The Rheology of Powders and Bulk Materials – a Multivariate Approach Using Dynamic, Shear and Bulk Property Measurements

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ABSTRACT

This paper will introduce the application of modern, computer controlled instrumentation to measure the dynamic, bulk and shear properties of powders. Comprehensive knowledge of this wide range of rheological properties can help with the design and troubleshooting of particular processes and will be demonstrated by using specific examples.

INTRODUCTION

Powders and bulk materials are widely used in industry as feedstock, intermediates and finished products – for example over 60% of the value of pharmaceutical sales worldwide is accounted for by powder formulations, either as tablet/capsule or in the form of an inhalable powder[1].

Whilst they are used extensively, they are among the most difficult materials to characterise and understand as evidenced by the frequent problems encountered when scaling manufacturing processes, from laboratory through pilot and on to full scale production.

The wide range of processes used to manipulate powders, at whatever scale, subject them to extremes of stress and shear – from high compaction loads seen in tableting machines to the highly dispersed state seen in fluidised bed reactors and dilute phase pneumatic conveying. Combine this with the inconsistent physical properties of powders and then introduce environmental variations, such as humidity, then the extent of possible variability is clearly large.

The key to processing powders is to appreciate their complex rheological behaviour, thus ensuring that the powders characteristics are compatible with the way they are to be processed – at whatever scale. However, such a requirement demands a thorough understanding of how a powder will behave over a range of stress/shear conditions (when stationary, in motion or about to move) and relying on simplistic single measures of a powder's response or physical property will, result in process interruption and/or poor product quality as such responses are invariably complex and often non-linear[2].

There are now technologies available that can assist industry in measuring relevant properties of powders and this paper illustrates how recent developments in powder characterisation allows process engineers to predict how a material will behave during processing and how best to configure equipment settings for optimal powder/process compatibility[3]. Furthermore, it will also demonstrate how this information can then be fed back in at the development stage to provide processability specifications that will assist with scale-up and also to evaluate the causes of process interruptions or reductions in the quality of final product.

MODERN INSTRUMENTAL POWDER CHARACTERISATION

Several techniques to measure a property of a powder have been traditionally used; Carr's Index; Hausner Ratio; Angle of Repose; flow through a funnel. Although pragmatic solutions for their day these techniques are basic and generally regarded as insensitive[3] and don't simulate all the conditions that powders experience in either manufacture or application.

More recently, shear cells have enabled researchers to measure powders under consolidation at the onset of flow – the transition from static to dynamic behaviour. This is extremely useful for understanding behaviour in hoppers.

Most recently, dynamic characterisation methods have been developed allowing the measurement of the powders response to various environments. It is now possible to directly measure response to aeration, consolidation and flow rate – all at low stresses within the powder. It is also possible to easily quantify powder bulk properties such as density, compressibility and permeability. In order to show how fully characterising a powder using multiple instrumental measurements can assist with the design and troubleshooting of processes, three examples at three different (relative) stress conditions are described.

HOPPER SYSTEMS – A MEDIUM/HIGH STRESS ENVIRONMENT

The most common design method for powder systems is the specification of hopper parameters for mass flow from storage vessels[4]. The design method requires shear, density and wall friction measurements and has been shown to give good, if somewhat conservative, results. With the relatively recent development of automated, computer controlled shear cells it is now possible to generate the data necessary to design a hopper within a few hours – compared to the, typically, 1-2 days required for manually operated cells.

It is also possible to use modern computers to rapidly calculate the hopper design parameters, without having to resort to manual graphical interpolation, further

Table 1. Descriptions of the wall materials and the results of the wall friction tests.

