Numerical modeling of collision of adhesive units: Stability and mechanical properties during handling

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A R T I C L E   I N F O

Article history:
Received 27 June 2019
Received in revised form 6 November 2019
Accepted 17 November 2019

Keywords:
Adhesive mixtures
Discrete element method
Dry powder inhalers (DPI)
Carrier particles

A B S T R A C T

Binary interaction between adhesive units formed from monodisperse spherical fines and carrier particles was studied with the discrete element method (DEM) in order to better understand phenomena such as lumping, bridging and flowability of adhesive units and mixtures. Three different surface coverage ratios (SCRs) representing different number of fines on the carrier, five different surface energies of interaction between fines and carrier, fifteen different relative velocities ranging from 0.04 m/s to 1.7 m/s were studied, with three replicates for each scenario. A total of over 700 independent simulations were conducted and stability ratios (retention, transfer and loss) and mechanical properties (coefficient of restitution) were determined. The critical velocity for the units, below which they tended to aggregate, was extracted. The units with high SCR and high surface energy were most stable and most cohesive. With increasing SCR, the fines tended to act as a damping pad, thus increasing the critical velocity. The adhesive units were found to be dynamic in nature and to undergo constant exchanges of particles. A detailed map of this behaviour was determined. The obtained findings constitute a first step towards the creation of multiscale DEM models for the mechanics of adhesive mixtures and provide insights into flowability and integrity of the mixtures.

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1. Introduction

Drug delivery through a dry powder inhaler (DPI) is a standard means of treating pulmonary and respiratory diseases (Islam and Gladki, 2008). DPIs use a special kind of mixture known as adhesive mixture, which consists of micronised active pharmaceutical ingredient (fines) (<5 μm) and comparatively larger carrier particles (~100 μm). Dry powder coating is one of the most commonly used techniques for formation of such units (Gradon and Sosnowski, 2014; Telko and Hickey, 2005). Adhesive units are complex (De Boer et al., 2012; Grasmeijer et al., 2015) and a lot of attention has been given to their formulation and manufacturing. There is an increasing interest being focused on dosage forms with higher drug loads (Rudén et al., 2018). Manufacturing and handling of these units rely upon the crucial cohesive-adhesive balance in the unit (Begat et al., 2004a; Begat et al., 2004b; Young et al., 2005).

Several numerical studies of adhesive mixtures and units have been performed using Computational Fluid Dynamics (CFD) and the Discrete Element Method (DEM), mostly focusing on dispersion performance in the inhaler (Yang et al., 2014; Yang et al., 2015a; Nguyen et al., 2014; Nguyen et al., 2015a). van Wachem et al. (2017) performed simulations of adhesive units at the micro, meso and macro scales in an attempt to study dynamics of the particles inside an inhaler. Collision of adhesive units with a static wall has been of considerable interest (Thornton et al., 1996; Ning et al., 1997; Thornton et al., 1999; Thornton and Liu, 2004; Moreno-Atanasio and Ghadiri, 2006). Yang et al. conducted further studies to probe the effect of electrostatic charge on the adhesive unit (Yang et al., 2015b).

