Statistical investigation of agglomerate breakage based on combined stochastic microstructure modeling and DEM simulations

Aaron Spettl^{a,*}, Maksym Dosta^b, Sergiy Antonyuk^c, Stefan Heinrich^b, Volker Schmidt^a

^aInstitute of Stochastics, Ulm University, Germany ^bInstitute of Solids Process Engineering and Particle Technology, Hamburg University of Technology, Germany ^cChair of Particle Process Engineering, University of Kaiserslautern, Germany

Abstract

The internal microstructure of agglomerates has a great influence on their stability and breakage characteristics. Therefore, to optimize production processes and to improve characteristics of the final product, it is very important to understand dependencies between structural and mechanical properties of agglomerates. In this paper, we discuss usage of the discrete element method (DEM) for understanding the breakage behavior of spherical agglomerates under uniaxial compression depending on their microstructure. A flexible stochastic model has been developed to generate agglomerates with various types of microstructures. As an example, we investigate the effect of the primary particle size distribution on agglomerate strength and breakage behavior. In particular, the size distribution of primary particles is specified by a mixing of two fixed particle sizes. The model construction ensures that the size and mass of agglomerates as well as primary particles and binder content remain constant in all experiments. From the obtained results it can be seen that the breakage behavior of agglomerates is influenced in different ways. Breakage energy and the maximum force applied before the primary break depend on the mixing ratio and the variability inside the microstructure. On the other hand, the size of fragments is very similar for all mixing ratios.

Preprint submitted to Advanced Powder Technology

^{*}Corresponding author. Tel.: +49 731 50 23555; fax: +49 731 50 23649. Email address: aaron.spettl@uni-ulm.de (Aaron Spettl)

Keywords: structure-property relationship, agglomerate breakage, DEM simulation, stochastic microstructure model, statistical analysis

1. Introduction

In recent years, more and more powerful computational resources permit the numerical investigation of bulk properties of particles based on the discrete representation of the material. The discrete element method (DEM) is a modern method to numerically simulate the detailed behavior of a large number of particles based on contact models describing their contact mechanics [1]. For example, DEM has become an important tool for understanding agglomerate breakage. Such knowledge about breakage mechanisms is used to optimize production processes, e.g., granulation [2] and grinding [3]. There are still many open questions and unknown relationships. One example is the relationship of the morphology of agglomerates to their mechanical behavior. Important influencing structural factors are agglomerate shape, the size, shape, packing structure and coordination number of primary particles as well as their bonding mechanism. Different aspects have been investigated in the past. The fracture behavior resulting from impact of agglomerates was investigated with the focus on the effect of impact velocity, impact angle, agglomerate size and material parameters [4, 5, 6, 7, 8]. Regarding morphology, it was seen that dense and loose agglomerates behave differently in terms of the mode of failure [9]. The bond parameters were determined to be one dominating factor, together with impact velocity [10]. The effect of agglomerate shape was analyzed by performing DEM simulations for spherical, cuboidal and cylindrical agglomerates [11]. Besides the dynamical behavior in such impact tests, the behavior under static loading is also important for understanding materials. A spherically shaped and an irregularly shaped agglomerate were compared and a vastly different behavior was observed under compressive load, although structural characteristics like particle size distribution and coordination number were the same [12]. Cylindrical agglomerates were investigated and the formation of cracks was described [13]. On the other hand, the size and shape of primary particles is also of relevance. Agglomerates consisting of nanoparticles exhibit much greater strength than agglomerates made of micron-sized particles [14]. This was known before from systematic investigations of the strength of agglomerates [15, 16, 17], an overview is given in [18]. Of course, the microstructure plays a central role for larger particles, too, e.g., in the crushing of rocks [19] or their mechanical behavior, which is influenced by the shape of primary particles [20]. In [21], it is shown that DEM is also suitable to investigate the effect of different microstructures under bending load. All these studies show that individual aspects can be explained, but a more general understanding is desirable.

