Abstract

Powder handling operations can give rise to the tribo-electrification of particles, causing a number of problems such as risk of fire and explosion, particle adhesion to the walls of processing equipment and segregation. Current methods available for measuring the dynamic charging of bulk powders are unsuitable for testing/handling small quantities of powders, some of which are highly active. Furthermore, very little work has been reported on the effect of tribo-electrification on the segregation of components of mixtures.

A methodology has recently been developed for investigating the tribo-electrification of small quantities of bulk powders using a shaking device. Two common pharmaceutical excipients, namely α-lactose monohydrate (α-LM) and hydroxypropyl cellulose (HPC) were used as model materials. The electric charge transferred to the particles was quantified as a function of shaking time, frequency and container material. The temporal trend follows a first-order rate process.

Using numerical simulations based on the Distinct Element Method (DEM), the charge accumulation of an assemblage of alumina beads inside the shaking device was analysed based on the single particle contact charge obtained from the experiments. It was shown that the inclusion of electrostatic mechanisms into the DEM model leads to an improved prediction of the charge build-up, but the difference with experimental data is still notable.

Using the above method, segregation induced by tribo-electric charging was characterised for binary mixtures comprising α-LM and HPC. The bulk and wall-adhered particles were analysed for the mass fraction of each component using selective dissolution of one component and filtration of the non-dissolving component, followed by a gravimetric analysis. The findings reveal that a considerable level of segregation can take place on the wall-adhered particles.

The method described here has the potential to be used to characterise small quantities of pharmaceutical powders including active pharmaceutical ingredients (API), which are sparse in the early development stages.

Keywords: tribo-electrification, electrostatics, segregation, DEM modelling

1. Introduction

Tribo-electrification is a common phenomenon that occurs in many powder handling industries such as pharmaceuticals, foods and detergents, etc. Powder handling operations such as pneumatic conveying, sieving, mixing and milling cause particles to make frequent contact among themselves and with the walls of the processing equipment. During these interactions, charge transfer takes place through shearing\(^1\), impact\(^2\) or friction\(^3, 4\), a process which is commonly known as tribo-electrification or tribo-electric charging. When materials become charged, their behaviour can change and as a result they can adhere to each other easier or repel other charged materials\(^5\). Excessive tribo-electrification of powders can be a nuisance as it causes problems such as dust
able tribo-charging devices, the cyclone charger has been developed by Šupuk et al. It can also lead to powder loss and difficulties in controlling the powder flow.

Pharmaceutical powders are usually semiconductors or insulators of small particle size and low bulk density, providing ideal conditions for electrostatic effects. In the pharmaceuticals industry, the problem extends further to the end-product quality, where the tribo-electrification of powders may cause segregation.

Segregation due to electrostatic effects is a relatively new area of research which has been identified as technologically important. A manifestation of this problem is susceptibility to a change in drug formulation in various processes such as tabletting. The pharmaceuticals industry is heavily regulated with a limited number of excipients and tight limits on content uniformity, hence an in-depth understanding is very important in order to control the electrostatic effects and to ensure that the end product is effective and safe to use.

At present, the industrial selection of appropriate excipients to form a stable blend is very often accomplished through trial and error. However, this approach is unattractive due to the significant resources required, including the use of large quantities of APIs which are sparse in the early development stages, in addition to the approach being very time-consuming. The ability to control the tribo-charging of pharmaceutical powders from an early stage of a process is therefore essential in improving the quality of the end product through minimising the deposition and powder loss in a process. From the currently available tribo-charging devices, the cyclone charger is probably the most prominent device for characterisation of the tribo-electric properties of pharmaceutical powders. The cyclone is fitted with interchangeable contact surfaces of steel and polymers. The particles are fed from the side with the aid of a carrier gas and are charged by means of collisions with the inner surfaces of the cyclone charger. The charge-to-mass ratio is measured by a Faraday cup and an electrometer. However, this device has not yet found widespread use, as it suffers from being an ‘open system’ with risk of exposure to APIs. A simple test method has been developed by Šupuk et al. for characterisation of the tribo-electric properties of powders in a shaking container by contacting the powder with imitations of common surfaces used in industry. In comparison, this is a closed system and has the added advantage that it is a rate process, from which the equilibrium condition can be quantified.

Šupuk et al. used α-LM and HPC as model materials due to their non-toxic nature, allowing for extensive testing with minimal health risk implications. In the pharmaceuticals industry, α-LM and HPC are widely used as excipients for tabletting and encapsulation due to their bland taste and wide interacting capabilities with other active and excipient ingredients.