Disk no.	Material[#]	Surface Finish	Notes	R_a value (µm)	WFA (°)
1	SS 316 L	Brushed		0.19	27.5 ± 0.2
2	SS 316 L	Satin finished		0.28	28.8 ± 0.4
3	SS 316 L	Electropolished		0.35	31.5 ± 0.0
4	SS 316 L	Glass pearl treated		0.45	29.0 ± 0.1
5	SS 316 L	Ground, fine		0.61	29.6 ± 0.1
6	SS 316 L	Brushed		1.2	31.0 ± 0.3
7	SS 316 L	Rhenolease MK V	Conductive, PTFE-based	1.85	24.8 ± 0.3
8	SS 316 L	Titanium nitride		N/A	32.1 ± 0.1
9	SS 316 L	CrNi-Coating		N/A	34.8 ± 0.1
10	SS 316 L	NEDOX SF2 coating	Nickel / polymer	0.7	28.1 ± 0.0
11	Aluminium	Tufram coating	Anodized, Polymer	0.91	27.6 ± 0.3
12	Aluminium	Hard slide HSS	Anodized, Polymer	N/A	27.8 ± 0.0
13	PEEK	Milled	Polyetheretherketone	2.39	24.3 ± 0.4
14	POM-C	Milled	Polyoxymethylene copolymer	0.06	13.0 ± 0.1
15	PETP	Milled	Polyethylene terephthalate	2.1	19.5 ± 0.3

improving the cost effectiveness of the design process. To illustrate this, the influence that the material of construction has on the mass flow design of a conical axisymmetric hopper is presented using a pharmaceutical excipient, Respitose® ML001 (DMV-Fronterra) and a range of wall materials based on finished or coated stainless steels (SS), aluminium and plastics used in process equipment (Table 1).

In parallel to generating wall friction angle (WFA) results (Table 1), data was gathered for the shear and density properties of the Respitose®. This enabled the rapid evaluation of the hopper design parameters using a proprietary computer based design program (Figure 1).

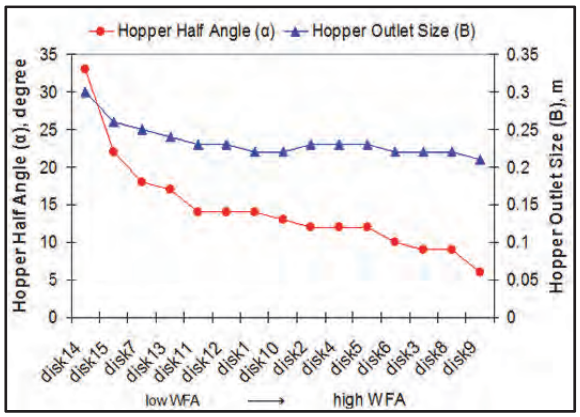


Figure 1. The calculated hopper half angle and outlet parameters for Respitose® with respect to wall friction material.

The WFAs of all 15 discs are highly reproducible and differentiating. They vary from 13° for polyoxymethylene copolymer, to 34.8° for CrNi-Coating on SS316L. For SS316L discs, WFA increases with increasing roughness, with electro-polished 316L an exception. For polymer based discs or polymer coating, the WFA also increases with increasing roughness. However, compared to the metal discs, the polymer discs have significantly lower WFAs despite their higher surface roughness, which indicates other properties of the wall material are important. Interestingly, the polishing of stainless steel does not improve its frictional properties with respect to this powder.

The influence of WFA on mass flow hopper design is substantial. For the materials in this study, hopper half angles range from 6° to 33°. Outlet size slightly increases with increasing hopper half angle (reducing wall friction) in order to maintain mass flow. Whilst perhaps counter-intuitive, this is because the shallow hopper walls tend to support a proportion of the major principle stress, leading to less stress acting directly on the arch.

This outcome shows that it is now quick and cost effective to evaluate multiple options for evaluating hopper constructional materials. Such an approach could result in significant costs savings from lower priced, but just as effective, wall materials as well as improvements in the overall geometry of the hopper system which could result in lower manufacturing and installation costs.

However, it is not only the shear, wall friction and density information that influences flow. Instances where can occur flow is pulsatile or even stops altogether despite the correct design procedure being followed. The work presented by Carlson and Hancock[5] shows how poor permeability affects powder's ability to flow through a feed hopper in a tablet press and shows the importance of this characteristic.