Recently there has been increased interest in studying particle mixing through DEM simulations (Tamadondar et al., 2017). There have been studies on agglomeration and deagglomeration of fines in DPIs (Yang et al., 2015a; Yang et al., 2013; Yang et al., 2005) and of the effect of interface energy on impact strength of agglomerates (Subero et al., 1999). Nguyen et al. have investigated breakage, adhesion of fine-particle agglomerates and mechanistic time scales in adhesive mixing (Nguyen et al., 2015b; Nguyen et al., 2018). Tamadondar et al. have focused on effect of collision velocity, collision angle, carrier shape (Tamadondar et al., 2019) and interaction energy (Tamadondar et al., 2018) between particles during high shear mixing (Tamadondar et al., 2017). However, little attention has been given to the particle dynamics during handling, packaging and storage (Le et al., 2012; Jashnani et al., 1995). The...
Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>SCR</td>
<td>Surface Coverage Ratio</td>
</tr>
<tr>
<td>DEM</td>
<td>Discrete Element Method</td>
</tr>
<tr>
<td>DPI</td>
<td>Dry Powder Inhaler</td>
</tr>
<tr>
<td>x_i</td>
<td>Position of Particle i</td>
</tr>
<tr>
<td>M</td>
<td>Torque</td>
</tr>
<tr>
<td>R</td>
<td>Radius</td>
</tr>
<tr>
<td>(v)</td>
<td>Poisson’s Ratio</td>
</tr>
<tr>
<td>(E)</td>
<td>Young’s Modulus</td>
</tr>
<tr>
<td>(\epsilon)</td>
<td>Equilibrium Separation Distance</td>
</tr>
<tr>
<td>(F_{ne})</td>
<td>Normal Elastic Force</td>
</tr>
<tr>
<td>(\delta_{n})</td>
<td>Normal overlap</td>
</tr>
<tr>
<td>(e)</td>
<td>Coefficient of Restitution</td>
</tr>
<tr>
<td>(\omega)</td>
<td>Angular velocity about center of mass</td>
</tr>
<tr>
<td>(F_{el})</td>
<td>Tangential damping force</td>
</tr>
<tr>
<td>g</td>
<td>Acceleration due to gravity</td>
</tr>
<tr>
<td>(f_{nc})</td>
<td>Normal component of force</td>
</tr>
<tr>
<td>(f_{tc})</td>
<td>Tangential component of force</td>
</tr>
<tr>
<td>(F_{fluid})</td>
<td>Fluid forces</td>
</tr>
<tr>
<td>I</td>
<td>Inertial tensor</td>
</tr>
<tr>
<td>M</td>
<td>Mass</td>
</tr>
<tr>
<td>G</td>
<td>Shear Modulus</td>
</tr>
<tr>
<td>(\mu)</td>
<td>Tabor Parameter</td>
</tr>
<tr>
<td>(\Gamma)</td>
<td>Surface Energy</td>
</tr>
<tr>
<td>(F_{ce})</td>
<td>Pull off force</td>
</tr>
<tr>
<td>(\delta_{c})</td>
<td>Critical overlap</td>
</tr>
<tr>
<td>(v)</td>
<td>Relative velocity</td>
</tr>
<tr>
<td>(F_{te})</td>
<td>Tangential elastic force</td>
</tr>
<tr>
<td>(F_{nd})</td>
<td>Normal damping force</td>
</tr>
</tbody>
</table>

where \(M\) is the applied torque, \(I\) is the inertial tensor and \(\omega\) is the angular velocity about the center of mass.

Interaction between two unequal sized particles is described in terms of effective properties of the interaction (Thornton and Ning, 1998; Thornton and Yin, 1991): The effective radius \(\bar{R}\), determined as

\[
\frac{1}{\bar{R}} = \frac{1}{R_i} + \frac{1}{R_j}.
\]

(3)

the effective mass \(\bar{M}\),

\[
\frac{1}{\bar{M}} = \frac{1}{M_i} + \frac{1}{M_j}.
\]

(4)

the effective Young's modulus \(\bar{E}\),

\[
\bar{E} = \frac{1 - \nu_j^2}{E_i} + \frac{1 - \nu_i^2}{E_j}.
\]

(5)

and the effective shear modulus \(\bar{G}\),

\[
\bar{G} = \frac{2 - \nu_i}{G_i} + \frac{2 - \nu_j}{G_j}.
\]

(6)

In these expressions, \(R_i\) is the radius, \(M_i\) the mass, \(E_i\) Young’s modulus, \(G_i\) the shear modulus and \(\nu_i\) Poisson’s ratio for particle \(i\) (and analogously for particle \(j\)). The derivation of Eq. (5) relies on the isotstress condition (Johnson and Johnson, 1987). Moreover, only two of the elastic constants are independent so that \(G_i = E_i/[2(1 + \nu_i)]\) (and analogously for particle \(j\)).

The Tabor parameter \(\mu\) (Tabor, 1977) is a measure of the extent to which adhesive forces are capable of deforming the particles and is used to identify the interaction mode to be used. Tabor parameter is defined as,

\[
\mu = \left( \frac{R^2 \Gamma E^2}{\Gamma^2 E^3} \right)
\]

(7)

where \(\epsilon\) is the equilibrium separation distance between two spheres. For \(\mu < 1\), the DMT (Derjaguin–Muller–Toporov) (Derjaguin et al., 1975) model is preferred and for \(\mu > 1\), the JKR (Johnson–Kendall–Roberts) (Johnson and Johnson, 1987) model is used. The parameter was calculated for all interaction between particles (fines-fines, fines-carrier, carrier-carrier) and was found to be greater than 1. Therefore, the JKR model is chosen.