The tribo-electrification of particles against various surfaces during powder handling gives rise to bipolar charges within a formulation which can give rise to attractive or repulsive forces between the individual particles. The charging of particles with the opposite polarity has been utilised in the formation of stable ordered mixtures which have proven to minimise segregation. However, in some cases, both components of a binary mixture may charge with the same polarity. This gives more chance for particles to adhere to the inner walls of the processing equipment rather than to each other. This may have a significant effect on the charging behaviour of powders and may cause segregation of particles during powder handling and processing. However, little work has been done on this topic. In addition to being highly dependent on particle size, shape and density, segregation may also be affected by electrostatic charges. It remains a challenge and an area which lags behind the rest of segregation studies, possibly due to the lack of simple tribo-electrification devices. Understanding the effects of particle adhesion and subsequent segregation of mixtures is therefore of particular interest.

To elucidate the temporal profile of tribo-electric charging, simulations by the Distinct Element Method (DEM) were carried out. This requires a model for single particle charging. Hence, experimental work was carried out on the tribo-electric charging of a single spherical alumina bead inside a shaking container. An empirical model is then fitted, relating the accumulated charge to the contact area of the bead with the capsule walls. This is then used in the DEM simulations with a number of beads to predict bulk charging and a comparison is made with experiments at different shaking frequencies. Furthermore, the effects of long-range forces, space charge and image charge at boundary conditions are investigated. At present, there are no methodologies available to predict the dynamic charging of bulk powders. A first attempt to analyse a simple system is herewith presented.

1.1 Tribo-electric charging devices
A common way of charging bulk particles tribo-
Another way of tribo-electric charging is to use a vibrating device on which a box is placed. Particles are put inside the box and are subjected to vibrations. The sample tested is then transferred into a Faraday cup connected to an electrometer, where the charge is measured. Mixing devices such as a high-shear mixer or a low-shear tumble blender have also been used, where the particles are charged as a result of collisions with the walls of the mixing devices and with each other. The charge measurement is done with a Faraday cup or the insertion of an induction probe inside the mixer.

Particle electrification is a common occurrence during pneumatic conveying due to numerous collisions between the particles and the pipe wall. One prominent method for measuring electrostatic charge transfer is to use a pipe in which the particles are pneumatically conveyed. A tribo-charging device based on this concept was developed by Matsusaka et al. to analyse the electrostatic charge distribution of particles. The set-up consisted of various lengths of tribo-charging pipes and an Electrical Single-Particle Aerodynamic Relaxation Time (E-SPART) analyser. A table feeder was used to introduce the particles into the pipe and compressed air was used to transport the powder. The charge and particle size were measured after travelling through the pipe.

A cyclone and more recently a dispersion device have also been used to perform tribo-electric charging. The cyclone is fitted with interchangeable contact surfaces of steel or polymers. The pharmaceutical powders are charged by means of collisions with the inner surfaces of the cyclone charger. The charge-to-mass ratio is continuously monitored by a Faraday cup and electrometer. In the dispersion device, a small quantity of powder, typically 36 mg, is sandwiched between two thin metal sheets, separated by a spacer. A pulse of pressurised air is applied to the cavity above the sheets, as a result of which the sheets burst open, dispersing the powder. The unit is mounted on a conventional Faraday cup connected to an electrometer to measure the net charge transfer due to dispersion.

Examples of other methods of tribo-electric charging include fluidised beds, rotary drums, vibrating device on which a box is placed. In both cases, particles are poured from the top of the cylinder/plate, and as they roll and bounce on the way down, the particles are collected in a Faraday cup and the charges are measured. The inclined surface material can be changed to test the effect of the surface material on charge transfer.

A simple way to charge powders is to shake them in a container, where powder-wall contacts can induce tribo-electrification. The method provides good control of temperature and humidity, as it is enclosed, and the charging rate can be assessed by monitoring the charge as a function of time until the saturation level is achieved.

Šupuk et al. used a Retsch MM200 shaking machine for this purpose. About one gram of powder is placed inside a 10-ml container and shaken to tribo-electrically charge the powder. The shaking container is subjected to reciprocal vibrations in a horizontal direction. Containers made of stainless steel, PTFE, PMMA (Perspex) or glass are used to test the effect of the contact surface material on tribo-electrification. The vibration frequency can be set between 3 and 30 Hz. The tribo-charging time can be digitally preset from 10 seconds up to 99 minutes. The amplitude of vibrations is fixed at 89 mm. After a specified time of shaking, the powder is emptied into a Faraday cage to measure its charge. A quantity of the powder sticks to the walls and would not come out. This is referred to as powder loss due to adhesion to the walls and correlates well with the charge level on the powder. The details of the device and its operation can be found in ref. To measure the electrostatic charge of the bulk powders, a Faraday cup is used which consists of two stainless steel cups isolated from each other by a PTFE spacer. The inner cup is connected to an electrometer (Keithley Model 6514) via a BNC cable, and the outer cup is earthed. The electrometer is connected to a computer and the data are recorded. The inner cup can be easily removed to measure the weight of the sample poured into the cup. A stainless steel lid, fitted to the outer cup, is used to reduce electric noise. The resolution of the charge measurement is in a nano-Coulombs (nC) order of magnitude.

