Assessing Powder Flowability at Low Consolidation Stresses

by

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Declaration of Originality

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Abstract

The inability of cohesive powders to flow consistently and reliably is a major cause of process
downtime and product wastage across a wide range of powder processing industries. Extensive work
has been carried out characterising powder flowability using a wide array of techniques, with the most
established method of powder flow measurement at moderate to high stresses being shear cells, with
theories developed for silo and hopper design. Many processes of great industrial interest though,
such as filling and dosing of powders in capsules and dispersion in dry powder inhalers (DPI), expose
particles to very low consolidation stresses (≤ 1 kPa), at which the determination of unconfined yield
strength by shear testing is often marred with inconsistencies in the measurement, or in comparison
to the observed behaviour. Therefore, there is a need for an alternative approach in order to develop
an understanding of powder flow for weakly consolidated powders, such as ball indentation, which is
a penetration technique capable of assessing powder flowability down to very low stresses, whilst
requiring only a very small amount of material. In this technique, a powder bed is consolidated to any
desired stress that provides a reasonably flat surface, and then penetrated by a spherical indenter.
The flowability is determined by calculating the hardness of the powder bed, from the force-
displacement response of the bed. Hardness can be linked to the unconfined yield strength, commonly
derived by shear testers, via the constraint factor, which is dependent on particle properties, although
cannot yet be determined a priori.

In this work, the constraint factor of a broad class of powders was quantified from indentation and
shear cell experiments at moderate to high stresses and was found to be generally independent of the
applied stress, while for four out of the twenty-five materials it exhibited fluctuations. In order to infer
the unconfined yield strength from hardness measurements at low stresses, it was assumed that the
constraint factor remains constant at lower stresses. Distinct Element Method (DEM) modelling was
also utilised to simulate the ball indentation system, allowing the powder bed internal failure stresses
to be realised in order to elucidate the behaviour of the constraint factor at low stresses. The
simulations validated the assumption that the constraint factor remains constant throughout the
applied stress range.

Furthermore, the applicability and reliability of both ball indentation and the FT4 shear cell were
assessed in a wide range of both low and moderate to high stresses. Ball indentation gave very
repeatable results throughout the whole range of stresses applied, whilst the FT4 shear cell was
deemed unreliable for most materials at pre-shear normal stresses of 1 kPa and below. For all
materials except the three powders that remain very cohesive throughout the stress range tested, the
increase of hardness (and therefore also the unconfined yield strength inferred from ball indentation)
with stress was observed to be much steeper at low stresses, as compared to higher stresses, due to a more rapid increase in packing fraction. For all model glass beads tested, except for the 0 - 20 μm samples, hardness was found to be independent of penetration depth in a certain depth range. In contrast, for most ‘real’ materials, plus the aforementioned very fine model glass beads, hardness was found to continually increase with depth, with a gradient that is independent of the applied stress and similar for all materials tested. The powders that are prone to stick-slip deviated from the above behaviour and exhibited a fluctuating force response.

The influence of a variety of particle properties on the constraint factor, and subsequently powder flowability, was also determined both experimentally and computationally. The effects of particle size, size distribution, and single particle and agglomerate shape were investigated experimentally, whilst static and rolling friction, and plastic yield stress were varied in DEM simulations. The influence of interface energy was studied both experimentally and by DEM modelling. All properties were found to affect the constraint factor and flow behaviour to some extent, denoting the complexity of powder flow behaviour.
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Dedicated to my beloved parents

Victor Aris & Eleftheria
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# Nomenclature

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<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>Normal overlap</td>
<td>m</td>
</tr>
<tr>
<td>$A$</td>
<td>Projected area of the impression of the indenter</td>
<td>m$^2$</td>
</tr>
<tr>
<td>$a^*$</td>
<td>Plastic flow limit overlap</td>
<td>m</td>
</tr>
<tr>
<td>$a_0$</td>
<td>Overlap at zero contact force</td>
<td>m</td>
</tr>
<tr>
<td>$a_{op}$</td>
<td>Overlap at which the extrapolated plastic loading curve intercepts the x-axis</td>
<td>m</td>
</tr>
<tr>
<td>$A_{bed}$</td>
<td>Area of the powder bed</td>
<td>m$^2$</td>
</tr>
<tr>
<td>$a_c$</td>
<td>Overlap at the pull-off force in Thornton and Ning’s model</td>
<td>m</td>
</tr>
<tr>
<td>$A_c$</td>
<td>Average interparticle contact surface area</td>
<td>m$^2$</td>
</tr>
<tr>
<td>$a_{co}$</td>
<td>Contact re-establishment overlap</td>
<td>m</td>
</tr>
<tr>
<td>$a_{cp}$</td>
<td>Overlap at pull-off force after plastic deformation</td>
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</tr>
<tr>
<td>$a_f$</td>
<td>Contact breakage overlap in the JKR model</td>
<td>m</td>
</tr>
<tr>
<td>$a_{fe}$</td>
<td>Elastic contact breakage overlap</td>
<td>m</td>
</tr>
<tr>
<td>$a_{fp}$</td>
<td>Plastic contact breakage overlap</td>
<td>m</td>
</tr>
<tr>
<td>$A_H$</td>
<td>Hamaker constant</td>
<td>-</td>
</tr>
<tr>
<td>$a_{imp}$</td>
<td>Radius of the impression</td>
<td>m</td>
</tr>
<tr>
<td>$a_{max}$</td>
<td>Maximum overlap</td>
<td>m</td>
</tr>
<tr>
<td>$a_p$</td>
<td>Plastic deformation overlap</td>
<td>m</td>
</tr>
<tr>
<td>$a_t$</td>
<td>Tangential overlap</td>
<td>m</td>
</tr>
<tr>
<td>$a_y$</td>
<td>Plastic yield overlap</td>
<td>m</td>
</tr>
<tr>
<td>$c$</td>
<td>Cohesion</td>
<td>Pa</td>
</tr>
<tr>
<td>$C$</td>
<td>Constraint factor</td>
<td>-</td>
</tr>
<tr>
<td>$C'$</td>
<td>Effective constraint factor</td>
<td>-</td>
</tr>
<tr>
<td>$Cl$</td>
<td>Carr Index</td>
<td>-</td>
</tr>
<tr>
<td>$d$</td>
<td>Separation distance between two bodies</td>
<td>m</td>
</tr>
<tr>
<td>$d_{10}$</td>
<td>Diameter of the particle that 10 % of a sample’s mass is smaller than</td>
<td>m</td>
</tr>
<tr>
<td>$d_{50}$</td>
<td>Mass median diameter</td>
<td>m</td>
</tr>
<tr>
<td>$d_{90}$</td>
<td>Diameter of the particle that 90 % of a sample’s mass is smaller than</td>
<td>m</td>
</tr>
<tr>
<td>$d_b$</td>
<td>Diameter of the indenter</td>
<td>m</td>
</tr>
<tr>
<td>$D_d$</td>
<td>Diameter of the die</td>
<td>m</td>
</tr>
</tbody>
</table>
$d_p$ Particle diameter \text{ m}

$d_v$ Particle equivalent volumetric size \text{ m}

e Coefficient of restitution -

$E$ Young’s modulus \text{ Pa}

$E^*$ Reduced Young’s modulus \text{ Pa}

$E_1$ Young’s modulus of element 1 \text{ Pa}

$E_2$ Young’s modulus of element 2 \text{ Pa}

$E_{flow}$ Flow energy \text{ J}

$F'_n$ Previous normal force \text{ N}

$F'_t$ Previous tangential force \text{ N}

$f_0$ Contact force at zero overlap in Luding and Pasha \textit{et al.} models \text{ N}

$f_{cp}$ Intercept of the linear fit to the pull-off force of Pasha \textit{et al.} with the force axis \text{ N}

$F_{base}$ Vertical force acting on the base \text{ N}

$F_{bed}$ Normal force applied to the powder bed \text{ N}

$f_{ce}$ JKR elastic pull-off (adhesion) force \text{ N}

$F_{cp}$ Plastic pull-off force in Thornton and Ning’s model \text{ N}

$f_{cp}$ Plastic pull-off force in Luding and Pasha \textit{et al.} models \text{ N}

$F_{det}$ Detachment force \text{ N}

$f_{fc}$ Flow factor -

$F_H$ Interparticle force exerted on each individual particle \text{ N}

$F_{HO}$ Adhesion force between particles with no external normal force \text{ N}

$F_j$ $j$-component of the contact force \text{ N}

$F_{max}$ Maximum indentation load \text{ N}

$f_{max}$ Maximum contact force in Pasha \textit{et al.} model \text{ N}

$F_{max,p}$ Maximum force during plastic deformation in Thornton and Ning’s model \text{ N}

$F_{\text{max}}^*$ JKR equivalent maximum contact force \text{ N}

$F_n$ Normal contact force \text{ N}

$F_t$ Tangential force \text{ N}

$F_{VW}$ van der Waals force \text{ N}

g Gravitational acceleration \text{ m/s}^2

$G$ Shear modulus \text{ Pa}

$G^*$ Reduced shear modulus \text{ Pa}

$G_1$ Shear modulus of element 1 \text{ Pa}
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G_2$</td>
<td>Shear modulus of element 2</td>
<td>Pa</td>
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<tr>
<td>$H$</td>
<td>Hardness</td>
<td>Pa</td>
</tr>
<tr>
<td>$H_{2,3}$</td>
<td>Distance between the pressure taps PT2 and PT3</td>
<td>m</td>
</tr>
<tr>
<td>$h_{\text{bed}}$</td>
<td>Height of the powder bed</td>
<td>m</td>
</tr>
<tr>
<td>$h_{\text{blade}}$</td>
<td>Blade penetration depth</td>
<td>m</td>
</tr>
<tr>
<td>$h_c$</td>
<td>Elastically-recovered depth</td>
<td>m</td>
</tr>
<tr>
<td>$h_d$</td>
<td>Dimensionless penetration depth</td>
<td>-</td>
</tr>
<tr>
<td>$H_d$</td>
<td>Dynamic hardness</td>
<td>Pa</td>
</tr>
<tr>
<td>$h_f$</td>
<td>Final depth of the impression</td>
<td>m</td>
</tr>
<tr>
<td>$h_m$</td>
<td>Penetration depth at maximum indentation load</td>
<td>m</td>
</tr>
<tr>
<td>$H_{\text{plug}}$</td>
<td>Height of the plug detached</td>
<td>m</td>
</tr>
<tr>
<td>$HR$</td>
<td>Hausner Ratio</td>
<td>-</td>
</tr>
<tr>
<td>$k_c$</td>
<td>Cohesive stiffness</td>
<td>N/m</td>
</tr>
<tr>
<td>$k_{cp}$</td>
<td>Slope of the linear fit to the pull-off force curve of Pasha et al. model</td>
<td>N/m</td>
</tr>
<tr>
<td>$k_e$</td>
<td>Elastic stiffness</td>
<td>N/m</td>
</tr>
<tr>
<td>$k'_{e}$</td>
<td>Maximum value of the elastic stiffness in Luding’s model</td>
<td>N/m</td>
</tr>
<tr>
<td>$k_{\text{largest}}$</td>
<td>Largest stiffness in the system</td>
<td>N/m</td>
</tr>
<tr>
<td>$k_n$</td>
<td>Normal stiffness</td>
<td>N/m</td>
</tr>
<tr>
<td>$k_n^1$</td>
<td>Normal stiffness of element 1</td>
<td>N/m</td>
</tr>
<tr>
<td>$k_n^2$</td>
<td>Normal stiffness of element 2</td>
<td>N/m</td>
</tr>
<tr>
<td>$k_p$</td>
<td>Plastic stiffness</td>
<td>N/m</td>
</tr>
<tr>
<td>$k_t$</td>
<td>Tangential stiffness</td>
<td>N/m</td>
</tr>
<tr>
<td>$k_t^1$</td>
<td>Tangential stiffness of element 1</td>
<td>N/m</td>
</tr>
<tr>
<td>$k_t^2$</td>
<td>Tangential stiffness of element 2</td>
<td>N/m</td>
</tr>
<tr>
<td>$m$</td>
<td>Mass of the particle</td>
<td>kg</td>
</tr>
<tr>
<td>$M$</td>
<td>Mass of the powder</td>
<td>kg</td>
</tr>
<tr>
<td>$M_{\text{ind}}$</td>
<td>Mass of the indenter</td>
<td>kg</td>
</tr>
<tr>
<td>$m_{\text{smallest}}$</td>
<td>Mass of the smallest particle in the system</td>
<td>kg</td>
</tr>
<tr>
<td>$n$</td>
<td>Shear index</td>
<td>-</td>
</tr>
<tr>
<td>$n/n_m$</td>
<td>Surface coverage</td>
<td>-</td>
</tr>
<tr>
<td>$N_c$</td>
<td>Number of contacts</td>
<td>-</td>
</tr>
<tr>
<td>$n_i$</td>
<td>$i$-component of the normal vector from a particle centroid to its contact</td>
<td>-</td>
</tr>
<tr>
<td>$N_p$</td>
<td>Number of particles</td>
<td>-</td>
</tr>
<tr>
<td>$p$</td>
<td>Proportionality constant</td>
<td>-</td>
</tr>
</tbody>
</table>
\[ PD \quad \text{Poured bulk density} \quad \text{kg/m}^3 \]
\[ p_y \quad \text{Contact yield pressure} \quad \text{Pa} \]
\[ r \quad \text{Surface roughness} \quad \text{m} \]
\[ R \quad \text{Particle radius} \quad \text{m} \]
\[ R^* \quad \text{Reduced radius} \quad \text{m} \]
\[ R_1 \quad \text{Radius of element 1} \quad \text{m} \]
\[ R_2 \quad \text{Radius of element 2} \quad \text{m} \]
\[ R_b \quad \text{Radius of the indenter} \quad \text{m} \]
\[ R_{\text{crit}} \quad \text{Critical radius} \quad \text{m} \]
\[ R_{\text{imp}} \quad \text{Radius of the impeller} \quad \text{m} \]
\[ R_{p1} \quad \text{Radius of particle size 1} \quad \text{m} \]
\[ R_{p2} \quad \text{Radius of particle size 2} \quad \text{m} \]
\[ R_p^* \quad \text{Contact curvature} \quad \text{m} \]
\[ T \quad \text{Torque acting on the impeller} \quad \text{N} \cdot \text{m} \]
\[ t_{\text{cont}} \quad \text{Contact time between the stub and the stopper} \quad \text{s} \]
\[ TD \quad \text{Tapped bulk density} \quad \text{kg/m}^3 \]
\[ T_R \quad \text{Rayleigh time-step} \quad \text{s} \]
\[ t_{\text{sim}} \quad \text{Integration time-step} \quad \text{s} \]
\[ U \quad \text{Unrelaxed volume of the indentation impression} \quad \text{m}^3 \]
\[ U_{\text{mf}} \quad \text{Minimum fluidisation velocity} \quad \text{m/s} \]
\[ U_{\text{ro}} \quad \text{Rain-off velocity} \quad \text{m/s} \]
\[ v \quad \text{Impact velocity} \quad \text{m/s} \]
\[ V \quad \text{Volume of the powder} \quad \text{m}^3 \]
\[ V_i \quad \text{Incident velocity} \quad \text{m/s} \]
\[ V_m \quad \text{Volume of the measurement cell} \quad \text{m}^3 \]
\[ x_i^c \quad i\text{-component of the contact location} \quad \text{m} \]
\[ x_i^p \quad i\text{-component of the particle centre location} \quad \text{m} \]
\[ z \quad \text{Bed depth} \quad \text{m} \]
\[ z_0 \quad \text{Distance between the base of the die and the piston at the starting point} \quad \text{m} \]
\[ z_f \quad \text{Final displacement of consolidation} \quad \text{m} \]
Greek Characters

