Agglomerate breakdown in fine alumina powder by multiple extrusion

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Repeated extrusion through dies of various diameters and die entry angles was used to determine the rate of agglomerate breakdown in a paste consisting of a fine alumina powder, carbon black and a binder of hydroxyl propyl methyl cellulose in water. It was found that three extrusion passes were enough to break up all but ~ 0.4% of the agglomerates. Dies with orifices of approximately 1 mm diameter and die entry angles of 45 to 90° (where the elongational strain and the deformation rates were highest) were the most efficient for disrupting and dispersing agglomerates and distributing the moisture evenly. This process of deagglomeration was studied by monitoring the load required to extrude and moisture distribution during five repeated extrusion passes of each test paste. The density, agglomerate area fraction and agglomerate circularity of dried extrudates were quantified and plotted.

1. Introduction

For many years pugging has been used to improve the quality of mixing in ceramic pastes before final shaping. Benbow *et al.* [1], working with alumina powders of relatively large particle size and square entry dies, found that pugging a paste three times prior to final extrusion improved the flow properties of the paste significantly. Physically based models were proposed for the flow of pastes during extrusion. The modelling work was expanded to include extrusion through conical dies [2]. The very fine powders used predominantly for the manufacture of technical ceramics are almost always to some degree agglomerated and therefore add to the difficulty of mixing of ceramic pastes. This subject was reviewed by Kendall [3]. Agglomerates are believed to be a major cause of defect formation in the final sintered body. Many methods have been reported for breaking down agglomerates to achieve uniform density and microstructure of the final product [4–6]. Alford *et al.* [7] also found that extruding a ceramic paste through a narrow orifice resulted in sintered products with fewer and smaller flaws and therefore higher strengths than die-pressed dry powders. Experiments have been carried out to follow systematically the breakdown of agglomerates and the moisture distribution by repeatedly extruding an alumina paste with a binder of hydroxyl propyl methyl (HPM) cellulose/water through (a) various barrel (D_0) to die (D) diameters with 90° die entry angle and (b) conical die entries of various angles and constant D_0/D. During five extrusion passes through each die the extrusion pressure and moisture content of the extrudates were recorded. Due to the addition of a small amount of carbon black to the paste the number, size and circularity of remaining agglomerates could be determined by image analysis of polished sections. After five passes the extrudates of all dies showed similar end-results, but the differences in the efficiency of the various dies in achieving the result are discussed here.

2. Experimental procedure

The alumina powder used (Baco RA107 LS Grade from BA Chemicals, UK) consists of tabular particles of 0.5 μm mean size (Fig. 1), agglomerated to aid its free flowing properties. The agglomerates were soft except for ~ 0.4%, which were small and too hard to be broken up even in high-shear mixing [8]. The powder was mixed with 1% carbon black and powdered HPM cellulose (Celacol Grade B2/15 from Courtaulds Fine Chemicals, UK) in sufficient quantity that when a total moisture content of 17.2–17.5% was achieved by the addition of distilled water, an 8% HPM cellulose solution formed the binder. After mixing the dry powders in a planetary mixer (Kenwood A901E, speed position 3) the water was added and mixed until a granular paste started to adhere to the whisk. The pastes were prepared three days prior to extrusion to allow for moisture equilibration. It had been shown by a preliminary experiment that the time of rest influenced the agglomerate breakdown rate in these powders.

For ram extrusion a barrel with a diameter of 25.4 mm and a length of 150 mm, a piston and interchangeable dies (Fig. 2) were placed in a universal load frame (Avery–Denison) with a 20 kN load cell. After preliminary tests had shown no significant difference

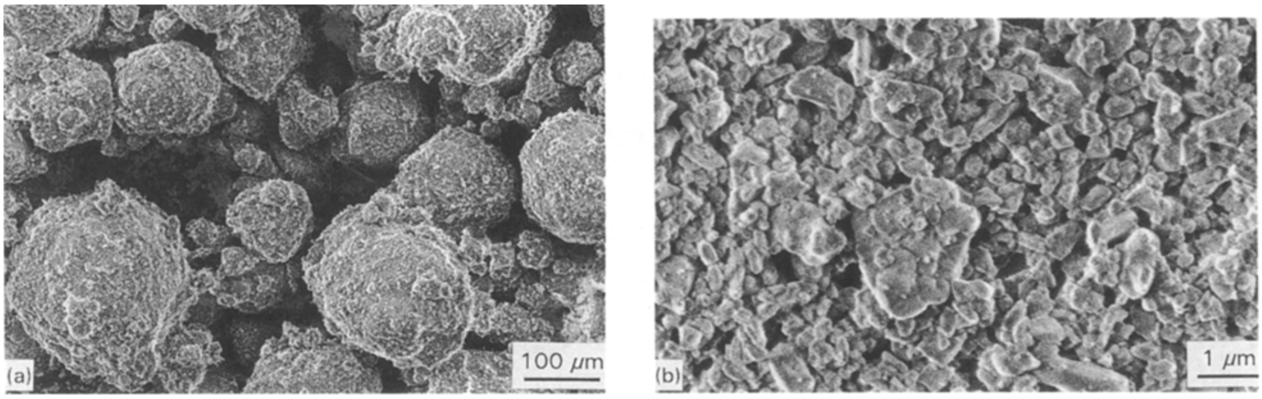

Figure 1 (a, b) Alumina powder agglomerates and individual particles.