In order to control the environmental conditions during the test, an isolator can be used wherein all of the test equipment, including the tribo-electric charging device, electrometer, Faraday cup, humidity and temperature meters and the test materials can be placed and sealed. Nitrogen can be supplied through an aperture on the side of the isolator to reduce humidity.
The test materials are placed inside the isolator via the side chamber. The humidity and temperature inside the isolator are monitored using a HydroPalm device. By adjusting the amount of dry gas coming into the isolator, the humidity can be reduced if required. With this arrangement, the active ingredients are easily contained, reducing the risk of exposure to dust and associated toxic hazards.

Tribo-electrification of the feed material in a shaking container is mainly achieved by impact and sliding against its inner wall. A high-speed video camera, (Redlake MotionXtra HG-100K) with a maximum acquisition speed of 100,000 frames per second (fps) is used to observe the particle movements. A glass container of the same geometry as the stainless steel and PTFE containers is used for this purpose.

2.1 Test materials
α-lactose monohydrate (α-LM) and hydroxypropyl cellulose (HPC) are widely used in the pharmaceutical industry as excipients for tableting and encapsulation, and were selected for this work based on the current industrial and scientific interest regarding their charging tendencies. The reasons behind selecting these materials also lie in the fact that they are of a non-toxic nature so that extensive testing could be conducted with minimal risks to health.

The above two materials are fine and irregular in shape and are unsuitable for more basic studies of tribo-electrification, for which information about various contact parameters such as the contact area is required. For this reason, alumina beads were also used for comparison between the experimental work and numerical simulations by the Distinct Element Method (DEM). These particles are strong enough not to break or chip easily during the tribo-charging experiments inside a shaking container at high impact velocities. The splitting of particles would create additional surface area thus affecting charge transfer; therefore it was essential this was kept to a minimum via the choice of beads. Physical properties of the test materials are presented in Table 1.

3. Analysis of the New Test Method

Saturation Level The saturation charge level, i.e. the amount of charge generated as a result of particle impacts for which no further charge would occur, is a characteristic of the system, and for a given powder-container system it should be independent of the shaking frequency. Šupuk et al. measured the charge-to-mass ratio as a function of shaking time for 1g of α-LM, HPC and a 50:50% by mass binary mixture in a PTFE container for 10, 20 and 30 Hz, and found this to be indeed the case. Their results are reproduced as Table 2, where for each system an equilibrium value is reached.

Šupuk et al. also report that the charging temporal profile follows a first-order rate (equation 1).

\[ q = q_{sat}(1 - e^{-\alpha t}) \]  

(1)

where \( q_{sat} \) is the saturation charge. The rate constant \( \alpha \) is obtained from the initial slope of the curves. The results show that increasing frequency increases the charging rate which follows the first-order process reasonably well for all the three frequencies.

The values of the rate constant and saturation

| Sample | Supply Source | Particle Density | Bulk Density | Tap Density | Particle Size Distribution (µm) | Aspect Ratio |
|--------|---------------|------------------|--------------|-------------|---------------------------------|-------------|
|        |               | kg/m³            | kg/m³        | kg/m³       | d₁₀ d₅₀ d₉₀                       |             |
| α-LM   | Mallinckrodt Baker, USA | 1520             | 725          | 825         | 196 334 527                       | 1.71        |
| HPC    | Sigma-Aldrich, USA | 1214             | 331          | 453         | 256 418 700                       | 2.12        |
| Alumina | IFP, France     | 1520             | N/A          | N/A         | Diameter: 2 mm                    | 1.05        |

Table 2 Saturated charge values for the test powders at 10, 20 and 30 Hz frequencies

| Frequency (Hz) | Saturated Charge (nC/g) |
|---------------|-------------------------|
|               | α-LM        | HPC          | Binary      |
| 10            | 24.6        | 2.3          | 12.1        |
| 20            | 24.7        | 2.7          | 11.8        |
| 30            | 22.7        | 3.0          | 11.9        |
charge were reported by Šupuk et al.\textsuperscript{9} and are reproduced in Table 3. An increase in the shaking frequency increases the rate constant. This is expected since the number of particle-wall collisions increases while the charge relaxation time between successive impacts is reduced. Furthermore, increasing the shaking frequency also leads to an increase in particle impact velocity, resulting in a larger contact area for charge transfer\textsuperscript{3}.

Wall Adhesion Tribo-electric charging gives rise to powder adhesion to the container walls, the extent of which was characterised for various samples and surface material by Šupuk et al.\textsuperscript{9}. The adhered powder is highly charged and its mass increases with the charge level. The powder does not empty into the Faraday cup without gentle tapping on the outside of the container. However, the adhered powder cannot be scraped into the Faraday cup as this would additionally charge the powder. The highest mass loss at all frequencies tested is for $\alpha$-LM. Approximately 10\% of total loaded particles of $\alpha$-LM adhere to the inner walls of the shaking container. HPC has the smallest mass loss at all the three frequencies, indicating a very low adhesion of particles to walls.

