Fluidity and dispersion of alumina suspension at the limit of thickening by ammonium polyacrylates

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The limit of thickening of an alumina suspension by ammonium polyacrylates (PAA) and its molecular weight dependence of the limit were determined from the lowering of the flow point to be a measure of simultaneous promotion of the thickening and the dispersion. PAA of a smaller molecular weight gave a lower flow point minimum and a thicker alumina suspension retaining fluidity up to 85 wt% alumina for PAA of molecular weight 2500. The suspension thickened to the limit has the smallest gap between the flow point and the wet point, supporting Daniel's statement on good dispersion. The average water layer thickness, calculated by dividing the amount of water of suspension at the limit of thickening by the particle numbers, indicated no linearity with the chain length of the PAA. The thickening for PAA with molecular weights smaller than 21 000 resulted in a limit in the average water layer thickness of $\sim$30 nm being accompanied by dilatant flow. The suspension at high solid loadings showed various extension features on the glass plate with changes in the PAA concentration around the flow point minimum. The flow behaviour of the alumina suspension around the limit of thickening was characterized by the Bingham model with two parameters of the yield stress, σ_0, and the Bingham viscosity, η. Increase in the fluidity on PAA addition was strongly attributed to a greater lowering of σ_0 than of η. A balanced ratio between the two parameters in the apparent viscosity under a suitable shear rate was suggested to be necessary for the flow of the castable thick suspension.

1. Introduction

Well-dispersed and thick suspensions could be obtained by adding dispersant in the slip-casting process. The simultaneous achievement of dispersion and thickening retaining fluidity in the preparation of suspension is characteristic of a superior dispersant [1]. However, the mechanism by which simultaneous achievement of dispersion and thickening by dispersants is not clear despite much colloidal research on the interaction between particles with an electrical double layer [2–4] and the polymer sheath [4–6]. The reason for this is the incomplete study of the thickening caused by the dispersant. The role of water in thickening is important. It is valuable to determine the limit of thickening and the fluidity around the limit to elucidate the roles of the dispersant and water.

The flow point, defined as the least amount of solvent required for a unit amount of powder to flow, represents the water content of the suspension at the limit of thickening retaining fluidity. The wet point is defined as the least amount of solvent required for a unit amount of powder to form a lump [7]. Daniel and Goldman [8] have pointed out that the smaller the gap between the flow point and the wet point, the better is the dispersion obtained. The lowering of the flow point by the addition of a dispersant is practically a measure of the smaller gap and also of the simultaneous achievement of thickening and a good dispersion of the slips retaining fluidity, because the change in the wet point on addition of dispersant is small.

Polyacrylate acts as a dispersant and also as a thickening or water-reducing agent [9]. The role of the polymers depends on the chain length. The limit of thickening of alumina suspension by PAA with four different molecular weights was determined from wet point and flow point measurements. The dispersing effect of PAA was evaluated by sedimentation tests and zeta-potential measurement. The flow behaviour, such as the shear rate–shear stress curve and the extension of flow on a glass plate, were examined. The flow characteristics of alumina slips around the limit of thickening for various amounts of PAA will be discussed.

2. Experimental procedure

2.1. Materials

The alumina powder used was α-Al_2O_3 (A-16 SG, Aluminum Company of America, Pittsburgh, USA) of average particle size 0.3 µm. Ammonium polyacrylates (PAA) of molecular weight 2500 (General Science Corporation, Tokyo, Japan), 5900, 21000 and 45000 (Dai-ichi Kogyo Seiyaku Co., Kyoto 600, Japan) were examined as dispersants for preparing

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alumina suspension. The polyacrylates are referred to below as PAA-2500, PAA-5900, PAA-21000 and PAA-45000, respectively.

2.2. Determination of wet and flow points

Alumina powder (20 g) was mixed with 2.5 ml (the amount being below the wet point) PAA solution with various concentrations. Water was added from a burette, and the amount of water required to form a lump was read as the wet point. On further addition of water, the amount of water at which the suspension starts to flow was read as the flow point.

2.3. Evaluation of the dispersing effect of PAA by the sedimentation method

Alumina powder (20 g) was dispersed ultrasonically in 20 ml water containing various amounts of PAA, and then the resultant suspensions were allowed to stand for 100 h at room temperature. The states of dispersion and sedimentation were observed.

2.4. Measurements of zeta potentials

Zeta-potential measurement was conducted using the improved electrophoretic mass transport apparatus with a modified Tison cell [10–13]. The pH of the suspension (without adjustment) varied between 8 and 9 for all composition ranges examined.