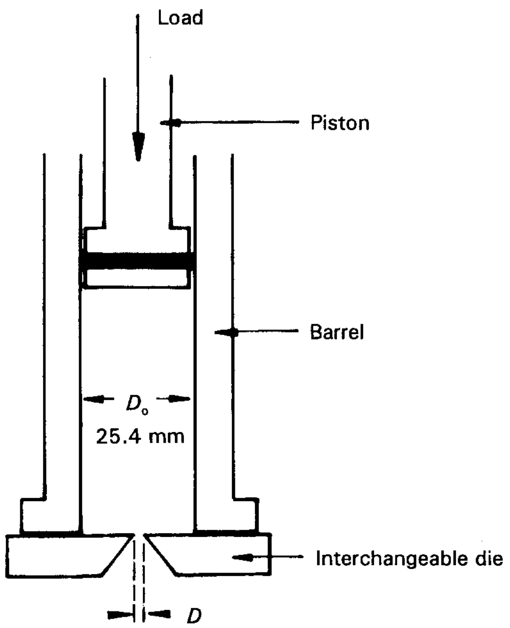

Figure 2 Ram extruder with interchangeable dies.

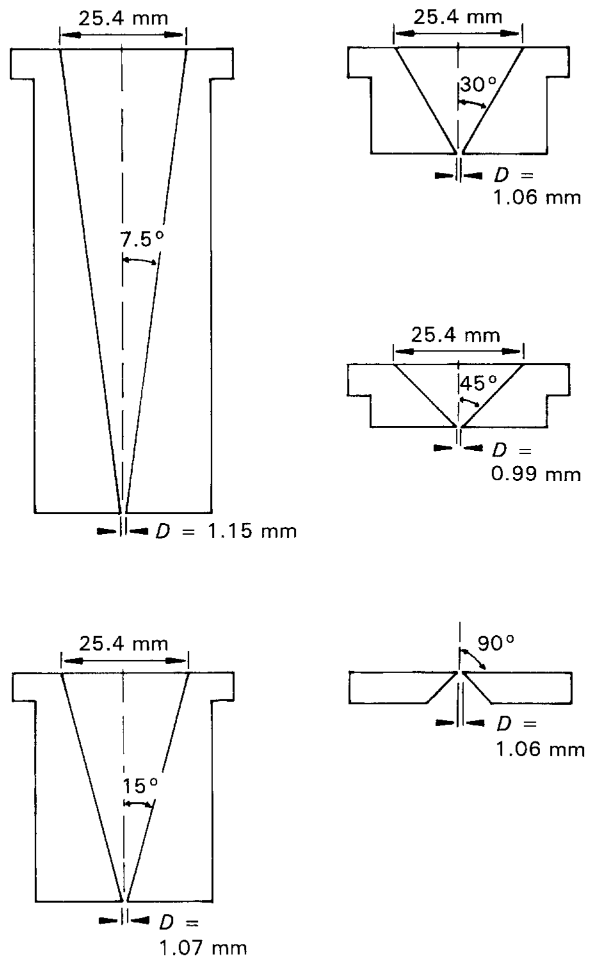

Figure 3 Dies with conical die entries and near-zero length die land.

in agglomerate break-up with speeds varying between 10 and 50 mm min^{-1}, extrusion speeds of 10 and 15 mm min^{-1} were used for the following tests. Two sets of dies were used:

(a) Varying diameters with 90° die entry angle and near-zero die land length. The final diameters were 6, 3, 2.05, 1.28 and 0.98 mm. D_0/D ranged from 4.23 to 25.9.

(b) Varying die entry angles with die diameters of as close to 1 mm as could be manufactured and near-zero length of die land. The semi-angles were 7.5, 15, 30, 45 and 90° as shown in Fig. 3. D_0/D varied from 22.1 to 25.6.

In Table I the deformation rates ($\dot{\gamma}$) and elongational strain (ε) for all the dies were listed, using the following equations for their calculation:

$$\dot{\gamma} = \frac{4Q}{\pi r^3}(s^{-1}), \quad Q = V_{\text{extrudate}} r^2 \pi (\text{mm s}^{-1}) \quad (1)$$

$$\varepsilon = 2\ln\left(\frac{D_0}{D}\right) \quad (2)$$

During each extrusion the load versus crosshead travel was recorded graphically and nine small samples of extrudate were collected for moisture determinations during each pass. Because extrudates lose water rapidly on exposure to the atmosphere, they were collected into glass jars and sealed between each pass. A total of five passes was made through the extruder for each die. During transfer of the extrudates back to the barrel some mixing occurred, in particular reorientation of the paste. This was unlikely to break up agglomerates, but assisted in dispersing the elongated, already disrupted agglomerates. Samples of extrudates from each pass were dried, cut through the centre in the direction of extrusion and polished. The white agglomerates could be identified easily against the grey background of the well-mixed paste. The

TABLE I All the dies with the calculated deformation rates and elongational strain

Die diameter (mm)	Die entry semi-angle (deg)	Crosshead velocity ($mm\,s^{-1}$)	Deformation rate (s^{-1})	Elongational strain
0.98	90	0.167	913.6	6.51
1.28	90	0.167	410.0	5.98
2.05	90	0.167	99.8	5.03
3.00	90	0.167	31.9	4.27
6.00	90	0.167	4.0	2.89
1.15	7.5	0.250	848.5	6.19
1.07	15	0.250	1053.4	6.33
1.06	30	0.250	1083.4	6.35
0.99	45	0.250	1227.3	6.41
1.06	90	0.250	1083.4	6.35

number, area size (sectional area per agglomerate), circularity and area fraction of the remaining agglomerates were measured by image analysis (Cambridge Instruments Quantimet 570, with Reichart-Jung microscope). For each sample 24 areas of 0.75 mm × 1.075 mm, equivalent to a length of 25 mm of extrudate, were analysed. Densities of the extrudates of the various diameters were calculated by their weight and dimensions.