According to the JKR model, the normal elastic force \(F_{ne}\) is obtained as a function of the contact area \(a\) as (Marshall, 2009),
\[
\frac{F_{ne}}{F_t} = 4 \left[ \left( \frac{a}{a_0} \right)^3 - \left( \frac{a}{a_0} \right)^2 \right]
\] (8)

Here, \( F_t \) is the pull off force, i.e. the force needed to separate particles in contact, calculated as
\[
F_t = 3\pi\Gamma R^2
\] (9)

where \( \Gamma \) is the surface energy of the interaction between the particles. Moreover, \( a_0 \) represents the finite contact area that due to force of adhesion exists when no external force is applied, obtained as,
\[
a_0 = \left( \frac{9\pi\Gamma R^2}{E} \right)^{\frac{1}{2}}
\] (10)

The contact area is in turn related to the normal overlap \( \delta_n \) by an expression of the form (Johnson et al., 1971)
\[
\frac{\delta_n}{\delta_c} = 6\left[ 2\left( \frac{a}{a_0} \right)^2 - 4\left( \frac{a}{a_0} \right)^2 \right]
\] (11)

where \( \delta_c \) is the particle overlap at the critical point, defined as
\[
\delta_c = \frac{a_0^2}{2(6)^{1/3}R^2}
\] (12)

The normal damping force \( F_{nd} \) is expressed as (Marshall, 2009)
\[
F_{nd} = 2\sqrt{\frac{5}{6}}\beta \sqrt{S_n} M^n v_n
\] (13)

where \( \beta \) is a parameter that is calculated from the coefficient of restitution \( e \) as
\[
\beta = -\frac{\ln(e)}{\sqrt{\ln^2(e) + \pi^2}}.
\] (14)

Moreover, \( S_n \), defined as
\[
S_n = 2E\sqrt{R}\delta_n
\] (15)

is a normal stiffness and \( v_n \) is the magnitude of the normal relative velocity between the particles. We note for future reference that the coefficient of restitution is a measure of the elasticity of the particle interaction, being defined as
\[
\varepsilon = \frac{v_{after}}{v_{before}}
\] (16)

where \( v_{before} \) and \( v_{after} \) is the relative velocity of the particles before and after collision respectively. The tangential elastic force is given by Mindlin (1953),
\[
F_{te} = S_t \delta_t
\] (17)

where \( S_t \), defined as
\[
S_t = 8G\sqrt{R}\delta_n
\] (18)

is the tangential stiffness. The tangential damping force is defined as,
\[
F_{td} = 2\sqrt{\frac{5}{6}}\beta \sqrt{S_t} M^n \nu_t
\] (19)

In summary, the normal and tangential forces both have elastic and damping contributions that are calculated from the normal and tangential overlaps and relative velocities between the particles.

3. Method

3.1. Particle description

Fines and carriers were modeled as elastic spheres of 3 and 100 \( \mu \)m diameter, respectively. The particle sizes and model parameters (Table 1) were chosen to be representative for mannitol as carrier and lactose as fines (Nguyen et al., 2014; Ning et al., 1997; Moreno-Atanasio, 2012; Tong et al., 2009). Various combinations of surface energies ranging between 0.01 and 0.05 J/m\(^2\) were investigated. Each specific combination is designated as \( \Gamma_x-y \), where \( x \) represents the surface energy of the carrier-carrier interaction and \( y \) represents the surface energy of the fines-fines interaction (both in J/m\(^2\)). The dash represents the cross interaction between carriers and fines.

The JKR cohesion model was used to model adhesive/cohesive interaction between particles and the mechanistic behaviour was modelled using the Hertz–Mindlin model. For simplicity, monodisperse elastic carriers and fines were assumed, with no breakage or plastic deformation, but the model can be extended to polydisperse particles.

3.2. Adhesive unit

Ordered units comprising of fines attached to large carriers are referred to as adhesive units. The adhesive units were formed by pseudo-randomly distributing fines onto the surface of carriers. The process of creation of an adhesive unit was divided into 4 stages as shown in Fig. 1.

Stage 1

A uniform envelope of evenly spaced fines was created around the carrier based on simple cubic packing, leaving a gap between the fines to prevent physical overlap at the point of particle creation.