\( \alpha \)  Adhesiveness \( \text{kg/m} \cdot \text{s}^2 \)
\( \Gamma \)  Interface energy \( \text{J/m}^2 \)
\( \gamma \)  Surface energy \( \text{J/m}^2 \)
\( \gamma^{AB} \)  Acid-base surface energy \( \text{J/m}^2 \)
\( \gamma^d \)  Dispersive surface energy \( \text{J/m}^2 \)
\( \gamma^o \)  Shear strain rate \( \text{s}^{-1} \)
\( \gamma^o* \)  Dimensionless shear strain rate -
\( \Gamma_{p1} \)  Interface energy of particle size 1 \( \text{J/m}^2 \)
\( \Gamma_{p2} \)  Interface energy of particle size 2 \( \text{J/m}^2 \)
\( \Delta F_n \)  Increment of the normal force \( \text{N} \)
\( \Delta F_t \)  Increment of the tangential force \( \text{N} \)
\( \Delta P_{plug \ (u_{mf})} \)  Pressure drop of the powder at minimum fluidisation velocity \( \text{Pa} \)
\( \Delta P_{plug \ (u_{ro})} \)  Pressure drop of the powder across the plug height at rain-off velocity \( \text{Pa} \)
\( \Delta P_{max} \)  Maximum applied pressure drop \( \text{Pa} \)
\( \Delta \alpha \)  Increment of the normal overlap \( \text{m} \)
\( \Delta \alpha_t \)  Increment of the tangential overlap \( \text{m} \)
\( \varepsilon \)  Void fraction -
\( \varepsilon_{av} \)  Average void fraction -
\( \kappa \)  Mean number of contacts per particle -
\( \lambda \)  Material’s contact consolidation constant -
\( \mu_r \)  Coefficient of rolling friction -
\( \mu_s \)  Coefficient of static friction -
\( \nu \)  Poisson’s ratio -
\( \nu_1 \)  Poisson’s ratio of element 1 -
\( \nu_2 \)  Poisson’s ratio of element 2 -
\( \rho_b \)  Bulk density \( \text{kg/m}^3 \)
\( \rho_p \)  Particle density \( \text{kg/m}^3 \)
\( \rho_t \)  True density \( \text{kg/m}^3 \)
\( \sigma \)  Normal stress \( \text{Pa} \)
\( \sigma_1 \)  Major principal stress \( \text{Pa} \)
\( \sigma_2 \)  Minor principal stress \( \text{Pa} \)
\( \sigma_3 \)  Intermediate principal stress \( \text{Pa} \)
\( \sigma_{\text{bot}} \) Consolidation stress at the bottom of the bed  Pa
\( \sigma_c \) Unconfined yield strength  Pa
\( \sigma \) \( ij \)-component of the stress tensor  Pa
\( \sigma_{\text{pre}} \) Pre-shear (normal) stress  Pa
\( \sigma_y \) Plastic yield stress  Pa
\( \sigma_t \) Tensile strength  Pa
\( \sigma_{\text{lim}} \) Limiting tensile strength  Pa
\( \tau \) Shear stress  Pa
\( \tau_0 \) Deviatoric stress  Pa
\( \tau_{\text{pre}} \) Pre-shear shear stress  Pa
\( \varphi \) Angle of internal friction  deg
\( \varphi_b \) Angle of the FT4 blade’s helical path to the horizontal plane  deg
\( \varphi_e \) Effective angle of internal friction  deg
\( \varphi_f \) Dimensionless plasticity depth -
\( \chi \) Packing fraction -
\( \psi \) Particle sphericity -
Abbreviations

AFI  Avalanche flow index
AFM  Atomic Force Microscopy
AOR  Angle of repose
AR   Aspect ratio
BI   Ball indentation
CLSM Confocal Laser Scanning Microscopy
Col  Cohesive interaction index
DEM  Distinct Element Method
FD-IGC Finite Dilution Inverse Gas Chromatography
GDR  Gravitational Displacement Rheometer
msFBR Mechanically Stirred Fluidised Bed Rheometer
MTA  Mean time to avalanche
NIBS Non-Invasive Back Scatter
PFA  Powder Flow Analyser
RH   Relative humidity
SEM  Scanning Electron Microscopy
SPT  Sevilla Powder Tester
XRMT X-ray Microtomography
Chapter 1 Introduction

First and foremost, this chapter serves the purpose of introducing the gap in current knowledge of powder flowability at low consolidation stresses, justifying the need for this research work. In addition to this, it sets the main objectives of this project, concluding with an overview and the structure of this PhD thesis.

1.1 Identifying the gap in present knowledge

Nowadays, a large proportion of the materials processed and the products manufactured in industry are in the form of particulate solids. Several industries, such as pharmaceuticals, chemicals, food, materials and fast-moving consumer goods, consist of processes that involve granular materials, such as fluidisation, granulation, mixing, tableting and storage in bins or hoppers, therefore they are particularly interested to understand their behaviour in order to properly design processes and equipment. One of the major concerns regarding bulk solids handling is the inability of cohesive powders to flow consistently and reliably. Cohesive materials can lead to the formation of stagnant regions or flow stoppages in process equipment, resulting in uncontrolled or erratic flow rates from industrial equipment, and potentially causing segregation problems (Johanson, 2009). Therefore, studying the flow behaviour of cohesive powders is vital, since poor flow can severely affect the manufacturing efficiency and the quality of the product in terms of its weight and content uniformity, consequently leading to equipment malfunction and product wastage, and finally to additional unwanted cost (Prescott and Barnum, 2000). In contrast to the study of fluids, where the term rheology is used to describe flow, for powders the not so well-defined term ‘flowability’ is used, which has been given various definitions such as the relative movement of a bulk of particles amongst neighbouring particles or along the container wall surface (Peleg, 1977), or more simply the ability of the powder to flow (Prescott and Barnum, 2000). Flowing, or yielding, means that a powder is brought to irreversible deformation by an external mechanical stressing event, which can be considered as a force or energy (Tomas and Kleinschmidt, 2009). The reason for the absence of a universally accepted definition is that particulate systems’ behaviour is multivariable, depending on both intrinsic particle properties such as particle size, size distribution, shape, density, surface roughness, porosity, cohesive and frictional forces between particles and system properties such as the stresses applied during storage and processing, and strain rate, as well as on external factors such as temperature and humidity (Rios, 2006).

Over the years, there have been a diverse array of techniques developed for assessing powder flowability, which mostly focused on silo and hopper design and/or qualitative assessment of bulk
solid flow, yet there is still a limited understanding on precisely how particle properties, stressing conditions and environmental factors affect flowability in a way that could lead to a reliable prediction of powder flow behaviour. None of the flow evaluation methods are universally applicable, since they usually measure a certain property of the powder that reflects the state of the powder in this specific experiment, and therefore their usage is meaningful in limited applications. Nevertheless, shear cells are the most widely accepted quantitative technique. Shear testing was introduced by Jenike (1961; 1964; 1967), with theories developed for the design of suitable hoppers and prediction of mechanical arching (Tang and Behringer, 2011) and cohesive arching (Enstad, 1975). Later various more robust shear cells followed (Schulze, 2008). Shear cells operate in the quasi-static regime, typically at moderate to high stresses that exist in large storage bins or hoppers, measuring the shear stress required to initiate flow under a given normal stress, and subsequently allowing the unconfined yield strength to be estimated from the measured yield locus. As with most traditional flowability assessment techniques, they typically fail to evaluate the flow behaviour of cohesive powders at low consolidation stresses (≤ 1 kPa). At such stresses shear cells are normally unable to generate steady-state shear, or the reproducibility of the measurement of unconfined yield strength is greatly reduced, or does not correlate with observed process behaviour (Schulze, 2008; Søgaard et al., 2014). The common practice is to assume linearity for yield loci, which are extrapolated towards zero normal stress, leading to an overestimation of unconfined yield strength and cohesion, since yield loci tend to curve downwards in the region of low stresses (Schulze, 2008). There are many processes of great interest during which granular materials are exposed to such low stresses and their flowability needs to be determined, such as flow in small scale hoppers, filling and dosing of powders in capsules, feeding powders for packing and tableting machines, and dispersion in dry powder inhalers (DPI). Under such stresses, small contact areas exist between constituent particles, and very little particle deformation occurs, leading to a low structural strength (Harnby et al., 1987). An aerated powder needs a lot less energy to make it flow than is required when the same powder is consolidated (Freeman, 2005). For all the aforementioned reasons, there is a need for established methods for powder flow measurement at low stresses, so that the results are generalisable to a broad class of powders.

To address these issues, over the last decade or so, a number of powder flowability assessment techniques capable of measuring at low stresses have emerged, or become more prominent. The focal point of this research work is the ball indentation (BI) technique, a penetration test, which falls in the above category. It was introduced by Hassanpour and Ghadiri (2007), with its operational window being thoroughly established experimentally by Zafar et al. (2017) and computationally by Pasha et al. (2013). In this method, a die is filled with powder and pre-consolidated by uniaxial compression,
following which a spherical indenter is driven into the sample, whilst its penetration depth and the resulting vertical force are measured. From the force-displacement response of the powder bed, hardness is the index that is directly measured, which corresponds to the resistance of the bed to plastic deformation. Ball indentation offers the capability of obtaining hardness measurements at any stress level, as long as a flat surface is available for indentation. However, it is commonly of interest to measure the unconfined yield strength, as determined by shear cells. Tabor (1951) demonstrated for continuum materials that for a given material, hardness is directly linked to the unconfined yield strength via the constraint factor. Currently the constraint factor of a powder is not known a priori, consequently in order to determine the unconfined yield strength of a powder bed by ball indentation it is necessary to determine the constraint factor of the powder. As such, it is beneficial to develop an understanding of how particle properties influence the constraint factor in order to predict its value for a given powder. In this regard, it is also necessary to understand if the constraint factor shows any variation with stress, i.e. whether the constraint factor determined at high stresses, by comparing indentation hardness with unconfined yield strength measured in a shear cell, can be applied to indentation measurements at lower stresses. Taking the above into consideration, this project, which is funded by the International Fine Particle Research Institute (IFPRI), aims to further the investigation on the ball indentation technique by emphasising on low stresses, both experimentally and computationally, with its ultimate goal being to elucidate the flowability of weakly consolidated powders.

### 1.2 Main research objectives

The overall goal of this PhD thesis is to improve the current understanding of powder flowability at low consolidation stresses, which is of great interest for many industrial processes, as discussed above, utilising both experiments and DEM modelling. The main objectives of this work are to:

i. Determine the operational range and reliability of the ball indentation technique
ii. Determine how powder flowability at low stresses (≤ 1 kPa) differs from that at high stresses
iii. Establish the influence of particle properties on powder flow behaviour
iv. Determine the variation of the constraint factor with stress level and powder properties

### 1.3 Project overview and structure of thesis

As mentioned above, this piece of research work employs particle characterisation and powder flowability determination experiments, as well as DEM simulations, in order to deliver its main aims.

An overview of the work of this project that encompasses how the different aspects interact with each other is presented in Figure 1.1.
Furthermore, the contents of the following chapters are as follows:

Chapter 2 constitutes a comprehensive literature review on powder flow. The main factors that influence bulk solid flow are presented, as well as the most established flow indices and powder flowability assessment techniques. The chapter closes with a thorough evaluation of the aforementioned techniques.

Chapter 3 summarises all the materials that were tested experimentally, including their particle size and shape characterisation. In addition to this, all the methods used for particle characterisation, surface treatment, surface energy measurement and powder flowability determination are described.

Chapter 4 is a study of the flowability of various samples of model glass beads at both high and low stresses using shear testing and ball indentation. In each experimental series, the samples under investigation differ in one certain property, which is isolated and studied at a time, with its influence on the constraint factor and powder flowability being established.

In Chapter 5, the same flowability measurement techniques as in the previous chapter are employed with the aim of studying the flow behaviour of a broad class of inorganic and organic powders in a wide range of stresses. The applicability and reliability of ball indentation are assessed, along with the reproducibility and reliability of the FT4 shear cell down to very low stresses. Moreover, the influence
of some properties on the constraint factor is explored, as well as the stick-slip behaviour which some organic powders exhibit during testing.

Chapter 6 is devoted to the DEM modelling work that was carried out as part of this project. First, the Distinct Element Method (DEM) is introduced and some of the most widely used contact models in DEM simulations are presented. Following this, a ball indentation system is simulated and the variation of the constraint factor with stress throughout a wide range of stresses is investigated. In addition to this, further investigation on various properties that influence the constraint factor and particulate flow at low stresses is conducted.

Finally, in Chapter 7, a summary of the main conclusions of the thesis is presented, together with suggestions for future research in this field.
Chapter 2  Literature Review

In this chapter, some basic principles of powder flow testing are presented first, followed by a discussion of the most dominant factors affecting bulk solid flow. After that, the most prominent powder flowability assessment techniques are introduced, and are evaluated based on some proposed criteria at the end of the chapter.

2.1  Basic principles and commonly used powder flow indices

2.1.1  Major principal stress, unconfined yield strength and flow function

For almost 60 years now, the most widely accepted and commonly used powder flowability index is the flow factor, \( ff_c \), which was introduced in the pioneering work of Jenike (1961; 1964), who studied bulk solid flow behaviour by treating them as a rigid-plastic Coulomb-solid, an approach that was already applied in soil mechanics. Based on this, plastic flow is governed by a limiting stress function, such that stresses lower than those determined by this function do not cause any plastic deformation; stresses equal to this critical stress state lead to plastic flow; and stresses exceeding this limit are not permissible (Ashton et al., 1965).

Perhaps the most vivid way of illustrating this is with a uniaxial compression test (Figure 2.1), which itself constitutes a flow measurement technique, which will be discussed further in section 2.3 along with the other flow evaluation methods. In this simple test, a sample is filled into a cylinder with low friction walls and is consolidated vertically by a piston, under a normal consolidation stress, which is equal to the major principal stress, \( \sigma_1 \) (assuming zero wall friction). After that, the stress is removed, and the cylinder is gently removed. At this stage, the stresses that act perpendicular to the direction of consolidation are all zero, while the material is in an unconfined state and possesses enough cohesive strength to stand alone as a column. Then, the sample is loaded with an increasing vertical normal stress up to the point that the powder bed fails, and consequently starts to flow. The stress at failure is the unconfined yield strength, \( \sigma_c \), of the material (Schulze, 2008).
Since the powder bed fractures at an exact stress, there is a specific yield limit of the material, which depends on its stress history (level of pre-consolidation). The flow factor is the ratio of the major principal stress applied over the unconfined yield strength of the material at this consolidation stress, as shown in Equation 2.1:

$$ff_c = \frac{\sigma_1}{\sigma_c} \quad (2.1)$$

The flow factor is not a material property, since it depends on the major principal stress that the powder undergoes. So, every time the flow factor is used, the pre-consolidation stress should be stated as well. Based on this parameter, Tomas and Schubert (1979) categorised bulk solids as shown in Table 2.1. The curve $\sigma_c$ vs. $\sigma_1$, shown in Figure 2.2, is called the flow function, or instantaneous flow function to highlight that the unconfined yield strength is measured directly after consolidation. An increase of the pre-consolidation stress under which the powder is compressed generally leads to an increase in its flowability (Schulze, 2008).

<table>
<thead>
<tr>
<th>$ff_c$ value</th>
<th>Flow behaviour</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 1</td>
<td>Non-flowing</td>
</tr>
<tr>
<td>1 - 2</td>
<td>Very cohesive</td>
</tr>
<tr>
<td>2 - 4</td>
<td>Cohesive</td>
</tr>
<tr>
<td>4 - 10</td>
<td>Easy-flowing</td>
</tr>
<tr>
<td>&gt; 10</td>
<td>Free-flowing</td>
</tr>
</tbody>
</table>
The test shown above depicts a simple case, in which only normal stresses are exerted on the material, whereas in realistic situations the bulk solid is subjected to shear stresses as well. Although seemingly it is a convenient way of determining the flow factor, the preferred way of measuring it is by shear testing, for reasons that will be discussed in section 2.3. Shear testing is based on the work of Jenike (1961; 1964), who not only developed the theoretical background for bulk solid flow from silos and hoppers, but also a tester to measure flow properties. In shear tests, a loose, uncompacted material is subjected to a constant pre-consolidation normal force, before being sheared until constant packing conditions have been achieved. Then, the material is sheared under different, either increasing or decreasing normal loads (depending on the protocol followed), with the bed being returned to the pre-consolidation constant packing condition prior to each shear to failure step, each of which provides a new shear force. Plotting shear stress, τ vs. normal stress, σ, gives a curve that is called the yield locus and represents the maximum shear stress at a specific normal load that the material can withstand before failing, with respect to the packing state of the pre-consolidation condition (Schulze, 2008). An example yield locus and its analogy to the previously discussed unconfined uniaxial compression are shown in Figure 2.3.
If the yield locus is known, various flow properties can be found. In order to determine the major principal stress and the unconfined yield strength, Mohr stress circle analysis has to be applied. A Mohr stress circle is a geometric representation of a coordinate transformation which identifies the principal stresses acting on all cutting planes of the material at a certain stress state. The principle, based on which Mohr circles are drawn, is described elsewhere (Schulze, 2008). If an uncompacted powder bed is loaded with a normal stress, its bulk density will increase. As the following shearing starts, particles begin to move against each other and frictional forces increase until a point where the frictional forces are maximised, and the bulk solid begins to undergo plastic deformation. A powder bed that exhibits an increase of bulk density when being sheared is called underconsolidated. The point at which the particles are fully mobilised and the bulk density and the stresses acting on the powder are constant is the point when steady-state flow initiates, with the bulk solid having achieved what is called a critically consolidated state with respect to the normal stress. In a shear test, instead of having a loosely compressed specimen, the bulk solid is overconsolidated before the shearing to failure step initiates, so in this case the plastic deformation will start only after the shear stress that is exerted on the bed is large enough to overcome the previous state of consolidation. Incipient flow
starts at point e in Figure 2.3, which constitutes the end point of the yield locus in the direction of increasing normal stresses, as well as the point where the yield locus contacts the Mohr circle of pre-consolidation, also known as steady-state Mohr circle. The aforementioned Mohr circle intercepts the normal stress axis at the major principal stress, which is the largest of all normal stresses acting during steady-state flow in all possible cutting planes of the specimen, and is comparable to the consolidation stress of the uniaxial compression test. The steady-state Mohr circle also intercepts the normal stress axis at the minor principal stress, \( \sigma_2 \), which is the smallest normal stress in all possible cutting planes. The principal stresses act on cutting planes along which the shear stress is zero, and are perpendicular to each other. The smaller Mohr circle that is depicted in Figure 2.3 is the Mohr circle representing failure, therefore having its minor consolidation stress at zero, while its other intercept with the \( \sigma \)-axis is the unconfined yield strength. Each yield locus gives one pair of values of the unconfined yield strength and the major principal stress, therefore enabling the calculation of the flow factor for a given pre-consolidation stress. Independent flow factor values can be determined for each yield locus derived at different pre-consolidation stresses. The angle \( \phi_e \) between the \( \sigma \)-axis and a straight line tangent to the steady-state Mohr circle which passes through the origin, known as the effective yield locus, is called the effective angle of internal friction, representing particle friction at steady-state flow, and is very important in the design of silos (Schulze, 2008). Similarly, friction at incipient flow is represented by the slope of the linearised yield locus measured against the \( \sigma \)-axis, which is called angle of internal friction, \( \varphi \) (not shown in Figure 2.3).

