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Dispersion of ZrO_2 particles in aqueous suspensions by ammonium polyacrylate

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The effects of poly anionic-electrolyte (ammonium polyacrylate, PAA) as a dispersant on two kinds of ZrO_2 (monoclinic and yttria-doped tetragonal zirconia) aqueous suspensions were examined by the measurements of ζ-potential and viscosity, the sedimentation test and the determination of the wet point and flow point of the powders. Additions above 2.5 wt% PAA to zirconia gave a negative high ζ-potential above −30 mV, and then −45 and −30 mV were obtained for monoclinic and tetragonal zirconia above 5 wt% PAA, respectively. A high negative ζ-potential above −30 mV was retained with 5 wt% PAA for a change in pH over a wider range (pH 6 to 10 for monoclinic ZrO_2, 7 to 9 for tetragonal ZrO_2) in comparison to that of ZrO_2 without dispersant. The increase of the ζ-potential resulted in a decrease in the viscosity. The evaluation of dispersion by the sedimentation test was correlated well with the value of ζ-potential and the viscosity of the suspensions. The presence of native positive charge of monoclinic and tetragonal zirconia powders required an excess amount of PAA to attain dispersion of the suspension. There was a small difference in the least amount of PAA required to attain good dispersion between monoclinic and tetragonal ZrO_2. The difference was also indicated by changes of the flow point on PAA addition. Addition of 0.1% PAA to monoclinic ZrO_2 and 0.25 wt% to tetragonal ZrO_2 gave a maximum value of the flow point, whereas the positive ζ-potential fell to zero. Measurement of the flow point was a simple and useful technique for rapid evaluation of a required amount of dispersant for ZrO_2 suspensions.

1. Introduction
The dispersion of ceramic particles is important in the forming process, such as slip casting [1]. The good dispersion of particles gives optimum packing state (high green density) which influences the sinterability in the fired process and then the physical and chemical properties of the final product [2]. Organic polyelectrolytes have been used in the slip casting process in order to obtain a suitable and stabilized slurry in the process [3, 4]. Ammonium polyacrylate was recommended by the several investigators for slip casting [5, 6]. We have reported that the molecular weight of ammonium polyacrylate affected the dispersion of alumina particles in aqueous suspensions. We proposed a selection criteria of ammonium polyacrylate for the suspensions of alumina by using the sedimentation method, measurement of ζ-potential and viscosity, and the determination of the flow point and wet-point [7]. In addition, an improved method for the ζ-potential measurement by our laboratory [8] was available for the concentrated alumina suspensions. Zirconia and its polymorphic form have been widely used in scientific and engineering investigations because of their superior mechanical properties [9–11]. In order to control the wet-forming process of these powders, it is important to examine the colloidal behaviour of particles in their suspensions.

The purpose of this paper is to elucidate the effects of ammonium polyacrylate on the dispersion of two kinds of ZrO_2 particles, monoclinic zirconia and tetragonal zirconia with 3 mol % yttria, in aqueous suspensions.

2. Experimental procedure
2.1. Materials
Commercial monoclinic zirconia (TZ-0) and tetragonal zirconia with 3 mol % yttria (TZ-3Y) (TSK Co., Shinnanyo, Yamaguchi 746, Japan) were used in this experiment as described in a previous paper [8]. The chemical analysis provided by the manufacturer gave an oxide content as follows: Al_2O_3 0.005, SiO_2 0.002, Fe_2O_3 0.005, Na_2O 0.007 wt %, for TZ-0; Y_2O_3 5.08, Al_2O_3 0.005, SiO_2 0.002, Fe_2O_3 0.004, Na_2O 0.007 wt %, for TZ-3Y. Chloride ions as an anionic impurity were determined by a potentiometric titration; TZ-0 and TZ-3Y included 0.03 and 0.09 wt % chloride ions, respectively. Polyammonium acrylate (PAA) was Celuna D-305, molecular weight approximately 2000 to 3000 (Chukyo Yushi Co., Nagoya 454, Japan).

2.2. Measurement of ζ-potential and viscosity
The measurement of ζ-potential for each particle in the suspensions was conducted by the method previously reported [8] using an improved mass-transport apparatus in order to measure the ζ-potential for the concentrated suspensions. Apparent viscosity was measured using a cone and plate viscometer (Visconic EMD, Tokyo Keiki Co., Tokyo 144, Japan).

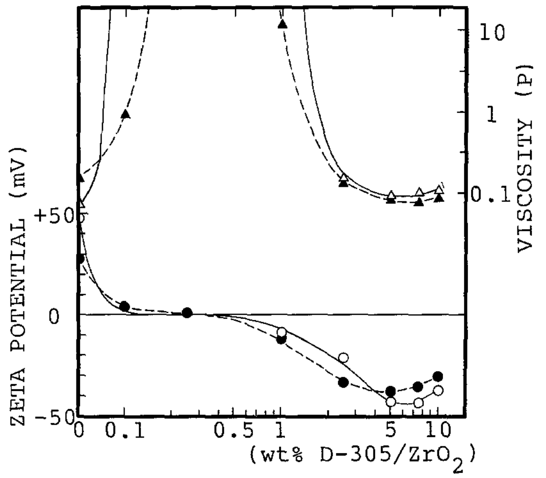

Figure 1 ζ-potential and viscosity of zirconia in suspensions of various amounts of ammonium polyacrylate. (○, ●) ζ-potential and (△, ▲) viscosity of monoclinic and tetragonal ZrO_2, respectively.