Stage 2

Each of the fines created in Stage 1 was given a random velocity between \(-1\) and \(1\) m/s which followed a gaussian distribution. Hence each of the fines followed a different trajectory, leading to collisions and the formation of smaller aggregates of fines in addition to randomly distributed individual fines on the carrier. The aggregation and movement depended upon the interaction energy between the particles.

Stage 3

Each of the fines in the enveloping cloud was given a constant velocity directed towards the centre of the carrier, so that the fines moved towards the carrier and were captured by the adhesion.

Stage 4

The simulation was continued until the system reached a stable equilibrium and most of the energy was dissipated away.

Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Coarse Particle (carrier)</th>
<th>Fine Particle (fines)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle Size (Diameter, ( \mu )m)</td>
<td>100</td>
<td>3</td>
</tr>
<tr>
<td>Poisson’s ratio (–)</td>
<td>0.29</td>
<td>0.12</td>
</tr>
<tr>
<td>Density (kg/m(^3))</td>
<td>1490</td>
<td>1520</td>
</tr>
<tr>
<td>Young’s Modulus (GPa)</td>
<td>0.1</td>
<td>4</td>
</tr>
<tr>
<td>Coefficient of Static Friction (–)</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Coefficient of Rolling Friction (–)</td>
<td>0.002</td>
<td>0.002</td>
</tr>
<tr>
<td>Surface Energy (J/m(^2))</td>
<td>0.01–0.05</td>
<td>0.01–0.05</td>
</tr>
<tr>
<td>Coefficient of Restitution (–)</td>
<td>0.89</td>
<td>0.5</td>
</tr>
</tbody>
</table>
Based on the number of fines on each carrier, a new quantity, the surface coverage ratio (SCR) is defined,

$$\text{SCR} = \frac{N \times \pi r_{\text{fines}}^2}{4\pi r_{\text{carrier}}^2}$$  \hspace{1cm} (20)$$

where \(N\) is the number of fines attached to the carrier, and \(r_{\text{fines}}\) and \(r_{\text{carrier}}\) are the radii of fines and carriers, respectively. The SCR represents the ratio between the projected area of fines on the carrier surface and the surface area of the carrier itself. There are different ways to represent the SCR (Rudén et al., 2018) but the current definition is chosen to simplify calculations. Adhesive units with different SCRs (0.5, 0.7, 1), as calculated by Eq. (20), were formed as shown in Fig. 2.

3.3. Simulation setup

Binary collisions of adhesive units were simulated with different velocities. In total, a set of 15 different relative velocities was investigated, ranging from 0.04 to 1.7 m/s, representing the handling phase. Simulations were performed for adhesive units of different SCRs (0.5, 0.7, 1) and surface energies between fines-fines and fines-carrier (0.01, 0.03 and 0.05 J/m²). In each case, head on collisions between adhesive units was studied.

To account for the variability resulting from random distribution of fines on carriers, three different initial seed values for the pseudo-randomisation were considered and examples of the resulting structures are shown in Fig. 3 for an SCR of 0.5. The simulations were evaluated in terms of the mechanical stability of the adhesive units and the effective mechanical behaviour of the adhesive units, as inferred from their restitution coefficients.

Specifically, the quantification of the stability of the adhesive units was based on three ratios: The Transfer Ratio, defined as the fraction of fines exchanged between the carriers during collision. The Retention Ratio, that represents the fraction of particles which remain adhered to the carriers during collision. The Loss Ratio that represents the fraction of particles which are lost from either of the carrier particles during collision. Fig. 4 shows an illustration of transfer, retention and loss of fines after a head on collision. The coefficient of restitution (e), defined in Eq. (16), was calculated as the ratio between the magnitude of the velocity of each carrier after collision and the magnitude of the initial velocity.

Based on the setup described in the previous section with different SCR, randomisation seed, surface energy and collision velocity, over 700 independent simulations were performed (Fig. 5) and results from each of the simulation were analysed in terms of stability ratios and restitution coefficient.

DEM simulations and analysis were conducted using EDEM© 2019 bulk material simulation software provided by DEM Solutions Ltd., Edinburgh, Scotland, UK with JKR cohesion contact model for a range of surface energy and morphological properties as explained in Section 3. A timestep of 2 ns was chosen which ensured that the overlap period at the interface of two particles was about 50 timesteps which reduces computational errors (Campbell, 2002).