Effect of Initial Mass Powder mass affects the charging rate as well as the equilibrium charge, as it affects the dynamic of particle wall collisions and the surface area available for charging. Šupuk et al.\textsuperscript{9} carried out tests with 0.33, 0.66 and 1 g of initial mass and report that the highest charge generation is with the smallest mass; i.e. 0.33g. This will be analysed later in Section 4.

Effect of Surface Material Šupuk et al.\textsuperscript{9} evaluated the tribo-electric charging of the test powders against three solid surfaces, namely PTFE, stainless steel and glass. Their results for pure $\alpha$-LM, HPC and a binary mixture (50:50\% by mass) at 20 Hz show that the powders become positively charged against PTFE surfaces and negatively charged against glass and stainless steel containers. The magnitude of charge is highest with the PTFE and lowest in the stainless steel shaking container. The stainless steel container may allow the charge on the wall-adhered particles to dissipate through the charge relaxation process, explaining the reduced magnitude of charge obtained for this container.

The primary factor affecting the charging process is the work function of the contacting surfaces and the resulting contact potential difference. This together with contact mechanics of impacting particles influences the charging process. To account for these effects, a more detailed study of particle movement taking account of electrostatic charge is being undertaken by the distinct element method. Preliminary results are reported in Section 4.

High-Speed Video Analysis of Particle Motion Šupuk et al.\textsuperscript{9} made observations of particle motion at three shaking frequencies by high-speed video recording, and report two patterns of particle dynamics: at 10 Hz the particles mainly slide at the bottom of the shaking container, with the number of particle-wall impacts considerably less than the other two frequencies. This suggests that particles are becoming charged primarily as a result of sliding friction which corresponds to the smallest amount of charge transferred at this frequency. At 20 Hz, a large proportion of the particles impact on the upper walls and rounded ends of the container and the rest slide at the bottom of the container. At 30 Hz, particle collisions are most prevalent. Particles are thus mainly charged as a result of particle-wall impacts and hence a rapid charging to the saturation level is expected for the 30 Hz frequency, as indicated by the rate constant for 30 Hz in Table 3. An analysis of the effect of particle motion is therefore helpful in understanding the charging process, and this is addressed further in Section 4 below.

4. Tribo-Electric Charging of Spherical Alumina Beads

In an attempt to elucidate the process of tribo-electric charging of particles by this method, spherical alumina beads were shaken in the same way as reported above and the charge level was characterised for two cases of a single bead and 230 beads.

4.1 Single bead experiments

A single alumina bead, 2 mm in diameter, was tribo-charged at 10, 20 and 30 Hz frequencies using the

| Frequency (Hz) | $\alpha$ | $q_{\text{sat}}$ |
|---------------|---------|----------------|
| 10            | 0.045   | 24.2           |
| 20            | 0.060   | 24.6           |
| 30            | 0.163   | 24.0           |

Table 3 Values of the rate constant and saturation charge reported by Šupuk et al.\textsuperscript{9} for $\alpha$-LM.
The average mass of a single alumina bead is 4.4 ± 0.1 mg based on a random selection of 30 beads. Initially, each alumina bead was treated with ethanol and dried in an oven at 35°C for one hour prior to the tribo-electric charging tests. Following charge measurement, the alumina bead was discarded. The inner surfaces of the PTFE capsule were wiped with ethanol and dried. Each test was carried out with a fresh bead. This procedure was repeated a minimum of three times for each tribo-electric charging test and the average value was calculated. It should be noted that there was no breakage of alumina particles during the single particle tests at all three frequencies. The temperature and humidity range during single particle testing was 20.1-24.1°C and 34.1-42.3% RH, respectively.

The experimental results for a single alumina bead tribo-charged at three test frequencies are shown in Fig. 1. The charge values for 20 and 30 Hz shaking frequencies are close to each other, whilst those at 10 Hz are distinctly different. At 10 Hz, the time taken to reach the saturation charge is longer. This is most likely due to a smaller number of shaking cycles, as compared with those of the other two frequencies, and consequently to a lower number of particle-wall contacts as well as lower impact velocities. A first-order charging rate equation (Eq. 1) proposed by Hogue et al.\textsuperscript{12} was fitted to the experimental data by linear regression. The fitted values are summarised in Table 4. The results show the charging rate constant is much higher at frequencies of 20 and 30 Hz as compared with that obtained at 10 Hz. For the last frequency, much longer times are required to reach saturation (not shown here).

### 4.2 Bulk shaking experiments

Two hundred and thirty alumina beads, corresponding to 1.012 ± 0.001 g, were used for bulk tribo-charging tests. These tests were carried out using the exact procedure described for the single bead above method.
with a PTFE shaking capsule at time intervals of 1, 3, 5 and 10 minutes. A minimum of three runs were performed for each test. The charge on the beads was measured for each run and then averaged. The beads were then weighed to determine any mass loss due to breakage.