The bonded-particle model (BPM) [22] is a common approach to simulate the mechanical behavior of agglomerates numerically using DEM, where the agglomerate microstructure is specified by a dense packing of spheres that are bonded together. Usually, agglomerate microstructures are generated such that these packings of (bonded) primary particles have similar properties as observed experimentally in real agglomerates, see e.g. [13, 23]. A flexible framework for generating tailored microstructures is a further step to deepen the understanding of relationships between structural and mechanical properties on a broad scale.

In this paper, DEM simulations are used to evaluate the mechanical behavior of spherical agglomerates whose microstructure is generated according to a flexible (parametric) stochastic model. Realizations of the proposed stochastic microstructure model are suitable as input to the BPM, i.e., primary particles are spherical, non-overlapping and connected by bonds. Advantages of the proposed stochastic model are precise control about the microstructure including its 'randomness' and reasonable properties like isotropy or connectivity of the agglomerate. The stochastic model is used to generate agglomerates with specific microstructural properties. As an example, two primary particle sizes are used to generate agglomerates and a mixing ratio describes the volume fraction of the larger primary particles. This mixing ratio is then varied, whereas material parameters and all other properties like agglomerate diameter, primary particle volume and binder volume are kept fixed. A statistical approach is used to draw conclusions about the breakage behavior, where a database of a large number of agglomerates with different mixing ratios is generated. Each of these agglomerates is uniaxially compressed, their evolving microstructure during compression is saved and their breakage is analyzed.

Note that the stochastic microstructure model considered in the present paper was not (yet) fitted to experimentally characterized agglomerate microstructures, although this would be an option for future research. This kind of fitting (simulated) microstructures to experimental image data has been done for the stochastic model proposed in [24], which was used in [25] to determine the mechanical behavior of real and virtually generated alloy microstructures by help of the finite element method. For more general quantitative relationships between microstructure and physical properties see e.g. [26], where a formula has been derived which expresses effective transport properties of porous materials by three important structural characteristics.

The stochastic model introduced in the following facilitates the automated generation of a large number of agglomerate microstructures. These are random, but nonetheless their structural properties can be controlled easily. Based on this stochastic microstructure model we investigate the effect of mixing of two primary particle sizes, where we show that relationships between microstructure and mechanical behavior can be revealed. These are partially expected, but also previously unknown behavior is observed.

2. Methods

In this paper spherical glass agglomerates with a diameter of 8 mm have been investigated. The primary particles have been bonded with a polymer binder, namely hydroxypropyl methylcellulose (HPMC). Main material parameters are listed in Table 1.

le 1. Main material parameters of prima	ry particles and be
parameter	value
primary particles (glass):	
density	$2500 \mathrm{kg/m^3}$
Young's modulus	$6\cdot 10^{10}\mathrm{Pa}$
Poisson ratio	0.21
binder (HPMC):	
Young's modulus	$4 \cdot 10^8 \mathrm{Pa}$
normal and tangential strength	$5\cdot 10^7\mathrm{Pa}$

Table 1: Main material parameters of primary particles and bonds

The primary particles are arranged with a packing density of 56 %, which corresponds to the very loose random packing of spheres. To determine the influence of primary particle sizes, two different sizes of primary particles are used: first, a radius of $r_1 = 0.5$ mm, and second, a radius of $r_2 = 0.25$ mm. Then, a mixing ratio $a \in [0, 1]$ specifies the volume fraction contributed by the larger particles with radius r_1 . Consequently, particles with radius r_2 contribute the remaining volume (i. e., a fraction of 1 - a). In dependence on the mixing ratio, the number of primary particles in agglomerates has been varied between 300 and 2 300. The binder volume is held constant at 10 % of the total volume of the primary particles. Solid bridges are represented by cylindrical bonds and the ratio of the bond radius to the radius of the smallest particle in the contact is 0.4.

The generation of agglomerate microstructures is explained in Section 2.1. Details of the compression experiment and DEM simulations are given in Section 2.2, whereas in Section 2.3 automated breakage detection is shortly discussed.