3. Results and discussion

The importance of moisture content and distribution is shown in Fig. 4. The three pastes were extruded at the same rate through the 6 mm diameter die ($D_0/D = 4.23$). Paste (a) was extruded three days after mixing; paste (b), of the same composition, was extruded immediately following mixing. Clearly, resting the paste for 3 days at room temperature caused seepage of moisture into the agglomerates, which weakened their structure causing them to disperse more easily during extrusion. Paste (c) was extruded as (b) but contained reduced moisture (15.8 as against 17.2 wt %); the agglomerates were elongated and

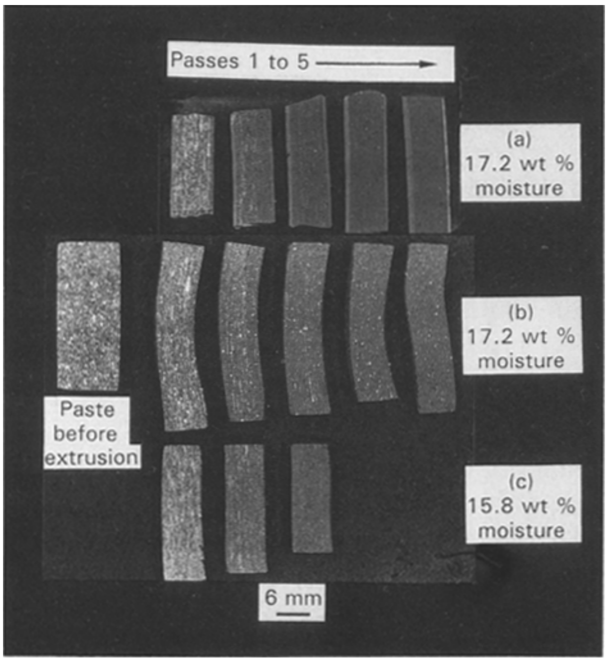

Figure 4 Extrudates of the 6 mm diameter die: (a) extruded 3 days after mixing, (b) and (c) extruded immediately after mixing.

broken down more efficiently than in either (a) or (b). The reduced moisture content increased the load necessary for extrusion, thus increasing the density of the paste and the contact areas between the particles, causing the agglomerates to disrupt at a higher rate. A similar effect has been shown by Bhargava [9] in the consolidation of dry agglomerates with lateral flow. Pastes similar to the one shown in Fig. 4a were used in the subsequent experiments.

The average moisture of the paste used for testing the influence of die diameters was 17.18% and for the die entry angles 17.50%. This slightly reduced the force required for extrusion of the latter materials. This is illustrated in Fig. 5, where in Fig. 5b the 90° entry angle die (1.06 mm diameter, $D_0/D = 23.96$) required a load of 1.9 kN for the first pass, while the 1.28 mm die (90° entry angle, $D_0/D = 19.86$) (Fig. 5a), despite the bigger die exit, required 2.2 kN after similar processing. This reflects the sensitivity of paste flow to moisture content.

Comparing the load curves of all the dies during the first extrusion pass (Fig. 5a and b) showed that the smaller the die diameter and the smaller the die entry angle the higher was the load needed for extrusion. The very sharp, high intensity peaks using the dies with small diameters indicated uneven moisture distribution: agglomerates containing lower moisture than the well-mixed paste around them needed a higher extrusion pressure to disrupt and pass through the narrow orifices. The height and frequency of the sharp peaks decreased systematically with the increase of the die diameters. In the dies with low entry angles, 7.5 and 15°, the paste was deformed gradually as it approached the orifice, disrupting the large agglomerates before they reached the die exit, resulting in load curves in which the peaks were less intense but broader. The higher overall load needed for the 7.5° angle die was attributed to the length of the die acting as an extension to the barrel rather than contributing efficiently to the agglomerate break-up. The standard deviation in the moisture of small extrudate samples is shown in Fig. 6. There was consistently greater variation after the first extrusion pass, confirming the initial uneven moisture distribution, which improved in the subsequent passes. The slight overall reduction in moisture was due to the handling of the paste between passes.

