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Effectiveness of a dispersant for the thickening of alumina slurries whilst retaining the fluidity

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Concentrated alumina slurries were fluidized in an optimum amount of polyacrylates (PAA) in the content region where a good dispersion was obtained. Dispersion was necessary, but not sufficient for fluidization. The expected role of PAA in the thickening was retention of a water-reducing ability to retain the fluidity. Thickening of the alumina slurry to the limit of retaining the fluidity was achieved by the amount of PAA at which the flow point showed a minimum. The flow of alumina slurries around the limit was approximated by the Bingham model which was characterized by the yield stress and the Bingham viscosity. The flow curves of the slurries containing insufficient PAA had a yield stress which decreased with increasing amount of PAA and disappeared at an optimum amount of PAA to give a minimum flow point. The yield stress again increased retaining the low Bingham viscosity with increasing amount of PAA, to exceed the optimum amount for molecular weights smaller than 10 000. On the other hand, the Bingham viscosity increased without increasing the yield stress with increasing amount of PAA, to exceed the optimum amount for molecular weights larger than 20 000. The effect of PAA on the dispersion and flow behaviour could be explained by the electrostatic stabilization based on the Derjaguin-Landau, Verwey-Overbeek (DLVO) theory for the PAA with a molecular weight smaller than 10 000, and by the steric stabilization for the PAA with a molecular weight larger than 20 000.

1. Introduction

It is desirable in slip casting to prepare concentrated slurries whilst retaining the fluidity [1]. We have reported elsewhere that ammonium polyacrylates (PAA) are effective for the thickening of the slurries and those polymers added as dispersant have a characteristic function in fluidizing slurries, other than in their dispersion and stabilization [2, 3]. It is, however, possible to thicken the slurries and to reduce their water content by the fluidizing effect of a limited kind of dispersant.

The measurement of the flow point has been used for the evaluation of the thickening by a dispersant [4]. The flow point refers to the least amount of a medium required for a definite amount of powder to start to flow [5]. The addition of PAA lowered the flow point of alumina, giving a minimum in the presence of an optimum amount. Slurries at the flow-point minimum correspond to the thickening limit of the slurries.

The fluidity of the slurries in the vicinity of the thickening limit was affected by the concentration and molecular weight of PAAs and the solid loading in the slurries [6]. The flow curves were determined using a viscometer around the thickening limit in the presence of PAAs. By applying the Bingham model to the flow curves of the slurries, the fluidities can be characterized by the yield stress and the Bingham viscosity [7].

The purpose of the present study was to examine the effects of the molecular weight of PAA on the thickening limit and on the flow behaviour of alumina slurries around the limit.

2. Experimental procedure

2.1. Materials

The alumina powder used was α-alumina (A-16 SG, Aluminum Company of America, Pittsburgh, USA) of average particle size 0.3 μm. Ammonium polyacrylates of molecular weights 2500 (General Science Corporation, Tokyo, Japan), 5900, 11 000, 21 000 and 45 000 (Dai-ichi Kogyo Seiyaku Co., Kyoto, Japan) were examined as dispersants and fluidizing agents for preparing alumina slurry. The polyacrylates are referred to below as PAA-2500, PAA-5900, PAA-11 000, PAA-21 000 and PAA-45 000, respectively.

2.2. Evaluation of the effect of PAA fluidization of alumina slurries

The effect of PAA on the thickening of a slurry was evaluated from the lowering of the flow point with change in the amount of PAA. The flow point, as mentioned above, is defined as the least amount of water that was necessary for a unit amount of alumina containing PAA to start to flow. It was determined as follows: alumina powder (20 g) was mixed with 2.5 ml

0022-2461

(the amount being below the wet point) PAA solution of various concentrations. Water was added from a burette, and the least amount of water required to form a lump as a whole was read as the wet point. Then, by adding water up to the amount at which the slurry started to flow from the inclined spatula, the total amount of liquid added was read as the flow point.