The temperature and humidity ranges during bulk particle testing were 20.7-23.3°C and 35.8-47.4% RH, respectively. The experimental results obtained at three test frequencies are presented in Fig. 2. Initially, the level of charge measured at 10 Hz was considerably lower than those at 20 and 30 Hz. However, as the length of shaking time is increased, the charge on the beads at the three test frequencies approaches asymptotically a saturated charge level. The saturated charge \( q_{sat} \) levels at each frequency are also shown in Table 4. As with the single bead results, a first-order charging rate equation (Eq. 1) was fitted to the bulk shaking data by linear regression. The values of the rate constant \( \alpha \) for bulk charging are also summarised in Table 4. The results show the charging rate constant is lowest at 10 Hz. Interestingly, the value of the charging rate constant is highest at 20 Hz (not 30 Hz) for bulk shaking. This may suggest that at 20 Hz, the bead-wall contact frequency as well as the impact velocity is the highest. This is investigated further using DEM in the next section. Furthermore, it may be noted that the charge on the bulk beads is not 230 times higher than on a single bead. This may suggest that when the beads are shaken in bulk, the probability of individual beads making contact with the capsule walls decreases. There are also other hindering effects due to long-range forces, space charge and image charge at boundaries, as will be considered in the simulation section below.

4.3 Analysis of tribo-electrification inside the container using Distinct Element Method (DEM) - simulation results

Numerical simulations by the distinct element method is used to analyse the tribo-electric charging of an assemblage of particles based on information obtained from charging a single particle in the same device. The effects of long-range forces, space charge and image charge at boundary conditions are investigated.

4.3.1 Calibration procedure

The simulations were performed using the distinct element method, originally proposed by Cundall and Strack\(^{23}\) and implemented in PFC\(^{3D}\) software (ITASCA). In this method, the interactions between contiguous particles are modelled as a dynamic process and the time evolution of the particles is advanced using an explicit finite difference scheme. The interactions between the constituent particles are based

![Fig. 2 Charge of 230 alumina beads following tribo-charging at 10, 20 and 30 Hz frequencies – lines show best fit using Eq. 1.](image-url)
on theories of contact mechanics. In this work, a linear contact model is used to simulate particle-particle and particle-wall interactions. The mechanical properties of the alumina beads were measured and are shown in Table 5. The ends of the capsule are designed by arranging five cone frustums around a cylinder positioned in the central region as shown in Fig. 3. The stiffness of the PTFE walls is lower than the alumina beads and was estimated using the elastic modulus.

Initially, a single sphere representing an alumina bead was simulated inside the capsule. The capsule was then vibrated at frequencies of 10, 20 and 30 Hz at an amplitude identical to the experimental device (simple harmonic motion). The maximum contact area for every particle-wall contact event was then calculated and recorded, as it is the main factor affecting the charge transfer. For a single contact event, the charge transfer was calculated by the linear relationship (Eq. 2) between the charge transfer $\Delta q$ and the charge, $q$, held by the particle just before the contact:

$$\Delta q = \beta \Delta S \left( 1 - \frac{q}{q_{sat}} \right) \quad \text{(2)}$$

where $\beta$ is the proportionality constant and $\Delta S$ is the maximum contact area, calculated based on the maximum overlap and Hertz analysis. $\Delta S$ is the main process parameter affecting the charge transfer. Integration of Eq. 2 for multiple impacts from $q=0$ yields:

$$q = q_{sat} \left( 1 - e^{-\beta \sum \Delta S / q_{sat}} \right) \quad \text{(3)}$$

For a long time scale, the accumulated maximum contact area can be treated as proportional to the operation time,

$$\sum \Delta S = \gamma t \quad \text{(4)}$$

therefore, Eq. 3 can be converted into Eq. 5:

$$q = q_{sat} \left( 1 - e^{-\gamma \beta \sum \Delta S / q_{sat}} \right) \quad \text{(5)}$$

This converts the time constant $\alpha$ in Eq. 1 to the accumulated contact area as a function of time, expressing a more practical term of physical event, and provides a basis to analyse the macroscopic charge development on single particles with the aid of DEM simulations. In the calculation, constants $\beta$ and $q_{sat}$ were fitted parameters obtained from the experimental data.

### 4.3.2 Bulk simulations

With the calibrated parameters, the simulation procedure was applied to bulk shaking with 230 particles. For a first attempt, the single particle procedure was simply applied without any extensions of electrostatic functions, which will be described in detail later. The results were simply given as 230 times of the single particle cases. However, the trends given by these values did not agree at all with the experimental results obtained (Fig. 4, dashed lines).