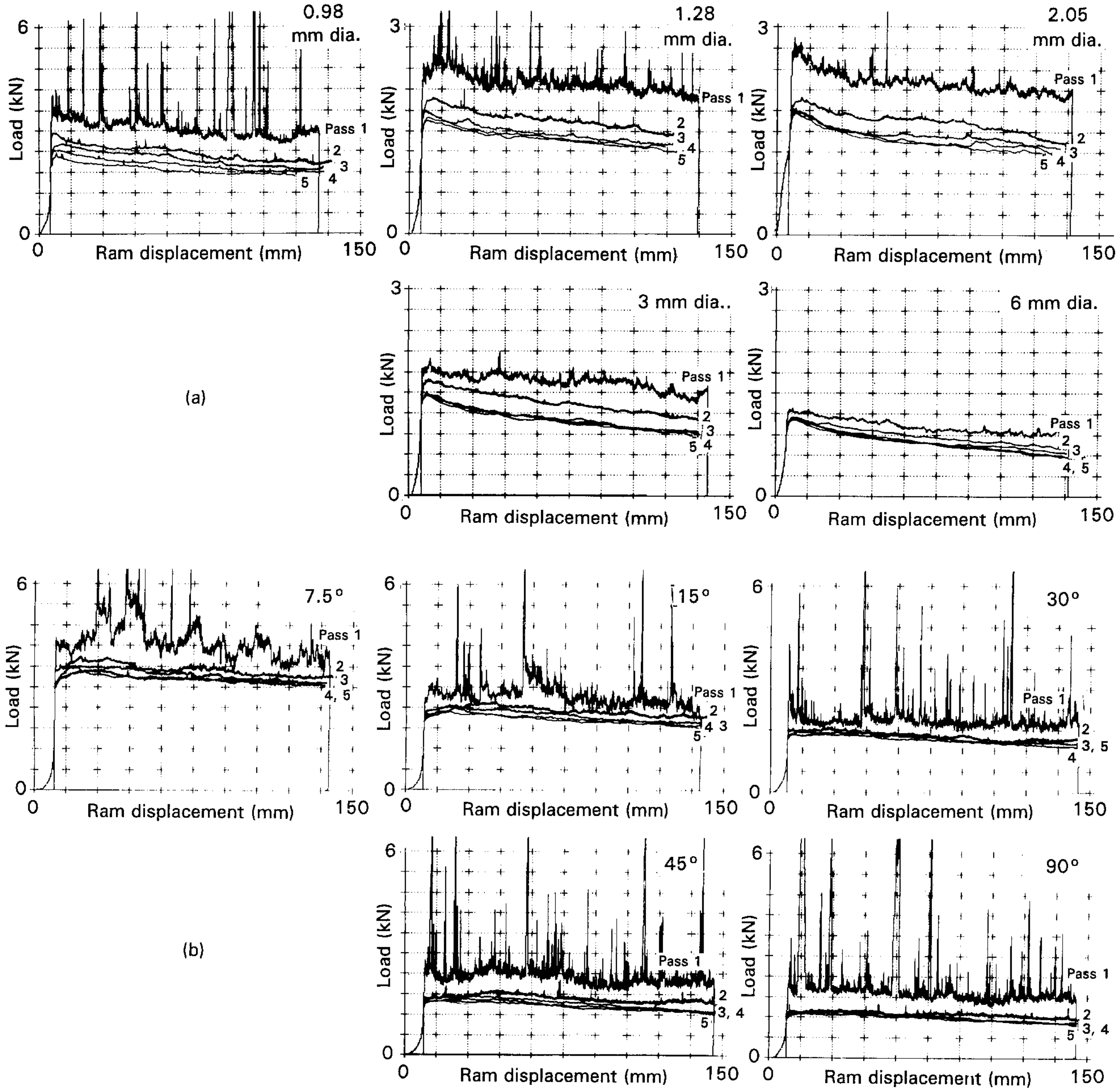

Figure 5 Load versus overhead travel curves during five extrusion passes using dies of (a) various diameters and (b) various entry angles.

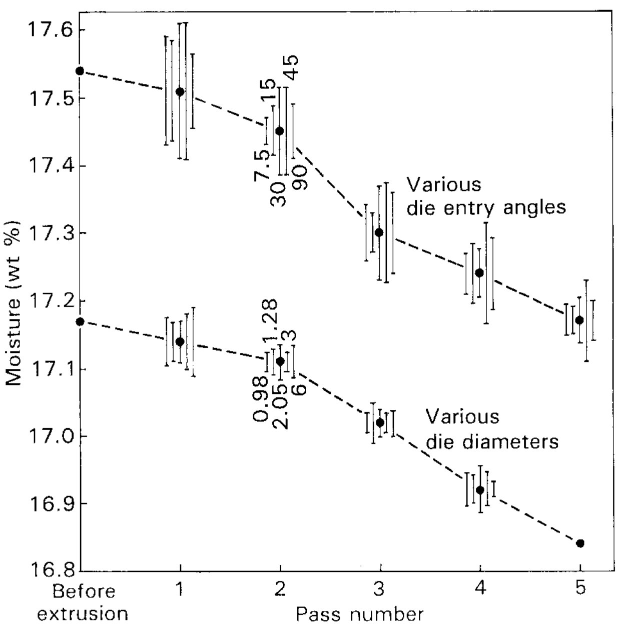

Figure 6 Drop in moisture during five extrusion passes and the scatter of the moisture of nine samples for each die in each pass.

The area fraction of remaining agglomerates (Fig. 7) after the first pass was lowest with the small-diameter dies and entry angles of 30° and above, where elongational strain rate was maximized. The wide and low peaks in the load curves of the 7.5 and 15° entry angle dies, in addition to the high agglomerate area fraction of their extrudates, compared to the die with small diameter but 90° entry angle, showed that the elongational forces due to a sudden change in diameter and large D_0/D were important factors for efficient deagglomeration. The density of the dried extrudates is plotted against their diameter in Fig. 8: the smaller the orifice the higher the extrusion pressure, resulting in higher density of the extrudate and therefore better agglomerate break-up. The seemingly higher agglomerate count in extrudates of large diameters compared to the paste before extrusion was attributed to the increase in density of the paste during the extrusion process. No change in densities could be measured between the first and fifth extrusion passes in any of the dies.