2.3. Rheological observations

The flow behaviour of the slurries was determined from shear rate–shear stress curves, obtained at 25 °C with a cone and plate type viscometer (Visconic EMD, Tokyo Keiki Co., Tokyo 144, Japan) in the range of shear rate from 10–400 s^{-1}. Apparent viscosity, as a linear ratio of the shear stress to the shear rate, was obtained at the shear rate of 76.6 s^{-1}, assuming the slurry to be a Newtonian fluid.

3. Results and discussion

3.1. Thickening effect of PAA on alumina slurries

In a previous paper [2], the dispersive effect of PAA on alumina slurries was examined. From the results of the sedimentation test of alumina slurry containing PAA-2500, it was found that the slurry was dispersed by the addition of PAA in amounts from 0.125–2.5 wt % PAA to alumina. The changes in zeta-potentials of the alumina slurries for the variation of the amounts of PAAs were also measured. The range in the amount of PAAs where the zeta potential was higher than − 30 mV agreed with that of PAAs where slurries were dispersed in the sedimentation tests.

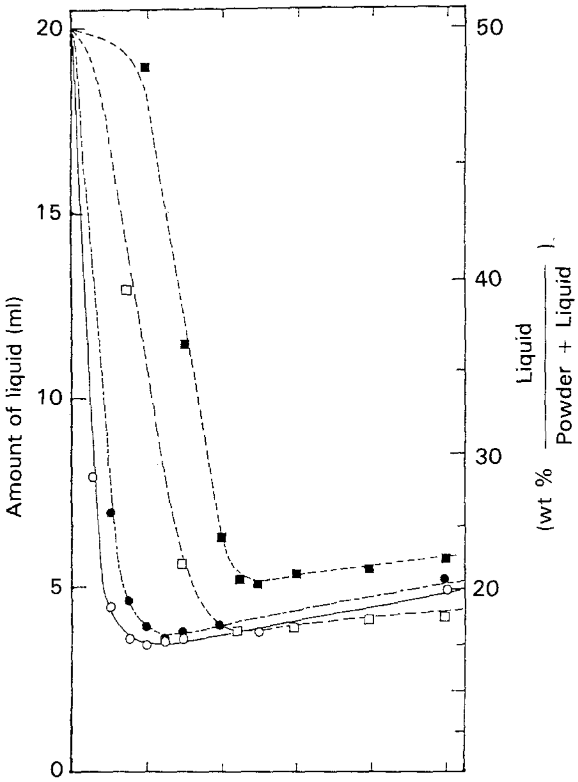

Figure 1 Flow points of alumina in the presence of various amounts of PAA of different molecular weights. (○) PAA-2500, (●) PAA-5900, (□) PAA-21 000, (■) PAA-45 000.

Fig. 1 shows the results of the determination of the flow points of alumina in the presence of various amounts of PAA of different molecular weights. The amount of PAA to give a minimum flow point corresponds to the most effective amount for fluidization. The amount agreed with that to give a maximum zeta potential of the slurry. The optimum amount for fluidization was obtained at a critical amount in the preferable range of amounts for dispersion. Dispersion was necessary, but not sufficient, for fluidization. In the presence of that amount of PAA, the slurries can flow in the least amount of water. The slurry at a flow-point minimum is at the limit of thickening of the slurry for it to retain its fluidity.

Table I shows the composition of slurries at the flow-point minimum for each PAA of different molecular weights. The slurries can be concentrated to the limit of the flow-point minimum in the presence of the optimum amount of PAA. The flow-point minimum increases with increasing molecular weight of PAA. The optimum amount of PAA also increases with increasing molecular weight of PAA.

3.2. Rheological properties of alumina slurries containing PAAs

It is valuable to characterize the flow of the slurries around the thickening limit in order to elucidate the interaction of adsorbed dispersants on the surfaces of the particles included in the concentrated slurries [8]. Fig. 2a and b represent the shear rate–shear stress curves of concentrated alumina slurries in the presence of PAA-2500 and PAA-45 000, respectively.