### 2.1.2 Cohesion and tensile strength

Two more noteworthy flow parameters are the cohesion, \( c \), which is the shear stress when the material is not subjected to an imposed normal load, and the tensile strength, \( \sigma_t \), which is the intercept of the yield locus on the abscissa at zero shear stress, and constitutes its end point. These parameters can only be evaluated if the yield locus is extrapolated towards zero and negative normal stresses, respectively, since conventional shear cells are not able to test in this regime. The common practice for the determination of the cohesion is to linearly extrapolate the yield locus towards low stresses, which may not always be very accurate, particularly for cohesive powders, since the yield locus is increasingly curved towards low stresses (Schulze, 2008). The tensile strength can be found experimentally with the use of tensile testers that will be discussed in section 2.3. The Warren Spring model was introduced by Ashton et al. (1965) to characterise the yield locus, and is described by Equation 2.2:

\[
\left( \frac{T}{c} \right)^n = \frac{\sigma}{\sigma_t} + 1 \quad (2.2)
\]
where $n$ is the shear index of the material. The shear index is a material-dependent parameter that varies between 1, for free-flowing materials, to 2, for cohesive materials, and has been found to be independent of packing conditions (Ashton et al., 1965). Data fitting is needed in order to determine the cohesion and tensile strength of the powder.

### 2.1.3 Compressibility Index and Hausner Ratio

Bulk density is a critical process-history-dependent parameter, and a material characteristic that depicts a powder’s consolidation state, and is therefore directly related to its flow behaviour. Based on this, there have been developed two flowability indices that have gained much popularity across a range of industries; most notably in the pharmaceutical industry. The first, Carr Index, $CI$, also known as Compressibility Index, was introduced by Carr (1965), and is given by Equation 2.3:

$$CI = \left(1 - \frac{PD}{TD}\right) \% \quad (2.3)$$

where $PD$ and $TD$ are the poured and tapped bulk densities, respectively.

Since, free-flowing materials can pack tightly with strong structure at low stresses, they will be less prone to particle rearrangement and further consolidation when tapped, in comparison to a cohesive powder that will collapse progressively with successive taps to fill the voids in its packing. Powder flowability based on compressibility is classed as fair from 16 - 20 %; passable from 21 - 25 %; poor from 26 - 31 %; very poor from 32 - 37 %; and extremely poor when greater than 38 % (Carr, 1965).

Similarly, based on the work of Hausner (1967), Grey and Beddow (1969) introduced the Hausner Ratio, $HR$, which is the ratio of tapped bulk density to the poured bulk density. This ratio expresses the interparticulate friction in a moving mass of powder (Grey and Beddow, 1969). Geldart et al. (1984) reported that the Hausner Ratio enabled one to distinguish quantitatively between the free-flowing, easy-to-fluidise Geldart group A and the cohesive, difficult-to-fluidise group C powders. Powders with an $HR$ larger than 1.4 belong to group C, whereas bulk solids with a ratio less than 1.25 belong to group A. Particulate solids with an $HR$ between 1.25 and 1.4 fall into a transitional category, AC, sharing properties with both of the aforementioned groups.

These two empirical correlations have been proven fast and easily applicable tools for a very rough classification of powder flow behaviour, especially on-line, but they suffer from serious limitations. They do not measure fundamental bulk properties, since they depend on a plethora of particle and process parameters, such as the material’s true density, size, external stresses applied, container wall friction, environmental conditions, as well as on the type of apparatus used and the total number of taps applied for their determination (Kulkarni et al., 2010; Abdullah and Geldart, 1999). Also, their correlation with well-established flowability techniques, such as shear cells is usually poor.
Standardisation of the test used for their calculation is suggested to ensure repeatable and comparable results, always with regard to the specific application for which they are intended to be used (Bell, 2001).

2.2 Factors affecting powder flow behaviour

Powder flowability is not an inherent material property, but the result of the combination of material physical properties, environmental conditions and the parameters of the processes that the bulk solid undergoes when handled, stored or processed (Prescott and Barnum, 2000). In respect of the above clarification, the most dominant factors affecting powder flow are discussed below.

2.2.1 Particle size, size distribution and shape

Particle size and shape constitute the most significant particle properties that concern the bulk solids industries, while they are directly linked to powder flow behaviour. Phenomena and processes such as agglomeration, attrition, segregation and mixing affect these properties, therefore influencing powder flowability.

For a given powder, reducing particle size tends to reduce flowability (Carr, 1965; Hausner, 1967, Farley and Valentin, 1968; Woulters and Geldart, 1996; Geldart et al., 2006; Hou and Sun, 2008; Kranz et al., 2009), because the particle surface area per unit mass increases as particle size decreases, providing a greater surface area for surface cohesive forces to interact, and therefore resulting in a more cohesive flow behaviour (Fitzpatrick et al., 2004). However, powders with similar size can exhibit different flow behaviours due to differences in other properties such as particle morphology and surface roughness (Fu et al., 2012; Hare and Ghadiri, 2013). Larger particles pack more efficiently due to the ease with which they flow past one another to fill voids in the bed, while as the particle size decreases flowability deteriorates and particles pack more loosely (Valverde et al., 2001). Cohesion becomes increasingly important as the particle size decreases and especially for powders that are very fine e.g. < 50 μm, since the interparticle forces are significant in comparison to the weight of the particles (Lumay et al., 2012). Though it should be noted that this threshold depends on other particle properties such as density, shape and roughness.

Lumay et al. (2012) tested five flour powders, finding that as the size distribution becomes narrower, and at the same time the $d_{10}$ becomes larger, flowability improves. Abdullah and Geldart (1999) studied the packing of binary mixtures of coarse and fine particles in aerated and tapped states, with their findings being easily translatable to powder flow behaviour. In the case of aerated mixtures, the poured density initially increased with a reduction in fines content, eventually reaching a plateau. On the other hand, for the tapped system the tapped density initially increased with a reduction in fines
content, and then decreased since insufficient small particles were available to fill the voids in between the larger particles. The Hausner Ratio exhibited a continuous decrease with a reduction in fines content, indicating an improvement in flowability. They also concluded that more spherical mixtures pack better than angular mixtures. Gold et al. (1968) showed that when fine particles are added to lactose granules, the flowrate of the mixture increases with an increase in the amount of fine particles until a given maximum flowrate is achieved. However, when this maximum is reached, any increase in the amount of fine particles results in a decrease in the flowability of the mixture. In addition, their finding shows that the quantity of fine particles required to reach the maximum flowrate for a given material decreases with a reduction of the size of the fines. Liu et al. (2008) showed that when the finest particles of a needle-shaped ibuprofen powder are separated from the bulk, the fine powders flow better than the bulk powder. This is attributed to the narrower size distribution.

For powders with equal median size, a narrower size distribution tends to lead to better flowability. A bulk mixture with a smaller mean size, but narrow size distribution, may flow better than a coarser mixture with a wider size distribution. Molerus and Nwylt (1984) found that for binary mixtures of coarse and fine limestone particles, an increase in the fines content results in an increase in the unconfined yield strength, eventually becoming equal to the strength of the fines alone with a fines content of 30% w/w. At fines contents equal or greater than this it is expected that the coarse particles are completely embedded by the fines, and so the flow behaviour is governed by the interparticle forces between the fines. In a binary mixture of coarse and fine particles, contacts between coarse particles dominate flow behaviour when the fines content is small, while contacts between fine particles dominate when the fines content is large, with the coarse-fine contacts not seen to dominate at any fines content (Kojima and Elliot, 2012).

Most studies indicate that powders containing spherical particles provide fewer contact points between neighbouring particles, and therefore show better flowability, as compared to those with elongated or irregular particles (Riley and Mann, 1978; Lahdenpää et al., 1996; Iida et al., 1997; Chan and Page, 1997; Kaerger et al., 2004; Hou and Sun, 2008; Liu et al., 2008; Horio et al., 2014). Irregularly shaped particles do not pack efficiently, creating structures with large voidage, subsequently being more compressible and permeable in comparison to spherical particles (Fu et al., 2012). Hausner (1967) found that the further the particle shape deviated from spherical, the higher the ratio of the tapped to the aerated density was. Especially for particles larger than 50 μm, particle shape has been found to be very important. When the elongation of the particles increases, the packing fraction decreases and the mobility of the particles inside the packing decreases (Lumay et al., 2012).
Mechanical interlocking occurs with particles of irregular or fibrous shapes, and with the aid of vibration or pressure, particles can form a stable structure (Peleg, 1977). Fibrous, bulky and flaky particles can interlock or fold about each other, resulting in ‘form-closed’ bonds, contributing to interlocking in addition to frictional strength developed under constant normal stress of the system (Pietsch, 1997). If particles are interlocked with one another for some time, strong mechanical bonds can be formed between them, which can potentially result in the formation of arches, cakes and ratholes (Bodhmage, 2006). Moreover, particle porosity (inner and outside pores) can influence friction and interlocking during shearing (Juliano et al., 2006). Mullarney et al. (2003) and Vlachos and Chang (2011) found needle-shaped powders to exhibit poor flow. Oshima et al. (1995) tested five limestone powders of very similar size distributions, each of which had been milled using a different type of mill, reporting that surface roughness had a major impact on flowability in comparison to the macroscopic shape of the particle itself.

Attempts have also been made to derive equations in order to theoretically determine the effects of particle size and shape on powder flow behaviour. Rumpf (1962) proposed an estimation of bulk tensile strength based on the strength of individual particle contacts, given by Equation 2.4:

\[
\sigma_t \sim \frac{2}{\pi} \kappa (1 - \varepsilon) F_H / d_p^2
\]  

(2.4)

where \( \kappa \) is the mean number of contacts per particle, known as the coordination number, \( \varepsilon \) is the void fraction (powder bed porosity), \( F_H \) is the interparticle force exerted on each individual particle and \( d_p \) is the particle diameter. This relationship demonstrates how the tensile strength scales with the individual interparticle force divided by the particle surface area, and depends on the packing fraction. The tensile strength is shown to be proportional to the inverse of the square of particle size, though this is not necessarily the case, since the interparticle forces may also depend on particle size. Furthermore, both the coordination number and porosity depend on the particle size distribution; e.g. a wider size distribution that results in smaller particles filling the spaces between large particles leads to more particle contacts and reduced porosity in the powder bed, as compared to a narrower size distribution.

This model does not account for the orientations of the contacts, although in reality the tensile strength depends on these, and on particle shape which can impact packing fraction and contact orientation, as well as mechanical interlocking. Furthermore, this model doesn’t consider the distribution of the magnitude of individual interparticle forces, which is influenced by the state of consolidation, due to its dependence on interparticle distance and the contact area.
Li et al. (2004) developed a model, described by Equation 2.5, to predict powder flowability based on the assumption that only van der Waals and gravity forces apply to the particles, and the condition that the gravitational force of loosely packed particles exceeds its limiting tensile strength.

$$\rho_p d_p^3 g \geq \frac{\alpha A_c}{\varepsilon} = \frac{1}{\gamma^3} \frac{A_c}{\sqrt{\frac{12\pi^2 r (1-v^2)^2}{E^2} \varepsilon}}$$

(2.5)

where $\rho_p$ is the particle density, $g$ is the gravitational acceleration, $A_c$ is the average interparticle contact surface area, $\gamma$ is the surface energy, $r$ is the surface roughness, $v$ is Poisson’s ratio, $E$ is the Young’s modulus and $\alpha$ is the adhesiveness, which is defined as the adhesion force exhibited on a unit effective surface area.

The limiting tensile strength, $\sigma_{\tau,\text{lim}}$, of spherical particles packed randomly and under isostatic stress is given by Rumpf (1970) via Equation 2.6:

$$\sigma_{\tau,\text{lim}} = \frac{(1-\varepsilon) F_{H0}}{d_p^2}$$

(2.6)

The cubic power relationship of particle size in Equation 2.5 depicts the sensitivity of powder flowability to particle size. The smaller the particle size or the broader the size distribution, the larger the contact surface area is, therefore leading to higher limiting tensile strength. The latter is also achieved with increasing non-sphericity of the particles. Moreover, Equation 2.5 shows the effects of particle density, adhesiveness and void fraction on powder flowability.

Similarly, based on the adhesion model of Thomas (2001), Liu et al. (2008) developed Equation 2.7 describing the incipient flow condition for monosized spherical particles based on the assumption that the gravity of the particles exceeds the total adhesive forces:

$$\rho_p d_p^3 g \geq \frac{(1+\lambda) F_{H0} + \lambda F_{\text{bed}}}{\varepsilon}$$

(2.7)

where $F_{H0}$ is the adhesion force between particles with no external normal force, $F_{\text{bed}}$ is the normal force applied to the powder bed and $\lambda$ is the material’s contact consolidation constant and is a measure of irreversible particle contact stiffness. Equation 2.7 illustrates that the net effect of particle size on the incipient flow of a powder is proportional to particle size to the cubic power, although in reality it is slightly reduced by the lower void fraction of the larger size particles of the bulk.

In addition to this, Liu et al. (2008) derived another relationship (Equation 2.8), similar to Equation 2.7, which takes into account the particle shape when determining the flow condition:

$$\rho_p d_p^3 g \geq \frac{(1+\lambda) F_{H0} + \lambda F_{\text{bed}}}{\varepsilon}$$

(2.8)
where \( d_v \) is the particle equivalent volumetric size, \( p \) is a proportionality constant and \( \psi \) is particle sphericity, which is defined as the ratio of the surface area of the equivalent volume sphere to the particle surface area. Equation 2.8 shows that the more regular the particles, the larger the minimum particle size for incipient flow is.

It should be noted that the above theory is developed under ideal conditions. It is assumed that the interparticle adhesion force, the interparticle separation distance and the particle surface roughness are constant for a particular type of powder. In reality, these properties may vary considerably within a sample, and as such their application may be limited by these assumptions.

Over the years, a few researchers have been studying the influence of powder shape using DEM. Höhner et al. (2014) investigated the mechanical interactions of spherical and non-spherical particles in a rotating drum numerically. They found that the dynamic angle of repose increased with decreasing particle sphericity, a finding that agrees with the work of Yamane et al. (1995). The increasing nonsphericity of the particle shapes increased the formation of pile-ups as well as the interlocking of particles, while limiting their free movement, subsequently resulting in greater angles of repose. Jensen et al. (1999) performed DEM simulations to compare the shear strength of clustered and non-clustered particles having varying surface roughness. They demonstrated that particle rotations were reduced in clustered particles due to particle interlocking, thus increasing the shear strength, as compared to non-clustered particles. Höhner et al. (2012) used DEM to show that particles with an increasing angularity exhibit reduced mass flow rate from a hopper, and in the case of a flat bottom hopper increase the residual quantity after discharge. An increased flow resistance was found, which led to arch-like void structures above the orifice of the hopper, indicating bridging. Hare and Ghadiri (2013) investigated the influence of aspect ratio (AR) (defined as the ratio of width to length of a particle) and roughness of particles on their flowability by simulating two systems, a standard shear box, and indentation of a powder bed with a spherical indenter. The results showed that the particles with a large aspect ratio experience reduced shear stresses, which may be due to particles aligning, thus allowing them to slide past one another more easily. An increase in particle roughness promotes interlocking; for a given aspect ratio, rougher particles were shown to experience increased shear stresses.

2.2.2 Environmental factors: humidity, moisture content and temperature
The control of the environmental parameters in powder processing is of utmost importance, since they can strongly affect the flowability of powders. Therefore, it is crucial to design equipment and
processes based on the worst-case scenario, or handling and storage should be done under controlled environmental conditions.

The amount of water present in a powder, where it is located and how it is associated with the particles are all crucial issues in bulk solids handling (Faqih et al., 2007). Water may interact only at the surface of solids (adsorption), or water may penetrate the bulk solid structure (absorption), possibly leading to a physicochemical change of the powder (Sandler et al., 2010). The smaller the particle size, the larger the surface area per unit volume available for sorbing water (Teunou and Fitzpatrick, 1999; Stoklosa et al., 2012). For a non-porous powder, at low relative humidity, the moisture associated with the particles is adsorbed water vapour. As the relative humidity increases, the thickness of the adsorbed layer also increases, subsequently leading to an increase of the interparticle distance and a decrease of van der Waals adhesive forces. Eventually, the addition of water leads to capillary condensation occurring at the contact points, with liquid bridges being created that result in greater powder cohesion. The boundary between the two forms of water retention is determined by the stability of the liquid bridges, with the relative humidity being the variable that defines the boundary condition rather than the moisture content of the powder (Coelho and Harnby, 1978). On the other hand, as the relative humidity decreases, the powders tend to desorb water, and liquid bridges will disappear for moist insoluble materials, such as glass beads. However, for soluble materials such as the majority of food powders, solid bridges may remain, causing the powder to cake (Teunou and Vasseur, 1996). For many powders, there exists a value of relative humidity (critical relative humidity) at a given temperature, above which the powder will cake, which is usually very detrimental to powder flow (Teunou et al., 1999).