2.1. Stochastic microstructure model

This section introduces the stochastic model used to generate agglomerate microstructures. Important properties of the random microstructure are isotropy, non-overlapping primary particles, connectivity and further userdefined constraints like a random mixing ratio or constant binder volume.

Configurations of primary particles are often obtained by sphere packing algorithms. One common method to obtain sphere packings is given by so-called *collective-rearrangement algorithms* [27], which repeatedly shift a given set of spheres with the aim to reduce and finally remove sphere overlapping. For example, the *force-biased algorithm* [28, 29] is a frequently used collective-rearrangement algorithm. Given that the initial configuration of overlapping spheres is generated homogeneously and isotropically, the resulting set of spheres is homogeneous and isotropic, too. This means that there is no preferred direction for e.g. contacts between particles and there is no spatial gradient in the packing density. These are reasonable assumptions for spherical agglomerates produced by e.g. spray granulation and we restrict ourselves to this case. However, non-homogeneous agglomerates occur in reality, too, e.g., agglomerates with spatially varying packing density or agglomerates having a core-shell structure—these could be modeled by extending the present approach.

For most collective-rearrangement algorithms direct contacts between particles are not guaranteed (or even unlikely) [28], because particles are shifted apart based on a rule considering all local overlappings. Therefore, bonds are required to connect the primary particles; this bond network corresponds to the solid bridges consisting of binder material. It is clear that all particles of a single agglomerate should be connected to each other, either directly or indirectly. One possibility to generate a set of bonds is to connect two particles if the distance between their surfaces is below a certain threshold. If this threshold is too small, then the system of particles may not be connected. A further problem with this approach is that the volume of the bonds is hard to control, especially if it should be small.

In the following, the developed stochastic model for random microstructures of agglomerates is explained, where these points are addressed. The positions of primary particles are random, and the sizes of primary particles follow a given distribution. In this paper, the size distribution of primary particles is controlled by a (randomly chosen) mixing ratio. Thus, the generation of primary particles forming an agglomerate is a two-stage procedure. First, a mixing ratio $a \in [0, 1]$ is sampled from the uniform distribution U(0, 1) on the interval [0, 1]. Then, given the mixing ratio $a \in [0, 1]$, the sizes of primary particles are sampled from a certain (conditional) size distribution. Bonds between primary particles are generated such that the agglomerate has no disconnected part, while targeting a given binder volume at the same time.

2.1.1. Parameters of the model

A spherical shape is assumed for agglomerates, where we denote the agglomerate radius by r. The sampling domain W is therefore a sphere $B(o,r) \subset \mathbb{R}^3$ located at the origin o with radius r. The primary particles are also spheres and their radii are drawn from (independent copies of) a random particle radius R_p . The targeted volume fraction of primary particles simulated in W is given by the packing density $\eta \in (0, \eta_{\max}]$, where the maximal possible packing density η_{\max} depends on the radius distribution of the primary particles (e.g., $\eta_{\max} \approx 0.71$ for equal spheres [29]). The total volume of bonds is given as a ratio b > 0 with respect to the total volume of the primary particles. The bonds are cylindric objects connecting two primary particles. For a bond connecting two particles with radii r' and r'', the bond radius r_b is given by $r_b = k_b \cdot \min\{r', r''\}$ for some factor $k_b \in (0, 1]$.

In order to look at mixtures of primary particles with two fixed sizes (i.e., radii r_1 and r_2 , $r_1 > r_2$), the random particle radius R_p mentioned above is defined as a discrete random variable. It takes the value r_1 with some probability $p \in [0, 1]$, and r_2 with probability 1 - p. The probabilities p and 1 - p can be interpreted as the number fractions of larger and smaller particles, respectively. The mixing ratio a specifies the volume fraction of the larger particles, i. e., $a \in [0, 1]$ is the volume fraction of the particles with radius r_1 , namely

$$a = \frac{p \cdot v_1}{p \cdot v_1 + (1 - p) \cdot v_2},$$
(1)

where $v_i = \frac{4}{3}\pi r_i^3$ denotes the volume of a sphere with radius r_i , for i = 1, 2.