Fig. 1. Stages of formation of adhesive unit with a surface coverage ratio (SCR) of 0.7 and surface energy of interaction 0.03 J/m². The images to the left represent fines particles and carrier particle and the ones to the right represent the particle velocities in vector form.

Fig. 2. Examples of adhesive units with different surface coverage ratios (SCRs) and interaction energy fixed at 0.01 J/m².

Fig. 3. Illustration of the effect of different seed values on the structure of adhesive units with a surface coverage ratio (SCR) of 0.5 and interaction energy fixed at 0.01 J/m².

Fig. 4. Illustration of transfer of fines between adhesive units with a surface coverage ratio of 1 and surface energy 0.05 J/m².
4. Results

4.1. Qualitative picture

Fig. 6 illustrates different steps during the collision process. In Fig. 6a, the two adhesive units approach each other at equal velocity. Based on the surface energy, SCR and the impact velocity, the fines are redistributed on or between the carriers or lost as indicated in Fig. 6b. The adhesive units either adhere to each other or rebound back based on the impact velocity and the interaction energy between them as indicated in Fig. 6c. The transfer or loss of fines occur either independently or as small agglomerates formed during the collision.

As can be seen in Fig. 7, which displays impact between adhesive units (C₀:01/C₀:01) at 0.4 m/s, the net energy and particle loss changes with SCR. This calls for a detailed analysis of stability ratios and the coefficient of restitution which is provided in the next sections.

4.2. Stability ratios

Stability ratios for adhesive units for which all surface energies are equal are shown in Fig. 8a–c, and the effect of more cohesive fines than carriers is shown in Fig. 8d and e. In all cases, averages of three simulations with different initial random seed values are plotted in the graph. These cases are discussed in turn below.

Gamma 0.01. Fig. 8a summarizes the results obtained from binary head on collisions between two adhesive units with the surface energy between the particles fixed at 0.01 J/m². Ratios obtained for the three investigated SCRs (0.5, 0.7 and 1) are displayed as a function of the relative velocity in the range 0.04–1.7 m/s, considered representative of handling conditions. A discontinuous y-axis is used for a better representation of loss and retention ratios. It can be seen that the transfer ratio is very low across the entire velocity range, irrespective of the SCR. The retention and loss ratio are similar for all three SCRs at low velocities. For an SCR of 0.5, more fines are lost from the units during collision when the velocity increases. There is sudden shift observed at 0.8 m/s and as much as 20% of the fines are lost from the units at the highest velocities investigated. The results for SCRs of 0.7 and 1 follow a similar trend, but the adhesive units are more stable than for an SCR of 0.5, as one would expect.

Gamma 0.03. Fig. 8b, provides data from binary head on collisions between two adhesive units with surface energy between particles fixed at 0.03 J/m². The retention ratio reduces with increasing relative velocity between units, and again a sudden shift is seen at 0.8 m/s. It can be seen that an SCR of 0.5 incurs the maximum loss of about 10% whereas SCR 0.7 and SCR 1 have somewhat lower losses. Since the transfer ratio is minimal in all cases, these trends are mirrored by the loss ratios.

Gamma 0.05. Fig. 8c represents data from binary head on collisions in a cohesive regime with the interaction energy between all particles fixed at 0.05 J/m². It can be seen from the graph that most of the fines tend to stay on carriers for all SCR.

Gamma 0.03–0.05. Fig. 8d represents binary head on collisions of adhesive units with surface energy of interaction between fines of 0.05 J/m² and between fines and carriers of 0.03 J/m². It can be seen from the graph that the ratios represent values between C₀:03/C₀:03 and C₀:05/C₀:05.

Gamma 0.01–0.05. Fig. 8e represents binary head on collision with surface energy between fines of 0.05 J/m² and between fines and carriers of 0.01 J/m². The regimes represent extremes for carrier-fines and fines-fines interaction energy, the latter being considered highly adhesive. The final net loss of particles is close to 10% and adhesive units with SCRs of 0.7 and 1 reach this plateau faster than the units with an SCR of 0.5.

4.3. Restitution

The restitution coefficient as defined in Eq. (16) was used to quantify the mechanical properties of the adhesive units. Examples of results obtained from the simulations are given in Fig. 9, which
displays the coefficient of restitution as a function of velocity. It can be observed that restitution is difficult to predict at low impact velocity, since the units may stick to each other or bounce back depending on the initial distribution of fines on the carrier surface. When the impact velocity increased beyond a certain threshold velocity, the restitution became more regular and reached a constant plateau value.