Hygroscopic powders tend to take up more water with increasing relative humidity and cake at lower relative humidities (Teunou et al., 1999). For non-hygroscopic powders, moisture content is independent of the surrounding environment (Emery et al., 2009). In contrast to hydrophilic powders, hydrophobic powders can only enhance their flowability with water intake, since they enable the water to remain on the surface of the particles as ‘free water’, making it act as a lubricant (Faqih et al., 2007; Karde and Ghoroi, 2015).

Humidity has a different effect on porous and non-porous materials according to the work of D’amore et al. (1979). In porous materials, most of the moisture content is found within the internal particle porosity and does not play a significant role in the determination of interparticle capillary forces due to liquid bridges, while non-porous materials (glass beads) were found to be sensitive to humidity changes.
In general, the greater the water content of a powder, the more cohesive the powder becomes and the more difficult it is to flow. Jenike (1964) and Walker (1967) showed that the powder flowability first decreases with the increase of moisture content until a critical water content, above which it increases, but the rate of decrease and the critical water content depend on the material and its behaviour in the presence of water. Furthermore, at low relative humidity levels a monolayer of adsorbed water can be formed, which might reduce the electrostatic charges that typically exist for small particles in dry conditions, subsequently leading to an increase in flowability. At high humidity levels the adsorbed water might have a lubricating effect, decreasing friction and interlocking that are caused by surface cracks and irregularities (Bravo-Osuna et al., 2007). Also, for some powders, at certain humidity levels the absorbed water can act as a plasticiser improving the compressibility (Bravo-Osuna et al., 2007).

Experiments performed by Emery et al. (2009) using pharmaceutical powders showed that only the shear cell was truly able to capture the complex influence of moisture content on flow behaviour, in contrast to the insensitive Hausner Ratio, Carr Index, and the static and dynamic angles of repose. Kamath et al. (1994) found for wheat flour powders that an increase in moisture content from 11.8 % to 14.7 %, and then 16.4 % led to a decrease in flowability and an increase in angle of internal friction. Teunou et al. (1999) conducted shear tests using food powders, finding that in the case of the difficult flowing flour, the unconfined yield strength does not change significantly from 25 % to 66 % RH, whereas whey-permeate powder readily cakes at low RH due to the presence of amorphous lactose, and improves its flowability with the increase of RH, up to a point where a strong cake is formed due to the formation of strong lactose crystal bridges between particles and cohesion is again increased. In another piece of research on food powders, Teunou and Fitzpatrick (1999) confirmed the aforementioned behaviour for flour and whey-permeate, also finding that tea powder adsorbs a lot of water with the increase of RH, transforming into a sluggish, rubbery material that cannot be sheared. Ganesan et al. (2008) found for distillers dried grains with solubles that flow factor decreased with increasing moisture content (10 - 20 %), but increased for 25 % and 30 % moisture content. Landi et al. (2011) sheared humidified fine glass beads (13 - 98 % RH), showing that powder cohesion increases with relative humidity, despite the very low moisture contents present in the powder (< 0.2 %), while the angle of internal friction is not significantly affected by humidity.

In another study, Landillon et al. (2008) observed that the flowability and mechanical strength dependence on water content of wheat powders was diverse, suggesting that the biochemical surface composition of the particles plays a more important role in evaluating flow behaviour than the bulk composition of the material. Opaliński et al. (2012) studied the flow behaviour of several materials at moisture contents 0 - 25 % using a Jenike shear cell, concluding that at low normal loads all the
materials exhibited increased shear stresses with increasing moisture content, because capillary adhesion prevails and liquid bridges are formed at such stresses when humidity is increased. However, when the moisture content was increased above a certain level under high normal loads, at which the adhesion forces can be neglected, an opposite trend was observed for some materials, for which there was the potential of a lubricating effect to develop, because a thin layer of water accumulates on particle surface due to adsorption. As they found, this ‘lubricating threshold’ is usually existent in beds of large, hard particles of approximately spherical shape, such as glass beads.

Cain et al. (2001) studied the influence of atmospheric humidity on stick-slip motion in granular media using mono-sized glass beads (150 - 180 μm) in an annular shear cell. The stick-slip phenomenon occurs when particles in contact and moving parallel across each other are alternating between sticking and slipping. During sticking the shear stress increases until the static friction is overcome and the particle suddenly starts to move consequently causing a sudden decrease of shear stress due to the change from static to a usually lower kinematic friction (Schulze, 2008). This behaviour is translated to shear stress oscillations during shear testing. In the work of Cain et al. (2001), the amplitude of the stick-slip response increased with increasing humidity from about 25 % to about 40 %, but the average value of the maximum and minimum shear stresses was not affected. Karde and Ghoroi (2015) showed that at the higher humidity range (> 60 % RH) the capillary force is the more dominant interparticle force for hydrophilic pharmaceutical powders, whereas at low humidity levels (< 45 % RH) electrostatic, frictional and van der Waals forces dominate. A stable humidity zone (45 - 60 % RH) was identified, where interparticle forces were minimal or stable. These findings are supported by a similar study by Sandler et al. (2010), with the latter finding also supported by the work of Forsyth et al. (2002), though depend on the material.

Temperature is another environmental parameter that can alter bulk solid flow in a variety of ways. The temperature dependence of the powder properties can be due to:

- Changes to the crystal structure of materials such as salts, which affect the rigidity and surface properties of the particles.
- Formation and alteration of adsorption layers. A change in temperature results in a change in the adsorption equilibrium, subsequently altering the adhesive forces, and therefore powder flow.
- Formation of liquid bridges. This has many causes amongst which are the exceeding in temperature of the softening point of the material and the escape of internal oil or water of hydration from the powder’s structure. This is particularly relevant to food powders.
• Formation of solid bridges. Solid bridges are strong bonds that can be formed when a material is stored at a temperature near its melting point, or when a rise in temperature is followed by a sudden drop in temperature. They can also form from drying or freezing liquid bridges.

• Visco-plastic deformation at the contact points of the particles. It results in alteration of the surface structure and possibly the particle structure, therefore influencing the adhesion and the frictional forces between the particles. Such changes usually take place in waxes or plastic granules (Ripp and Ripperger, 2010).

Teunou and Fitzpatrick (1999) performed shear tests using flour, tea and whey permeate, observing a decrease in flowability with increasing temperature, except for flour, which showed an increase in flowability with increasing temperature, possibly due to the reduced moisture content and therefore the amount of liquid bridges. In the case of tea, it was thought that increased temperature resulted in increased dissolution of surface layers of the particles, thus agglomeration, whereas in the case of whey permeate, the plasticity of its main component, lactose, could have increased, rendering the powder more cohesive. Tomasetta et al. (2013) used a High Temperature Annular Shear Cell to measure the flow properties of powders at very high temperatures. Using a model material, a mixture of pure glass beads and 1 % w/w of HDPE, they observed that when the temperature of the shear test was higher than the melting temperature of HDPE, capillary forces occurred, and a significant increase of the cohesive behaviour of the powder was measured. This can be attributed to melting of one of the solid phases and the consequent formation of liquid bridges. Pilpel and Britten (1979) conducted flow rate and tensile strength tests with a variety of powders, founding that, under compression, the asperities on the particle surfaces deform plastically, and may melt, if the temperature is raised above about 90 % of the melting point (in K). The effects of temperature and pressure, due to the melting of asperities at the points where the particles are in contact, are analytically described by York and Pilpel (1972).

A change in environmental conditions drives changes within the particles or bed structure until an equilibrium condition is reached. It should therefore be noted that the influence of humidity and temperature on the flow behaviour of bulk solids significantly depends on the time that the material is exposed to these environmental changes until an equilibrium condition is reached (Teunou and Fitzpatrick, 1999).

2.2.3 Adhesion

The flow behaviour of a powder depends on the forces between particles and those between particles and their neighbouring surfaces. The former fall into the category of cohesive forces, whilst the latter
are adhesive forces. In both cases these mainly consist of van der Waals, electrostatic and liquid bridges or capillary forces (Stewart, 1986). Analytical descriptions of van der Waals forces are given by Tomas (2007), Castellanos (2005) and Schulze (2008), electrostatic forces by Tomas (2007) and Schulze (2008), and capillary forces by Tomas (2007), Schulze (2008) and Butt and Kappl (2009), whereas adhesion phenomena and mechanisms in general are extensively discussed by Zimon (1982).

Throughout this thesis, the term ‘adhesion’ and all similar terms are used to refer to both particle-particle and particle-surface forces, as is the typical convention in the field.

*Van der Waals forces*

It is known that for dry powders and inert agglomerates without chemical bonds and in the absence of an external electric field, the particle-particle and particle-surface adhesion force is usually dominated by van der Waals interactions. Hamaker (1937) introduced a mathematical model in order to assess the van der Waals force, $F_{VW}$, between a spherical particle and a semi-infinite body, which is described by Equation 2.9 (Seville et al., 2000):

$$F_{VW} = \frac{A_H R}{12d^2} \quad (2.9)$$

where $A_H$ is the Hamaker constant, which is a material property that is difficult to determine, $R$ is the particle radius and $d$ is the separation distance between the two bodies. Later, analytical models were developed to predict the mechanical behaviour of ideal sphere-sphere or sphere-plane contacts, with the most widely accepted being the Johnson, Kendall and Roberts (JKR) (Johnson et al., 1971) and the Derjaguin, Muller and Toporov (DMT) (Derjaguin et al., 1975) models, which are based on the interfacial energy between the two surfaces in contact. For two surfaces in contact, the interfacial energy determines the strength of the adhesion. For ideal, smooth, flat substrates and perfect spheres in contact, the force of adhesion is directly proportional to the interfacial energy. Both of these models consider elastically deformable solids in contact, predicting a pull-off force necessary to separate them. The JKR model assumes that attractive forces act only inside the two surfaces’ contact area, whereas the DMT model includes long-range surface forces operating outside the particle-substrate contact area. The JKR model is more suitable for softer, elastic materials, larger particles and particles with high surface energy, whereas the DMT model is valid for harder, stiffer materials, smaller particles and particles with lower surface energy (Rimai et al., 2000). More advanced models have been developed that also take into account the physical deformation component between the interacting surfaces, which have been reviewed by Tomas (2007) and Prokopovich and Starov (2011), however they use a range of approximations in order to evaluate adhesion, therefore failing to evaluate adhesion phenomena with the same accuracy as experimental techniques. Such
experimental techniques include Atomic Force Microscopy (AFM) (Mizes et al., 2000; Bowen et al., 2001; Price et al., 2002; Zhou et al., 2003), the Centrifugal Detachment Technique (Podczeck and Newton, 1995; Podczeck et al., 1995; Mizes et al., 2000; Zhou et al., 2003; Takeuchi, 2006; Salazar-Banda et al., 2007), the Electric Field Detachment Technique (Mizes et al., 2000; Takeuchi, 2006), the Vibration Method (Ripperger and Hein, 2004), the Needle Separation Method (Shimada et al., 2002), the Drop Test (Zafar et al., 2014) and Inverse Gas Chromatography (Ho and Heng, 2013).

The physics of particle adhesion is a complex subject that depends on the interaction mechanisms and the mechanical properties of the contacting materials (Rimai et al., 2000), while which type of forces prevail depends on environmental conditions and the physicochemical properties of the materials that are in contact (Salazar-Banda et al., 2007). For larger particles, gravity and inertia are generally greater than the interparticle adhesion force, hence they normally flow easily. For fine particles, the interparticle adhesion force is noticeable compared to gravity, as such they tend to adhere to one another, and are challenging to handle (Li et al., 2004; Tomas and Kleinschmidt, 2009). The most important factor influencing adhesive forces is the geometry of the contact of the adherents, which is linked to the roughness of their surfaces. In general, it is known that van der Waals forces decrease with the increase of surface roughness, since the actual contact of the surfaces is made via the asperities, and increased roughness results in greater separation between the centres of mass (Bowen et al., 2001; Takeuchi 2006), but this is not always the case (Podczeck et al., 1995). The size of the particle and its relation to the asperity height are also critical factors. Particles smaller than the asperity height can be trapped in the valleys between the asperities, leading to an increase in contact area, and consequently van der Waals forces. On the other hand, larger particles might have only a few contact points with the asperity tips of the surface, resulting in lower adhesive forces (Zimon, 1982; Takeuchi, 2006).

Salazar-Banda et al. (2007) studied the adhesion force of manioc starch and phosphatic rock particles with a flat surface using the Centrifugal Detachment Technique. They observed that the adhesion force of both materials with a flat surface increased linearly with the increase of particle size, thus suggesting that the van der Waals interactions predominate in the adhesion phenomena of their work. During contact, a large particle will usually lead to a great number of contact points with a plane surface. Thereby exhibiting a greater adhesion force due to the growth in the contact area (Zimon, 1982). Podczeck (1998) investigated the adhesion force between micronized drug particles (Salmeterol Xinafoate) and lactose monohydrate carrier particles of varying size distribution in interactive powder mixtures. It was found that the adhesion force between drug and carrier particles increased with the increase of the amount of fine carrier particles in the mixture, due to the improved packing and subsequent increase of the total surface area of the powder.
In a similar manner to surface roughness, particle shape influences adhesive forces. Irregular particles can detach easier from a flat surface (Salazar-Banda et al., 2007), with the adhesion decreasing with the increase of aspect ratio. In the extreme case of a needle-shaped material, particles can preferentially align themselves along the valleys between surface asperities of contacting particles, therefore leading to a larger contact area (Podczeck et al., 1996). Furthermore, contact mechanics of the surfaces have to be taken into account. Surface roughness can greatly reduce the adhesion between soft, elastic solids, since the higher asperities can prize the surfaces apart and break the adhesions occurring at the lower asperities, whereas in the case of very hard, elastic solids with high Young’s moduli, very small adhesions may be observed for surface roughness only just greater than atomic dimensions, even if the surfaces are extremely clean. If, however, the surfaces are ductile, the junctions can accommodate the prizing action of the higher asperities, resulting in high adhesion (Tabor, 1977). Moreover, the hardness of surfaces plays an important role in adhesion. Softer materials can present a greater plastic deformation on a surface during the compression stage, which increases the true area of contact, and subsequently the adhesion forces (Salazar-Banda et al., 2007). However, elastic deformation due to relaxation processes can then reduce the adhesive forces (Podczeck and Newton, 1995).

**Electrostatic forces**

Zhou et al. (2003) studied the influence of particle charge on adhesion force, which may dominate when the distance between the adhesive partners is large enough to make the van der Waals force negligible. They observed that the contact charge of adhesive partners of the same material is negligible. Furthermore, the charge distributed on particles with surface asperities may be concentrated on the peaks of the asperities, therefore influencing the surface charge distribution. The particle charge in the vicinity of the contact area comprises a very high contribution to the electrostatic force at short particle-substrate distances, because the electrostatic force is inversely proportional to the squared separation distance. The charge of the contact area dominates the electrostatic force at short distances up to 100 nm, whereas at larger distances it is negligible in comparison to the mean particle charge. Mizes et al. (2000) found that non-uniform charging of particles, as in the case of toners, can increase adhesion over an order of magnitude. They also showed that the number of neighbouring particles is not an important parameter. Takeuchi (2006) observed that the adhesion forces of toner particles increased with an increase in either particle size or particle charge. The relative contribution of van der Waals forces to the total adhesive force increases with a decrease in particle size, since the contribution of the electrostatic force decreases more rapidly than that of the van der Waals force with decreasing particle size. This work also showed that the adhesive force of irregularly shaped toner particles is larger than that of spherical toner particles of the same size and
charge, explaining this finding due to the non-uniformity of surface charge. The electrostatic Coulomb forces reduce as relative humidity is increased, hence are more likely to be the dominant contributor to adhesive force when the relative humidity is low.

*Capillary forces*

The contribution of capillary forces to the total interparticle force increases above a certain critical humidity level, and can exceed van der Waals forces in the case of non-hydrophobic surfaces (Ata et al., 2002; Forsyth et al., 2002; Price et al., 2002). Forsyth et al. (2002) showed that the aforementioned critical humidity increases with the increase of particle size for spherical glass and iron powders. Beyond the critical humidity the capillary force may act due to capillary condensation or capillary bridges. Capillary forces are the result of two mechanisms that lead to the formation of a liquid meniscus between two lyophilic solids. If the two solid surfaces are lyophilic with respect to a vapour present in the intervening medium, the vapour will condense into a liquid phase if the gap is sufficiently close. In the absence of a gaseous environment, menisci can be formed by capillary bridges of one liquid in another immiscible liquid (Butt and Kappl, 2009). The adhesive force between hydrophilic surfaces may increase continuously with increasing humidity, or pass through a maximum before reduction at greater humidity. Only for macroscopic, perfectly smooth spheres is the capillary force independent of humidity (Butt and Kappl, 2009). In general, it depends critically on the shape and size of the contact region, and the vapour pressure if the meniscus forms by capillary condensation. A reduction in surface roughness leads to an increase of the contact angle, which results in reduction of the capillary force (Butt and Kappl, 2009). Moreover, the elastic properties of the materials in contact do not contribute significantly to the magnitude of capillary forces, since moisture can act as a plasticiser and turn elastic into plastic deformation (Podczeck et al., 1997).

### 2.3 Techniques for assessing powder flowability

#### 2.3.1 Traditional qualitative techniques

This category comprises techniques that have been used for a long time by both academia and industry with the aim of providing quick, qualitative results. In these techniques, the stress state is not controlled, thus they are not suitable for design purposes.