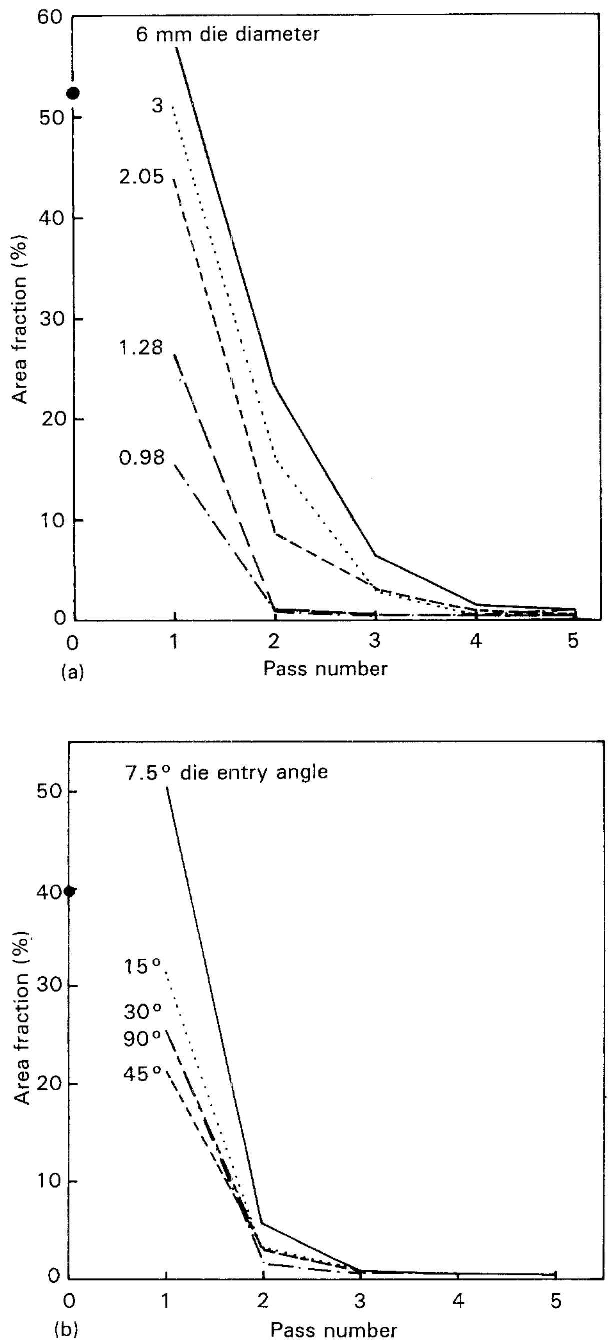

Figure 7 Area fraction of remaining agglomerates during five extrusion passes using dies of (a) various diameters and (b) various entry angles; (●) before extrusion.

The variations in extrusion pressure for the various dies can be predicted for the paste using analysis methods and models of Benbow and Bridgwater [1, 10]. The pressure drop in square-entry dies is given by

$$P = 2(\sigma_0 + \alpha V)\ln\left(\frac{D_0}{D}\right) + \frac{4L}{D(\tau_0 + \beta V)} \quad (3)$$

and for conical entry dies of zero die land it is given by

$$P = 2(\sigma_0 + \alpha V + \tau_0 \cot\theta)\ln\left(\frac{D_0}{D}\right) + \beta V \cot\theta \quad (4)$$

where D_0 is the barrel diameter, D the die diameter, V the extrudate velocity and θ half the die entry angle (semi-angle); the other variables are paste parameters.

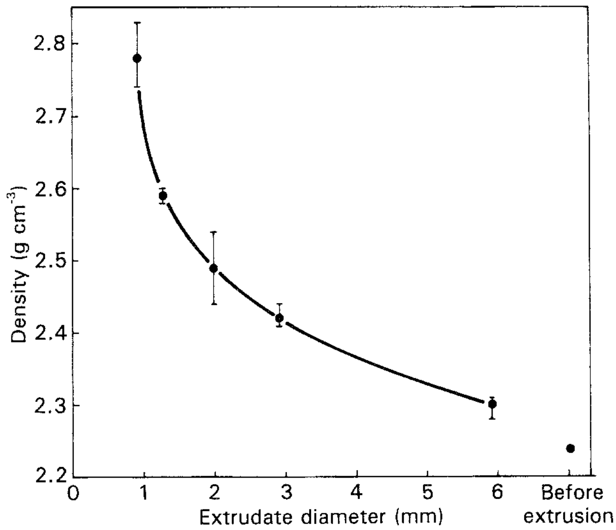

Figure 8 Green density of paste before extrusion and extrudates of dies of various die diameters.

The rheology of the paste at pass 1 was characterized using methods proposed by Benbow *et al.* [1]. The paste was passed through dies of 3 mm diameter and L/D ratios of 1, 8 and 16 at extrudate velocities between 0.001 and 0.053 m s^{-1}. The paste parameters σ_0, α, τ_0 and β were derived for the velocity range of concern for the two sets of dies, i.e. for the 90° die entry angles

$$\sigma_0 = 0.53 \text{ MPa}$$
$$\tau_0 = 0.047 \text{ MPa}$$
$$\alpha = 5.08 \text{ MPa s m}^{-1}$$
$$\beta = 1.97 \text{ MPa s m}^{-1}$$

and for the conical entry dies

$$\sigma_0 = 0.60 \text{ MPa}$$
$$\tau_0 = 0.050 \text{ MPa}$$
$$\alpha = 0.72 \text{ MPa s m}^{-1}$$
$$\beta = 0.17 \text{ MPa s m}^{-1}$$

The predicted values for extrusion pressure were obtained by substitution of these derived parameters into Equations 3 and 4 and compared well with the experimental data (Fig. 9).