2.5. Measurement of viscosity and other flow characteristics of the suspensions

Alumina powder (75 g) with 25 ml water was tumbled with various amounts of PAA in a plastic bottle for 24 h. The ratio of shear stress, σ, to shear rate, $\dot{\gamma}$, for the suspension was determined at 25 °C using a cone and plate viscometer (Model visconic EMD, Tokyo Keiki Co., Tokyo, Japan).

The apparent viscosity, η', was obtained from the ratio of the shear stress to shear rate at the shear rate of 76.6 sec^{-1} using Equation 1 and assuming the suspension to be a Newtonian fluid

$$\eta' = \sigma/\dot{\gamma} \tag{1}$$

3. Results and discussion

3.1. Wet and flow points of alumina in the presence of various amounts of PAA

Fig. 1 shows the flow and wet points of alumina in the presence of various amounts of PAA of different molecular weights. The change in the wet point is negligible with varying amounts of PAA. On the other hand, the flow points dramatically decrease to a minimum value and then gradually increase with the increase in the amount of PAA. That amount of PAA giving the flow-point minimum is the most effective for the suspension to flow in the least amount of water. Table I shows the flow-point minimum for each PAA of different molecular weights. PAA of a smaller molecular weight gives a lower flow-point minimum and thicker alumina suspension retaining fluidity. PAA-2500, therefore, is the most effective for thickening in the examined series of PAA of different molecular weights and it can thicken the suspension up to 85 wt % alumina retaining fluidity. The smallest gaps between the flow point and the wet point were obtained at 0.20 wt % PAA-2500.

The average thickness of the water layer at which water does not contribute to the flow of the suspension, was calculated by dividing the amount of water at the flow-point minimum by the number of alumina particles. The chain length of each PAA was also

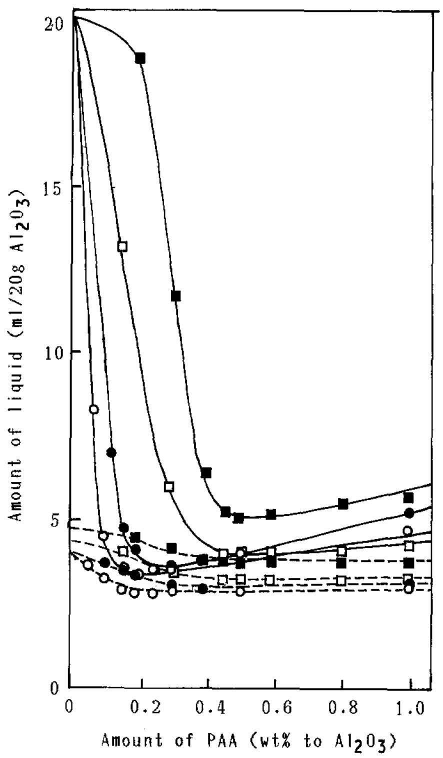

Figure 1 (——) Flow points and (- - - -) wet points of alumina in the presence of various amounts of PAA of different molecular weights: (○) 2500, (●) 5900, (□) 21 000, (■) 45 000.

TABLE I The flow-point minima for the concentrations of different molecular weight PAA

	PAA mol. wt			
	2500	5900	21 000	45 000
Length of PAA (nm)	7	20	73	156
Concentration of PAA at the flow-point minimum (wt % PAA to Al_2O_3)	0.20	0.25	0.44	0.50
Wet point at the minimum (ml/20 g Al_2O_3)	2.90	3.05	3.15	3.70
Flow point at the minimum (ml/20 g Al_2O_3)	3.50	3.70	3.85	5.20
The difference between the flow point and the wet point (ml/20 g Al_2O_3)	0.60	0.65	0.70	1.50
Average water-layer thickness not contributing to the flow of suspension (nm)	29	30	32	40

calculated. These data are given in Fig. 1. There was no proportionality between the PAA chain length and the average water-layer thickness. The average water-layer thicknesses are approximately one-fourth or one-half of the length of PAAs for PAA-45 000 or PAA-21 000, respectively, which are smaller than the chain length of each PAA. These polymers might be adsorbed on the solid particles suspended in such a thin water layer, contributing to the flow of the suspension. On the other hand, the thickening for PAAs with a molecular weight smaller than 21 000 resulted in a limit in the average water-layer thickness of ~30 nm being accompanied by the dilatant flow. The water-layer thicknesses for PAAs of molecular weights 5900 and 2500 are larger than the chain length of each polymer; approximately one and one-half or four times each chain length of PAA-5900 or PAA-2500, respectively. The appearance of dilatant flow tends to underestimate the limit of thickening, i.e. apparently giving a thicker limit of average water-layer thickness than that with no dilatancy, by overlooking the flow resulting from lower shear stress than that in the conventional flow-point determination. The suspension which shows dilatant fluidity might possibly thicken when passing over the conventional flow point, until the suspension loses fluidity even at low shear stress.

