The effects of liquid-phase rheology on the extrusion behaviour of paste

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A description is given of experiments carried out to determine the effect of liquid-phase rheology on the extrusion behaviour of particulate pastes. These were prepared by mixing alumina powder with chosen amounts of four liquids. Measurements show that the properties of the pastes are directly related to those of the liquids from which they were made. Rheological properties of the pastes and the liquid phases are related by factors which are independent of liquid type, liquid content and extrusion rate. An additional set of experiments used pastes made from ballotini particles and one of the liquids.
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1. Introduction

The amount of liquid needed to make an extrudable particulate paste depends in part on the packing efficiency of the particles in it. Before the mixture can be extruded at practical pressures, sufficient liquid must be present to fill the inter-particle voids and to separate the particles. If the particles are porous, such as those used in the fabrication of heterogeneous catalysts, additional liquid must be added to fill the internal and open pores of the high surface area particles. The volume of voids between non-porous particles can be approximately deduced from packing theories. These methods were originally described by Furnas [1] and have since been extended by several other authors [2, 3]. Mixtures of approximately spherical particles with short fibres have recently been shown to follow the same laws [4, 5]. It has also been demonstrated that the precise degree of packing is influenced by the shear conditions employed during paste preparation [6]. The effectiveness of this process, pugging as it is known in the ceramic industry, is in turn influenced by the nature of the liquid phase.

In contrast to the amount of research done into particle packing, relatively little attention has been given to the influence of the rheology of the liquid phase on paste properties. It has been established that at low shear stresses a high viscosity or a significant yield value help to avoid phase separation during extrusion. Similar rheological behaviour promotes shape retention of the extrudate. There is, however, a need to relate more closely the liquid properties to those of the paste during extrusion through a die.

In the past 30 years or so, the properties of many pastes have been measured by ram extrusion. "Extrusion parameters" derived from the results have been used to design dies and to characterize a number of ceramic pastes [7].

In earlier research a series of pastes was prepared using mixtures of α-alumina, glucose solutions and bentonite clay [6]. This type of liquid phase was chosen because such pastes had the advantage of having approximately constant plastic viscosities at moderate shear rates. This feature allowed extrapolation of the measurements made at moderate shear rates to predict those at the high rates which are expected to be relevant to paste extrusion. In the present work this extrapolation was avoided by measuring the liquid properties in the appropriately high range of shear rates.

The resistance of a paste to deformation is expected to depend on the thickness and rheological properties of the liquid layer around the particles. The thickness of this layer depends on the excess of liquid above that required to fill the inter-particle voids. For a given paste this can be estimated from the change in extrusion properties with liquid content. If the reciprocals of extrusion pressure are plotted against the volume of liquid, the critical value is indicated by extrapolation to zero, see Fig. 1. This is where the liquid just fills the interparticle voids and extrusion becomes feasible. The critical value, V^*, depends on the packing propensity of the particles and on the mixing procedure and it hence varies with particle-size distribution.

In the present work, one alumina powder was mixed with different amounts of four liquids, two of which are typical of those employed in the ceramics industry. Thus the work has direct relevance to commercially important materials.

Another feature of the work to be described here is that the rheological properties of the liquids were measured by using two distinctly different methods. These enabled their rheological properties to be measured over a wide range of shear rates, from 10^{-1}–10^4 s^{-1}.