DIE FILLING – A MEDIUM / LOW STRESS ENVIRONMENT

The filling of dies to generate 'tablets' is a common practice in several process industries - pharmaceutical, food, household products, and powder metallurgy/ceramics, to mention a few.

There are, however, many ways of designing and operating a tableting process, but the main aim is to achieve a low porosity, densely filled die, without compromising production capacity.

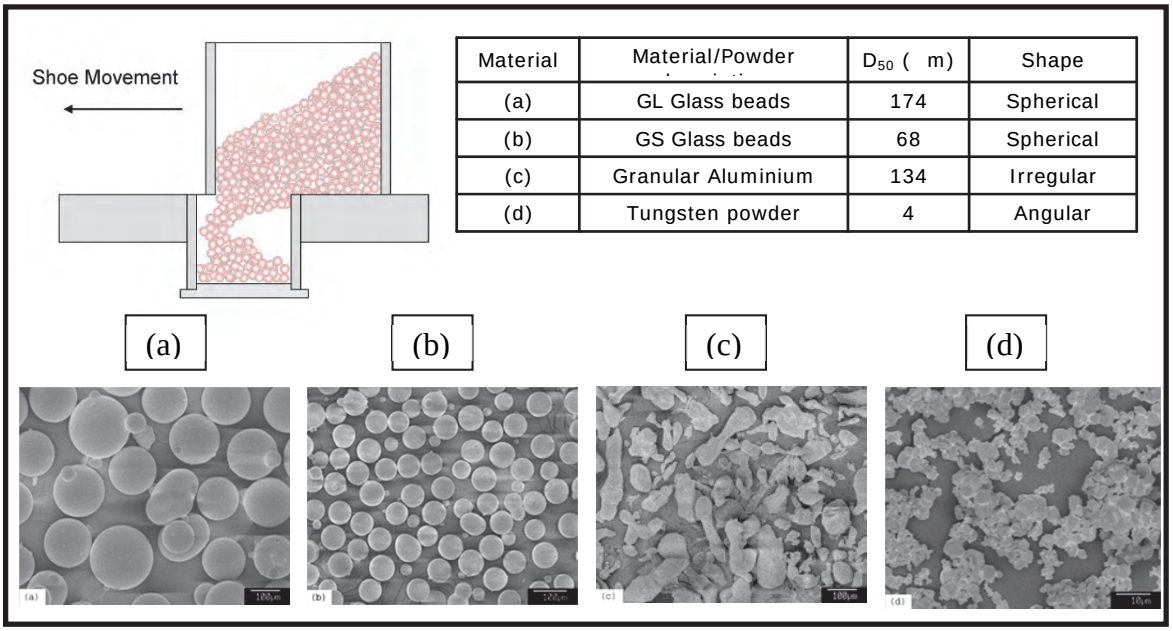
If one considers the way that powders flow into the die then a range of powder properties appear to be influential:-

• Cohesion – powder which displays high cohesion may not flow into the die under gravity in a regular manner.

• Mechanical interlocking – size and shape of the particles may result in bridging, restricting efficient filling of the die.

• Low permeability – if air in the die cannot escape during filling then a back pressure may be generated reducing the flow into the die.

To evaluate this, a series of experiments was carried out with four test materials, as described in Figure 2. The results are shown in Figure 3.



Material	Material/Powder	D_{50} (m)	Shape
(a)	GL Glass beads	174	Spherical
(b)	GS Glass beads	68	Spherical
(c)	Granular Aluminium	134	Irregular
(d)	Tungsten powder	4	Angular

Figure 2. Schematic of the shoe/die and physical properties of the four test materials.