In the next stage, a number of electrostatic functions were incorporated into the DEM simulations for bulk shaking. These were long-range Coulombic forces, space charge effects, and boundary conditions. For the boundary conditions, equipotential or conductive conditions on the capsule surfaces were considered. However, this differed from the actual experiments, where the capsule was made of PTFE, a non-conductive polymer, and hence this assumption could have affected the calculation results. This point should be addressed in future investigations. There are a range of options to calculate the electric field distribution inside the capsule. In this work, a charge simulation method was employed with discrete image charge array located outside the capsule. The electrostatic field was calculated by the superimposition principle, whereby the contributions from every particle charge were added, including the vir-

| Property             | Value   |
|----------------------|---------|
| Particle diameter    | 2 mm    |
| Particle friction    | 0.5     |
| Particle normal stiffness | 0.3 MN/m |
| Particle tangential stiffness | 0.25 MN/m |
| Particle density     | 1100 kg/m³ |
| Contact damping factor | 0.12 |
| Wall normal stiffness | 0.1 MN/m |
| Wall tangential stiffness | 0.082 MN/m |
| Wall friction        | 0.5     |

*Table 5 Alumina beads and PTFE wall properties.*
The resulting electrostatic field affects an object not only by way of the external force (the long-range force) but also in the charge exchange (space charge effect). In the simulation procedure, the long-range force was calculated by Coulomb’s law. For the space charge effect, an electric-field-equivalent method was used in which the charge \( q \) in Eq. 2 was modified with an additional charge, giving an equivalent field to the external field (space charge effect) at the particle surface.

The results following the incorporation of all the electrostatic functions are shown in Fig. 4 (solid lines), where a drastic improvement is observed. The level of saturated charge was significantly reduced; however, it is still overestimated. There are several factors that might affect the level of saturated charge such as the boundary conditions. In the simulations, the walls are conductive and do not represent the actual experimental conditions. Additionally, the field-equivalent method used to calculate the space charge effect may be too simplistic. Such factors should be studied in detail in the future. It should also be noted that the long-range force resulted in expansion of the particle bed to some extent due to repulsion; however, the effect of the shaking frequency was more notable and the role of the bed expansion is not clear at this moment.

### 4.3.3 A comparison of experimental and simulation particle dynamics

Figs. 5.1 – 5.3 illustrate images of 230 alumina bead particles moving at shaking frequencies of 10, 20 and 30 Hz inside the container. The top images are obtained from high-speed video recordings of alumina beads inside a glass container. The bottom images are a product of the simulation work with the level of charge indicated by ball colour, given in the bar under simulated containers. In general, a qualitative comparison of the movement of particles, both from the experimental and simulation results can be achieved. The figures below show the particles moving from the left to right side of the container and back again at 80 seconds of tribo-charging time. The observations from the video recordings reveal two patterns of particle movements. At 10 Hz (Fig. 5.1), most of the particles slide along the bottom of the container with a minimal number of particle-wall impacts. However, at 20 Hz and 30 Hz (Figs. 5.2 and 5.3), the number of particles impacting on the top wall and becoming airborne increases, respectively. In the simulation results shown in the figures below, the colour variation of the balls and their charge distribution bar are a snapshot in a very narrow time window and represent the minimum charge to the maximum charge in that snapshot; i.e. they do not correspond to the absolute value of charge of the par-
As the shaking frequency is increased to 20 Hz (Fig. 5.2), a large proportion of the particles impact on the upper walls and rounded ends of the container and the remainder continues to slide along the bottom of the container.

A further increase in frequency to 30 Hz (Fig. 5.3) results in most particles impacting rather than sliding on the bottom.
5. Analysis of Segregation Post Tribo-Electrification

A range of \( \alpha \)-LM and HPC mass ratios (charging positively against a PTFE container as a result of tribo-electrification) was analysed for the level of material that had adhered to the walls. The particles were tribo-charged using the shaking device and container made from PTFE. The mixture composition post shaking was analysed by dissolution and filtration to determine the proportion of \( \alpha \)-LM in comparison to the proportion of HPC. An attempt was made to link the tribo-electric charging tendencies of the selected excipients with the segregation tendencies by comparing the composition of particles adhered to the walls with that of the original formulations.

5.1 Segregation method

Binary mixtures were tribo-charged using the shaking device and the charge was measured by the Faraday cup and an electrometer. The powders were charged inside a PTFE container at 20 Hz. The shaking time was selected based on the time required to reach the saturated charge level for each binary system as shown in Table 6. The length of time that each binary mixture was tribo-charged prior to analysing the segregation study depended on the composition ratio of a mixture. A binary mixture was charged at time increments until no further increase in the net charge was measured, i.e. three consistent readings were obtained. At this point, it was anticipated that the charge had reached a saturation level.

The wall-adhered material was then recovered using an electrostatic gun together with a gentle tapping on the outer wall of the shaking container. Scraping the material from the sides was avoided to ensure that no particles were lost or broken. Following tribo-electric charging, the sample from the wall was collected, dispersed in the solvent and filtered. A known amount of wall-adhered mass of \( \alpha \)-LM and HPC was dispersed in 50 ml of 2-propanol. The HPC particles dissolved, leaving only \( \alpha \)-LM particles dispersed in the liquid. After filtering and drying in the oven at 35°C for one hour, the \( \alpha \)-LM particles were weighed. Table 6 below shows the binary mixture compositions by weight of \( \alpha \)-LM and HPC particles. Systems 1 and 7 were used for calibration purposes and were not analysed. Approximately 1 g of pure \( \alpha \)-LM was placed in 50 ml of 2-propanol. The dispersion was agitated and left for a period of 72 hours to allow enough time to test the extent of dissolution of the \( \alpha \)-LM particles in 2-propanol. After this time, the sample was filtered and dried and the mass of \( \alpha \)-LM was measured again. The procedure was repeated three times. The same procedure as above was carried out for the HPC sample including repeats. The HPC sample dissolved completely. The amount of \( \alpha \)-LM recovered is slightly less than originally used.