3.2. Observation of the dispersing effect of PAA on alumina suspensions by the sedimentation method

Fig. 2 shows the results of the sedimentation tests on the dispersive effect of PAA-2500. Alumina suspensions containing more than 0.125 wt % PAA are well dispersed. However, precipitation by flocculation occurred at more than 2.5 wt % PAA. A suitable range in the amount of PAA required for the dispersion is from 0.125 to 2.5 wt %.

3.3. Zeta potentials of alumina suspension in the presence of different molecular weight PAAs

Zeta potential is a measure of the charge of particles which causes electrical repulsion in the suspension. The zeta potentials of the alumina suspension in the presence of various amounts of PAAs are shown in Fig. 3.

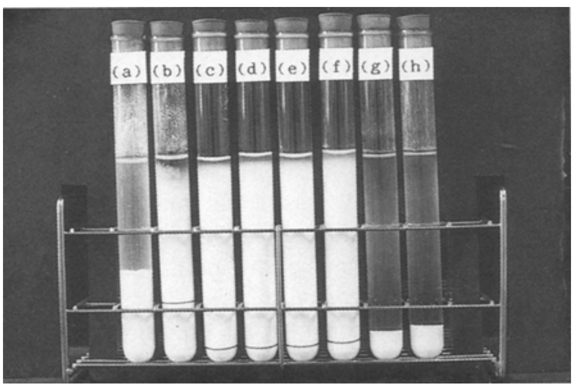

Figure 2 Sedimentation tests of alumina suspension containing PAA of molecular weight 2500 at the solid loading of 17 wt % Al_2O_3. Amount of PAA, (a) 0, (b) 0.0025, (c) 0.125, (d) 0.25, (e) 1.25, (f) 2.5, (g) 12.5, (h) 25 wt % to Al_2O_3, respectively.

The potentials increased sharply in negative value with increase in the amount of PAA, passing through a broad maximum approximately −45 mV at 0.25 to 0.5 wt % PAAs of molecular weight 2500 to 45 000, and then gradually decreasing. Good dispersion in the sedimentation test was obtained when the zeta potential exceeded approximately −30 mV showing that the electrical repulsive force is effective for the dispersion; the range corresponded to the region of the small gap between the flow points, read from Fig. 1. These facts support the statement made by Daniel and Goldman [8] that the smaller gap between the flow point and the wet point leads to better dispersion. The concentration range of PAA in which the zeta potential exceeds about −30 mV tends to shift slightly to higher concentrations of PAA for higher molecular weight PAAs.

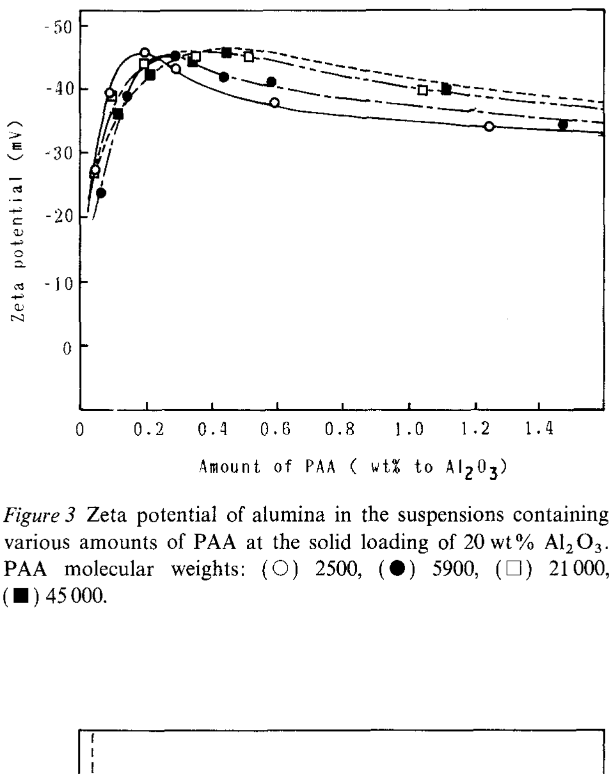

Figure 3 Zeta potential of alumina in the suspensions containing various amounts of PAA at the solid loading of 20 wt % Al_2O_3. PAA molecular weights: (○) 2500, (●) 5900, (□) 21 000, (■) 45 000.