Restitution coefficients for adhesive units for which all surface energies are equal are shown in Fig. 10 a–c, and the effect of more cohesive fines than carriers is shown in Fig. 10 d and e. For better graphical representation, only values of restitution for which the profile exhibited a consistent increase with velocity are included (i.e. the random region described above is not shown). In all cases, averages of three simulations with different initial random seed values are plotted in the graph. The solid lines represent fits of a Kawakita type equation (Kawakita and Lüdde, 1971) to the data displayed in the figure. Specifically,

\[
e = \frac{a(v - v_c)}{c + (v - v_c)},
\]

where \(v_c\) is the critical velocity above which the incident energy is high enough for the particle to rebound and \(a\) and \(c\) are constants.

The results obtained for different surface energies are described in more detail in what follows.

**Gamma 0.01.** In Fig. 10a, the restitution coefficients obtained for a fixed surface energy of 0.01 J/m² and different SCRs are plotted against relative impact velocity. The restitution coefficients of carrier-carrier collisions (i.e. an SCR of 0) are plotted as reference values. From Table 1 it can be seen that the restitution coefficient for carrier-carrier interactions is 0.89, which is reflected in the graph. The restitution coefficient at an SCR of 0.5 plateaus close to 0.89 and a downward shift is observed for the SCRs of 0.7 and 1. The error bars represent the variation (standard deviation) across different seed values for the same parameter setup.

**Gamma 0.03.** Fig. 10 b summarizes results obtained for simulations analogous to the ones in the previous paragraph but with the interaction energy fixed at 0.03 J/m². For an SCR of 0.5, the restitution coefficient increases in agreement with the Kawakita type equation and plateaus at a value lower than the carrier-carrier restitution coefficient. For SCRs of 0.7 and 1, the restitution coefficient does not reach a constant value but otherwise follows a similar pattern as for an SCR of 0.5.

**Gamma 0.05.** In Fig. 10c, corresponding to an interaction energy of 0.05 J/m², it can be seen that the critical velocity above which the units do not adhere to each other is higher compared to the
results obtained for the lower interaction energies, especially for SCRs of 0.7 and 1. For an SCR of 0.7, the restitution coefficient follows a pattern similar to that of an SCR of 1, but reaches a higher restitution coefficient for the same impact velocity. The plateau at high velocities is not reached in these simulations.

**Gamma 0.03–0.05.** Fig. 10d reports the results obtained for adhesive units with surface energy of interaction between fines of 0.05 J/m² and between fines and carriers of 0.03 J/m². We observe a similar increasing trend as in the previous cases with the restitution coefficient being highest for an SCR of 0.5 followed by 0.7 and 1.

**Gamma 0.01–0.05.** In Fig. 10e, the interaction between fines was modelled to be cohesive in nature with surface energy of interaction being 0.05 J/m² whereas the carrier-fines and carrier-carrier interaction was fixed at 0.01 J/m². The profiles obtained for this system are similar to the previous ones with a tendency of the restitution coefficient for SCRs of 1 and 0.7 to converge at large velocities, at a value lower than the one obtained for an SCR of 1.

Simulations were not performed for higher impact velocities as these are not typically encountered during handling.

### 5. Discussion

One of the most common mechanisms of handling the manufactured product and filling capsules is through hopper flow. A common problem encountered during such handling of adhesive mixtures is bridging of adhesive units, which causes clogging and reduces flowability. In this study, the restitution coefficient \( e \) and its dependence on the incident velocity are used as indicators of the flowability of the adhesive mixtures. In particular, the critical velocity \( v_c \) is expected to provide an indication of the tendency of the adhesive units to form aggregates. During handling, there is also an evident risk of segregation, which may occur since adhesive units undergo constant collisions with each other. As a result of these collisions, fines are lost from each of the units and may be taken up by other units or lost to the walls. These events are captured by the loss and transfer ratios. It can be noted that the loss ratio represents the maximum loss of fines which could occur in a single collision, since all fines lost during a binary collision are assumed to be lost to the walls and not taken up by other units.