The second extrusion pass showed relatively smooth load curves, the average load being lower than during the first pass. The number and height of sharp peaks was significantly reduced, indicating a much improved moisture distribution and a much lower number of agglomerates. The drop in agglomerate area fraction in all dies was highest here, where the large proportion of agglomerates disrupted and elongated during the first pass were dispersed into the paste, in addition to further agglomerate breakdown.

The load curves for the third to fifth pass were smooth and lay very close together, but generally systematically lowered with each pass. This was observed despite the moisture loss of handling the paste, which without enhanced mixing would have caused a small increase in the force required for extrusion. The

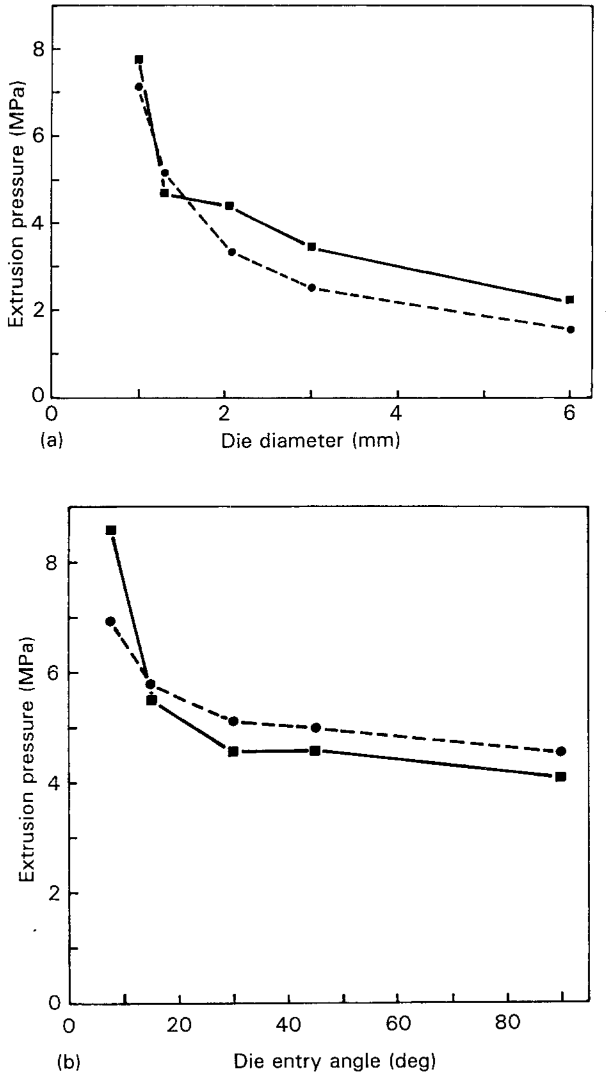

Figure 9 Comparison of (●) predicted and (■) experimental extrusion pressures in pass 1 for dies of (a) various diameters and (b) various entry angles.

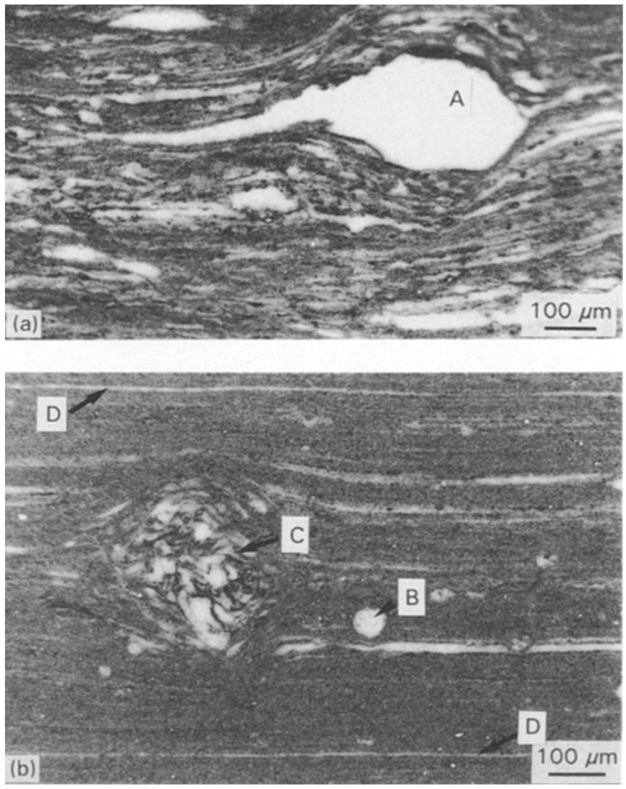

Figure 10 Typical examples of agglomerate break-up during the first and second extrusion passes showing (a) paste flowing around and thereby elongating a dry agglomerate (A), and (b) an unaffected, hard agglomerate (B), a disrupted one (C) and very elongated agglomerates (D).

area fraction of agglomerates was not reduced significantly after the third pass; about 0.4% of mainly small agglomerates of high roundness remained. These could not be broken down by the imposed shear rates and elongational forces of this experiment. A similar fraction remained when high-shear mixing or kneading was applied to the same paste system [8].

The agglomerates are broken down by elongation and shear. Examples of the flow patterns are shown in Fig. 10. Elongation of the dry agglomerates by densification of the paste and by their resistance to flow as well as spalling into the surrounding matrix predominate. The elongated agglomerates are fragmented and dispersed in the barrel packing and re-extrusion of the next pass, this accounting for the rapid dispersion in pass 2 of all the die systems.