The flow of particulate pastes along a die-land of constant cross-section has been likened to that of a lubricated solid plug [8]. When liquid is added there is an increase in the thickness of liquid surrounding particles and between the outer particles and the die wall. At a
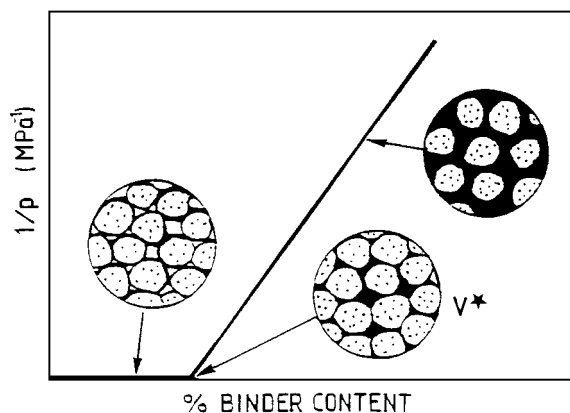
Figure 1 The dependence of the reciprocal of extrusion pressure on liquid volume. The abscissa is the ratio of (liquid/solid) volume. The critical value, V^*, where extrusion is possible, depends on the packing ability of the solid powder.

fixed extrusion speed this will result in a decrease of the shear rate between the particles and the die wall. It has, however, long been recognized that it is not easy to relate the yield properties of the liquid and paste based on this simple picture and that the micro-structure near the wall is, in reality, rather more complex.

2. Experimental procedure

The experimental pastes were made with the same blend of fine ceramic particles but with four different types of liquid as binders. These liquids were chosen so that their rheological properties were appreciably different from each other, but all were capable of combining with the ceramic powder to produce extrudable pastes. Additional pastes were made from glass ballotini of a mean diameter of 0.3 μm and the most viscous of the liquids.

2.1. Materials and paste preparation
2.1.1. Powders

The particulate phase of the pastes was a blend of non-porous α-alumina (White Bauxilite from Universal Ceramic Materials PLC, Stafford, UK). The proportions of the various size fractions used are given in Table I. This distribution of particle sizes was chosen because it was known to produce extrudable pastes with a variety of liquids without being unstable.

2.1.2. Liquids

The four liquid systems employed to prepare the pastes and the details of the formulations are given in Table II.

TABLE I Powder fractions in the solid phase

α-alumina	d_{50} (μm)	(wt %)
F1200	4.6	40
F 600	8.4	40
F 400	13.5	10
F 280	28.0	10
Glass ballotini	0.3	100

TABLE II Liquid phase compositions (wt %)

Type	HPMC[a]	Wyoming bentonite clay[b]	Glucose[c]	Glucose syrup[d]	Water (de-ionized)
Liquid A	8				92
Liquid B		20			80
Liquid C		20	56		24
Liquid D		20		57	23

[a]Hydroxypropyl methyl cellulose, Celacol B2/15, Courtaulds Chemicals, UK.
[b]Steatley Minerals, UK.
[c]Fisons Chemicals, UK.
[d]"Glucose syrup", consisting of a mixture of various sugars, Thornton and Ross Ltd, Huddersfield, UK.

Having examined the relation between the paste and liquid properties with the alumina powder, an additional set of measurements was made with pastes made from glass ballotini and liquid D. This system was added to show the relationships with high packing of spherical particles of a different solid. Liquid D was chosen because, being relatively viscous, it formed stable pastes even with the open packing spheres. These pastes allowed the comparison between liquid rheology and paste extrusion properties with a different powder (from the alumina) which would be more amenable to a quantitative description of the paste structure at the die wall.

2.1.3. Paste preparation

A series of pastes was prepared, containing different proportions of the four liquids. All the pastes were made using the same procedure, i.e. the dry or powdered ingredients (alumina, HPMC or clay) were mixed in a planetary mixer (Kenwood) for 1 min, then the liquid phase (water or glucose solution) was added and mixing continued for a further minute. The pre-mixes were then transferred to a high shear rotary mixer (Werner and Pfleiderer LUK 3III-2VAK) for 40 min. The pastes were extruded 2 h after mixing. The surface structure of a dried extrudate is shown in Fig. 2. Stereoscopic examination of transverse fracture surfaces showed the structure in the bulk of the pastes to be uniform after mixing and extrusion.

## 2.2. Preparation of liquids for viscosity measurements

Liquid A, HPMC: the water was heated to 70 °C, dry HPMC was added, stirred, and the suspension cooled. The water lost during heating was added before the cellulose gelled and could still be stirred without excessive air entrapment.