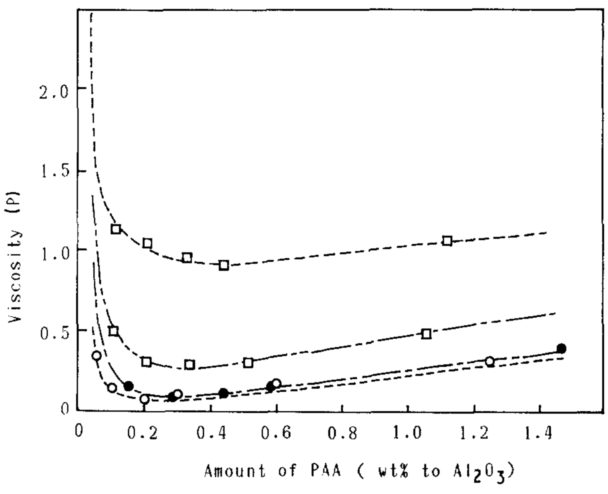

Figure 4 Viscosity of alumina suspensions containing various amounts of PAA of molecular weights: (○) 2500, (●) 5900, (□) 21 000, (■) 45 000, at the solid loading of 70 wt % Al_2O_3.

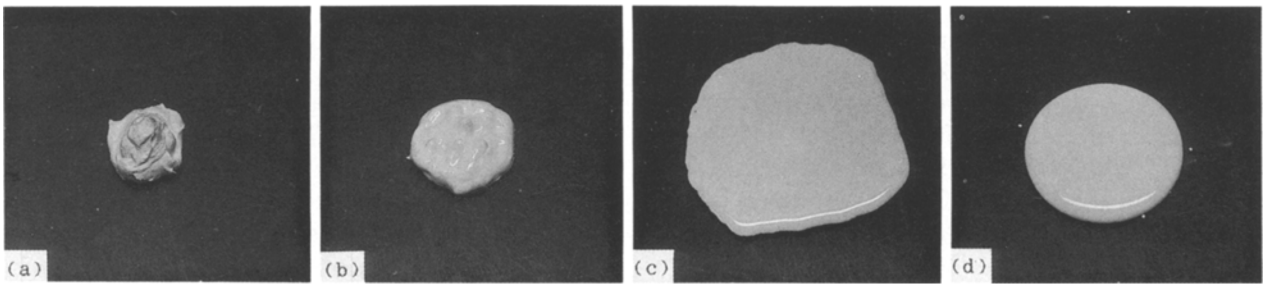

Figure 5 Extension of 5 ml alumina suspensions containing various amounts of PAA of molecular weight 2500 on a glass plate at the solid loading of 75 wt% Al_2O_3. (a) No addition, (b) 0.05 wt % PAA, (c) 0.2 wt % PAA, (d) 2 wt % PAA.

3.4. Viscosity and flow of thick alumina suspension in the presence of various amounts of PAA

The apparent viscosity of the thick suspension was determined in order to study the fluidity around the limit of thickening retaining dispersion by PAA. The apparent viscosity, η', at the shear rate of 76.6 sec^{-1} was calculated using Equation 1 for the suspension with varying amounts of PAA at 75 wt % solid loadings, and is shown in Fig. 4.

Apparent viscosities showed a minimum with increasing amount of PAA. The amount of PAA which gave the minimum viscosity coincided with that giving a minimum flow point. It is not possible, however, to predict the limit of the thickening from the viscosity change. Only the flow-point minimum could give directly the limit of the thickening, indicating by how much the amount of water should be reduced to obtain the thickest suspension retaining fluidity. Therefore, flow-point measurement is preferable for the evaluation of thickening effect.

The lowest minimum of apparent viscosity was obtained for the smaller molecular weight PAA in the series of PAAs examined with molecular weights from 2500 to 45 000. A smaller molecular weight of PAA is effective in lowering the viscosity by the amount which gave a minimum for the apparent viscosity. Satoh *et al.* [14], however, reported that a PAA of lower molecular weight produced an increase in the minimum viscosity of an alumina suspension for a PAA of molecular weight from 400 to 2800. Therefore, the most effective molecular weight of PAA to produce the thickest and simultaneously well-dispersed alumina suspension retaining fluidity, should be around 2500 for the series of PAA examined with molecular weights from 400 to 45 000.