#### 5.1. Stochastic behaviour at lower velocity

Fig. 9 represents raw data for the restitution coefficient obtained for impact velocity in the entire range with a surface energy of interaction of 0.03 J/m². On impact between two adhesive units, exchange of energy among fines or fines and carrier depends on the initial spatial distribution of the fines on the carrier surface, summarized in terms of the SCR and obtained with different initial seed values. Depending on the specific initial spatial distribution of the fines, a total or partial loss of energy may occur during collisions at low velocities, resulting in zero (sticking) to low coefficients of restitution. As a result, the behaviour at low impact velocity is more stochastic in nature and hence difficult to predict. However, the net loss of particles from the system during head on collision is minimal in this range (cf. Fig. 8), indicating that the stochasticity at lower velocity does not play any significant role for the loss or transfer of fines.

#### 5.2. Effect of surface energy and impact velocity

In order to understand the flowability of adhesive units during handling, the velocity of rebound, expressed as restitution coefficient \( e \), is plotted as function of the impact velocity. In order to analyse the effect of surface energy at fixed incident energy of the system, it is preferable to present the data as in Fig. 11, which compares the results obtained for different surface energies at fixed SCRs. This also enables a more natural representation of data obtained for systems comprising particles with different surface energies (i.e. more adhesive fines than carriers).

**SCR 0.5.** In Fig. 11a, summarizing the results obtained for an SCR of 0.5, it can be seen that adhesive units with weakly bound fines (low surface energies) behave similarly as systems with no fines at higher velocities. This could be due to the high loss of fines (20%) from the adhesive units during collision as seen from the ratios on the right. Higher losses imply that fines are displaced and so that the net interaction approaches the one between bare carriers. For higher values of the surface energy, the energy required to overcome the cohesive and adhesive interactions is higher, which results in a reduction of the restitution in the order of increasing surface energy.

**SCR 0.7.** In Fig. 11b for an SCR of 0.7 it can be observed that there is minimal loss of fines for lower velocities and that the critical velocity above which the units do not tend to agglomerate is higher compared to an SCR of 0.5. This could be explained by the fact the collisions among fines increase as the number density of fines on the carrier surface increases, thereby resulting in a higher energy dissipation and thus a lower net restitution coefficient and increase in critical velocity for rebound. The effect of surface energy follows a similar pattern as explained for an SCR of 0.5 (Fig. 11a). It could also be seen in the stability ratios plot that the net loss of particles is reduced compared to an SCR of 0.5 as a result of higher energy dissipation.

**SCR 1.** In Fig. 11c, for an SCR of 1, the restitution coefficients do not plateau and the final restitution is lower than for SCRs of 0.5 and 0.7. One plausible explanation is that clusters of cohered fines are formed at higher SCRs that more easily are displaced upon...
collision. The particle losses at lower surface energy are higher compared to an SCR of 0.7 as is also seen in Fig. 10a. This may be due to the formation of multi-layer units which are more easily dispersed compared to the ones closer to the carrier. Predominantly in the case of $C_{01}$, the kinetic energy is high enough to disperse a considerably larger fraction of fines from the surface of the carriers compared to units with higher surface energy and thus the loss ratio follows a pattern similar to that of the previous cases. The explanation for the overall changes in restitution and ratios is similar to the one previously stated.

For a higher value of $e$ there is less loss of energy and more energy is retained by the fines. The retained energy further excites the fine and loses are higher. For higher SCR and high surface energy, $e$ is lowest which implies most of the energy is lost form the system.

Adhesive fines. For adhesive units with fines modelled as more adhesive than carriers, it could be hypothesised that the fines-fines interaction dominates at lower velocity and that the behaviour at a higher velocity is an effective interaction resembling that of the units with lower surface energy. For higher velocities, the net loss of particles is equal for different surface energies even for different SCRs. For the sake of clear representation the stability ratios for adhesive fines is omitted from Fig. 11 but can be found in Fig. 8.

5.3. Relationship between SCR, critical velocity and surface energy

As already mentioned, particles tend to stick to each other at low velocities, something that may adversely affect the flowability of the material. The results in Fig. 10d and e tend to support the hypothesis that the fines-fines interaction dominates at lower velocity. The layer of fines may act as a damping pad between the carriers. Consistent with this, the effect is more prominent at higher SCR than for the lower SCR. At lower impact velocity, the initial energy is low and most of the energy tends to dissipate thereby resulting in an effective interaction dominated by the fines. This is further corroborated by the ratio plots, where the net particle loss is minimal for low velocity impacts. The data are also consistent with the notion that the interaction between the adhesive units at higher velocity tends to be governed by an effective interaction energy that is an average of the carrier and fines surface energy. A possible explanation is that most of the fines, at higher velocity, are displaced from the contact surface between the two units thereby giving an effective interaction resembling that of the units with lower surface energy. For higher velocities, the net loss of particles is equal for different surface energies even for different SCRs. For the sake of clear representation the stability ratios for adhesive fines is omitted from Fig. 11 but can be found in Fig. 8.