Table 2 provides an overview of the parameters of the stochastic microstructure model. All parameters except the mixing ratio are fixed. The mixing ratio a is varied in the interval [0, 1]. It is chosen uniformly from [0, 1] for every sampled agglomerate, i. e., a random variable $A \sim U(0, 1)$ is considered to generate samples of a. Note that for each given mixing ratio a, the probability p of larger particles (with radius r_1) is determined using Eq. (1).

Table 2: Parameters of stochastic microstructure model		
parameter	value	
agglomerate:		
radius of agglomerate	$r = 4 \mathrm{mm}$	
primary particles:		
radius of large primary particles	$r_1 = 0.5 \mathrm{mm}$	
radius of small primary particles	$r_2 = 0.25 \mathrm{mm}$	
(random) mixing ratio	$A \sim U(0, 1)$	
binder:		
binder volume fraction	b = 0.1	
radius factor for bonds	$k_b = 0.4$	

2.1.2. Random packing of primary particles

Given the sampling domain W = B(o, r) of a spherical agglomerate, the random variable R_p for radii of primary particles and the packing density η (see Section 2.1.1), the algorithm to obtain a random packing of primary particles is given by

- 1. Initialize the set of spheres/particles: $P = \{\}$.
- 2. Choose the center x' of a new sphere candidate uniformly inside the sampling domain W and sample the radius r' from the random variable R_p .
- 3. If the volume fraction η of particles is not exceeded, i.e.,

$$\left(\sum_{(x_p,r_p)\in P} \frac{4}{3}\pi r_p^3 + \frac{4}{3}\pi (r')^3\right) / \operatorname{vol} W \le \eta \,,$$

then accept the sphere candidate, i.e., $P = P \cup \{(x', r')\}$, and repeat step 2, else proceed with step 4.

4. Apply the *force-biased algorithm* [28, 29] to the set of spheres P, which rearranges them iteratively to avoid interparticle overlaps. To obtain an approximation of the agglomerate shape specified by the boundary of W, spheres are pushed back into the sampling domain at each iteration step.

Figure 1 illustrates the results of steps 1-3 and 4 in the two-dimensional case.



Figure 1: Illustration of initial arrangement of spheres and spheres after collective rearrangement by force-biased algorithm.

2.1.3. Bond network model

At this point, the set of sphere centers and radii $P = \{(x_i, r_i), i = 1, \ldots, n\}$ is known. These primary particles have to be connected by bonds such that the union of all bonds has a given volume. This volume is obtained as a fraction b with respect to the total volume of primary particles. The idea is to construct an agglomerate where all particles being sufficiently close together are connected and further bonds are only inserted where necessary to obtain connectivity. Then, the volume of bonds can be controlled by the thresholding value used to connect particles. If this threshold is zero, then only as many bonds as necessary are generated to obtain connectivity. For larger thresholds, the number of bonds (and their total volume) is increased.

This can be implemented as an algorithm using ideas from graph theory. For a given distance threshold $l \ge 0$, we will construct a graph $G^{(l)} = (V, E^{(l)})$ that connects the set of vertices (particles) V = P by the set of edges (bonds) $E^{(l)}$. A bond between two particles is only put if the smallest distance between their surfaces is less than or equal to l or if the bond is required for complete connectivity, i.e., every primary particle has be connected directly or indirectly to all others via the bond system. Such a graph $G^{(l)}$ can be obtained by the following algorithm, which is illustrated in Figure 2.