The apparent viscosity, η', is the ratio of the shear stress, σ, to the shear rate, $\dot{\gamma}$, as given by

$$\eta' = \frac{\sigma}{\dot{\gamma}} \qquad (1)$$

A concentrated slurry does not, usually, behave as a Newtonian fluid [9]. The apparent viscosity of the non-Newtonian fluid varies with shear stress [10]. By applying the Bingham model to the non-Newtonian fluid, η' can be approximated by the sum of the Bingham viscosity, η, and the ratio, σ_0/γ shown in Equation 2

$$\eta' = \eta + \frac{\sigma_0}{\dot{\gamma}} \qquad (2)$$

TABLE I Concentration of PAA required to obtain a minimum flow point for alumina and the thickening limit of alumina slurries

	PAA molecular weight				
	2500	5900	11 000	21 000	45 000
Amount of PAA (dwb of alumina) (%)	0.20	0.25	0.30	0.44	0.50
Solid loading (alumina powder) (wt %)	85.2	83.8	83.5	83.2	79.6

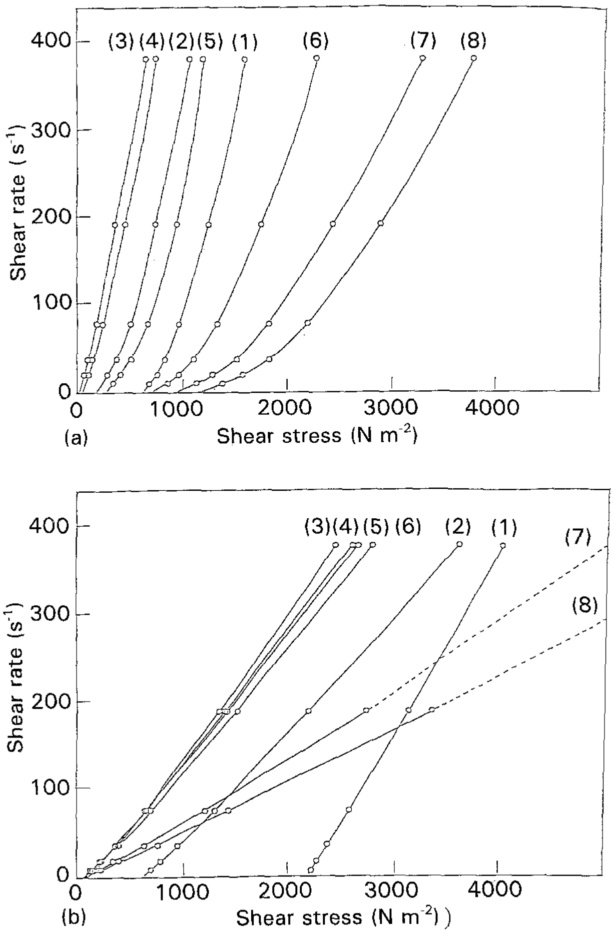

Figure 2 (a) Shear stress–shear rate curves for the alumina slurries containing various amounts of PAA-2500 at the solid loading of 75 wt % alumina. Amount of PAA: (1) 0.05, (2) 0.12, (3) 0.18, (4) 0.23, (5) 0.70, (6) 1.2, (7) 1.7 and (8) 2.1 wt % (dwb of alumina). (b) Shear stress–shear rate curves for the alumina slurries containing various amounts of PAA-45 000 at the solid loading of 70 wt % alumina. Amount of PAA: (1) 0.2, (2) 0.4, (3) 0.6, (4) 0.7, (5) 0.9, (6) 1.1, (7) 1.8 and (8) 2.7 wt % (dwb of alumina).

where σ_0 is the yield stress. This equation can be transformed into

$$1 = (\eta/\eta') + \frac{\sigma_0/\dot{\gamma}}{\eta'} \qquad (3)$$

In the Bingham model, therefore, the fluidity of a slurry can be characterized by high or low η/η' in the sum. For fluidization, the state at which η/η' is close to unity, as well as being possible, i.e. the state at which σ_0 and the second term in Equation 2 is close to zero, is preferable and necessary to give a low apparent viscosity.