Liquid B, water + clay: the constituents were placed in a plastic bag and worked by hand until a homogeneous suspension was formed.
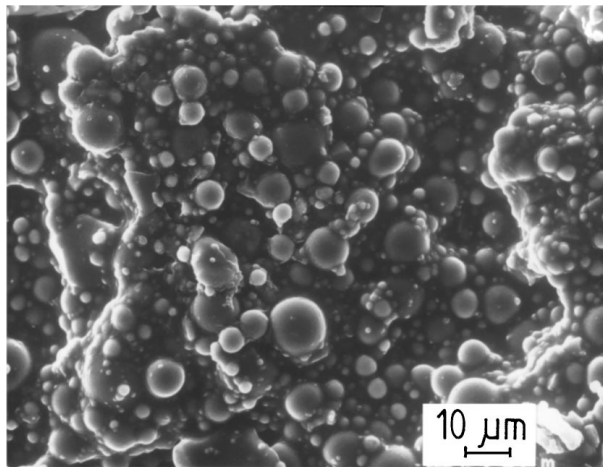
Liquid C, glucose solution + clay: the same procedure was adopted as that used for the water and clay binder.

Liquid D, diluted "glucose syrup" and clay: as for liquids B and C.

Liquids A and B are similar to those frequently used to prepare ceramic extrudates. Liquids C and D were
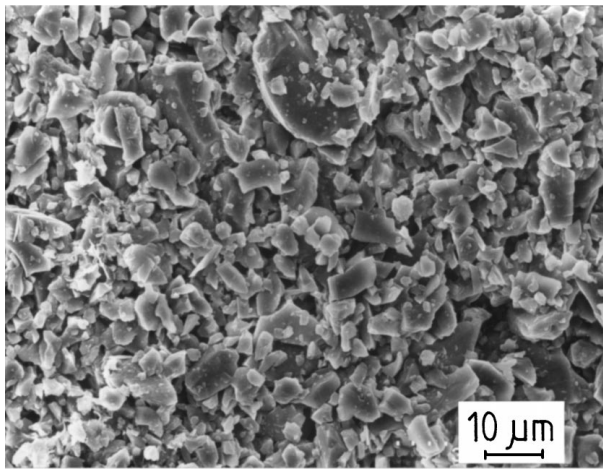
(a)

(b)

Figure 2 Scanning electron micrograph of extrudate surfaces of pastes prepared with (a) alumina powder, (b) ballotini.

chosen to introduce liquids of significantly different rheological properties, although they are not likely to be used to make commercial ceramic products.

2.3. Rheological measuring techniques
2.3.1. Liquids
Rheological properties of the liquids were measured in two ways:

(a) with a cone and plate rheometer (Carrimed Constant Stress CSL500) using 1, 2 or 4 cm diameter, 2° cones.

(b) by ram extrusion through two small bore dies from a barrel having a diameter of 20 mm. Both dies had a diameter of 0.72 mm; their lengths were 10.5 and 30.3 mm, respectively. The L/D ratio eliminating the die entry effects was thus 27.5. The ram extruder was mounted in a universal load frame (Avery-Denison, Leeds, UK). The liquids were extruded at six ram speeds of 1, 2, 5, 10, 20 and 50 mm min^{-1}.

From the differences in the extrusion forces through the two dies, the shear stresses at the die walls were calculated for each of six extrusion rates. By assuming no slip at the die walls and a parabolic distribution of shear rates, the apparent viscosities were subsequently calculated from the shear stresses.

Some problems were met due to leakage past the ram when extruding liquid D through the longer die. For this reason, additional measurements were made using dies of larger diameter (1.33 mm). At the lower stresses involved with these dies, no leaking occurred, but the shear rates were also lower at the same ram speeds as used with the finer dies. Results from the larger dies were found to be proportional to the L/D, so there was no entry effect with this liquid. Having established that this was so, the results for the short fine die were used to calculate the stresses and velocities directly without the subtraction step. Although the shear rates through this die were up to 7100 s^{-1}, the stresses were low enough to avoid leakage.