1. Compute the relative-neighborhood graph (RNG) [30] $G_{\text{RNG}}^{(l)}$ of the primary particles, using a suitable distance function $d: V \times V \to [0, \infty)$ (see below). In the RNG, an edge is put between two vertices when there is no third vertex closer to both vertices (with respect to d). Using this technique, the vertices (primary particles) are always completely connected by the edges in the RNG [30]. A suitable distance function d is given by

$$d((x',r'),(x'',r'')) = \max\{0, \|x'-x''\| - r' - r'' - l\}.$$

By this construction, the RNG contains all edges that connect two particles within a given distance l and further edges ensuring complete connectivity. Therefore, $G_{\rm RNG}^{(l)}$ fulfills most properties desired for $G^{(l)}$, but it may contain more edges than necessary for connectivity. More precisely, it is a superset of the graph we are interested in, whose construction is explained in the next step.

- 2. Compute the minimum spanning tree (MST) [31] $G_{\text{MST}}^{(l)}$ of $G_{\text{RNG}}^{(l)}$, again using the same distance function d, now applied to the existing edges. In the MST, as much edges as possible are deleted while minimizing the sum of distances and upholding connectivity.
- 3. The result $G^{(l)}$ is given by the edges of the graph $G^{(l)}_{\text{MST}}$ combined with all edges in $G^{(l)}_{\text{RNG}}$ having 'length' zero, i.e., their primary particles' surfaces have at most a distance of l.

Note that the MST of a complete graph (where every pair of vertices is connected by an edge) is always a subgraph of its RNG [30], therefore we consider the RNG in the first step and then compute the MST. Obtaining the MST is the main goal. In principle, it would also be possible to construct the complete graph and compute the MST directly from it, the result is exactly the same. But this can be much more expensive from the computational point of view if the number n of primary particles is large. A further technical detail is that the MST is only unique if all edges have different lengths. In our case, there are many edges with length zero (obtained by distance function d). However, this is not a problem, because step 3 of the algorithm stated above ensures that all these edges are re-added, i. e., it does not matter which ones remain in the MST.



Figure 2: Illustration of relative-neighborhood graph (RNG) for l = 0 (direct contacts are shown in solid black, further connectivity bonds are gray) and minimum spanning tree (MST) for the same graph.

Recall that for a given threshold value $l \ge 0$, $G^{(l)}$ is the graph connecting all particles that are within distance l to each other, plus further bonds that are required for connectivity. Detection of the 'optimal' threshold value l^* can be formulated as a minimization problem

$$l^{\star} = \arg\min_{l \ge 0} \left| \sum_{e \in E^{(l)}} \operatorname{vol} B(e) - b_{\operatorname{abs}} \right| ,$$

where b_{abs} is the absolute binder volume targeted and vol B(e) denotes the volume of the bond specified by edge e. Note that this minimization problem may not have a sufficiently good solution if there are e.g. large spaces between primary particles, large bond radii or very small targeted total binder volumes. In these cases it is possible that even for l = 0 the bonds generated for connectivity have a total volume that is too large and not within an acceptable tolerance.

2.1.4. Statistical analysis

Before investigating the breakage behavior of the agglomerates generated by the proposed stochastic model, it is interesting to look at some characteristics of the simulated microstructures. The agglomerate diameter as well as the porosity are always the same, but it is useful to analyze the primary particle radii, coordination numbers and bond radii in dependence on the mixing ratio. For an optical impression, three agglomerates with different mixing ratios are shown in Figure 3. For all evaluations, 300 agglomerates have been generated according to the stochastic microstructure model. (Note that the number of realizations has been chosen as high as possible such that computing time required for generation and DEM simulations is still acceptable.)



Figure 3: Three realizations of agglomerates for mixing ratios a = 0.0 (top), a = 0.45 (middle), and a = 0.99 (bottom). The larger primary particles are visualized in blue, the smaller primary particles in yellow. For all three agglomerates one eighth has been cut out for visualization of the interior microstructure.