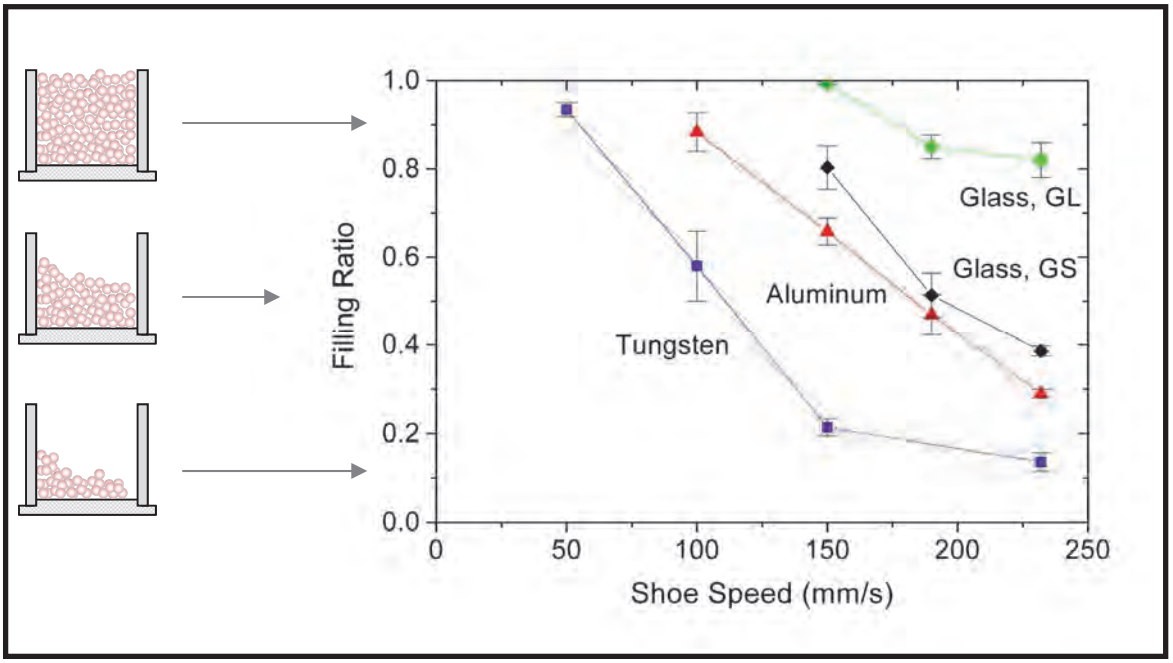


Figure 3. Variation of die filling ratio for four different powders over a range of shoe speeds.

From the data presented in Figure 3 and Table 2, it can be seen that the Tungsten performs the worst out of the four, followed by the Aluminium, the Glass GS and the Glass GL. Comparing the processing performance with the powders' physical characteristics; it is clearly not possible to link a single measurement to observed behaviour.

The dynamic testing of powders using a powder rheometer employs a specially shaped blade to establish a particular flow pattern in a precise volume of powder and evaluates the ability of the sample to resist the motion of the blade. The flow pattern is downward anti-clockwise motion generating a compressive, relatively high stress flow mode in the powder. The Basic Flowability Energy (BFE) is calculated from the work done in moving the blade through the powder from the top of the vessel to the bottom. In the same test the Specific Energy (SE) is also derived during the upward movement of the blade through the powder. Using the same flow pattern, but established on the upward traverse of the blade where the powder is now unconfined (powder can lift up), the energies measured are more dependent on the cohesive and mechanical interlocking forces between the particles and less influenced by compressibility, for example.

The Aeration Energy (AE) is an obvious extension to this dynamic test of the powder using a powder rheometer; measuring the energy required to pass a blade through a specific volume of powder whilst passing a continuous stream of air through the base of the test vessel. As the flow rate of air is increased, the amount of energy required to pass the blade through the sample will reduce as the individual particles begin to be separated and partially supported by the air stream. More cohesive powders will show a relatively small reduction in AE compared to free flowing powders, as they do not permit the air to permeate through the powder bulk – instead forcing the air to escape through channels or rat-holes. The resulting change in flow energy is therefore relatively small. However, in less cohesive powders, air is able to permeate throughout the entire bulk of the powder, mechanically separating particles and hence the reduction in AE is large. In some cases virtually all particles are separated and the bed fluidises.