2.3.2. Pastes
All the pastes were extruded from a ram extruder at the same six ram speeds as the liquids through two dies of 3.2 mm diameter and lengths 3.2 and 50.8 mm, to give aspect ratios of $L/D = 1$ and 16, respectively. The barrel diameter was 25.4 mm. This ram extruder was mounted in the same universal load frame that was used for the liquids. Full details of the apparatus are given by Benbow *et al.* [6].

To compare the paste properties to those of the corresponding liquids, the shear stresses in the pastes were calculated by subtracting the forces for flow through the dies, thus giving an effective length to diameter of 15. By these methods the shear stresses relating to flow of pastes and liquids along dies of uniform bore were obtained, and in both cases the entry forces were eliminated. The wall shear stresses σ, for the pastes were calculated from the extrusion pressures by using the relation $\sigma = (\Delta P L/4D)$, where ΔP is the pressure drop over the die length. This is derived from the force balance at the die wall and is independent of the type of material involved.

3. Results
3.1. Liquid-phase rheology
The properties of the liquids measured in the Carrimed rheometer at low shear rates are shown in Fig. 3, where
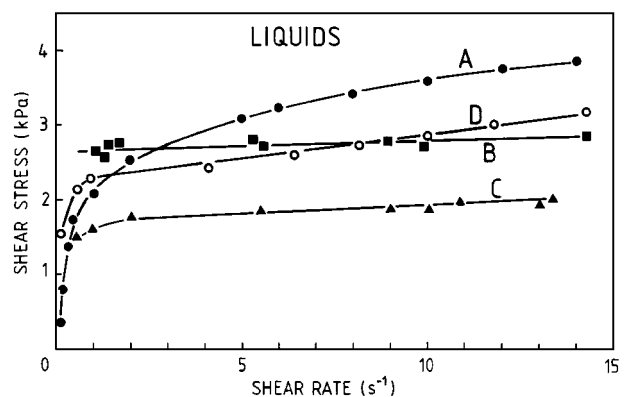

Figure 3 Shear stresses versus shear rate for the four liquid phases, obtained by shearing between a cone and plate in a Carrimed rheometer; (A) HPMC, (B) clay + water, (C) clay + glucose, and (D) clay + glucose syrup.
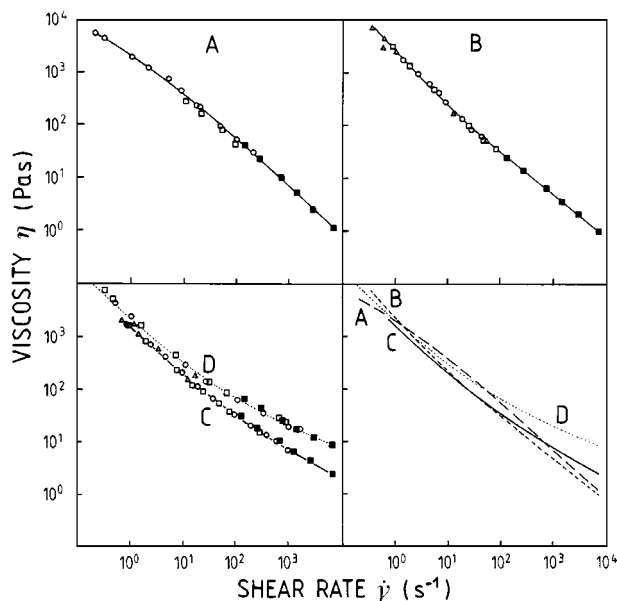
Figure 4 Combined results of cone and plate, and capillary measurements for the four liquids A, B, C and D separately and comparing the four: (□) cone and plate results obtained by using cones of various diameters; (■) capillary results.

the shear stresses are plotted as a function of the apparent shear strain rate for the four liquid systems A, B, C and D. It can be seen that two, the clay plus water (B) and the clay plus glucose solution (C), both exhibited apparent yield stresses whereas the HPMC (A), whilst non-Newtonian, is highly pseudo-plastic. The "glucose syrup" (D) has an apparent yield value, but due to its higher and more Newtonian viscosity, the shear stresses it shows at high rates are more rate dependent.

