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Microstructure of single-droplet granules formed from ultra-fine powders

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ABSTRACT

A quantitative analysis of variations in granule microstructure based upon changes in primary particle size and bed preparation is presented. The granule microstructures are obtained using X-Ray Computed Tomography (XRCT). An algorithm is developed to measure the number and size of macro-voids (pore space with volume equivalent size greater than or equal to 30 μm or 3 times the primary particle size). Four size fractions of alumina, ranging in primary particle size from 0.5 μm to 108 μm, are sieved using three different sieve sizes to create static powder beds from which single-droplet granules are produced. The analysis shows that large macro-voids exist in ultra-fine powders (0.1–10 μm). The macro-voids take up to 7% of the granule volume and the largest macro-voids are 200–700 μm in volume equivalent size. Changing the sieve preparation changes the size and total volume of macro-voids. In contrast, there are very few macro-voids in granules formed from coarser powders. This study shows that micron sized powders have the opportunity to form complex structures during granulation and that the handling history of the materials should receive greater scrutiny than it currently gets.

1. Introduction

Wet granulation is a process by which small particles are formed into larger agglomerates through the use of a liquid binder. It has found application in a variety of industries, from pharmaceuticals, agriculture and food to ore processing and pigments [1]. A common application is to take fine particles and bind them to form high density agglomerates. These agglomerates may be the final product or they may be further compacted to make ribbons or tablets.

Most fundamental studies of wet granulation have used model materials, such as glass ballotini, or lactose. These materials often have a relatively large mean size (>20 μm). The study of ultra-fine particles (0.1–10 μm) behavior in wet granulation is uncommon, despite the fact that many powders of industrial interest for detergents, pigments, agricultural chemicals and ceramics are in this size range. As the primary particle size is reduced below 10 μm, van der Waals forces increase to a point at which they become non-negligible and capable of countering the weight of the individual particles [2]. The exact magnitude of this force also depends on particle shape and roughness, surface properties and the particle size distribution. Van der Waals forces can lead to self-agglomeration of the dry primary particles, resulting in complex and potentially unwanted behaviors and making the powder behavior very sensitive to its prior history. In their study of drop penetration time, Hapgood et al. [3] found that their model was effective in all cases except when used for ultrafine powders (zinc oxide and titanium dioxide). Their penetration model assumes an effective porosity which is not as accurate for ultrafine powder beds which are expected to have a more complex microstructure than model materials. The study of hydrophobic nucleation mechanisms by Eshtiaghi et al. [4–6] showed the formation of hollow and collapsed granules while using X-ray computed tomography (XRCT) to confirm their structural observations. However, their work used a variety of materials, ranging in size from 0.01–320 μm and these structures are not unique to the ultrafine powders. There are a few other studies in the wet granulation literature which make use of ultrafine powders [7–19]. Often, only one of several materials used was in the ultrafine range [3–9].

Hapgood et al. [3] and Emady et al. [7] studied the granule nucleation mechanism and their external structures. Emady et al. [7] identified that static bed granules will nucleate either through the Tunneling or the Spreading/Crater mechanism dependent upon the granule Bond number. Ultra-fine powders had high bond numbers and generally exhibited Tunneling behavior. Rough et al. [11,14,16] studied a semi-solid paste in a high-shear mixer for detergent granulation using an ultra-fine sodium alumino-silicate powder. Their work looked at the agglomeration mechanisms, bulk density characterization, and effects of solid formulations. Afarani et al. [13] showed, for alumina in a high-shear environment, that increasing binder content led to a wide size distribution, enhanced attrition and bulk compression strength of sintered granules, but provide only some SEM images for structural examination. There is additional work on hydrophobic granulation from Hapgood and

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Khanmohammadi [9] as well as Charles-Williams et al. [10] showing layering of hydrophobic particles on the outside of granules that are either hollow or filled with hydrophilic particles. None of these papers examine the potentially interesting behaviors that are unique to ultrafine powders. It is necessary to look outside of traditional wet granulation processes to find information about the interesting and complex behavior of ultrafine powders.

There are examples of other processes using ultrafine powders to create granules and agglomerates with a variety of internal structures. The internal structure of these agglomerates has an impact on its behavior during further processing. For example, Eckhard and Nebelung [20] showed a change from ductile to brittle behavior in the compaction of spray dried agglomerates by changing the structure from homogeneous to inhomogeneous. Inhomogeneous or "hollow" spray-dried granules can be created by using a well dispersed suspension which allows for particle mobility during drying. A different technique used by Pagnoux et al. [21] makes large, spherical granules in suspension through continuous stirring of primary agglomerates created from alumina (0.4 μm average) and silica (25 nm). The granule structure was changed from solid to hollow by adding a step to the primary agglomeration stage, producing a narrower primary agglomerate distribution. Fluidized beds have also been used to create soft agglomerates (non-permanent bonds) in cohesive nano- and micro-powders where the van der Waals forces are dominant [22–29]. Fluidized nanoparticles are expected to first form particle-particle clusters and then to form soft agglomerates from the clusters while the micron sized particles form particle-particle clusters [22]. The fluidized agglomerates were found to have a fractal dimension of 2.57 close to the predicted simulation value for diffusion limited agglomeration [22]. Wang et al. [23] showed a tiered arrangement of cluster sizes with large aggregates made of fine particles at the bottom (2.8 mm aggregates with 7 μm particles) and 0.3 mm aggregates from 17.8 μm average sized particles in the upper layer from particles 0.01 μm–18.1 μm in size. Several studies have shown that the application of force, through ultrasonic vibrations or other methods, will improve the fluidization behavior and generate a consistent agglomerate size [22,24–27]. It is hypothesized that the internal granule structures can also be controlled through changes in handling and the powder bed structure in traditional wet granulation applications. An imaging technique, such as X-ray tomography, capable of quantifying internal structures must be used to verify this hypothesis.