The sensitivity of a powder to aeration is predominantly dependant on the strength of the cohesive forces acting between particles and therefore relates well to performance in a gravity feed system and processes such as volumetric filling, where cohesive strength is important. Typically an AE of 10mJ or less would indicate that the powder has zero cohesion and is likely to fluidise.

Thus, the cohesion – as described by the AE – shows the Tungsten to have the highest value, but cannot differentiate the other materials, categorising them all as non-cohesive (<10mJ). The particle interlocking – as described by the SE – shows that the Glass GS sample has the lowest value, however this is counterintuitive as the Glass GS only performs half as well as the GL (40% fill compared to 82% fill).

Clearly the Tungsten has a very high pressure drop which, in combination with the AE and SE data, clearly identifies

Table 2. Process and powder property data for die filling experiment.

Measurements:	**Glass GL**	**Glass GS**	**Aluminium**	**Tungsten**
Fill Ratio @ 230mm/s shoe speed	0.82	0.40	0.29	0.14
Aeration Energy, AE (mJ)	< 10	< 10	< 10	~300
Specific Energy, SE (mJ/g)	3.4	2.4	4.4	6.7
Pressure Drop across the powder bed at 2mm/s air velocity, PD_{15} (mbar)	0.8	5.2	1.4	15.3

this as the worst performer. However, the permeability and SE measurements enable us to begin to differentiate between the other samples. This is a function of a change in dominance of a purely cohesive flow resistance to a balance between mechanical interlocking and gas/solid interchange mechanisms. The Glass GS has a much higher pressure drop across its powder bed than the Glass GL. A low permeability limits the interchange of powder and air that must occur as the shoe moves across the die inlet. If the air in the die cannot quickly escape through the incoming powder, then a back pressure is created preventing the powder from flowing into the die – no matter how good it's other flow properties. In such instances the speed at which dies can be filled is significantly reduced, limiting the productivity of the process. The Glass GL shows increased mechanical interlocking when compared to the Glass GS (higher SE), but its greater permeability helps it to fill the die better than Glass GS over the entire range of shoe speeds, as shown in Figure 4.

Considering the aluminium and Glass GS, the aluminium has lower permeability and, given the rationale described previously, one might expect it to show better filling performance, however Figure 4 shows that this is not the case. Clearly the cohesion does not explain the differences between these materials as the aeration data shows both to be non-cohesive. The specific energy – as a measure of mechanical interlocking – indicates a significantly higher value for the aluminium, almost certainly due to its irregular morphology. This balance between permeability and SE is clearly important for these materials.

Evidently there is a complex equilibrium between all three properties that were described previously. Such relationships will be challenging, if not impossible to model, without test data from a significantly larger number of materials in order to validate the relationships between cohesion, mechanical interlocking and permeability. In many instances, the generation of empirical relationships based on measurable powder assembly properties is a necessary first stage in capturing the range of behaviours that are observed.

MIXING – A LOW STRESS ENVIRONMENT

Increasing the rate of rotation of a tumble mixer usually increases the rate a formulation achieves optimal dispersion of its components.