![Image](image-url)
This is less likely to have happened due to \( \alpha \)-LM particles dissolving in 2-propanol, but rather due to some fine particles being lost as they adhered to walls following the drying stage.

### 5.2 Tribo-electrification of binary mixtures

Table 6 above shows the saturated charge-to-mass ratio \( \frac{Q}{m} \) for each binary mixture following tribo-electrification inside a PTFE container. \( \frac{Q}{m} \) decreases with the amount of \( \alpha \)-LM present in a binary mixture decreasing. This is expected as the saturated charge measured on pure \( \alpha \)-LM particles (24.7 nC/g) following tribo-electrification (inside a PTFE container at 20Hz) and the specific saturation charge are significantly higher in comparison with those measured of HPC (3.0 nC/g) in similar test conditions. The introduction of more \( \alpha \)-LM particles into the system increases the chance of \( \alpha \)-LM particles impacting on the walls of the shaking container.

In Table 6, the mass percentage of \( \alpha \)-LM for an ideal mixture measured by the filtration method is shown for each binary mixture system. The amount of particles adhered to walls increases as the \( \alpha \)-LM in the initial system is increased. The 80:20 system has the largest difference between the ideal and measured amounts of \( \alpha \)-LM, and it is expected that this system will cause the largest extent of segregation in the main mixture.

### 5.3 Segregation of the main mixture

The level of segregation of the binary mixture in the bulk of the sample and in the powder mixture adhered to the walls of the container was analysed. The term “the main mixture” is used to refer to the mass recovered from the shaking container following tribo-electrification and it excludes the amount of powder adhered to the walls. In contrast, the term “wall-adhered mixture” is used to refer to wall-adhered material only. The change in \( \alpha \)-LM concentration in the system can be used as an indicator of the extent of segregation of \( \alpha \)-LM in the main mixture (SM). The segregation extent for the main mixture was determined by calculating the ratio between the amount of \( \alpha \)-LM recovered at the end of tribo-electrification and the amount of \( \alpha \)-LM initially used for each sample, as shown by:

\[
S_{M} = 1 - \frac{\text{Conc. of } \alpha-\text{LM in the main mixture after}}{\text{Conc. of } \alpha-\text{LM in the main mixture before}} \quad (6)
\]

An extent of segregation that is equal to one indicates a fully segregated system, whilst a value of zero indicates a system where no segregation has taken place. Therefore, an increase from zero indicates that more \( \alpha \)-LM particles have adhered to the container walls and this indicates that the binary mixture has undergone segregation. In Fig. 6, the extent of segregation of \( \alpha \)-LM in the main mixture is shown as a function of the charge-to-mass ratio. Despite the data scatter, a clear trend is observed. With higher charge-to-mass ratios, the extent of segregation is increased, which implies that the tendency of a binary mixture to segregate is adversely affected by tribo-electric charging of the mixture. However, the extent of segregation is relatively small (below 0.1).

### 5.4 Segregation of the wall-adhered mixture

In order to determine the extent of segregation of \( \alpha \)-LM on the wall (SW), the following equation was used:

\[
S_{W} = 1 - \frac{\text{Amount of } \alpha-\text{LM present on walls}}{\text{Ideal amount of } \alpha-\text{LM on wall}} \quad (7)
\]

Fig. 7 shows the extent of segregation of the wall-adhered mixture as a function of the amount of \( \alpha \)-LM in a binary mixture. The results show that the extent of segregation of \( \alpha \)-LM decreases with an increase in the amount of \( \alpha \)-LM present in a binary mixture. This is expected because an increase in the \( \alpha \)-LM concen-

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Table 6 The average charge and adhesion of binary mixtures

| System | \( \alpha \)-LM:HPC | Shaking Time | \( \frac{Q}{m} \) | \( M_i \) | \( M_a \) | \( M_{\alpha-\text{LM}} \) | \( M_{\text{HPC}} \) |
|--------|------------------|--------------|---------------|--------|--------|-----------------|----------|
| 1      | 10:00            | 45           | 24.68         | 1.0018 | 0.0827 | 0.0827          | -        |
| 2      | 80:20            | 30           | 16.67         | 1.0024 | 0.0802 | 0.0764          | 0.0039   |
| 3      | 60:40            | 30           | 14.21         | 1.0007 | 0.0757 | 0.0546          | 0.0210   |
| 4      | 50:50            | 20           | 11.89         | 1.0021 | 0.0695 | 0.0454          | 0.0241   |
| 5      | 40:60            | 20           | 10.49         | 1.0014 | 0.0673 | 0.0332          | 0.0342   |
| 6      | 20:80            | 15           | 5.01          | 1.0034 | 0.0552 | 0.0144          | 0.0408   |
| 7      | 00:100           | 10           | 3.03          | 1.0025 | 0.039  | -               | 0.039    |