X-ray computed tomography (XRCT) is increasingly being used in a variety of applications as it provides detailed information about the internal structures of objects of interest [30]. This technique is capable of producing a 3-D recreation of the entire internal structure which allows for quantitative rather than qualitative structure analysis. Other techniques commonly used to describe granule structure, such as SEM, optical microscopy, and porosity measurements, do not provide information about the entire structure. XRCT has been used to calculate pore shape, size, connectivity and overall porosity for granules made from large particles. These values have been compared with those obtained from mercury porosimetry and were found to predict lower porosity and a larger pore size [31]. A different issue arises when attempting to determine porosity through tomography for ultra-fine powders. The smallest reported voxel resolution is on the order of 0.5–1 μm on a side, meaning that a single particle may be equal to or smaller than a single voxel. This resolution is insufficient to make a determination of granule micro-porosity and compare it to other methods [30]. XRCT is instead useful for examining meso-structures in ultrafine powder granules rather than porosity alone, which can be obtained from other methods. Recently published work by Dale et al. [32] describes a novel technique for measuring and describing phase distributions in granule microstructure which will be used for this study. The quantitative nature of this technique means that the impact of bed preparation, compaction, or other processing can be measured and compared to see which methods have the greatest impact.

This study tests the hypothesis that changes in powder bed preparation for ultra-fine powders will result in changes to the microstructure of wet granules. The effects of particle size on the complex behaviors will also be tested. It is hypothesized that the smallest particles will have the most complex behavior and increasing the particle size will simplify the behavior. Four different size fractions of alumina powder are used. X-ray computed tomography is employed to examine and quantify changes in microstructure.

2. Materials and methods

α-Alumina particles with 4 different median particles sizes ((d_{50} = 0.5 μm, 5 μm, 25 μm, 108 μm Inframat Advanced Materials) were used to form granules for study. Particle size characterization was performed by wet dispersed laser diffraction (Malvern Mastersizer 2000). The 25 μm alumina dispersed easily in water with ultrasonics at 50%. A dispersant solution of IGEPAL CA-630 (Sigma-Aldrich) in water (1 g/1000 g water) was used to disperse the 0.5 and 5 μm powders. Particles were in the system for 5 min at 50% ultrasonic intensity before measurements were taken. The 108 μm particles broke up when dispersed (to around 1 μm) so a Tyler Ro-Tap Model E Sieve Shaker was used for sizing. The sieve shaker was run for 5 min using the Fine Analysis option. The powder flow properties have been evaluated using a Jenike & Johanson RST-XS Schulze Ring Shear Tester using 1,2, and 4 kPa pre-shear values with automatic shear-point selection.

Granules were prepared through single droplet nucleation in static, sieved beds. The powder was sifted through a single sieve into a petri dish (9 cm diameter) to prepare the powder beds. The two finest powders were sieved using 1.4 mm, 710 μm and 500 μm sieves. The 25 μm alumina easily passed through the 1.4 mm sieve and was sieved through the 710 μm and 500 μm sieves. The 108 μm alumina was very free flowing and passed easily through the 1.4 mm, 710 μm, and 500 μm sieves. Approximately 300 granules were created in each experiment using a 22 gauge needle from each powder/sieve combination. Water (2.71 ± 0.03 mm diameter droplets) was used as the binding liquid for submicron and 5 μm alumina powder beds. A solution of 0.05 g PVP K32 (Acros Organics) per gram of distilled water (2.76 ± 0.06 mm diameter droplets) was used for the 25 μm and 108 μm granules because the granules did not have sufficient dry strength for analysis with water as the binder. Granules were dried in a Mettler Toledo Halogen Moisture Analyzer at 100 °C. A Nikon SMZ1500 microscope was used for optical imaging of granules.

Ten granules were chosen at random from a tray of the granules for each experiment for XRCT imaging to examine and analyze the internal structure. A Scanco Medical μCT 40 (Scanco Medical) housed at Purdue University was used for the scans at its high resolution settings, resulting in a 6 × 6 × 6 μm voxel size. The material and sieve preparation will be referenced using the letter and number combinations in Table 1, such as Powder A1 or Powder B3. The letters (A,B,C,D) refer to the primary particle size, from smallest to largest, while the attached number (1,2,3) refers to the sieve size used for powder preparation. Powder A1 refers to 0.5 μm primary particles that have been passed through a 1.4 mm sieve and Powder C3 refers to 25 μm primary particles that have been passed through a 500 μm sieve.

The analysis of XRCT granule images was performed using ImageJ and MATLAB based on the analysis methodology developed by Dale et al. [32]. A binary threshold was applied in ImageJ using the automatic

Table 1
Reference table of different powder and sieve combinations.

Alumina size (μm)	1.4 mm Sieved1	710 μm Sieved	500 μm Sieved
0.5	A1	A2	A3
5	B1	B2	B3
25	C1	C2	C3
108	D1	D2	D3