The mean radius of primary particles (unweighted, i.e., not weighted by their volume or mass) clearly depends on the mixing ratio a, see Figure 4, because a larger fraction of the large primary particles increases the mean radius directly. As a consequence, the mean radius of bonds is also increased. More interesting is the behavior of the coordination numbers, i. e., the number of bonds per primary particle. A larger value of the mean coordination number implies that the system of particles is better connected. Figure 5 shows that the mean coordination number is a bit smaller for very small and very large mixing ratios a than for intermediate 'mixing' scenarios. On the other hand, the standard deviation (SD) is obviously largest in the range of $a \in [0.6, 0.8]$, where it achieves a value of almost 4 in comparison to about 2 for very low/high mixing ratios. This can be interpreted as a higher variability of the microstructure.



Figure 4: Effect of mixing ratio on the radii of primary particles (black) and bonds (gray): mean radius (left), standard deviation of radii (right).

2.2. DEM simulations

For all 300 agglomerates discussed in Section 2.1 uniaxial compression experiments have been simulated with the help of DEM. A wall with the typical material parameters of steel is lowered with a constant speed, see Figure 6 for a schematic illustration of the experiment. Displacement of particles, breakage of bonds and applied forces are recorded. For every DEM simulation, the result is a force-displacement curve and the time-resolved agglomerate microstructure.



Figure 5: Effect of mixing ratio on the coordination numbers of primary particles: mean coordination number (left), standard deviation of coordination numbers (right).



Figure 6: Schematic illustration of the experiment, forces are visualized using colors (blue, green and red for low, medium and high forces, respectively).

All DEM simulations were performed with the command line version of the MUSEN system [32]. To describe particle-particle and particle-wall interactions the soft sphere contact model is employed. The normal component of the force is calculated according to the Hertz theory [33] and the tangential component according to the model proposed in [34], see also [35]. The solidbridge bond model is based on the BPM [22]. However, modifications have been implemented. For each bond the unique normal and tangential stiffness has been calculated depending on material parameters and bond length. As the breakage criteria the maximum of shear and tensile stresses in the bonds are used. If one of them reaches the corresponding bond strength, then the bond breaks and is removed from the calculation procedure. All material pa-

rameters required for the DEM simulations are given in Table 1 and Table 3.

Table 3: Further material parameters for the DEM simulations		
parameter	value	
interactions between primary particles:		
static friction	0.2	
rolling friction	0.05	
wall (steel):		
Young's modulus	$2\cdot 10^{11}\mathrm{Pa}$	
Poisson ratio	0.3	
interactions between primary particles	and wall:	
static friction	0.2	
rolling friction	0.05	

The DEM simulation time step used is chosen as 10% of the Rayleigh time. Usually, in compression experiments the compression velocities in the order of 0.01 mm/s to 0.1 mm/s are employed. However, to speed-up the computations, the wall velocity in the numerical studies has been chosen equal to 0.02 m/s. A set of additional simulations was done and it was pointed out that the proposed increase of the velocity does not have significant influence on simulation results. The DEM simulations have been performed until a deformation of 35% of the agglomerate is observed. At this deformation, all agglomerates were fractured. The force-displacement diagram and the time-resolved microstructure were saved with a time resolution of 0.4 ms.

2.3. Agglomerate breakage

Agglomerate breakage has to be detected using automated methods to analyze the compression results of all agglomerates statistically. Especially with varying mixing ratios, it is not useful to aggregate all force-displacement diagrams directly. Available data for breakage detection is the force-displacement curve for every agglomerate, its complete initial microstructure and the displacement of primary particles as well as breakage of bonds over time.

Figure 7 shows the force-displacement curves for agglomerates with different mixing ratios, i. e., mixing ratios in the intervals [0.0, 0.04], [0.18, 0.22], [0.78, 0.82] and [0.96, 1.0]. A sudden drop in the force means that one or more bonds got broken, a large drop occurs at more significant defects. In most cases these curves show a clear drop in the force when the primary break occurs. This seems to be the case for almost the same displacement values (which is proportional to the time due to constant wall speed), but the maximum force applied before is different. This will be discussed in Section 3.



Figure 7: Force-displacement curves obtained for different mixing ratios *a*: almost only small primary particles (top-left), about 80 vol% small primary particles (top-right), about 80 vol% large primary particles (bottom-left) and almost only large primary particles (bottom-right).

