889.

[5] Y. Hirata, K. Onoue, Y. Tanaka, Effect of pH and concentration of aqueous alumina suspension on pressure filtration rate and green microstructure of consolidated powder cake, Journal of the Ceramic Society of Japan 111 (2003) 93–99.

[6] Y. Hirata, Y. Tanaka, Pressure filtration model of ceramic nanoparticles, Journal of the American Ceramic Society 91 (2008) 819–824.

[7] Y. Tanaka, Y. Hirata, N. Matsunaga, M. Nakamura, S. Sameshima, T. Yoshidome, Pressure filtration of nanometer-sized SiC powder, Journal of the Ceramic Society of Japan 115 (2007) 786–791.

[8] Y. Hirata, N. Matsunaga, S. Sameshima, Phase transition and consolidation of colloidal nanoparticles, Ceramic Transactions 223 (2010) 101–112.

[9] Y. Hirata, K. Matsushima, S. Baba, N. Matsunaga, S. Sameshima, Theoretical and experimental analyses of colloidal processing of nanoparticles, Advances in Science and Technology 62 (2010) 131–140.

[10] Y. Hirata, K. Matsushima, N. Matsunaga, S. Sameshima, Viscoelastic properties of flocculated alumina suspensions during pressure filtration, Journal of the Ceramic Society of Japan 118 (2010) 977–982.

[11] Y. Otsubo, K. Watanabe, Dynamic viscoelasticity of flocculated suspensions, Colloids and Surfaces 41 (1989) 303–310.

[12] L.B. Garrido, A.N. Califano, Effect of an excess of polyelectrolyte on viscoelastic properties of suspensions of alumina and zircon mixtures, Colloids and Surface A: Physiochemical and Engineering Aspects 302 (2007) 24–30.

[13] T. Belza, V. Palinek, P. Saha, O. Quadrat, Effect of field strength and temperature on vicoelastic properties of electrorheological suspensions of urea-modified silica particles, Colloids and Surface A: Physiochemical and Engineering Aspects 316 (2008) 89–94.

[14] Y. Hirata, X.H. Wang, Y. Hatate, K. Ijichi, Electrical properties rheology and packing density of colloidal alumina particles, Journal of the Ceramic Society of Japan 111 (2003) 232–237.

[15] Y. Hirata, T. Kodama, K. Shimada, Y. Ishihara, Charcterization of ZSM-5 zeolite synthesized from silica stone (Ioh island, Kagoshima prefecture), Journal of the Ceramic Society of Japan 99 (1991) 1255–1259.

[16] S. Usui, in: The Chemical Society of Japan (Ed.), Colloid Science I, Kaguku Dojin, Tokyo 1995, p. 185.

[17] Y. Hirata, Y. Tanaka, Thermodynamics of colloidal suspensions, Journal of Ceramic Processing Research 9 (2008) 362–371.

[18] T. Fukunaga, Y. Hirata, S. Sameshima, unpublished data.