With variation in amount of PAA-2500 added, the yield stress gave a minimum at a optimum amount of PAA, retaining the low Bingham viscosity, as indicated in Fig. 3. The values of η/η' have a maximum at the optimum amount of PAA-2500. The flow of the slurries containing PAA-2500 is a characteristic of the yield stress which changes with the amount of PAA added. Only on the addition of the optimum amount of PAA does the yield stress disappear, and is a high η/η' obtained. The effect of PAAs of molecular weights less than 10 000 was similar to that of PAA-2500. On the other hand, flow without yield stress is characteristic for the slurries containing PAA 45 000, as shown in Fig. 4. The Bingham viscosity increased with increasing concentration of PAA on increasing the excess amount of PAA to the optimum amount for fluidization. The flow is characterized by high η/η', being almost unity. The effectiveness of PAAs of molecular weights larger than 20 000 was similar to that of PAA-45 000. The change in the flow of slurries containing PAA occurred with molecular weights of PAA between 10 000 and 20 000.

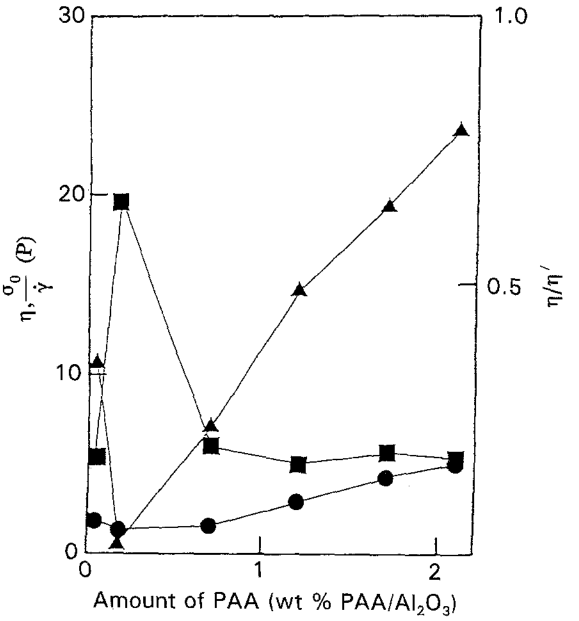

Figure 3 Calculated parameters, (●) η, (▲) $\sigma_0/\dot{\gamma}$ and (■) η/η' as a function of PAA-2 500 concentration.

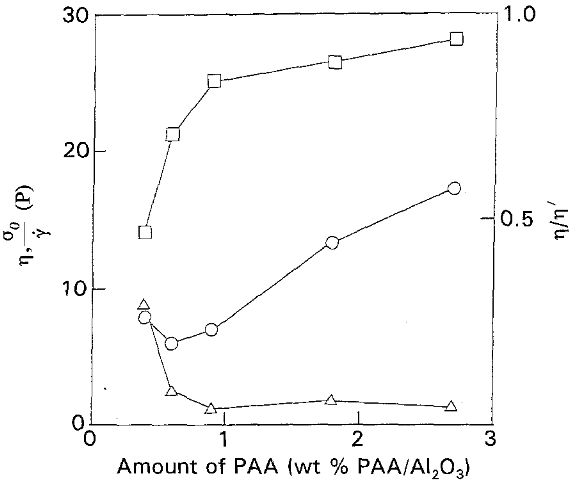

Figure 4 Calculated parameters, (○) η, (△) $\sigma_0/\dot{\gamma}$ and (□) η/η' as a function of PAA-45 000 concentration.

All the flow curves of the slurries containing insufficient PAA exhibited a yield stress. The yield stress decreased with increasing amount of PAA and disappeared at an optimum amount of PAA which gave a minimum flow point. The yield stress, however, increased again, retaining the low Bingham viscosity, on increasing amount of PAA to eventually exceed the optimum amount for molecular weights less than 10 000. For thickening and fluidization with PAAs of molecular weights less than 10 000, the yield stress should be reduced first and then high η/η' should be realized, with a value of η as low as possible.

On the other hand, the Bingham viscosity increased without the yield stress on increasing the amount of PAA to exceed the optimum amount for molecular weights larger than 20 000. For fluidization with PAA of molecular weight larger than 20 000, low η should be selected at the optimum amount of PAA added, because high η/η' values have already been realized, irrespective of the η value. Thus high η/η' for fluidization, with η as low as possible, should be realized with the amount of PAA that gave a minimum flow point in both cases.