There exist two grades of damages that occur in agglomerates: the microscopic destruction, when the breakage of individual interparticulate contacts occurs, and the macroscopic, when a granule is detached into two or more disjoint parts [36]. In many research works the primary breakage event is determined based on the analysis of force-displacement curves only, as the point where the force curve has the first significant drop [13, 37]. However, it should be noted that such an approach does not allow to distinguish between the microscopic and macroscopic damages and hence cannot be used for detection of agglomerates' fracture. For example, granules with core-shell structures are often investigated: it is necessary to analyze their microstructure to determine their breakage mechanisms, i.e., to determine whether only the shell or both core and shell are fractured, which cannot be decided using only force-displacement data [38]. For this reason, the breakage detection by evaluation of the microstructure has been employed in this work. This is clearly the best method to obtain precise information about the energy required for fracture and the new specific surface area which is formed during the fracture [39]. When the total volume of small fragments is negligible, in many cases the fracture process is considered as attrition. Therefore, the breakage event in the developed algorithm was detected only when the initial agglomerate was splitted into two or more disjoint parts and the volume of the largest part was less than 90% of the initial agglomerate volume. Moreover, the small fragments consisting of less than four primary particles were considered as debris and therefore were excluded from the volume-ratio analysis. Several randomly selected agglomerates are visualized in Figure 8, where the two largest fragments are highlighted.

3. Results and discussion

Two very important characteristics describing agglomerate strength are the maximum force applied before breakage and the required breakage energy. As can be seen in Figure 9 (top-left), the breakage force is smaller for mixing scenarios (scenarios where both fractions of particle sizes are 'relevant', i. e., $a \in [0.2, 0.8]$) than in the "non-mixing" cases. A possible reason is the higher variability in agglomerates with both small and large particles (cf. standard deviation of coordination numbers, Figure 5). This leads to more weak points in the microstructure, where forces are not evenly spread and individual bonds are heavily loaded. Therefore, local fracturing occurs before a high (global) force is applied. This implicates that even for almost only small primary particles (i. e., a < 0.2) the force is considerably higher, which is an interesting observation that was unexpected. The (mass-related) primary breakage energy does not show this behavior, cf. Figure 9 (top-right). It



Figure 8: Six randomly selected agglomerates (ordered by increasing mixing ratio) at the time point determined by the breakage criterion 'at least 10% loss of volume excluding debris'. The largest fragment is drawn in blue, the second largest fragment is in red, further fragments are in dark gray, debris is in light gray. (Note that the optical impression of the size of fragments depends heavily on the point of view, therefore red fragments seem to be larger in some cases.)

seems to increase almost linearly with the mixing ratio, i.e., agglomerates consisting of larger primary particles and thicker bonds are more stable. This means that even though the maximum force is smaller for mixing scenarios, this does not influence the energy required for breakage. Therefore, the average force before breakage has to be similar or the related deformation has to be larger. Figure 9 (bottom) shows the deformation of the agglomerates relative to their original diameter. It can be seen that the deformation at the breakage point really tends to be larger for mixing scenarios, but the fluctuations are in a wide range for all mixing ratios.

A structural characteristic of the agglomerates is the damage ratio, i.e.,



Figure 9: Effect of mixing ratio on maximum force applied before primary break (top-left), mass-related primary breakage energy (top-right), and deformation of the agglomerates at their primary breakage point (bottom). A quadratic function fitted to the data points is shown in red.

the number of broken bonds divided by the initial number of bonds. Looking at the damage ratio in dependence on the mixing ratio, cf. Figure 10 (topleft), the optical impression is similar as for breakage energies. Figure 10 (topright) shows that there is an almost linear relationship between the number of broken bonds and the breakage energy, which is intuitive. Figure 10 (bottomleft) shows the volume fraction of broken bonds (which one could call "volumetric damage ratio"), which is probably a more accurate characteristic in the case of bonds with very different volumes. The optical impression is very similar, but thin bonds are less relevant in scenarios with higher mixing ratios, which leads to smaller values in comparison to the number-based damage ratio. More interesting is the volume fraction of the broken thin and thick bonds individually, see Figure 10 (bottom-right). For a < 0.8, most broken bonds are thin, but beginning at about a = 0.6 the volumetric proportion of broken thick bonds increases fast. Of course, this is caused by the decreasing number of thin bonds. Note that $a \ge 0.6$ is about the same region where the maximum force required for agglomerate breakage increases clearly, too.