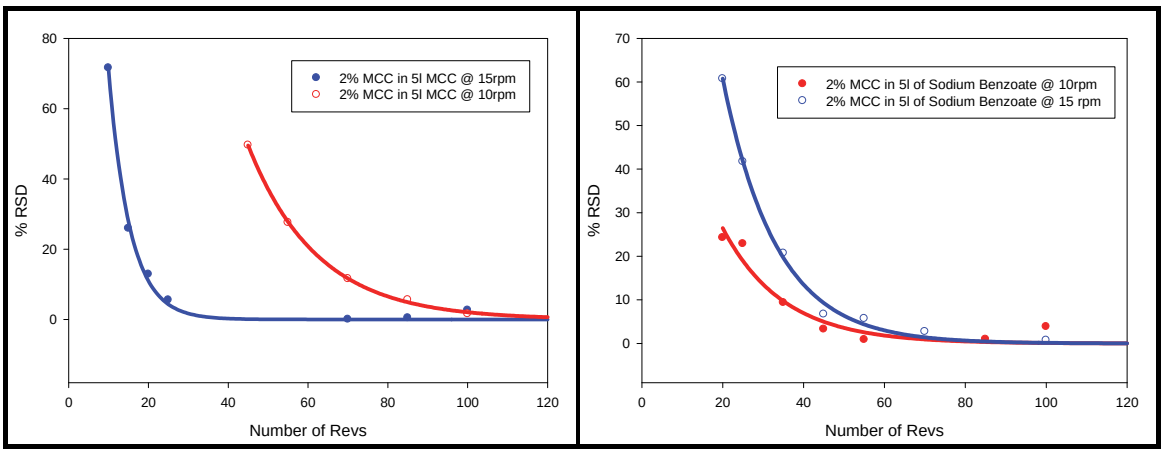


Figure 4. The rate of dispersion of a radioactive bolus in MCC (left) and Sodium Benzoate (right) substrates.

The graph displayed on the left of Figure 4 shows the rate of dispersion of a radioactively labelled bolus of microcrystalline cellulose (MCC) in an MCC substrate (as measured using positron emission tomography[6,7] for two different rotational speeds of a 10litre laboratory IBC tumble blender at a fill level of ~50%. As expected, operating the blender at a high rotational speed (the maximum system speed of 15rpm) achieves an acceptable level of mixing much earlier than at a lower rotational speed (10rpm).

The graph shown on the right of Figure 5 shows the same experiment except that the substrate has been changed to a food grade of sodium benzoate. In this case it can be seen that increasing the rotational speed actually slows the rate of dispersion. Clearly there is a significant difference between the dispersal mechanisms of the two substrates which is not immediately apparent from a visual assessment of the samples or from the results of a range of typical powder characterisation methods.

However, when the two materials were studied using the dynamic methodology available using a powder rheometer, there was a clear difference in the response of these two powders to changing the rate at which they were made to flow – analogous to the change in rotational speed of the blender which induces higher shear rates in the powder. As can be seen in Figure 6 there is an increase in the resistance to flow (Total Flow Energy) as the blade tip speed increases for the sodium benzoate compared to the spherical MCC particles which flow more readily at higher blade tip speeds.

Further investigation showed that the sodium benzoate particles are mostly platelets and the MCC was more spherical. This explains the difference in mechanism – the platelets have significantly larger surface contacts and more mechanical interlocking due to their irregular particle morphology than the spherical particles. The ability of the platelets to pass over each other and the blade (due to mechanical interlocking interference) during higher rates of shear is