Suspended ceramic particles are commonly of submicroscopic size and have a large specific surface area. Various kinds of forces, repulsive or attractive, act between them, i.e. van der Waals attractive force, electrostatic repulsive force and steric attraction and/or repulsion by adsorbing a polymer on the particle surfaces [11, 12]. Depending on the balance of those forces, the particles attract each other to form agglomerates or repel each other to become dispersed [13]. In general, a yield stress appearing in the flow curve of a concentrated slurry would be caused by a rigid structure formed by the particle–particle attractive interaction [14, 15].

Fig. 5 shows schematic diagram for the stabilization of alumina particles in the slurries in the presence of small or large PAA molecules. The function of PAA with a molecular weight less than 10 000 could be explained by the DLVO theory based on the electrostatic dispersion mechanism [16]. The least amount of PAA with their carboxylic negative charges to be balanced against the van der Waals attraction (the zone within this force is marked by the dotted line in Fig. 5) would be necessary for the dispersion and the fluidization, as indicated by the solid line in Fig. 5, for the effective zone. On the other hand, the function of PAA with a molecular weight larger than 20 000 could be explained by the steric stabilization [17]. Adsorbed PAAs on the solid particle surfaces keep the particles at a distance, indicated by the solid line, at which the van der Waals attraction did not affect the particles, leading to a low yield stress. This could be the reason why the flow curves of the slurries containing PAA of large molecular weight did not exhibit a yield stress. Thickening to the limit attained by PAA of smaller molecular weight, is difficult for PAA of large molecular weight even on the addition of the optimum amount to give a minimum flow point.

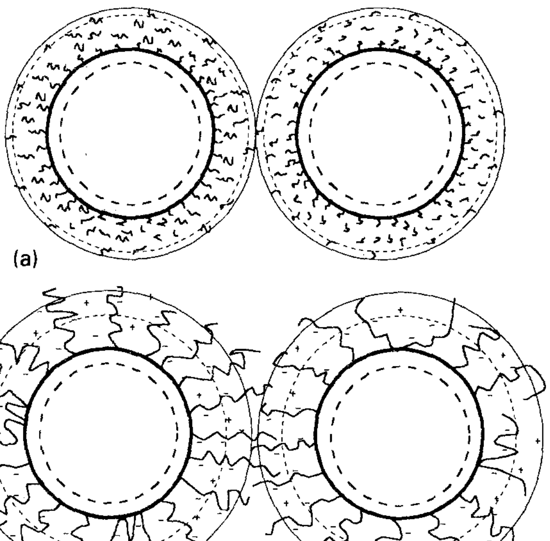

Figure 5 Schematic diagram of (a) the electrostatic and (b) the electrostatic stabilization (not to scale). (a) Molecular weight of PAA < 10 000, (b) molecular weight of PAA > 20 000.

4. Conclusions

Alumina slurries were fluidized by the addition of PAAs in amounts at which a good dispersion was obtained. Dispersion and thickening of alumina slurry whilst retaining fluidity can be simultaneously achieved by the addition of appropriate amounts of PAA and the limit of thickening with fluidization attained by that amount of PAA.

Flow behaviour of the slurries was determined around the thickening limit. The flow curves were characterized by the yield stress and the Bingham viscosity, approximating to the Bingham model. The flow of alumina slurries with PAAs of molecular weights smaller than 10 000 and higher than 20 000 is characterized by the flow with and without the appearance of a yield stress, respectively. The change in the flow of slurries containing PAA occurred at molecular weights of PAA between 10 000 and 20 000.

Except for the addition of the optimum amount of PAA, an excess or insufficient addition of PAA of molecular weight less than 10 000 caused a loss of fluidity with increasing yield stress, although a good dispersion was obtainable. An excess or insufficient addition of PAA of molecular weight larger than 20 000 caused a loss of fluidity with increasing Bingham viscosity or with high yield stress. In spite of the necessary conditions, dispersion was not always a sufficient condition for fluidization of the slurries.

The effect of PAAs on the dispersion and flow behaviour could be explained by the DLVO mechanism for PAAs of molecular weight less than 10 000, and by the steric stabilization of the powder particles for PAAs of molecular weights higher than 20 000.

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