Fig. 5 shows the extension of the suspensions on a glass plate at 75 wt % alumina in the presence of various amounts of PAA-5900. Qualitative differences in the extension (e.g. extended area, wrinkles and gloss) are present even for the suspensions with 0.2 to 2 wt % PAA/Al_2O_3, which show a small gap between the flow point and the wet point and good dispersive property.

It is necessary to characterize the flow of a suspension by the least amount of water, and to elucidate the effect of PAA on the flow characteristics of the suspensions around the limit of thickening and good dispersion.

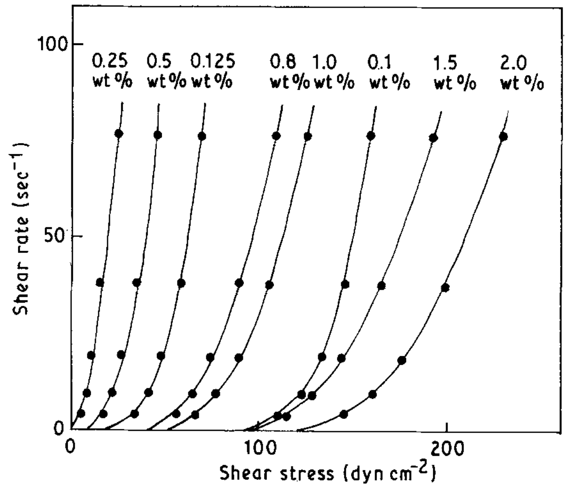

Figure 6 Shear stress–shear rate curves for the alumina suspension containing various amounts of PAA of molecular weight 5900.

3.5. Flow behaviour of thick alumina suspension around the minimum flow point in the presence of various amounts of PAA

Fig. 6 shows the shear rate, $\dot{\gamma}$,–shear stress, σ, curves of thick alumina suspension at 75 wt % alumina in the presence of various amounts of PAA-5900. The flow approximated to the Bingham fluid as expressed in Equations 2 and 3 characterized by the Bingham viscosity, η, and the yield stress, σ_0, indicated in Table II.

$$(\sigma - \sigma_0) = \eta\dot{\gamma} \qquad \sigma > \sigma_0 \qquad (2)$$

$$\dot{\gamma} = 0 \qquad \sigma \leq \sigma_0 \qquad (3)$$

The yield stress, σ_0, had a minimum at 0.25 wt % PAA which coincided with the amount of PAA at the minimum flow point, and gradually increased with further increase in PAA. On the other hand, the change in Bingham viscosity, η, with the variation of the amount of PAA was small and the viscosity showed only a dull minimum at the same concentration of PAA as that in the flow-point minimum.

The apparent viscosity, η', can be expressed by Equation 4, transformed from Equation 2 for the stress above the yield stress.

$$\begin{aligned}\eta' &= \sigma/\dot{\gamma} \\ &= \eta + (\sigma_0/\dot{\gamma}) \qquad (4)\end{aligned}$$

The contribution rate of the Bingham viscosity to the apparent viscosity, η/η', is calculated as shown in

TABLE II Yield stress and Bingham viscosity of alumina suspension containing various amounts of PAA of molecular weight 5900 at solid loadings of 75 wt % Al_2O_3

	PAA concentration (wt %)							
	0.10	0.125	0.25	0.50	0.80	1.0	1.5	2.0
Yield stress (dyn cm^{-2})	136	50.9	7.3	22	64	80	136	166
Bingham viscosity, η (P)	0.35	0.25	0.22	0.33	0.59	0.60	0.74	0.83
Apparent viscosity, η' (P)	2.1	0.91	0.31	0.61	1.42	1.65	2.52	3.00
η/η'	0.17	0.27	0.71	0.54	0.42	0.36	0.29	0.28

Table II. The increase in the fluidity of the suspension, i.e. the decrease in the apparent viscosity η', possibly results from the decrease in the contribution rate of the yield stress or the increase in the Bingham viscosity. The dependence of yield stress on the amount of PAA added is larger than that of the Bingham viscosity. The increase in fluidity therefore results from the decrease in the yield stress with variation in the amount of PAA.

Empirically, the suitable amount of PAA of molecular weight 2500 for the slip casting of this alumina is a little under 0.2 wt % PAA, and casting is possible from a little under 0.2 to 0.8 wt % PAA. A balanced contribution rate of the yield stress or the Bingham viscosity to the apparent viscosity is important for the castable slips to adjust the fluidity of the thick suspension around the amount of PAA added which results in a flow-point minimum. Qualitative differences in the flow of the suspension might possibly be related to the balance of the ratio of η/η' under a suitable shear rate.

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