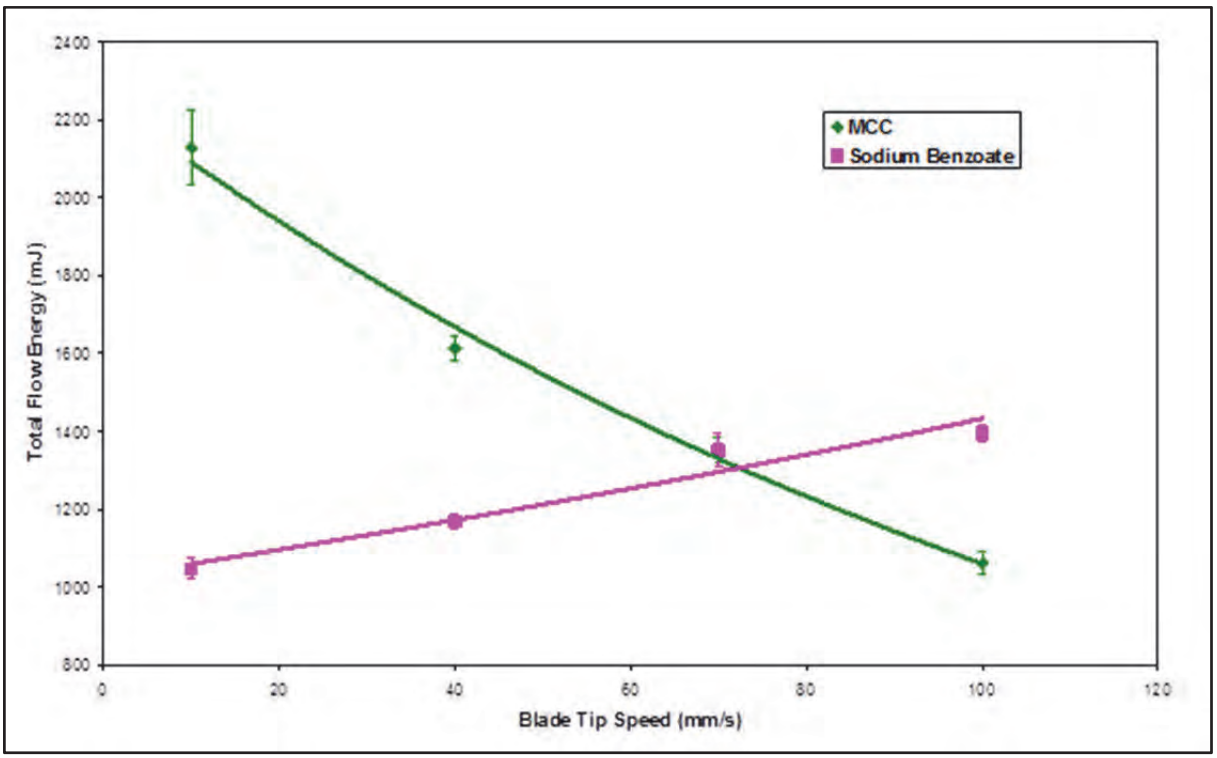


Figure 6. Powder response to blade tip speed in a powder rheometer.

clearly reduced – 'rotational frustration'[8] – and this is replicated during the higher speed blending experiment. The platelets have a reduced ability to be mobilised and thus interstitial spaces that would otherwise allow the minor component to disperse within this substrate are not promoted with increased blender speed. In contrast, the spherical particles can move over each other with greater ease, creating interstitial gaps (i.e. more air is entrained within the powder) when mobilised, allowing the minor component to move more easily between the substrate particles. This is enhanced at higher blade speeds and blender rotational speeds.

Without measuring the powder properties using the dynamic method, specifically the rate at which the powder is made to flow, such behaviour cannot be predicted or quantified, as no other powder characterisation technique showed such a difference as they were unable to replicate the process conditions.

CONCLUSIONS

The variability of powder systems is not in doubt and, to date, very few definitive relationships which link one or more of a powder's measurable characteristics to specific process design parameters have been identified[9]. Although it is nice to believe that one can say Powder A is better than Powder B, the reality is that a single index or characteristic will not enable a complete understanding of any given powder's performance in all situations. This paper has shown that a range of characterisation methods are required to ensure a complete understanding of how multiple powder properties can influence the performance in different processes.

Comprehensive characterisation quickly leads to an understanding of why certain powders behave in a specific way within a particular process. Limiting powder characterisation to a single measurement – whatever method is used – is unlikely to provide sufficient information to design or troubleshoot any given process. Equally, knowledge of the stress regimes and shear rates experienced by powders in a specific process bottleneck or failure will assist with the range of tests required to replicate the same powder response in the laboratory. Building on this concept will allow the development of a 'database' of powder and process relationships which allows the capture of current and historical data. With such a foundation, it will be possible for formulators, process engineers and equipment manufacturers to improve their efficiencies and productivity.

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