Figure 10: Effect of mixing ratio on damage ratio (top-left), relationship of damage ratio and breakage energy (top-right), volume fraction of broken bonds (bottom-left), volume fraction of broken thin and thick bonds (bottom-right).

Figure 11 shows the volume fraction of the largest and second largest fragments depending on the mixing ratio. In the average, the largest fragments stands for 48% of the volume, the second largest fragment corresponds to 34%. The mean volume of the first and second largest fragments together is 83%, which means that 17% of the volume belong to remaining fragments and debris. ('Remaining' fragments are the third, forth etc. largest fragments, which are not yet considered as debris.) A surprising fact is that the size of the two largest fragments does not really depend on the mixing ratio. The volume fraction of debris increases a bit with larger primary particles — but of course even a small number of large debris particles has a visible effect on the volume.



Figure 11: Effect of mixing ratio on volume fraction of largest fragment (top-left), second largest fragment (top-right) and remaining fragments together with debris (bottom).

4. Conclusions and outlook

In this paper, a stochastic model for agglomerate microstructures is introduced. It is constructed such that the microstructural features can be controlled easily. The stochastic model is used to vary the mixing ratio of two sizes of primary particles. Special care is taken to obtain comparable agglomerate microstructures even for different mixing ratios. For example, primary particle volume and binder volume are the same in all cases. A large number of spherical agglomerates with the same diameter are realized, assuming spherical glass primary particles and HPMC as binder. A statistical analysis of the generated microstructures shows that the mean coordination number is almost constant, but the standard deviation is considerably larger for mixing scenarios, which can be interpreted as a higher variability of the microstructure. All agglomerates have been simulated at the compressive normal load using the MUSEN software, where the force-displacement curves and the time-resolved microstructure is obtained for analyses. Finally, evaluation of agglomerate breakage based on these data shows that the behavior of agglomerates is influenced in different ways. Breakage energy depends on the mixing ratio almost linearly, but the maximum force applied before the primary break is influenced by the variability of the microstructure. Larger forces are necessary for agglomerates that are very homogeneous, i.e., consisting almost only of particles of one size. This is not only the case for large primary particles (where thick bonds are dominating the behavior), but also for small primary particles and thin bonds. The fracture behavior itself on the other hand is very similar in all cases and does not depend on the mixing ratio.

These results show that sophisticated models for random microstructures with a high control about individual structural features are a promising approach for revealing previously unknown behavior or confirming existing hypotheses. They should be applied in future work to improve the general understanding of agglomerates and particulate materials. Therefore, this paper is only a first step to further investigations of relationships between microstructure and mechanical behavior and to usage of obtained data for e.g. macroscopic flowsheet simulations [40]. For quantitative statements about relationships between microstructure and mechanical stability, a larger range of scenarios should be investigated, e.g., for other materials, other agglomerate diameters (and agglomerate shapes), other primary particle size distributions and other bond networks. Furthermore, an important step is to assess the accuracy of the predicted behavior. Therefore, experiments are planned to validate the obtained numerical results. In a forthcoming paper, we will represent real agglomerate microstructures using our stochastic modeling approach. Then, the results obtained from DEM simulations will be validated with experiments that were previously performed for the same agglomerates.

Acknowledgements

This work was funded by the Deutsche Forschungsgemeinschaft under grant number SCHM 997/14-1 in the priority program 1679 "Dynamische Simulation vernetzter Feststoffprozesse".

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