\( M_a \): wall adhesion, \( M_{\alpha-\text{LM}} \): amount of \( \alpha \)-LM in \( M_a \), \( M_{\text{HPC}} \): amount of HPC in \( M_a \), \( M_i \): initial mass.
Concentration in the mixture causes segregation to approach zero asymptotically. The extent of segregation in the wall-adhered powder mixture is remarkable and, in some instances, this value is over 0.3. However, even though the extent of segregation is high on the wall-adhered material, when considering the whole of the mixture, the extent of segregation is less than 0.1. Nevertheless, in an industrial context such as the pharmaceuticals industry, end products of high purity and good content uniformity are essential. The

**Fig. 6** The extent of segregation of α-LM in the main mixture as a function of the charge-to-mass ratio.

**Fig. 7** Extent of segregation of α-LM in the wall-adhered mixture as a function of the initial ratio of α-LM.
variations of components within a binary mixture adhered to walls play a significant role in the content uniformity. The mixture which is built up on the walls of the process equipment due to tribo-electric charging may fall off under its own weight due to gravity and upset the formulation. This phenomenon can take place further down the processing line, after the mixing and blending stages, leading to the formation of aggregates on the walls. These aggregates may be segregated and if falling into the main mixture at the packaging stage, they will cause a transient change in the mixture composition, thus having an immense and adverse impact on the content uniformity.

6. Conclusions

A new methodology has been developed for characterisation of the tribo-electric charging properties of powder materials. \( \alpha \)-LM and HPC powders were used as model materials. The tribo-electric charging and segregation due to preferential wall adhesion were analysed. Furthermore, a simulation model based on the distinct element method was developed to predict the dynamic charging of bulk powders inside a shaking container. The key conclusions are summarised as follows:

- The tribo-electrification propensities of \( \alpha \)-LM, HPC and a 50:50-by-weight binary mixture of the two powder materials were characterised by a mechanical shaking test method.

- All three powders charge positively against the PTFE container at all frequencies. The highest magnitude of charge observed at all three frequencies was with \( \alpha \)-LM. The results show that the saturated charge is independent of the shaking frequency. Increasing the shaking frequency decreases saturation time, as intuitively expected. The charging trend follows a first-order rate process. All three test powders charge negatively against stainless steel and glass. The magnitude of charge is low compared to PTFE and is lowest against stainless steel.

- High-speed video recording was used to observe particle motion at different frequencies. The results show that particle motion can be classified into two types of flow regimes, i.e. sliding and impact. At the lowest frequency, the particle movement is mainly by the sliding of the powder bed. At intermediate frequency, particles are divided between sliding at the bottom of the bed and impacting on the ends and upper wall of the container. At the highest frequency, the particles seem to be more suspended.

- Tribo-electrification of spherical beads inside a horizontally shaken sealed capsule was analysed experimentally and simulated using a DEM model. An empirical first-order rate equation, based on experimental data obtained from a single particle charging rate, was incorporated in the DEM simulations. It was found that the model significantly overestimates the total charge build-up for bulk shaking, as compared with the experimental results. However, the inclusion of long-range forces, space charge effects and boundary conditions into the DEM model significantly improves the prediction of total charge build-up.

- The results of the segregation analysis show that the extent of segregation in the main mixture increases linearly with an increase in the amount of \( \alpha \)-LM and consequently with the net charge on binary mixtures. The extent of segregation is highest in the 80:20 and lowest in the 20:80 ratio binary mixtures. However, the extent of segregation does not exceed 0.1 when the main mixture is considered. The extent of segregation measured for the wall-adhered mixtures shows an opposite trend to that of the main mixture, i.e. decreasing linearly with the amount of \( \alpha \)-LM increasing in the binary mixture. In this case, the extent of segregation is considerably higher than that of the main mixture with the highest value being 0.31 for the 20:80 ratio mixtures and the lowest of 0.19 for the 80:20 ratio mixtures.

It may be concluded that tribo-electric charging of powders can be carried out by the shaking container evaluated in this work. It can be used to quantify the electrostatic charge interactions between pharmaceutical powders and equipment surfaces. The interactions between particles and walls, which often result in particles adhering to walls, are relevant to many pharmaceutical operations. An understanding of the charge magnitude and polarity of pharmaceutical powders due to contact with containing surfaces is useful in the development of pharmaceutical formulations, where excipients and APIs are mixed together, as otherwise particles can be lost through particle-wall adhesion and could possibly cause segregation problems during mixing processes.
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