As particles appeared to be disrupted by being drawn out through elongation, the average circularity of the remaining agglomerates gave a numerical indication of this process. Measurements were made on dried extrudates, cut in the direction of extrusion and polished. From the image analysis, circularity was derived by dividing the square of the object perimeter length by 4π times the area of the object. Thus a perfect circle gives unity and a straight line infinity. In the conical die test sequence (Fig. 11a) there was a strong decrease in circularity following the first pass due to the elongation of the agglomerates; this is clearly shown in Fig. 10. The streaky agglomerates were dispersed rapidly in the second pass with the average circularity increasing as a result. Disruption and attrition of the agglomerates was such that by pass 3 most were well rounded and of constant shape. In the orifice size tests (Fig. 11b) a similar trend was observed, but initial elongation and the rate of subsequent circularity development were reduced with increasing orifice size.

Generally the agglomerate size distribution (in terms of the area exposed) decreased with increasing number of passes, Fig. 12 showing a typical example. The different mechanisms of first elongation without dispersion (pass 1), then dispersion with more elongation (pass 2) and attrition of harder agglomerates (passes 3, 4, 5) were reflected in the size distribution changes, with little change between the non-extruded paste and pass 1, a large reduction between pass 1 and 2 and little change between passes 2 to 5. After pass 5 only the harder, rounded agglomerates remained, of which 75% showed an average radius of about 13 μm. Most of the deagglomeration occurred during the second pass, when the density of the paste, and thus the contact areas, had been increased by the extrusion process, confirming the observations in Fig. 7a and b. This fast rate of deformation is also shown in Fig. 13, where the circularity of agglomerates was shown to be

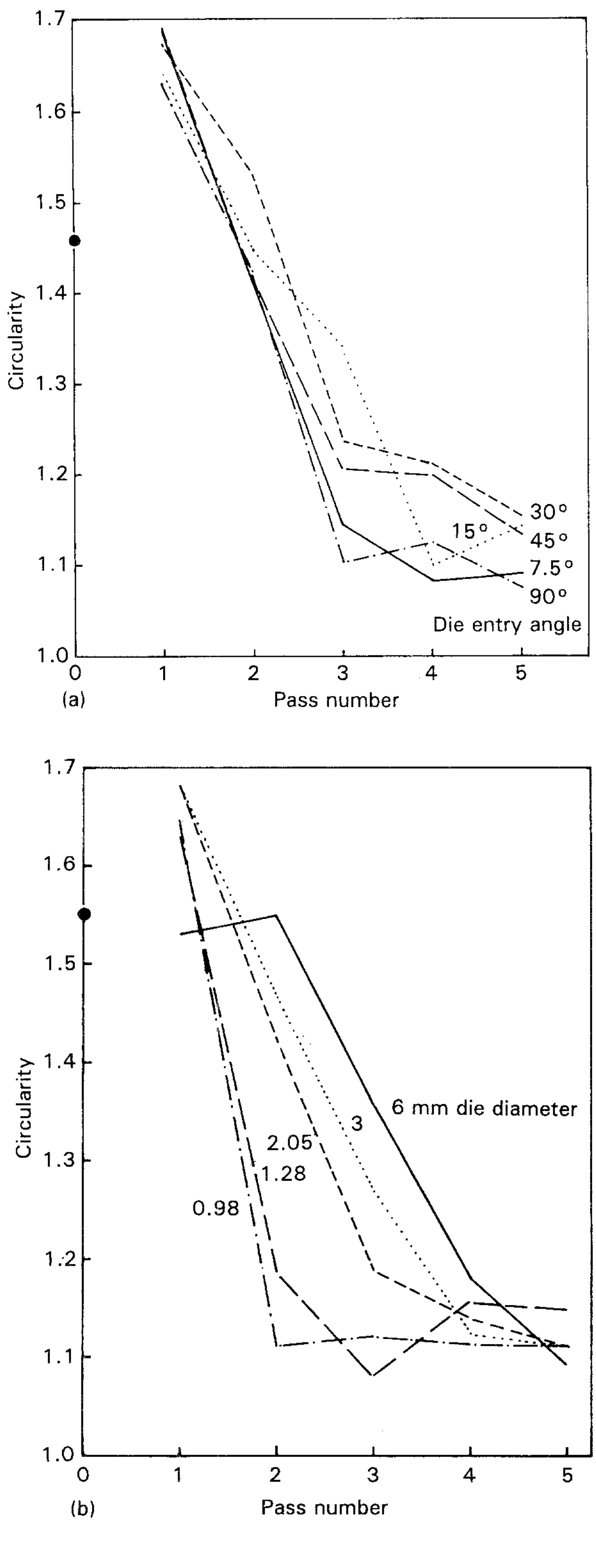

Figure 11 Average circularity of remaining agglomerates during five extrusion passes in (a) the conical dies and (b) the dies of various diameters; (●) before extrusion.

fairly constant before extrusion, while the circularity per sectional area size decreased significantly in the first and more so in the second pass, especially when the die entry angle was large. Measurements of passes 3 to 5 showed mostly small agglomerates of high circularity. At the same time the number of agglomerates for an equal area size on all samples had decreased from an average of 2100 before extrusion to 110 after pass 5. The rate of deagglomeration for the various dies in pass 2 is shown in Table II.