In Fig. 4 the apparent viscosities of the four liquids measured in the cone and plate system and by the capillary flow methods described above, are plotted together against the apparent shear strain rates on log–log scales. They show that there is good agreement between the two sets of measurements. The shear rate at the wall cannot be calculated exactly as the paste is a two-phase system in which it is speculated that the paste flows by plug flow on a thin liquid layer or depleted layer [9]. The ram extruder measurements were made to obtain the high shear strain rates which have been estimated to occur near the wall of the die land, when a thin liquid layer is being sheared. If a layer of liquid which is 1 μm thick is being sheared by a plug of paste moving at a speed of 1 mm s^{-1} the shear rate would be 1000 s^{-1}. As there remain many unknowns, a more elaborate calculation of the shear rate is unnecessary.

Because the thickness of the liquid layers has not yet been precisely determined and the paste measurements are made over a range of extrudate speeds, it is appropriate to determine the liquid properties at high shear rates, i.e. in the range 10^2–10^4 s^{-1}. The total range of shear rates over which the viscosities have been measured is five decades.

3.2. Paste properties
The extrusion properties of all the pastes are shown in Fig. 5. These indicate the wide range of rheological

behaviour encountered. Their properties extended from soft pastes which would be difficult to handle after extrusion, to rather stiff ones which required very high extrusion pressures. The curves also show the different ways in which the stresses depended on the ram speeds or extrusion velocity.

3.3. Relations between paste and liquid
During ram extrusion the applied pressure gradient balances the forces resisting flow along the barrel, into the die-entry and along the die-land. To account for these flows, pastes can be characterized by four extrusion parameters, if the viscous properties are proportional to the velocity (pastes B, C and D) and by six, when the flow is more complex (pastes A). Similarly, in the capillary flow of the liquid phases, both extension and shear are involved. Extensional flow occurs at the die entry and shear flow takes place where the dies have a constant cross-section.

To relate the paste and liquid by comparing the above derived properties would compound any errors in the descriptions of the pastes and liquids by such parameters. Instead the paste and liquid properties were expressed directly in terms of their shear stress, σ, versus ram speed, R. By separating out the flow into the die and concentrating on only the flow through the die-lands, the extension behaviour was avoided.

The paste and liquid extrusion properties were expressed directly in terms of the wall shear stresses at the corresponding ram speeds. The ratios of the shear stresses for pastes to those of the corresponding liquids at the same ram speeds (not extrudate velocities) are given in Fig. 6. It is clear that there is a systematic change of the values as the liquid content is changed. The ratios are independent of ram speed for all the pastes in spite of their different flow behaviour.

In Fig. 7, the ratios for liquid to powder volume in the range 0.95–1.01 are plotted against ram speed. There is seen to be only very little difference in the values for the four liquids. Differences which do occur may be due to unequal amounts of packing during the high shear mixing during the preparation of the pastes.

4. Discussion
The shear stresses in the pastes during capillary flow change systematically when the amounts of liquid phases are altered. The factors of proportionality between the paste and liquid stresses are fairly constant over a 50-fold range of extrusion speeds. This shows that the flow properties of all the pastes are closely related to those of their constituent liquid phases, even though the latter exhibited a variety of flow behaviours.