2.3. Evaluation of dispersion by sedimentation method

4 g zirconia powder and various amounts of PAA were mixed with 20 ml water under an ultrasonic processor, and then the suspensions were allowed to stand for 100 h, and the states of precipitation were observed.

2.4. Determination of wet point and flow point

The wet point and flow point of powders were defined as the least amount of solvent required to make a lump from a unit amount of powder and the least amount of solvent required for the suspension to begin to flow, respectively. The wet point and flow point were determined as follows: 20 g zirconia powder was mixed with 2.5 ml (below the wet point) of an aqueous solution including a fixed amount of PAA. Adding the solution from a burette, the total amount of the solution required to make a lump was obtained as a wet point. Furthermore, on adding water, the amount of solution at which the suspension began to flow was obtained as a flow point.

3. Results and discussion

3.1. The variation of ζ-potential and viscosity of suspension with the addition of various amounts of PAA

Fig. 1 shows the ζ-potentials and viscosities of monoclinic (TZ-0) and tetragonal (TZ-3Y) ZrO_2 in suspensions including various amounts of PAA. The ζ-potentials for both ZrO_2 particles with no addition of PAA indicate high positive values, i.e. these particles had a positive charge on their surfaces. The positive charge is neutralized and reduced to zero by the addition of 0.1 to 1.0 wt % PAA. Further additions of PAA above 2.5 wt % to the suspension gave a high negative ζ-potential, and resulted in a maximum negative value of −30 mV for tetragonal and −45 mV for monoclinic ZrO_2 at 5 wt % PAA.

A certain amount of PAA was consumed first to neutralize the positive charge of the ZrO_2 particle surfaces, and further addition of PAA led to negative ζ-potential to disperse the particles.

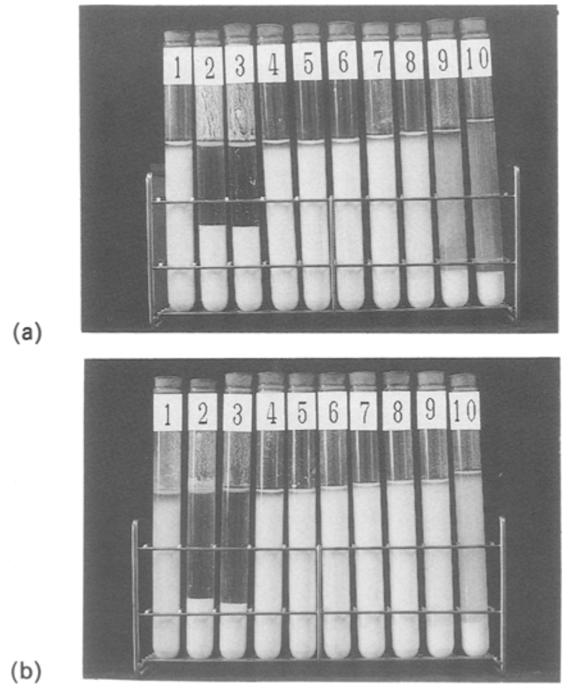

Figure 2 Sedimentation tests of (a) monoclinic and (b) tetragonal zirconia particles in aqueous suspensions in the presence of PAA. The amounts of PAA (wt % to ZrO_2) are (1) no addition, (2) 0.25, (3) 0.5, (4) 1, (5) 2.5, (6) 5, (7) 8, (8) 10, (9) 15 and (10) 25.

In a previous paper [7], we showed that PAA also had a dispersive effect on an alumina suspension in the amounts of only 0.2 wt % because alumina particles had a negative native charge on their surfaces due to the alkaline nature of alumina suspensions. An excess amount of PAA was, therefore, necessary to prepare a dispersion of ZrO_2 suspensions, compared to Al_2O_3.

Anderson *et al.* [12] have reported that the properties of a suspension with a high value of ζ-potential correspond to that with a low value of viscosity. A same correlation was also obtained for both zirconias in this experiment.

3.2. Observation of the effects of PAA on zirconia suspensions by the sedimentation method

Fig. 2 shows the results of the sedimentation test for the suspensions with or without various amounts of PAA, i.e. the photographs indicate the state of dispersion or precipitation of ZrO_2 particles. The suspensions without PAA dispersed well owing to their acidic properties (pH = 3.61 for monoclinic ZrO_2 and 5.51 for tetragonal ZrO_2) of the ZrO_2 surfaces. Additions below 0.25 and 0.5 wt % PAA inhibited the dispersion for monoclinic and tetragonal ZrO_2, suspensions, respectively, because of consumption of the positive charge of each zirconia by neutralization with the carboxylate of PAA. These results indicate that a good dispersion corresponds to the high ζ-potential and low viscosity with additions of various amounts of PAA.