##### 2.3.1.1 Angle of repose

Stimulated by the needs of powder-related industries to find a quick and simple indicator of powder flowability, many researchers have resorted to angle of repose (AOR) measurements. Angle of repose is defined as the angle formed between the horizontal plane and a sloped line extending along the
surface of a pile when material is dropped from some designated elevation (Figure 2.4) (Fayed and Otten, 1984).

Angle of repose is dependent on particle size, size distribution, surface roughness, porosity and moisture content (Train, 1958), among a plethora of other parameters too. Many scientists have investigated the relationship between angle of repose and the flowability of powders, such as Wouters and Geldart (1996), Geldart et al. (2006) and Bodhmage (2006), reporting that better flowing powders exhibit lower angles of repose, while more cohesive materials have higher values of AOR. Based on AOR values, powders have been allocated to groups by Carr (1965) as shown in Table 2.2.

<table>
<thead>
<tr>
<th>AOR value</th>
<th>Powder characterisation</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 30°</td>
<td>Very free-flowing</td>
</tr>
<tr>
<td>30 - 38°</td>
<td>Free-flowing</td>
</tr>
<tr>
<td>38 - 45°</td>
<td>Medium-flowing</td>
</tr>
<tr>
<td>45 - 55°</td>
<td>Cohesive</td>
</tr>
<tr>
<td>&gt; 55°</td>
<td>Very cohesive</td>
</tr>
</tbody>
</table>

Numerous apparatus and techniques have been developed to measure the angle of repose, all of which can be classified into two major categories: the methods that measure the static angle of repose and the methods determining the dynamic angle of repose. Techniques that measure the latter are based on moving surfaces, while the ones for the former value are based on the formation of a conical heap on a fixed surface. The AOR-value is dependent on the measuring method, thus results are difficult to be compared among researchers.

Geldart et al. (2006) found a near-perfect linear relationship between AOR and HR. Grey and Beddow (1969), while working with metal powders, found that HR tends to measure the friction condition in a
moving powder mass rather than a static situation, and therefore corresponds more closely to the dynamic angle of repose. Geldart et al. (2006) determined that the weight of the sample has an effect on the value of AOR measured; defining the optimum sample size as 100 g for the particular AOR tester that they used.

Advantages of measurement of the repose angle of powders to assess their flowability include the fact that it is a simple, low-cost method that can be performed on the plant and provide quick, qualitative results. On the other hand, the scientific community has always been hesitant to accept this as a reliable flowability characterisation method, due to the fact that it does not represent real industrial procedures, since there is no control on the consolidation stresses of the powders, and the parameters of the technique used to measure it have a huge impact on the result e.g. the frictional forces between the supporting surface and base particles (Carstensen et al., 1980). There is also a restriction of the particle size that can be used, since at large particle size the AOR reaches virtually constant values, whilst as particle size decreases additional interparticle forces rise, eventually accumulating to the point where avalanching becomes the dominant factor and prevents any sensible measurement of AOR (Wouters and Geldart, 1996). Last but not least, most of the methods used to measure AOR aren’t suitable for cohesive powders, which are of great industrial interest, as they can block the exit of the funnels used, or form multiple angles at the top of the pile. Due to the small powder mass used and the absence of an applied stress, the AOR test is naturally indicative of a low stress state condition.

2.3.1.2 Hosokawa Powder Tester

The Hosokawa Micron Powder Characteristics Tester is an apparatus designed by Hosokawa Alpine (https://www.hosokawa-alpine.com/powder-particle-processing/laboratory-technology/pt-x-powdertester/) and launched in 1969. This instrument’s operating principle is based on the work of Carr (1965) and is capable of giving a plethora of measurements, such as aerated and tapped bulk densities, angle of repose, angle of spatula, coefficient of compressibility, a cohesion index and index of uniformity. Schwedes (2003) reported how these properties are measured and analysed. Numbers are appointed to each of the quantities measured with the sum characterising flowability on a scale 0 - 100 (100 being free-flowing). For example, in relation to the operation of a silo, it is stated that no flow promoting devices are necessary if the number exceeds 80, that flow promoting devices might be necessary, if the number is between 60 and 80, and that they are necessary for numbers < 60 (Schwedes, 2003). In the test, powder is poured on to vibrating screens of different sizes, positioned in a vertical stack, and the relative mass passing through each screen is monitored (Zafar, 2013).
Hosokawa Powder Tester’s main assets are its reproducibility and accuracy for measuring powder properties. The incorporation of automation minimises human error that is usually present in these kinds of experiments (Abdullah and Geldart, 1999). Apart from its reliability for a qualitative method, an advantage of this device is that it can perform a series of experiments to estimate a complete set of powder properties. Regarding its drawbacks, it can only be used for a very rough classification of bulk solid behaviour, and most importantly the vibrations that the powder undergoes when it passes through this machine affect its consolidation state. Therefore, the level of stresses that act on the powder are not known.

2.3.1.3 Avalanche technique

Kaye et al. (1995) developed a new, dynamic in nature, method for characterising powder flow based on the deterministic chaos theory and fractal geometry of powders. This technique involves a translucent rotating drum, partially filled with powder. As the drum rotates, the powder rides up the drum wall and flows down in a series of avalanches. The powder movement is monitored by a light in front of the disc and a photocell arrangement which is located behind the drum, receiving the light passing through the drum and recording light variations resulting from the formation of the avalanches (Hobbs and Rhodes, 2000). In this test, the time taken for the consecutive avalanches to form is recorded, while data are presented in the form of a discrete phase space map known as a strange attractor plot, and flowability is characterised from the centre of the plot and the deviation of the data. The centre of this plot is represented by the mean time to avalanche (MTA), which refers to the average time between the formation of two successive avalanches. The spread of points around the centre is denoted by the scatter and it refers to the standard deviation between the times to avalanche (Soh et al., 2006). Better flowing powders exhibit shorter MTA and reduced scatter. Lee et al. (2000) suggested that it is of utmost importance to also focus on the visual observation of the types of motion in the rotating drum. Bhattachar et al. (2004) stated that from the six types of flow inside a rotating drum, only two, cascading and rolling, are considered to give reliable data.

There have been a myriad of studies conducted on the avalanching behaviour characterisation technique. Lavoie et al. (2002) performed avalanche tests with various materials and developed two new quantitative indices, one for flowability and one for cohesion. The first depicts the resistance of a powder to initiate movement during an avalanche, while the second gives information on the capacity of a powder to be agglomerated. For some powders the flowability index was found to correlate well with Carr Index, whereas for others it did not correlate, possibly due to both methods’ limitations. Similarly, Soh et al. (2006) attempted to quantify the flow behaviour of powders from the avalanche technique, introducing the avalanche flow index (AFI) (one over the gradient of the graph for MTA against drum speed) and the cohesive interaction index (CoI) (the gradient of the graph for
scatter against drum speed), which are meant to supplement each other. A greater AFI value indicates better flowability, whilst a greater CoI value indicates increased cohesion. Moreover, AFI was shown to correlate well with angle of repose and mean particle size, whereas CoI correlated well with both Hausner Ratio, Carr Index and angle of repose, since the degree of cohesion affects both flow and compressibility. Further details regarding the aforementioned indices can be found in the respective papers.

Crowder et al. (1999) suggested that the variability in the size of powder avalanches represents a more discriminating method of determining flow properties of similar materials rather than their frequency, and the avalanche size standard deviation provides a quantitative measure of the uniformity of flow. Based on this, Alexander et al. (2006), Faquih et al. (2006) and Vasilenko et al. (2011) employed a new apparatus, the Gravitational Displacement Rheometer (GDR), which utilises a load cell to measure the shift in the centre of gravity of the powder bed as it avalanches within a rotating cylinder. Faquih et al. (2006) showed that the GDR measurement is directly proportional to the cohesion of a material and can be used to define a flow index that predicts flow through small hoppers, while Vasilenko et al. (2011) found that the correlation between the GDR’s measured flow index and cohesion is near-perfectly linear at low consolidation stresses. On the other hand, the correlation between the GDR’s flow index and the flow factor is not good, because of the difference in powder behaviour upon consolidation.

Regarding the benefits of the avalanche method, it is fully automated and the drum is sealed, preventing the loss of material. It is also fast, reproducible and utilises relatively small powder samples; roughly 60 ml (Hobbs and Rhodes, 2000). There is no stress control, therefore it is suitable only for quality control and especially for comparative purposes e.g. for powders that have poor flow properties, to which a flow agent shall be added to improve the flow (Schwedes, 2003). Furthermore, while in a rotating drum, powders flow under low stress conditions (Vasilenko et al., 2011). On the other hand, cohesive powders may stick to the walls of the drum, thus affecting the validity of the measurements, and the continuous movement of the bulk solid might lead to segregation, agglomeration, or air entrainment, resulting in fluidisation (Schulze, 2008).

2.3.1.4 Funnel discharge techniques

There are various instruments that measure the time needed for a specific quantity of powder to outflow from a funnel or tube, or other flow indices that are associated with the discharge of powder, the most widespread of which are presented below.

The Hall Flowmeter is a commercial instrument, which is known for its simplicity and ease of operation, being very popular in the powder metallurgy industry (Kulkarni et al., 2010). It measures
the time required for 50 g of a powder to flow through the orifice of a calibrated funnel of standardised dimensions (BS EN ISO 4490:2008). This method is originally suitable for qualitatively assessing the flowability of free-flowing powders, but by fluidising the Hall Flowmeter, which uses a fluidised funnel instead of the standard funnel, so that gases are injected into the funnel to ‘lubricate’ the powder and enhance powder flow, the flowability of very cohesive powders can be estimated too (Wu and Cocks, 2004). Yang and Evans (2005) used this apparatus to measure the flowrate of free flowing powders at reduced and elevated air pressure, praising its versatility to be incorporated into a high vacuum chamber, since it offered the possibility to observe the effects of pressure and humidity. The fundamental problem with the Hall Flowmeter is that there are two different discharge patterns that could occur in the funnel, mass flow (where all material moves down evenly) or core flow (where material flows down a vertical channel), and the discharge rate of the powder is a function of the type of flow pattern. Furthermore, during the filling of the funnel the powder may be overconsolidated, and also the contribution of wall friction affects the measurement (Kulkarni et al., 2010).

Another technique that is based on the same principle as the Hall Flowmeter is the Flodex Flowmeter, with its main difference being that it is a cylinder with a series of replaceable disks of different sized openings, which serve as a discharge orifice in the base of the cylinder rather than a conical funnel. The material is loaded into the cylinder, and then a stopper at the base is removed. The flowability index is given as the orifice diameter of the smallest opening through which the powder falls freely (Taylor et al., 2000; Wu et al., 2012).

In addition to these testers, Patil et al. (2012) developed the Flomex device, which practically consists of a funnel into which powder is poured, and from which the powder falls onto a round glass plate that has a controllable incline. Four flow indices which have been defined by Patil et al. (2012), namely flow rate index, hopper index, cohesive index and adhesive index, are determined.

Ruppel et al. (2009) developed a new measuring technique, the modified outflow funnel, to evaluate the flow enhancing potential of glidants, which features a stirrer inside a hopper that acts to break up bulk arches, which otherwise obstruct the discharge of a cohesive powder out of the hopper. By destruction of the bulk arches, powder outflow is enabled and several proposed flow indices can be measured for a constant rotational speed. These include the time needed for discharge of a certain quantity of material, the average arch destruction time, the mean maximum torque and the integral of the torque. The latter is a combination of the time and force required to destroy the bulk arches, therefore being a sensitive parameter, which can be correlated with HR and shear testing results. However, the test’s measuring range is limited, because materials that can flow freely out of the
hopper cannot be tested, as well as materials which are too cohesive, whose arches cannot be broken with the stirring.

All of the aforementioned methods are good for qualitative studies, as they are very quick and do not require a skilled operator, but their operational window is not well established. More importantly, the user has no control over the consolidation stresses, so they cannot be used to simulate real industrial procedures, e.g. to predict the limiting feed shoe speed or the flow rate through a feed hopper (Wu and Cocks, 2004). The filling method, as well as the discharge pattern (mass or core flow), affect the measurement (Schulze, 2008). Also, in most cases cohesive powders cannot be tested, due to funnel blockage.

2.3.1.5 Vibrating capillary method

Vibrating capillary method is a technique for the evaluation of powder flowability proposed by Jiang et al. (2006). It is based on studies of Matsusaka et al. (1995), who developed a micro-feeding system for fine powders by using a vibrating capillary. A schematic diagram of the experimental apparatus is shown in Figure 2.5.

![Figure 2.5. Vibrating capillary method apparatus (Jiang et al., 2009)](image)

The apparatus consists of two vertically aligned tubes: a larger diameter glass tube at the top, followed by a smaller diameter capillary tube. The material is fed to the glass tube by a hopper on the top, which is kept full with powder during the measurements. The capillary tube is narrow enough to
prevent the powder flow without vibration. The capillary tube is vibrated in the horizontal direction, while the frequency and amplitude of the vibration are controlled, and the particles start to discharge. The mass of particles discharged from the capillary is measured by a balance. During the experiment the vibration amplitude is gradually increased, and at a specific value of vibration acceleration, the particles start to flow with an increasing rate until an upper limit is reached, beyond which the rate declines. The vibration acceleration that initiates flow, termed critical vibration acceleration, is a flowability evaluation factor, with its decrease implying an increase of flowability. Another flow assessment index of this method is the maximum mass flow rate of the bulk solid, which is related to the dynamic friction and flow, whereas the aforementioned critical vibration acceleration is related to the static friction and adhesion (Jiang et al., 2009).

This apparatus is simple to operate, shows good repeatability and has high resolution in comparison to conventional flowability measurement methods (Jiang et al., 2009). Also, it does not require a large amount of material, e.g. 10 g (Ishii et al., 2011). However, where the adhesion forces between particles are too large, bridging will occur in the capillary, thus making the measurement difficult even though the vibration is increased, and consequently rendering it inappropriate for the evaluation of extremely cohesive or fibrous powders that do not flow through the narrow capillary (Zainuddin et al., 2012). Other significant disadvantages of this technique include the absence of any control of the consolidation state of the bulk, as well as the inability to link its results with the unconfined yield strength. Furthermore, the fixed capillary tube diameter limits the range of particle size distributions that can be assessed by this technique, and the relative influence of wall friction for different powders is not considered. In general, it can be considered adequate only for qualitative measurements.

2.3.1.6 Warren Spring Cohesion Tester

This apparatus, which is also known as the Warren Spring-Bradford Cohesion Tester, consists of a vanned paddle, hollow inside, that is inserted into a uniaxially consolidated sample of powder inside a cell. A gradually increasing torque is applied via a calibrated spring until the point where its value is sufficient to cause the annular ring of powder to rotate. This value of the torque is assumed to be the maximum shear resistance, hence the cohesion is measured, since the normal stress applied perpendicular to the plane of shear is considered negligible. This ‘absence’ of an applied normal stress is the only basic difference between this technique and the annular shear cell (Orband and Geldart, 1997). As in the case of the uniaxial compression test, there is no strain in the lateral direction, therefore the steady-state Mohr circle will be smaller than that of the steady-state flow condition present in a shear cell, thus resulting in a lower unconfined yield strength, as well as cohesion (Schwedes, 2003).
This cohesion tester is considered to be a trustworthy instrument for qualitative assessment of flowability, which is easy and quick to operate. The measured ‘cohesion’ is not the same as in shear tests, since it is based on a specific stress history (Schwedes, 2003). On the other hand, tests require around 200 ml of material (Mohammed et al., 2011), and the state of stress and strain is neither homogeneous, nor well-defined, therefore it is not recommended to use this device to generate data for modelling or design purposes (Geldart et al., 2009). Furthermore, the geometry of the vanes of the paddle defines the way in which the powder bed is deformed, and the extent of wall friction is unknown.

2.3.2 Traditional quantitative techniques

The techniques of this class are quantitative and offer stress control to the user, with the shear cells standing out, as they are the most established powder flowability determination technique, due to their reproducibility and diversity of properties that they can measure.

2.3.2.1 Uniaxial compression test

The uniaxial compression test, which has been introduced in section 2.1.1 and shown in Figure 2.1, constitutes a simple method to obtain the flow factor, but this is partially true. The measurement depends on the wall friction angle, and consequently if the walls of the cylinder are not completely frictionless (as is practically always the case), the Mohr circles obtained, as well as the bulk density and unconfined yield strength, are smaller compared to those obtained with shear tests, therefore leading to an overestimation of powder flowability, which can potentially be significant (Schulze, 2008). In addition to this, contrary to shear tests, normal compression is not accompanied by shear, thus a steady-state cannot be achieved.