In general, the behaviour of the particulate pastes during extrusion depend on

1. the amount of liquid present in excess of that needed to fill the inter-particle voids,
2. the rheological properties of their liquid phases,
3. the interference between particles,
4. the extrusion conditions (whether the paste is free to expand or not), and
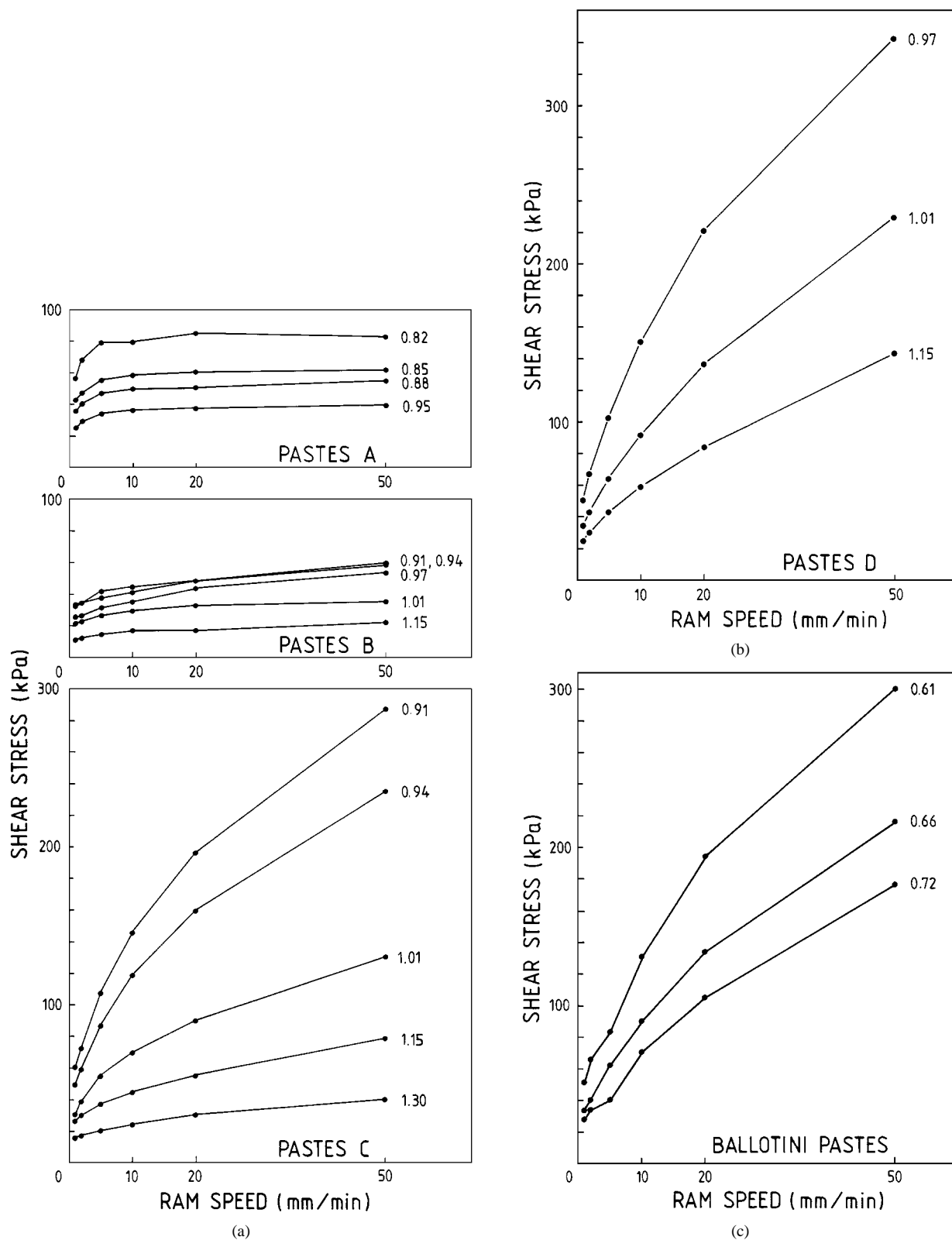5. the time scale of the experiments.