3.3. Dependence of ζ-potential and viscosity on pH of suspension with or without PAA

Fig. 3 shows the variation of the ζ-potential of each

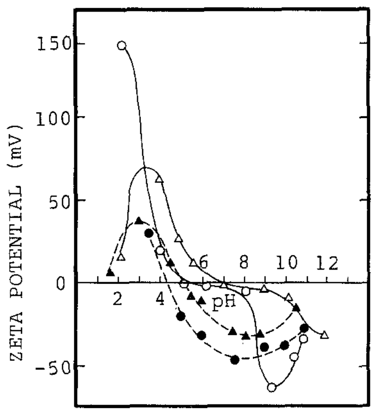

Figure 3 ζ-potential of zirconia as a function of pH in the presence of 5 wt % PAA. ζ-potential of monoclinic and tetragonal ZrO_2 (●, ▲) with and (○, △) without PAA, respectively.

ZrO_2 as a function of pH. The ζ-potentials of each ZrO_2 in the absence of PAA exceeded −30 mV only in the highly alkaline pH range (pH range = 9 to 11 for monoclinic ZrO_2, 12 for tetragonal ZrO_2). On the other hand, the ζ-potentials of each ZrO_2 in the presence of 5 wt % PAA retained a high negative value above −30 mV over a wider pH range (pH = 6 to 10 for monoclinic ZrO_2, 7 to 9 for tetragonal ZrO_2) than those in the absence of PAA. On addition of PAA, the range of pH where ζ-potential exceeded −30 mV was shifted to lower values of pH and extended to a wider pH range. A high ζ-potential is also obtainable in an acid medium as a positive charge without PAA. An acidic suspension, however, caused contamination by dissolving gypsum in practical slip casting [13], thus a neutral or weak alkaline suspension is preferable for this technique. The zirconia suspensions including PAA exhibited a higher ζ-potential around neutral or in the weak alkaline range.

3.4. Wet point and flow point of ZrO_2 powders

One of the purposes of adding a dispersant is to obtain a suspension as thick as possible whilst retaining fluidity, i.e. to reduce the water content of the suspension. In the case of an alumina suspension, PAA has a strong effect on the reduction of water [7]. The flow point represents the thickest suspension attainable to retain fluidity, and thus the lowest water content. Daniel and Goldman [14] have pointed out that a smaller gap between the flow point and the wet point results in a better dispersion of the suspension. The wet point represents the least amount of water required for a unit amount of powder to form a lump.

Lowering the flow point by the addition of PAA is, therefore, one means of thickening the suspension, i.e. a measure of the reduction of water content whilst retaining fluidity. The flow point and the wet point of both kinds of ZrO_2 powder were determined in the presence of various amounts of PAA, as shown in Fig. 4. The value of the wet point is almost constant for the addition of various amounts of PAA. Addition of a small amount of PAA up to 0.25 wt % allows an increase in the flow point value because of the neutralization of the positive charge and an increase of the viscosity of the suspension. On the other hand, further

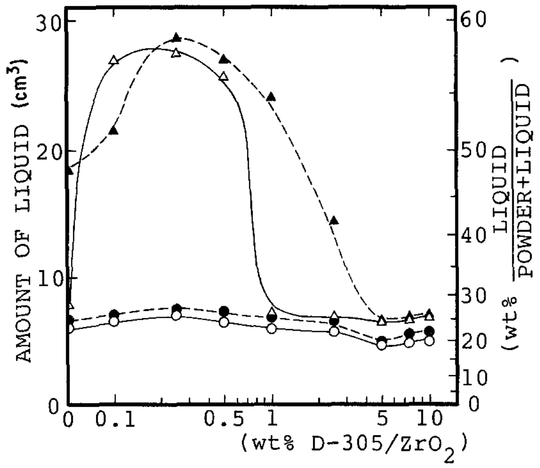

Figure 4 Wet point and flow point of zirconia powders with various amounts of PAA. (○, ●) Wet point and (△, ▲) flow point of monoclinic and tetragonal ZrO_2, respectively.

addition of PAA up to an optimum concentration to attain a good dispersion, allows a decrease in the flow point value because of the increase of ζ-potential by increasing the negative charge and decreasing the viscosity of the suspensions. The decrease of the flow point with further addition of PAA is slower for tetragonal ZrO_2 than for monoclinic ZrO_2. Monoclinic ZrO_2 is able to disperse in a smaller amount of PAA addition than is tetragonal ZrO_2, and to attain the minimum flow point in a much smaller amount of PAA addition. Excess amounts of PAA were required to attain a good dispersion of the suspension due to the consumption of a certain amount of PAA for the neutralization of ZrO_2 powders. The addition of 0.25 wt % PAA to monoclinic and 0.5 wt % to tetragonal ZrO_2 gave a maximum value of the flow point, whereas the positive value of ζ-potential fell to zero. The difference in the surface charge between monoclinic and tetragonal ZrO_2 affected the amount of PAA required to obtain a preferable dispersion, which indicated the least amount of PAA and water. Measurement of the flow point and wet point is a simple and useful technique for a rapid evaluation of the dispersion of ZrO_2 suspensions.

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