Transfer ratio during the handling phase. Transfer ratios during the collision of adhesive units is negligible as can be seen from Fig. 11; most of the fines are either retained on the carriers or lost from the system (but could potentially be picked up by other carrier in a real mixture). This is in sharp contrast to the situation when collisions between an adhesive unit and a carrier have been studied during shear mixing (at higher impact velocities) (Tamadondar et al., 2019).

Fig. 8. Stability ratios for binary head on collision with varying velocity, surface coverage ratio (SCR) and surface energy (a) $\Gamma_{0.01-0.05}$, (b) $\Gamma_{0.03-0.05}$, (c) $\Gamma_{0.05-0.05}$, (d) $\Gamma_{0.03-0.05}$, (e) $\Gamma_{0.01-0.05}$.

Fig. 9. Coefficient of restitution plotted as a function of impact velocity, showing the stochastic behaviour of units at a lower velocity.
of the adhesive mixture and its performance in e.g. hopper flow leading to operational problems such as arching or bridging. The propensity for sticking is expected to be captured by the critical velocity, as extracted from the fits to Eq. (21). Fig. 12 shows the propensity for sticking is expected to be captured by the critical leading to operational problems such as arching or bridging. The restitution coefficients vs. impact velocity for different surface coverage ratios (SCRs) and surface energies. The data are grouped according to the fines–fines and carrier–fines surface energies: (a) $\Gamma_{0.01-0.01}$, (b) $\Gamma_{0.03-0.03}$, (c) $\Gamma_{0.05-0.05}$, (d) $\Gamma_{0.01-0.05}$ and (e) $\Gamma_{0.05-0.05}$. Each data point represents the mean obtained from three independent simulations and the error bars indicates the standard deviation.

6. Conclusions

Dynamics of adhesive unit is complex and difficult to represent by a simple mathematical equation parameterized by surface energy and SCR. This work reports a characterization of the behaviour of adhesive units in a velocity range representative of the handling phase. A detailed analysis of binary collisions of adhesive units formed from mono disperse spherical fines and carriers was performed and the restitution coefficient and stability ratios were determined. These parameters are expected to reflect the flowability and stability of the adhesive mixtures.

At low velocities, restitution of adhesive units depended critically on the precise spatial arrangement of the fines on the carrier surface, thus introducing a significant randomness in the values obtained for the restitution coefficient. For higher velocities, still in the handling regime, the randomness decreased considerably and the restitution coefficients exhibited a consistent and rapid increase with velocity followed by a more gradual increase. The restitution coefficient of adhesive units was generally smaller than that of bare carriers, the smallest values being obtained for adhesive units with high SCR and high surface energy. Further, for adhesive units formed from fines that were more adhesive than the carriers were (i.e. had a higher surface energy), the fines-fines interaction dominated the restitution at lower velocity whereas the behaviour at a higher velocity was an average effect of fines and carrier surface energy.

As expected, the integrity of adhesive units following binary impacts was most strongly influenced by the surface energy. However, for weak to modestly strong adhesive forces, a significant dependence on SCR was also seen, such that a larger fraction of fines were lost for higher SCRs, especially at higher impact velocities. Hence, adhesive units do not behave as static, independent units but are more complex in their dynamics.

The knowledge of interaction between adhesive units is a first step in understanding the complex micromechanics of adhesive mixtures. This knowledge could be used to improve flowability, reduce segregation and improve handling of adhesive mixtures for inhalation. An understanding of behaviour of adhesive units at low velocities could be used to improve movement of units through hoppers, whereby identifying potential velocities which could lead to arching in the system. The model developed can further be extended to include other mechanical properties and interaction and handle polydisperse complex shaped particles.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
Acknowledgment

This study is part of the science program of the Swedish Drug Delivery Forum (SDDF) and financial support from Vinnova (Dnr 2017-02690) is gratefully acknowledged.

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