This method is an easy, quick way of assessing flowability, suitable for quality control. It needs a sufficient amount of sample in order to minimise wall friction, but its main drawback is that the sample is not brought to a reproducible state. Also, it cannot be used for low stress operations; the minimum stress needed to prevent the consolidated sample from falling under gravity is greater than the minimum stress level at which shear testers can operate (Parrella et al., 2008). Tests can only be performed using materials which are cohesive enough to stand unconfined as a column, and the results usually exhibit greater scatter than by shear cell analysis, due to the inhomogeneous compaction of the powder column. That said, it is among very few characterisation techniques that enable the user to have control of the consolidation stresses, as well as the strain rate, since it is performed with mechanical testing instruments. Moreover, it is highly suitable for time consolidation tests, provided that the walls are lubricated (Schulze, 2008).
2.3.2.2 Split Cell and Lifting Lid Tensile Testers

In the Split Cell technique (Figure 2.6), the powder is placed in a cylindrical cell, half of which is fixed and the other half is moveable. The sample is vertically compressed, and then a horizontal tensile stress is applied via a spring that splits the cell diametrically and the tensile strength is measured at a given consolidation stress (Ashton et al., 1964). An improvement of this apparatus was used by Yokoyama et al. (1982), who named it ‘Swing Method measuring instrument’, with its difference being that the powder cell is suspended by a very thin metal plate, while the original split cell is supported on ball bearings. This extra feature led to the minimisation of friction and consequently to better measurement accuracy. Since bulk solids are not very elastic, it has to be assumed that the tensile stress is not evenly distributed along the height of the sample, being highest at the bottom, therefore the measured tensile strength (force divided by area) depends on sample height (Schwedes, 2003). Also, in this method the consolidation does not result in steady-state flow, and the directions of major principal stress at consolidation and failure are perpendicular to each other rather than being aligned as recommended by Schwedes (2003). Based on a similar principle, there is another device, called the Lifting Lid Tensile Tester (Figure 2.6), which measures the tensile strength of the sample by pulling it vertically in the opposite direction of compaction (Castellanos et al., 2004). However, it can only work if the tensile strength between the underside of the piston, which is coated with an adhesive, and the sample is larger than the tensile strength of the material itself (Schulze, 2008). Both of these techniques underestimate the tensile strength, but in the case of the Lifting Lid Tester the underestimate of tensile strength is less, due to the fact that the orientations of the major principal stress at consolidation and failure coincide, in contrast to the Split Cell Tester.

These methods may be easy to use, and represent known stress states, but they lack the reproducibility to reliably measure the tensile strength of fine cohesive powders, since the powder is not initialised to a reproducible state. Moreover, the preparation of the sample does not lead to an isotropic state of stress, and the instruments are unable to assess powder flowability at low stresses (Castellanos et al., 2004).
2.3.2.3 Shear cells

Over many years, shear cells have served both industry and academia as the most widely accepted quantitative flow measurement technique, with issued ASTM standards. They remain the preferred method for storage silo and hopper design. Shear cells are geometries in which shear tests are carried out, and the flow factor is determined, along with many other flow parameters, as has been shown in section 2.1. The design of the shear cell defines the location of the shear band, subsequently affecting the measurement. The first shear cell that emerged was the Jenike translational shear cell (Jenike 1961; 1964). In this technique, the base of the cell is fixed, and a shear ring is placed on the base. The cell and the ring are filled with powder and then covered with the shear lid. The lid is loaded centrally by means of a weight hanger to consolidate the sample, and a horizontal force is applied on a bracket attached to the lid at a steady rate to shear the sample. After the Jenike shear cell, the Peschl circular rotational shear cell, which was the first automated shear cell, became popular (Bell, 2001). As with the Jenike shear cell, in this device a circular base which has a shear ring on it is first filled with material, and a roughened lid is placed on the specimen. In contrast to the Jenike shear cell, the lid is stationary, and the bottom half is rotated relative to the lid, generating a shear deformation that corresponds to a torque that is actually being measured (Schulze, 2008). Currently, the most widely used shear tester is the Schulze ring shear cell (Figure 2.7), which constitutes a major breakthrough and improvement of the Jenike translational shear cell and the Peschl circular torsional shear tester (Bell, 2001), which were previously most commonly used.
As shown in Figure 2.7, for the Schulze shear cell, first, a ring is placed on top of the base. Then, the sample is poured into the annular base of the cell. After that, an annular lid attached to a crossbeam is placed on top of the powder bed. The shear cell bottom and the underside of the lid are rough to prevent the material from sliding relative to these surfaces. There are also two tie rods that are connected to the crossbeam, which not only serve the purpose of preventing rotation of the lid, but also allow shear stresses to be measured. The normal force is mechanically controlled. Shearing of the sample is performed by driving the cell (in the direction of the arrow, $\omega$) whilst the lid is fixed with the support of the tie rods. Consequently, a shear stress is generated, due to the relative displacement of the cell to its lid. From the exerted horizontal forces on the tie rods, the shear stress is obtained (Schulze, 2008).

The powder is sheared in two steps in order to obtain a point on the yield locus. At first, the material is sheared under a normal stress until steady-state flow is achieved, providing the steady-state (large) Mohr circle. This process of consolidation and shear to steady-state flow is known as pre-shear, and the shear stress at this point is called the pre-shear shear stress, $\tau_{\text{pre}}$, whilst the normal stress is called the pre-shear (normal) stress, $\sigma_{\text{pre}}$. The shear stress is constant for this reproducible state. After the pre-shear, the shear stress is reduced to zero by reversing the direction of rotation. This is followed by shearing under another (lower) normal load until a peak shear stress is achieved, corresponding to incipient flow. This is known as the shear step and provides a set of normal and shear stresses that constitute a point on the yield locus. The process of pre-shear to steady-state flow and shear to failure is repeated for the same pre-shear normal stress, but increasing normal stresses in the shear process, though the order shouldn’t matter. This results in a number of shear points that form the yield locus.

Figure 2.7. Schulze shear cell (Schulze, 2008)
(Schulze, 2008). This represents the typical process applied in both Jenike and Schulze shear cells, though the method of load application, the stress measurement, the cell geometry and operation, and the determination of steady-state failure are aspects which may vary across different shear cell devices.

The Schulze shear cell constitutes the most established powder characterisation technique and has been used by the majority of researchers in the field. It is a quick, reproducible method of assessing flowability, which only requires one sample to be used to obtain the yield locus, with the RST-XS version being fully automated and thus not operator-dependent. Annular ring shear testers, one of which is the Schulze instrument, can achieve unlimited strain, along with the torsional ones, in contrast with the Jenike cell, rendering it unsuitable for testing elastic materials and particles with high aspect ratios (Bell, 2001). The Schulze shear cell can perform measurements at relatively low stresses, whereas its results have been correlated with various other powder flow characterisation techniques, including traditional methods such as the Jenike cell (Schulze, 2011), along with other methods such as ball indentation, the Sevilla Powder Tester and the raining bed method (Zafar et al., 2015). It is also capable of performing other tests, such as wall friction, time consolidation, attrition and compressibility tests (Schulze, 2008). The Peschl shear cell suffers from inhomogeneity of deformation due to the dependence of shear stress on radius (0 shear stress in the centre, increasing towards the perimeter), thus overestimating flowability, whereas the Schulze cell does not, provided that the ratio of the inner to outer shear cell diameters is not significant (Bell, 2001; Schulze, 2008). In contrast to the Jenike shear cell, the Schulze and Peschl shear cells are time-efficient, requiring only one third of the time required for the Jenike cell in order to carry out a test, and do not require a skilled operator. Also, the Schulze shear cell is more accurate and more repeatable than the Jenike cell (Bell, 2001). A drawback of all shear cells is that they are incapable of measurements at very low consolidation stresses, in contrast to recently developed techniques such as ball indentation, the Sevilla Powder Tester and the raining bed method (Zafar et al., 2015). Moreover, the normal stress distribution in the Schulze shear cell is not as uniform as in the case of the circular Peschl cell (Bell, 2001).

Recently, two new torsional shear cells have been developed, the Brookfield Powder Flow Tester and the FT4 Powder Rheometer Shear Cell, which are becoming increasingly common in industry. The Brookfield shear cell is a fully automated annular shear cell, with the only operator involvement in the testing being filling powder in the trough, attaching the required lid to the compression plate and loading the filled cell onto the drive of the instrument (Berry et al., 2014). It operates over a significantly lower consolidation normal stress range (0.3 - 4.8 kPa in the case of its standard volume cell), in comparison to other shear cells, but the available tests do not provide the operator with a lot
of flexibility in terms of customising the consolidation and shear stresses. Moreover, it is cheaper than the Schulze shear cell, whereas the shearing procedure has minor differences from Jenike’s protocol, which Schulze shear cells follow. Its drawbacks include that the consolidation normal stress range that can be applied is very narrow and that it requires a larger sample quantity than the Schulze shear cell (Berry et al., 2014). The other recently introduced shear cell, the FT4, which has a circular cross-section similar to the Peschl cell, is fully automated and highly repeatable. Its shearing protocol is again different to the widely used Jenike method. Koynov et al. (2015) studied the correlation of the results among the Schulze, the Brookfield and the FT4 shear cell, concluding that there was good agreement at higher consolidation stresses, with the FT4 and Brookfield shear cells giving a lower unconfined yield strength at low stresses. It has been expressed that caution should be taken when conducting tests with cells that have a circular cross-section, since, as mentioned previously, in the centre of the rotating cylinder no shear stress can be exerted on the sample, leading to an underestimation of unconfined yield strength (Schwedes, 2003). Contrary to this, to allow rotation of the cell relative to the lid, a gap must be present in all shear cells, through which material can be lost from the powder bed. This influence may be more pronounced in annular cells, since a gap is required at the inner and outer diameter of the ring. Similarly, the wall friction may be more significant in annular cells compared to cylindrical cells.

2.3.3 Quantitative low stress techniques

The techniques that fall in this category are relatively new and their operational windows are mostly yet to be fully established. The distinctive feature of these techniques is that they can measure flowability down to very low consolidation stresses (considered to be ≤ 1 kPa).

2.3.3.1 Sevilla Powder Tester

The Sevilla Powder Tester (SPT) is an automated apparatus based on the fluidisation of a powder bed, which measures the tensile strength of powders. A schematic view of the experimental setup is displayed in Figure 2.8.
The powder is placed into a cylinder with a filter base, up to a level which gives a ratio of powder bed height over width about equal or smaller than unity in order to minimise the wall effect. Dry nitrogen is then supplied (with its flow velocity and direction being adjustable) either directed upwards or downwards, as indicated by the arrows in Figure 2.8. The pressure drop across the bed is measured by a differential pressure transducer, while the height of the powder bed, $h_{bed}$ is measured by means of an acoustic pulse technique (Valverde et al., 1998, 2000, 2001; Watson et al., 2001).

The bed is initially fluidised by an upward gas flow, therefore bringing the powder to a reproducible state of consolidation. In case the powder is very cohesive, initialisation of the powder can be assisted by a vibration technique in order to break up channels and bubbles that prevent the fluidisation. The gas flow is then switched off, at which point the consolidation stress at the bottom of the bed, $\sigma_{bot}$, is given by Equation 2.10 (Valverde et al., 1998, 2000, 2001, Watson et al., 2001):

$$\sigma_{bot} = \frac{Mg}{A_{bed}} \quad (2.10)$$

where $M$ is the mass of the powder and $A_{bed}$ is the area of the powder bed.

The average void fraction, $\varepsilon_{av}$, for a given degree of consolidation is calculated from Equation 2.11 (Valverde et al., 1998, 2000, 2001; Watson et al., 2001):

$$\varepsilon_{av} = 1 - \frac{M}{\rho_p A_{bed} h_{bed}} \quad (2.11)$$
Once the bed has settled, the gas flow is gradually increased. If the powder had zero cohesion, it would become fluidised at the moment when the pressure drop across the bed balanced the consolidation stress. In reality, all powders demonstrate a degree of cohesion, so the gas flow continues to increase, exceeding the aforementioned point, which is known as minimum fluidisation velocity, putting the bed under tension. At some point, the powder bed will fail, with failure initiating at the base. The phenomenon described above is demonstrated in Figure 2.9.

![Figure 2.9. Pressure drop across the powder bed against gas flow for a xerographic toner (Valverde et al., 2000)](image)

The tensile strength, $\sigma_t$, is measured as the difference between that maximum applied pressure drop, $\Delta P_{\text{max}}$, and the consolidation stress at the bottom of the bed, where the fracture starts, as shown in Equation 2.12 (Valverde et al., 1998, 2000, 2001; Watson et al., 2001):

$$\sigma_t = \Delta P_{\text{max}} - \frac{Mg}{A_{\text{bed}}} \quad (2.12)$$

From the process described above, the tensile strength of the powder for the consolidation stress given by its weight per unit area is obtained. For consolidation stresses below the bed weight, the experimental procedure followed involves an increasing direct gas flow until the fluidisation of the bed, followed by a decrease to a non-zero value (point A in Figure 2.10) and then again an increase up to a new breaking point (point A' in Figure 2.10), where a new tensile strength is measured (Figure 2.10). As expected, the tensile strength decreases as the consolidation stress is reduced. Through this procedure the tensile strength can be assessed down to stress levels of about 10 Pa (Valverde et al., 2000; Valverde et al., 2001). For a set of toners it was found that at low stresses there is a linear relationship between tensile strength and consolidation stress (Valverde et al., 2001). Another
procedure that utilises both upward and downward gas flow is used to measure the tensile strength of the bed at consolidation levels above the weight of the sample (Valverde et al., 2000; Watson et al., 2001). Watson et al. (2001) found a sub-linear relationship between tensile strength and consolidation stress at high stresses for a set of cohesive powders.

Figure 2.10. SPT below powder bed weight consolidation (Valverde et al., 2000)

In addition to the function of this apparatus described above, it also offers the possibility to measure the yield loci of cohesive powders down to low stresses, by quasi-statically tilting the fluidised bed after the initialisation step (Castellanos et al., 2004). Nevertheless, no comparison has been made between the yield loci derived with this method and that of the well-established ring shear testers, as such the reliability of this technique is not known.

Two already mentioned promising elements of this method are that it yields fully repeatable results, due to the fluidisation of the material, and its capability to measure the tensile strength of powders down to consolidation stresses that most techniques cannot reach. Furthermore, the tensile strength measured is not sensitive to the rate of increase of the gas flow. Another advantage is that this apparatus is fully automated, while it requires a relatively small volume of powder (typically 50 ml) to perform the test (Castellanos et al., 2004). Regarding its disadvantages, Sevilla Powder Tester is not commercially available. It does not measure cohesion at yield stress, but only tensile strength. Moreover, it is not suitable for all powders, because the samples need to be able to be fluidised, and cohesive powders exhibit channelling rather than being lifted as a plug. This problem is mitigated to some extent by vibrating the column during fluidisation.
2.3.3.2 Raining bed method

This technique constitutes another tensile tester which shares some common elements with the Sevilla Powder Tester. It was first introduced by Buysman and Peersman (1967) and was later employed by Seville and Clift (1984) and Formisani et al. (2002). The schematic diagram of the method’s experimental setup is demonstrated in Figure 2.11. The first step of this method is the fluidisation of a powder bed by an upward air flow in order to remove the stress history of the bed. Following this, the air supply is turned off, the powder bed is tapped to get a better packing, and the air flow is inverted for the purpose of compressing the bed until the point where the pressure drop across the bed is higher than the weight of the sample. Then, the column and air flow are rotated 180°, so that the bed is upside down with the air flow holding the bed against gravity. The gas velocity is then gradually reduced until the powder starts to ‘rain’ from the bed. If the powder had zero cohesion, this would occur at the point where the pressure drop became equal to the bed weight. In reality, the tensile strength resists the powder raining off, and can be determined from Equation 2.13, by assuming that the pressure drop per unit height is constant, and considering that at the point of bed failure the upward fluid drag and cohesive forces balance the bed weight (Zafar et al., 2015):

\[
\sigma_t = \frac{[\Delta P_{\text{plug}}(u_{mf}) - \Delta P_{\text{plug}}(u_{ro})]H_{\text{plug}}}{H_{2-3}} \quad (2.13)
\]

where \(H_{\text{plug}}\) is the height of the plug detached, \(H_{2-3}\) is the distance between the pressure taps PT2 and PT3 in Figure 2.11, \(\Delta P_{\text{plug}}(u_{ro})\) is the pressure drop of the powder across the plug height at rain-off velocity, \(U_{ro}\) and \(\Delta P_{\text{plug}}(u_{mf})\) is the pressure drop of the powder at minimum fluidisation velocity, \(U_{mf}\). The exerted forces are shown in Figure 2.12.
As with the SPT, the raining bed method offers repeatability by bringing the powder bed to a reproducible state, and can test down to very low consolidation stresses. In a comparative study of different flowability techniques conducted by Zafar et al. (2015), it was found that the measurements of tensile strength from the raining bed method did not agree as closely with extrapolated values from shear cell measurements as did the measurements of tensile strength from the SPT. This may be in part due to the bed consolidation procedure applied for the raining bed method in this study (by
tapping), however the consolidation method used in the SPT could instead be applied. A major drawback of this apparatus is that it requires a large sample quantity, though in principle it could be designed to a similar scale as the SPT. However, in similarity to the SPT, this technique is not suitable for very cohesive powders. Furthermore, the stress state may change when the bed and air flow are inverted.

2.3.3.3 Centrifuge Powder Tester

This novel tester has been constructed at the University of Seville by Castellanos et al. (2007) with the purpose of calculating the angle of internal friction and the cohesion of powders. The experimental apparatus is shown in Figure 2.13.