Figure 5 (a–c) Wall shear stresses versus ram speed for all the alumina and ballotini pastes examined. Each part represents a particular liquid phase.

During paste extrusion, the die-land region can be considered in four parts, i.e. (1) the die-wall (usually metal), (2) a thin layer of liquid between particles and the die wall, (3) the thin layer of paste which is depleted of particles owing to local packing restraints, and (4) the body of paste (which for stiff pastes is un-sheared). Any roughness on the die-wall which is comparable in scale to the average particle diameter may increase the shearing resistance. If there is contact between the particles and the die wall, frictional forces will occur and wear

will take place. Electro-chemical effects can be important, as illustrated by the alterations in extrusion pressure produced by Perspex and steel dies and the changes which have been shown to occur when potential differences are applied between the paste and the die [9, 10].

Considering the liquid layer between the outer particles and the die-wall, the thickness of this depends for a given powder on the excess of that needed to fill the inter-particle voids. Increasing the quantity of liquid increases the layer thickness. At first sight it is tempting to
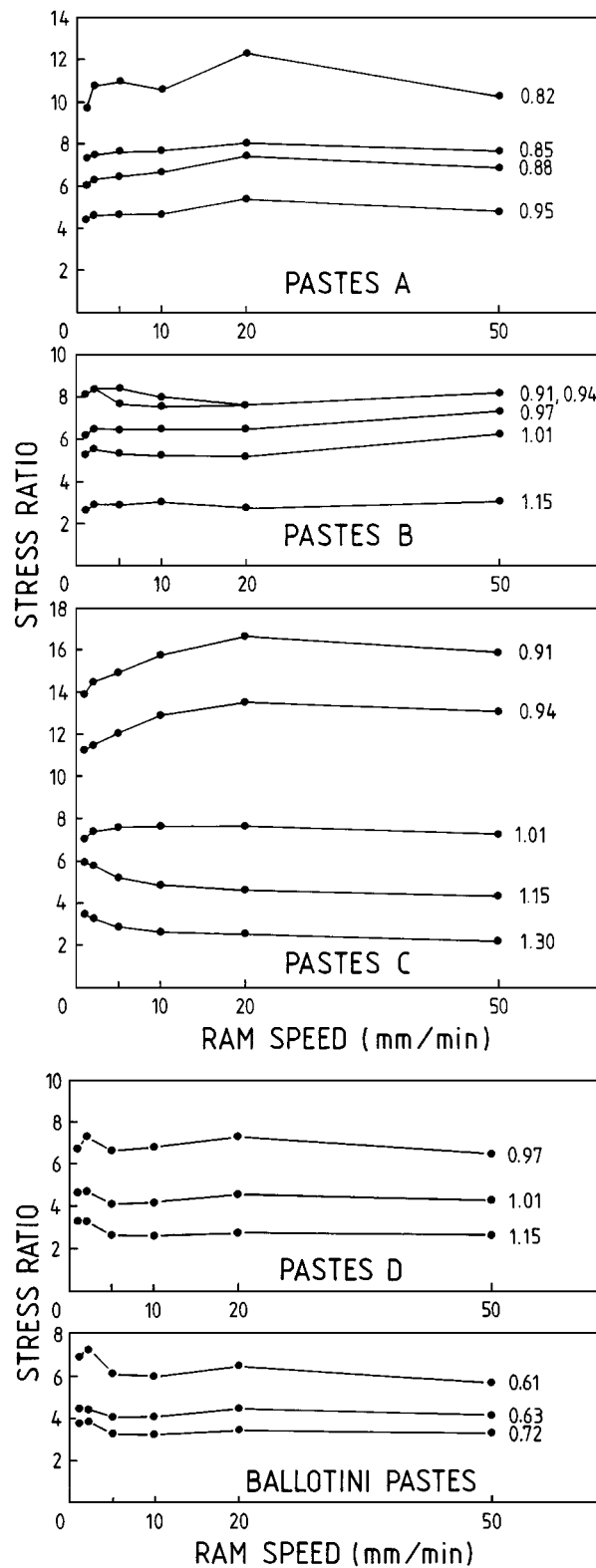
Figure 7 Stress ratios for approximately the same values of liquid to powder volume ratios for the four paste systems. The numbers associated with each line are the liquid to powder volume ratios of the pastes.