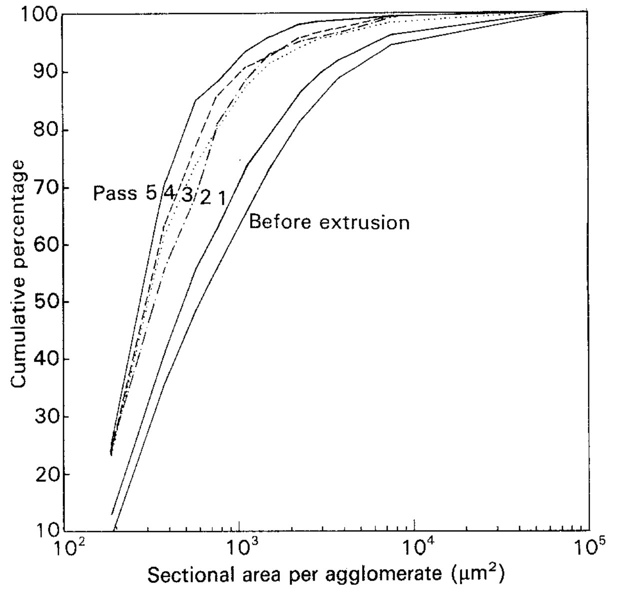

Figure 12 The area size of exposed agglomerates versus their cumulative percentage in five passes for 45° entry angle die. The curves for all the other dies were similar.

While it was difficult to establish the correct number of agglomerates before extrusion and after the first pass, as many of them were touching and gave an exact figure for their area fraction only, Table II again illustrates the efficiency of small orifices in combination with a large die entry angle, with lower moisture of the paste being of advantage.

4. Conclusion

The rate at which agglomerates in pastes were dispersed by ram extrusion has been examined by passing poorly mixed pastes repeatedly through dies of various entry angles and ratios of barrel to die diameter. The resultant agglomerate character and concentrations were determined by image analysis of stained polished sections.

The smaller the die diameter the higher was the load needed for extrusion, causing an increase in density of the paste. This consolidation increased the shear and the elongational forces necessary for disruption of agglomerates. The large agglomerates, being drier than the well-mixed paste around them, resisted extrusion through small orifices causing sharp, high peaks in the load curves before breaking up. Thus, the load curve was a sensitive indication of the rate of deagglomeration. A small die diameter and the sudden change of diameter from the barrel to the small orifice was more effective in agglomerate break-up than the gradual change of the 7.5 or 15° die entry angles, shown in the measurements of the area fraction of remaining agglomerates and their circularity, despite their equally high calculated deformation rates and elongational strain. Breakdown may therefore be considered to be influenced by a function of elongational strain though not strictly elongational strain rate. As the diameters of the dies with 30 to 90° varied slightly, resulting in significantly different deformation rates, but with image analysis results lying close together,

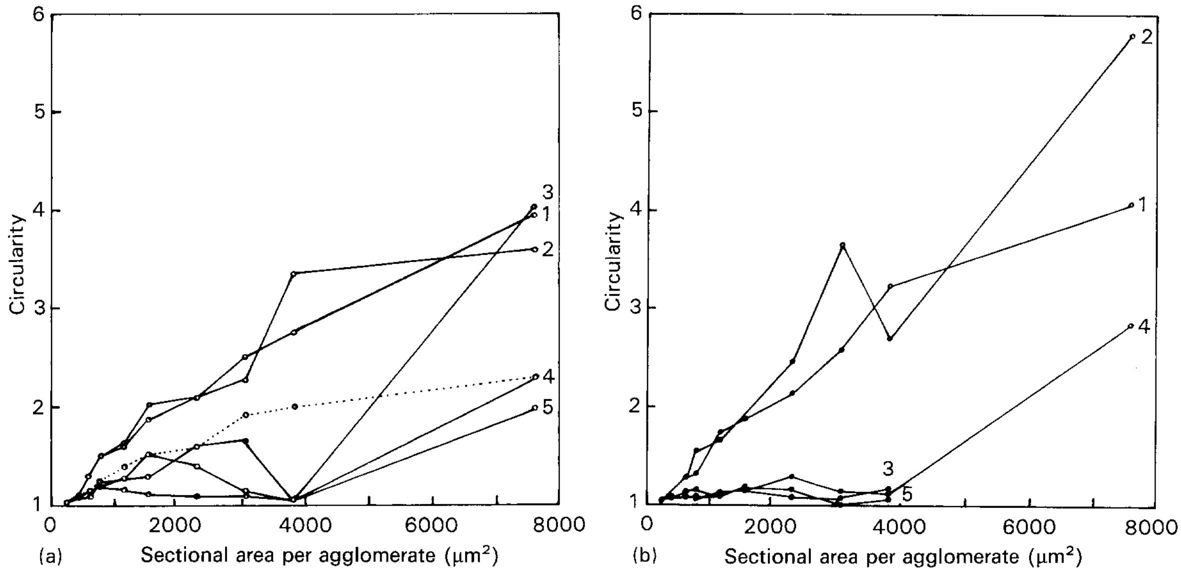

Figure 13 (——) Average agglomerate circularity plotted against agglomerate area size in (a) 15° and (b) 90° entry angle dies, after passes 1 to 5; (· · ·) before extrusion.

TABLE II Number of remaining agglomerates after pass 2

Die entry angle (deg)	Die diameter (mm)	Number of agglomerates
7.5	1.15	1234
15	1.07	633
30	1.06	545
45	0.99	642
90	1.06	332
90	6.00	2844
90	3.00	2134
90	2.05	1788
90	1.28	134
90	0.98	100

they could not be ranked here, except to say that the 45 and 90° angles, being closest to the natural formation of the static zone at the bottom of the barrel, performed better.

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