![Centrifuge Powder Tester (Castellanos et al., 2007)](image)

Figure 2.13. Centrifuge Powder Tester (Castellanos et al., 2007)

Regarding the experimental procedure, a rectangular cell (C in Figure 2.13) is partially filled with a few grams of powder. The bed is initialised by shaking the cell horizontally in the case of coarse particles, or by assisted fluidisation in the case of fines. Following this, the cell is placed on a rotary table and is rotated around its vertical axis by a motor (M in Figure 2.13). At a critical point, the shear stress generated from the exerted centrifugal force is large enough to drive material avalanches, which are recorded by a camera. From a theoretical analysis of these avalanches, based on Coulomb’s method of wedges, the angle of internal friction and cohesion are obtained (Castellanos et al., 2007). Soria-Hoyo et al. (2008) used this apparatus, but changed the initialisation step of the procedure by
subjecting the bed to low-intensity vertical vibrations of controlled frequency and amplitude for a fixed period of two minutes in order to compact it, after horizontal shaking. This initialisation step enables the user to vary the effective consolidation of the powder bed by varying the period of vibration. The results of tests using glass beads showed a significant increase of cohesion and a slight decrease of the angle of internal friction as the effective consolidation of the bed increased, and correlated well with the values of cohesion and angle of internal friction obtained from a Schulze ring shear tester (Soria-Hoyo et al., 2008).

The Centrifuge Powder Tester enables measurements at very low consolidation stresses (less than 0.5 kPa), while the rotor offers strain rate control. It is easy to operate, requiring only 2 - 4 g of material, and it enables the operator, via the usage of a camera, to detect exactly at which point the powder bed failure occurs. A drawback of this method is that whenever a higher consolidation stress needs to be applied, this is translated to higher vibration needed to break up the bed, which could potentially lead to auto-agglomeration for some cohesive materials (Ku, 2015). The powder volume used is a crucial parameter of this method in order to minimise the effect of wall friction, since the geometry of the cell means there is significant wall friction in any case. Furthermore, it would be an important improvement if the bed was consolidated to a known stress rather than vibrated.

### 2.3.3.4 SSSpin Tester

This power strength tester is developed by Material Flow Solutions Inc. and is capable of measuring the unconfined yield strength of bulk materials at consolidation stresses ranging from 10 Pa to 40 kPa. The SSSpin Tester houses the powder in a conical cell, which first consolidates the material using centrifugal force at a constant rotational speed. Then, the rotational speed is reduced to zero and the cell lid gates are removed. Following this, the rotational speed is increased until the compacted material yields. The yield point is determined by detection of material flowing from the cell, by temporarily blocking the path between a laser and a transducer. This apparatus is time-efficient, since a strength measurement is obtained in 3 minutes. Another feature of this tester is that it only requires 0.5 g of material to run a test in contrast to the long-established techniques for assessing powder flow behaviour, such as the Schulze shear cell. However, such a small cell ultimately results in an increased wall effect. Most other techniques require significant extrapolation to predict flow behaviour at low stresses, whereas the SSSpin Tester does not. On the other hand, the reliability of determining the yield point by a laser has not been reported in the literature, and the device’s operational window has not been well established yet (https://vimeo.com/icheme/review/128119934/fc65086fed).
2.3.4 Quantitative dynamic low stress techniques

Although this class of techniques is able to assess flowability at low stresses, they are described in this separate section, due to their unique potential to operate at higher strain rates above the slow, frictional regime as described by Tardos et al. (2003), which is of great interest, since a variety of powder industrial processes are dynamic in nature.

Tardos et al. (2003) defined approximate boundaries between the different types of flow based on the dimensionless shear strain rate, $\gamma^o*$, given by Equation 2.14:

$$\gamma^o* = \gamma^o \sqrt{\frac{d_p}{g}}$$  \hspace{1cm} (2.14)

where $\gamma^o$ is the shear strain rate. The shear stress as a function of strain rate for the different regimes is depicted in Figure 2.14. At zero shear, the condition is static without any flow. At very low shear rates, there is a very narrow regime in which the flow exhibits stick-slip motion. At low dimensionless shear rates, in the slow, frictional flow regime (also known as quasi-static regime), the frictional forces between particles prevail. At the opposite side of the spectrum, at very high shear rates, particles move very fast, with the friction between them being negligible, and the flow is governed by short collisions between particles. This regime is called rapid granular flow regime. Between the slow, frictional and the rapid granular flow regimes is the intermediate regime where both collisional and frictional interactions between particles are considered. In this regime, stress and strain rate fluctuations are present, which increase as the strain rate increases. It is noteworthy that the boundaries between the slow, frictional flow regime and the intermediate regime are not clearly defined.
In Figure 2.14 the dependency of shear stress on the strain rate is also demonstrated. It can be seen that at low shear rates, the shear stress is independent of the strain rate, while as the flow transitions from the slow, frictional to the intermediate regime, it becomes dependent on the strain rate to an increasing power that becomes 2 in the rapid granular regime.

2.3.4.1 Couette device

A Couette device constitutes a geometry in which powder is sheared between two vertical, concentric cylinders by rotating the inner cylinder at a certain rotational rate whilst keeping the outer cylinder stationary (Figure 2.15). Devices like this have traditionally been used for studying the rheology of fluids (Savage and McKeown, 1983), with Savage and Sayed (1984) employing it for the first time to study dry granular solids. The vertical shear gap forms between the rotating and the stationary cylinders, and its width and height can be adjusted by appropriate choice of the radius and height of the rotating cylinder. The material can be fed from above using a vibratory feeder and discharged by a screw feeder to a precision balance for flow rate measurement. The walls of the Couette are made rough by gluing sand paper on the shearing surfaces of both cylinders to match or exceed the coefficient of internal friction of the material, thus ensuring a non-slip boundary condition. It can be operated in batch mode by closing the discharge section, or continuously by feeding and removing powder to achieve a vertical steady-state flow (Kheiripour Langroudi et al., 2010). If the outer cylinder is chosen to be taller than the inner one, material can be added in the empty space formed, creating
a stationary layer that acts as a dead weight (not rotating with the inner cylinder), so that it can control the applied pressure and prevent the material in the shearing gap from expanding, thus keeping the porosity constant (Kheiripour Langroudi et al., 2010; Tardos et al., 1998). Normal stresses are measured on both the outer, stationary wall as well as the inner, rotating wall of the device, while shear stresses are measured indirectly from the torque on the rotating cylinder (Kheiripour Langroudi et al., 2010). In this apparatus, the powder is sheared in a plane perpendicular to the compressive force and gravity (Tardos et al., 1998).

If a dead weight is not used, then the free upper surface allows the packing density to adjust via feedback between shear-induced dilation and gravity (Mueth et al., 2000). Prior to shearing, air can be pumped at an air velocity below minimum fluidisation conditions through a porous base to obtain a reasonably uniform packing, and to erase any stress history (Mehandia et al., 2012). Additionally, the shearing itself can be assisted by gas flow, so that the powder can dilate to the critical state to accommodate the imposed shearing, and avoid flow problems that can be found in hopper flow, such as the repeated formation and breakage of arches (Tardos et al., 1998).

This geometry can operate from the frictional regime to the dynamic regime, thus it has been used by a number of researchers to investigate flow in the three different shear rate flow regimes (frictional, intermediate, rapid flow regimes) (Tardos et al., 1998; Tardos et al., 2003; Kheiripour Langroudi et al., 2010; Vidyapati et al., 2012; Mehandia et al., 2012; Kumar et al., 2013; Gutam et al., 2013). Apart from the significant benefit that this geometry provides to link the stresses with shear rate, the fact that

![Figure 2.15. Couette device (Kheiripour Langroudi et al., 2010)](image)
any size powder can be used from millimeter down to micron size, as well as that it is easy to operate, can be listed as its advantages. Measurements can be performed down to low stresses, since consolidation is controlled by adding/removing material. On the other hand, sufficient amount of material is needed in order to avoid wall effects (Tardos et al., 2003), and it still poses a challenge for granular materials in comparison to fluids, due to the rate independence and pressure-dependence of the deviatoric stress (Kumar et al., 2013). Contradictory results of vertical and radial normal stress variation throughout the bed height have been reported, with Tardos et al. (1998) finding the stress varying with $\rho_bgz$ and Tardos et al. (2003) finding stress scaling with $3\tan(\phi)\rho_bgz$, where $\rho_b$ is the bulk density and $z$ is the bed depth, while Gutam et al. (2013) showed an exponential growth of stress with bed depth. Furthermore, Gutam et al. (2013) showed that the direction of $\sigma_r$ switches upon onset of shearing and that the stress variation across the powder bed is dependent on the gap width. It is suggested that this could potentially be due to an upward flow of particles near the outer wall, or due to the anisotropy of the bed rheology. Since anisotropy of the bed fabric has been shown for static sand piles (Vanel et al., 1999) and during shear (Howell et al., 1999), it is expected that this would indeed be the case in a Couette flow.

2.3.4.2 Powder rheometers

Powder rheometers are a branch of powder characterisation techniques that can provide repeatable, sensitive and quick measurements with a high degree of automation. The most well-known powder rheometers are presented below.

FT4 Powder Rheometer

The FT4 Powder Rheometer, which is developed by Freeman Technology, UK, is a versatile tester capable of performing a plethora of measurements regarding bulk flow behaviour. The rheometry testing with this instrument involves a twisted blade displacing powder inside a cylindrical vessel, as it moves along a helical path through the sample. Depending on the direction and speed of vertical movement and rotation, a broad range of flow patterns and rates can be achieved. Axial and rotational forces acting on the blade at given vertical and rotational speeds are measured, and this data form the basis of the flowability assessment. Force and torque measurements are converted into ‘flow energy’, $E_{flow}$, to determine the total (translational and rotational) work done by the blade during the traverse (Freeman and Fu, 2008; FT4 Powder Rheometer Manual), as shown in Equation 2.15:

$$E_{flow} = \int_0^{h_{blade}} \left( \frac{T}{R_{imp}\tan(\phi_b)} + F_{base} \right) dh_{blade} \quad (2.15)$$
where $h_{\text{blade}}$ is the blade penetration depth, $T$ is the torque acting on the impeller, $R_{\text{imp}}$ is the impeller radius, $\phi_b$ is the angle of the blade’s helical path to the horizontal plane and $F_{\text{base}}$ is the vertical force acting on the base.

Before every measurement with this instrument it is suggested to perform powder conditioning, which is a full cycle of the blade moving downwards and then upwards in order to remove residual compaction and excess air from the bed, to achieve the best possible uniformity, and to bring the bed to a reproducible state. The downward traverse would typically use a positive 5 degree helix (clockwise) in order that the blade action is more slicing than compacting. The upward traverse would typically use a 5 degree negative helix (clockwise) that gently lifts the powder and drops it over the blade, each particle coming to rest behind it (Freeman and Fu, 2008; FT4 Powder Rheometer Manual).

After conditioning, the main test methodology, ‘dynamic testing’, is employed for the flow energy measurement in a high stress environment and is a downward anti-clockwise bull-dozing motion of the blade from the top to the bottom of the vessel; generating a compressive, higher stress flow mode in the powder. Alternatively, the methodology employed for testing in an unconfined, or low stress environment, is an upward clockwise motion of the blade from the bottom to the top of the vessel. The blade is still contacting the powder at the same angle as in the downward test, however it is driving it upwards, towards a free surface, and hence results in testing under a lower stress state. Unlike the first test, where powder compressibility can be very significant, the measurement of the low stress test is said to be most dependent on the shear forces that act between particles (Freeman and Fu, 2008; FT4 Powder Rheometer Manual).

For both tests, a greater value of flow energy is considered to indicate a reduced flowability (Freeman and Fu, 2008), however this is not always the case for the high stress test, because sometimes the density of the bed should also be considered (FT4 Powder Rheometer Manual). Along with these test methods there are also some accessories, such as a shear cell for measuring the powders shear strength, a wall friction kit to quantify how the powder shears against the wall of the apparatus, and various other tests can be carried out to measure density, compressibility, permeability and aeration, as well as other bulk properties. Freeman and Fu (2008) studied the die filling performance of three very different materials by measuring a comprehensive set of powder properties with the FT4 tester, concluding that die filling efficiency was predicted with a high level of confidence. Figure 2.16 shows the dynamic downward, upward and shearing modes.
In recent years, several studies have been published using the FT4 powder rheometer, praising the instrument’s repeatability of measurements, as well as the agreement of its results with those of conventional methods (Lindberg et al., 2004; Freeman, 2007; Zhou et al., 2010; Leturia et al., 2014).

**Powder Flow Analyser**

The Powder Flow Analyser (PFA) has been developed by Stable Microsystems, UK, and is very similar to the FT4. The PFA comprises a helical blade, which moves either upwards or downwards inside a cylinder and rotates either clockwise or anti-clockwise. The software of the instrument measures sample displacement, the reactive axial force caused by it, and time, generating force vs. displacement curves. It is noteworthy that the torque acting on the blade is not measured. The area under the curve indicates the work required for the powder to flow around the blade, enabling the measurement of various powder properties, including flowability (Abu-hardan and Hill, 2010). Shah et al. (2008) measured the cohesion, caking ability and strength, and flow stability of powders and granules with the PFA, highlighting the importance of the blade’s helical design that can cut through the column of the powder bed reproducibly without an aid of torque systems.

**Mechanically Stirred Fluidised Bed Rheometer**

Recently, Bruni et al. (2005) employed the Mechanically Stirred Fluidised Bed Rheometer (msFBR), displayed in Figure 2.17, to characterise the flow properties of powders in their aerated/fluidised state under realistic process conditions.
The msFBR consists of a powder bed placed in a cylindrical vessel, in which a fluidising gas (nitrogen) is introduced at the base with an upward flow in order to bring the bed into a reproducible state. The pressure drop across the bed is measured by means of an ultralow pressure differential sensor. An impeller with two flat blades is then lowered into the bed to a specified depth, and the torque is measured whilst the impeller is rotated. At aeration rates below the minimum fluidisation velocity, which is a state of low stress, the torque measurements were found to be dependent on the stirring time, with values of the torque reaching the same constant value at different impeller speeds after a sufficient time was allowed before each reading. The time-step was found to be longer at slower impeller speeds. The torque profiles with increasing impeller depth matched very well the normal stress profiles in silos, with the torque following a non-linear increase with increasing impeller depth and reaching a plateau at high values of impeller depth in the bed. In contrast, at minimum fluidisation conditions, the torques measured for both alumina and ballotini powders were found to be dependent on the impeller speed. Moreover, the effect of increasing impeller depth showed in this case a linear increase of the normal stresses in the bed, therefore showing the change in behaviour from solid- to liquid-like behaviour when minimum fluidisation is achieved.

**Anton Paar Rheometer**

The Anton Paar Rheometer is an instrument which is based on the same principles as the msFBR. The first step of the experimental procedure involves an air stream, which is introduced to the powder through a porous material at the base of a powder column to fluidise the bed, followed by a flat,
vertically aligned blade, which moves through the sample, while force and torque are measured and converted to a ‘flow energy’, like for the FT4. Torque and force are simply added up, but no defined shear surface is taken into account. Also, by following the same conditioning procedure, but instead measuring only the torque exerted at a constant rotational speed, a qualitative index called the ‘Cohesion strength’ of the sample can be derived (Anton Paar, n.d.).

Powder rheometers have been proven reliable characterisation methods, which provide results with a good level of differentiation in comparison to the traditional, quasi-static techniques seemingly due to their ability to operate at higher strain rates. They are capable of operating above the frictional regime of shear strain rates (Hare and Ghadiri, 2017) and at low stresses, since they can operate even without any vertical stress applied, under the low consolidation stress supplied by the powder bed. One significant problem of these devices is that measurements are based on the interaction between the blade and the sample, which are complex, depending on the design and material of the blade, as well as on the blade-wall clearance and particle properties, therefore it is challenging to compare the results among different materials. There has been no conclusive analysis of the stress state within the flowing region in these devices, thus utilising their measurements for process design is challenging. Hare et al. (2015) carried out DEM simulations of the FT4 and found the shear stress to be constant across the length of the blade, and increasing with blade penetration depth, a finding implying that shear stresses will not be constant across blades with other designs (e.g. vertical flat blades) and highlighting the importance of the blade shape. Furthermore, the predicted shear stress variation with particle sliding friction correlated with the flow energy. However, the relationship between the flow energy and shear stresses, depending on particle properties, is yet to be established. Also, flat, horizontal blades are reported to give rise to undesirable powder compression below the blade (Shah et al., 2008). Last but not least, a noteworthy drawback of powder rheometers is the amount of material needed for these tests (e.g. > 160 ml for FT4 tests using the 50 mm diameter vessels).

2.3.4.3 Ball indentation

Indentation tests have long been used for the study of continuum solids. In powder technology, Knight and Johnson (1988) were the first to introduce a penetration test. They used a metallic cone with a half-angle of 5° to measure the cohesive caking strength of compacted powder samples, suggesting this method to be used to supplement shear cell measurements. Several researchers in the field have used indentation techniques for powder flowability characterisation, but the results weren’t consistent, because they were dependent on the test method (Zatloukal and Šklubalová, 2008). Hassanpour and Ghadiri (2007) introduced ball Indentation for assessing powder flowability by evaluating the hardness of a powder bed. The first step of this method involves a powder bed that is
placed inside a cylindrical die made of low friction material, and is pre-consolidated by a piston to a desired stress at a specified strain rate. Then, the piston is unloaded, and the compressed bed is penetrated by a spherical indenter at the same strain rate until a certain depth is reached, and then unloaded (Hassanpour and Ghadiri, 2007), as shown in Figure 2.18.

![Figure 2.18. Indentation step of the procedure (Pasha, 2013)](image)

The curvature of a sphere results in a smoother transition from elastic to plastic deformation in the failure zone below the indenter, in comparison with other indenter shapes such as pyramids or cones, and allows the powder to be sheared rather than consolidated (Zafar, 2013).