Figure 6 The ratios of paste shear stresses to those of the corresponding liquids plotted as a function of ram speed. The numbers associated with each line are the volume of liquid/volume of powder in the pastes.

values in the paste, whereas much higher values were measured. Because the shear stresses are at maximum at the die-wall and the density of particles adjacent to the wall is reduced, it is likely that some shearing will occur in this region.

The ratios of the shear stresses are shown to be not very dependent on the type of liquid, because equal amounts produce similar ratios (Fig. 7). Given the size of the particles involved in the study, combined with the uniformity of the particulates present and the neutrality of the liquid systems in terms of pH, it was felt that the variations in the results due to surface charge differences would be small compared to the other factors, in particular the shear forces, active in the system.

Increases in liquid, therefore, increase the liquid layer in direct contact with the wall, but also reduce the inter-particle interference and the resistance to relative motion. At some high liquid content the whole paste will flow, but this lies outside the range of extrudable pastes, because they would not retain their post-extrusion shape.

In a paste containing mono-sized particles, the distance between adjacent particles can be approximately estimated from the volume of excess liquid and the surface area of the particles. In the case of the alumina powders, the above reasoning suggests that this value is less than a particle radius for a typical extrudable paste.

4.1. Ballotini powder
In Fig. 5 the shear stress results for pastes made from a ballotini powder mixed with three different amounts of liquid D are shown. The ratios of the paste shear stresses to those of liquid D are given in Fig. 6. These again do not depend significantly on ram speed and change with liquid content in a similar way to the alumina pastes. The values of the stress ratios depend on the amount of added liquid, but because the packing is different for this powder much less liquid is present.

5. Conclusion
The results show that there is a close qualitative link between the rheology of the four liquids and the extrusion behaviour of the pastes which were made from them. The ratios of the shear stresses increase as the amount of liquid decreases and ratios for the different liquids are numerically similar. The small observed differences

assume that all shearing takes place in this layer. If this was so, at a given extrusion speed, the shear rate would decrease as the amount of liquid was increased. But this would not affect the shearing stresses with liquids B and C (Fig. 3), because their shear stresses are almost independent of shear rate at shear rates above 2 s^{-1}. Hence there must also be some flow within the paste. Another factor which supports this is the view that a liquid having a yield value would only produce comparable yield
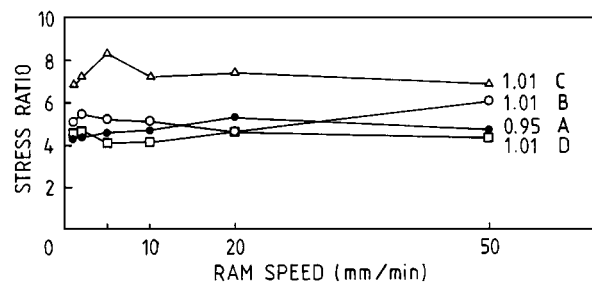
could be due to the unequal amounts of packing induced by each liquid during the high shear when they were being prepared.

The absolute values of the ratios suggest that a thin layer of paste is being sheared near the die wall and that an increase in the liquid content allows relative motion between the particles to take place more easily. This mechanism suggests that the effects of different liquids will be similar, as our results show, and that additional liquid affects the relative motion of the particles in a thin region near the die wall. As the concentration of particles is further diluted there comes a region in which there is no inter-particle interference. Finally, we consider, more research is required to explain in more detail the physical mechanisms taking place near the die-wall.

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