The penetration depth/load data are continuously recorded throughout the indentation process, to produce a depth/load curve as shown in Figure 2.19, which includes two discrete regions of loading and unloading (Hassanpour and Ghadiri, 2007).

![Figure 2.19. Indentation load against penetration depth (Zafar, 2013)](image)
During the unloading cycle, the elastic deformation of the sample recovers until the load reaches zero and displacement reaches its final value, \( h_f \). However, the end of the curve may deviate from the unloading slope due to adhesion of the indenter to the specimen, causing a slight rise of the powder bed surface as the indenter is unloaded. This effect has been observed for continuum solids and may not be significant for particulate specimens. Nevertheless, it can be discounted by using the elastically-recovered depth, \( h_c \), in the calculation of hardness rather than \( h_f \). \( h_c \) is taken as the depth-axis intercept of the tangent to the initial elastic part of the unloading curve (Zafar, 2013).

The aim of this method is to evaluate the hardness of the material, \( H \), representing flow stress, which is its resistance to plastic deformation, and is given by Equation 2.16. This measurement is well established for continuum solids, and has been extended to testing of cohesive powder beds by Hassanpour and Ghadiri (2007).

\[
H = \frac{F_{\text{max}}}{A} \quad (2.16)
\]

where \( F_{\text{max}} \) is the maximum indentation load and \( A \) is the projected area of the impression of the indenter, calculated from Equation 2.17:

\[
A = \pi(d_b h_c - h_c^2) \quad (2.17)
\]

where \( d_b \) is the indenter diameter. If unloading has negligible effect on the material’s recovery, the penetration depth at maximum indentation load, \( h_m \) (see Figure 2.19), can be used in place of \( h_c \).

Furthermore, it is of utmost importance to avoid further consolidation of the sample during the indentation step, because in this case the hardness value that is measured won’t represent the consolidation stress that was initially chosen to be applied (Pasha, 2013; Zafar, 2013).

Penetration of continuum solids leads to the formation of a local plastic zone around the indenter, where the volume of material under yielding condition is surrounded by an elastically deforming region, and cannot easily flow. This leads to an increase in the local yield strength, represented by the hardness (Kozlov et al., 1995). The hardness is related to the unconfined yield strength by Equation 2.18 (Tabor, 1951):

\[
H = C \sigma_c \quad (2.18)
\]

where \( C \) is the constraint factor, which represents the additional resistance caused by the elastically deforming region around the plastically deforming indentation zone.

Based on wedge cutting theory, Hill (1950) reported that the value 3 can be applied to the constraint factor for rigid-perfectly plastic materials, while according to Tabor (1951) this value is applicable only
for ductile metals. In addition, Johnson (1985) introduced the following relationship between indentation hardness and unconfined yield strength for elastic-perfectly plastic materials, which covers a wide range of organics and polymers:

\[ \frac{H}{\sigma_c} = \frac{2}{3} \left[ 1 + \ln \left( \frac{E a_{imp}}{3 R_b \sigma_c} \right) \right] \] (2.19)

where \( a_{imp} \) is the radius of the impression and \( R_b \) is the indenter radius. Equation 2.19 is applicable for continuum solids, but hasn’t been validated for particulate systems.

This additional elastic constraint around the plastically deforming indentation zone has also been found in particulate systems (Hassanpour and Ghadiri, 2007; Zafar, 2013). In the case of continuum solids, the constraint factor is known to depend on material properties (Tabor, 1996). For particle systems, the constraint factor is dependent on single particle properties (Hassanpour and Ghadiri, 2007; Wang et al., 2008; Zafar, 2013). Wang et al. (2008) conducted indentation hardness experiments, as well as uniaxial compression tests, using three pharmaceutical powders, Avicel, starch and α-lactose, concluding that both the indentation hardness and unconfined yield strength increase with pre-consolidation stress, and showing that the constraint factor is independent of pre-consolidation stress, but depends on the powder tested. This dependency is attributed to differences in single particle properties such as particle shape, roughness and friction coefficient. Using the same techniques to quantify \( C \), Zafar (2013) reported values of the constraint factor for various materials, ranging from 1.5 - 3 for silanised glass beads, to 6 - 8 for different size distributions of Lactohale. In addition, he found \( C \) to be independent of the stress level applied in a range of moderate to high consolidation stresses, also showing it to decrease with the increase in particle size by testing coated glass beads. Moreover, Zafar et al. (2015) conducted indentation and shear cell tests using a range of powders, reporting a good correlation between hardness and unconfined yield strength for stresses down to 3 kPa. The influence of particle properties on \( C \) remains unknown and constitutes one of the main objectives of this thesis.

Although the ball indentation technique is used to measure hardness, if the constraint factor is known, then the unconfined yield strength, which is typically determined from shear cells, can be inferred from Equation 2.18. The operational criteria of the ball indentation technique in terms of die filling method, penetration depth, bed height, indentation position, indenter size, shape and stiffness in order to get reliable hardness measurements have been established both experimentally (Zafar et al., 2017) and by DEM simulations (Pasha et al., 2013).

The experimental procedure mentioned above is typically followed by utilising a mechanical testing instrument in order to obtain measurements in the quasi-static regime of strain rates. However, this
technique has also the potential to operate at higher strain rates, and in the case of dynamic measurements a different setup is employed. The spherical indenter is dropped from a predetermined height in order to accelerate under gravity into a pre-compacted powder bed (Zafar, 2013). For dynamic indentation, hardness is given by Equation 2.20:

\[ H_d = \frac{M_{\text{ind}} V_i^2}{2U} \]  

where \( H_d \) is the dynamic hardness, \( M_{\text{ind}} \) is the mass of the indenter, \( V_i \) is the incident velocity and \( U \) is the unrelaxed volume of the indentation impression on the specimen (Tirupataiah and Sundararajan, 1990). By dynamically indenting a range of powder beds, Zafar (2013) found that hardness is independent of the strain rate in the quasi-static regime, but becomes dependent as the strain rate increases, with the transition boundary to the intermediate regime still unknown, a finding supported by the work of Tardos et al. (2003). Pasha et al. (2015) performed a numerical analysis of strain rate sensitivity in the ball indentation method on model glass beads using DEM, resulting in similar trends.

The ball indentation method constitutes an easy, quick and cheap test to evaluate powder flowability which needs only a small quantity of material, typically a few grams. For a larger sample, multiple tests can be done on the same pre-consolidated bed, and as such it can be used for assessing caking tendency (Chen et al., 2017). Another benefit of this technique is its capability to conduct measurements at very low stresses (≤ 1 kPa) and at strain rates beyond the quasi-static regime. Disadvantages include the lack of knowledge regarding the stress distribution within the powder bed, and that the determination of unconfined yield strength is indirect. In addition, the bed isn’t brought to a reproducible state, thus the point where steady-state flow is achieved is unknown. At present, the constraint factor is not known for a given powder, therefore the relationship between the constraint factor and particle properties needs to be established in order for the unconfined yield strength to be determined from hardness measurements.

### 2.4 Evaluation of powder flowability assessment techniques

Over the years, both academia and industries that deal with bulk solids handling have been using a plethora of techniques in order to study powder flow, as described in section 2.3. Some of these techniques have proven particularly useful for quality control, due to the fact that they are quick, easy to operate and low-cost, while others are quantitative, providing control of the consolidation stress, thus allowing the measurement to be informative in the design of real industrial procedures. A few of the techniques fall into a unique category of being able to measure flowability at very low consolidation stresses, and even fewer are capable of operating at this range of stresses and at the same time at higher strain rates, in the intermediate and rapid granular flow regimes.

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In this section, the existing techniques are evaluated based on a number of criteria. The criteria chosen consist of those proposed by Schulze (2008) for a tester in order to give quantitative results, as well as three additional criteria, which are directly linked to the needs of specific powder processes or industries:

Schulze’s criteria (Schulze, 2008):

1. Consolidation procedure with corresponding measurement of strength
2. Consolidation of the bulk solid sample up to steady-state flow
3. Rough coincidence of the directions of major principle stresses at consolidation and failure
4. Reproducible stressing conditions of the bulk solid sample at consolidation (4a) and failure (4b)
5. Known average stresses and uniform stress distribution in the plane of interest at consolidation (5a) and failure (5b)
6. Possibility for varying the consolidation stresses (with regard to application)
7. Possibility for measuring time consolidation

Additional criteria:

8. Small sample quantity needed (≤ 10 ml)
9. Capable of measuring at low consolidation stresses (≤ 1 kPa)
10. Capable of measurements at high strain rates beyond the quasi-static regime

It should be noted that criteria 1 - 6 refer to the ability to control and measure a quantitative value of flowability in relation to stresses, whilst criteria 7 - 10 refer to beneficial capabilities of a flow measurement device. A method may not meet most of the chosen criteria, but could be perfectly suitable for quality control of a given process, however caution should be taken in then applying the measurement of the method to a new process. The comparison of the techniques is displayed in Table 2.3.
<table>
<thead>
<tr>
<th>Technique</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4a/b</th>
<th>5a/b</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>Evaluative comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Angle of repose</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no/no</td>
<td>no/no</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>yes</td>
<td>no</td>
<td>Simple, quick, only suitable for quality control, not suitable for very cohesive powders, or very large particles</td>
</tr>
<tr>
<td>Hosokawa Powder Tester</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no/no</td>
<td>no/no</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>yes</td>
<td>no</td>
<td>Automated method, offers reproducibility and accuracy, capable of estimating a set of powder flow related properties, manipulated by vibrations consolidation state, suitable only for qualitative tests</td>
</tr>
<tr>
<td>Avalanche technique</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no/no</td>
<td>no/no</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>yes</td>
<td>no</td>
<td>Fast, reproducible qualitative technique</td>
</tr>
<tr>
<td>Funnel discharge techniques</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no/no</td>
<td>no/no</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>yes</td>
<td>no</td>
<td>Only for qualitative analysis, operational window not fully established, cohesive powders lead to funnel blockage</td>
</tr>
<tr>
<td>Vibrating capillary method</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no/no</td>
<td>no/no</td>
<td>no</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
<td>High resolution compared to other qualitative methods, cohesive powders block the capillary tube, limited range of PSDs can be tested</td>
</tr>
<tr>
<td>Uniaxial compression test</td>
<td>yes</td>
<td>no</td>
<td>yes</td>
<td>yes/yes</td>
<td>yes/yes</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>Easy, needs sufficient amount of sample to avoid wall friction, measures, but underestimates unconfined yield strength, provides consolidation stress control, only sufficiently cohesive powders can be tested</td>
</tr>
<tr>
<td>Warren Spring Cohesion Tester</td>
<td>yes</td>
<td>no</td>
<td>no</td>
<td>yes/yes</td>
<td>yes/no</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>Qualitative method, measures cohesion, not based on a specific stress history, state of stress and strain rate not well defined</td>
</tr>
<tr>
<td>Split Cell Tensile Tester</td>
<td>yes</td>
<td>no</td>
<td>yes</td>
<td>yes/yes</td>
<td>yes/yes</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>Measures tensile strength, sample preparation does not lead to an isotropic state of stresses, poor reproducibility</td>
</tr>
<tr>
<td>Lifting Lid Tensile Tester</td>
<td>yes</td>
<td>no</td>
<td>yes</td>
<td>yes/yes</td>
<td>yes/yes</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>Similar to Split Cell Tensile Tester, but the direction of major principal stress during consolidation and failure are aligned</td>
</tr>
<tr>
<td>Shear cells</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes/yes</td>
<td>yes/yes</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>Most established technique, repeatable, time-efficient using rotational shear cells, suitable for quantitative measurements and silo and hopper design, they either do not operate or are not consistently reliable at low stresses</td>
</tr>
<tr>
<td>Sevilla Powder Tester</td>
<td>yes</td>
<td>no</td>
<td>yes</td>
<td>yes/yes</td>
<td>yes/yes</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
<td>yes</td>
<td>no</td>
<td>Good repeatability, can measure tensile strength down to very low stresses, not suitable for very cohesive or free-flowing powders, not commercially available</td>
</tr>
<tr>
<td>Raining bed method</td>
<td>yes</td>
<td>no</td>
<td>yes</td>
<td>yes/yes</td>
<td>yes/yes</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
<td>yes</td>
<td>no</td>
<td>Similar to SPT, inversion of the powder bed may affect the stress state</td>
</tr>
<tr>
<td>Centrifuge Powder Tester</td>
<td>yes</td>
<td>no</td>
<td>no</td>
<td>yes/yes</td>
<td>no/no</td>
<td>yes</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
<td>Determines cohesion and angle of internal friction, cell geometry raises concern over the exhibited wall friction</td>
</tr>
<tr>
<td>Technique</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4a/b</td>
<td>5a/b</td>
<td>6</td>
<td>7</td>
<td>8</td>
<td>9</td>
<td>10</td>
<td>Evaluative comments</td>
</tr>
<tr>
<td>----------------------------</td>
<td>---</td>
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<td>------</td>
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<td>---</td>
<td>---</td>
<td>---</td>
<td>----</td>
<td>-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>SSSpin Tester</td>
<td>yes</td>
<td>no</td>
<td>yes</td>
<td>yes/yes</td>
<td>yes/yes</td>
<td>yes</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
<td>Measures unconfined yield strength, utilises only 0.5 g of material, can go down to 10 Pa, failure is determined visually by a laser, therefore raising concern over its reproducibility, reliability not established yet</td>
</tr>
<tr>
<td>Couette device</td>
<td>yes</td>
<td>no</td>
<td>no</td>
<td>yes/yes</td>
<td>yes/yes</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
<td>The first technique to operate at high strain rates, can measure at low consolidation levels, suitable for investigating all flow regimes</td>
</tr>
<tr>
<td>Powder rheometers</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>yes/yes</td>
<td>yes/no</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
<td>Do not measure strength, measurements are based on the complex interaction between blade and sample, operational windows not fully established</td>
</tr>
<tr>
<td>Ball indentation</td>
<td>yes</td>
<td>no</td>
<td>yes</td>
<td>yes/yes</td>
<td>yes/no</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>Simple method with only a few grams of sample required, can operate at very low stresses, can achieve high strain rates, does not measure unconfined yield strength directly, the stress state under the indenter is not well understood</td>
</tr>
</tbody>
</table>

Reported by Schulze (2008)
Chapter 3  Materials and Methods

In this chapter, all the materials used for this research are presented, along with their size and shape analysis. Furthermore, all experimental methods employed throughout the thesis, both for particle characterisation and powder flowability assessment, are described.

3.1 Materials and their characterisation

3.1.1 Material characterisation overview

This project focuses on cohesive powders, aiming at determining the influence of particle properties on flowability. A broad class of materials that includes glass beads coated with a hydrophobic silane to be made cohesive as a model material, as well as ‘real’ powders, both inorganic and organic, were investigated in order to evaluate the suitability of ball indentation as a low stress flow assessment technique and establish how the constraint factor varies with particle properties and its range of values. An overview of the size and shape characterisation of all materials, along with their particle densities, is presented in Table 3.1 and later discussed in detail in the following sections.
<table>
<thead>
<tr>
<th>Material</th>
<th>$d_{10}$</th>
<th>$d_{50}$</th>
<th>$d_{90}$</th>
<th>Span $[(d_{90}-d_{10})/d_{50}]$</th>
<th>Sphericity</th>
<th>AR</th>
<th>Shape description</th>
<th>Particle density (kg/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>45 - 53μm glass beads*</td>
<td>48.9</td>
<td>58.4</td>
<td>72.1</td>
<td>0.40</td>
<td>0.91</td>
<td>0.85</td>
<td>spherical</td>
<td>2,500*</td>
</tr>
<tr>
<td>53 - 63μm glass beads*</td>
<td>58.8</td>
<td>67</td>
<td>80.5</td>
<td>0.32</td>
<td>0.92</td>
<td>0.88</td>
<td>spherical</td>
<td>2,500*</td>
</tr>
<tr>
<td>63 - 75μm glass beads*</td>
<td>68.3</td>
<td>79.9</td>
<td>98</td>
<td>0.37</td>
<td>0.92</td>
<td>0.89</td>
<td>spherical</td>
<td>2,500*</td>
</tr>
<tr>
<td>75 - 90μm glass beads*</td>
<td>84</td>
<td>92.9</td>
<td>112.1</td>
<td>0.30</td>
<td>0.93</td>
<td>0.91</td>
<td>spherical</td>
<td>2,500*</td>
</tr>
<tr>
<td>90 - 106μm glass beads*</td>
<td>96.7</td>
<td>108</td>
<td>128.3</td>
<td>0.29</td>
<td>0.93</td>
<td>0.92</td>
<td>spherical</td>
<td>2,500*</td>
</tr>
<tr>
<td>53 - 90μm glass beads*</td>
<td>65.1</td>
<td>81.2</td>
<td>103.5</td>
<td>0.47</td>
<td>0.92</td>
<td>0.89</td>
<td>spherical</td>
<td>2,500*</td>
</tr>
<tr>
<td>45 - 106μm glass beads*</td>
<td>61.9</td>
<td>81.5</td>
<td>106.8</td>
<td>0.55</td>
<td>0.92</td>
<td>0.88</td>
<td>spherical</td>
<td>2,500*</td>
</tr>
<tr>
<td>63 - 75μm + 10% coarse glass beads*</td>
<td>67</td>
<td>80.1</td>
<td>159.3</td>
<td>1.15</td>
<td>0.93</td>
<td>0.9</td>
<td>spherical</td>
<td>2,500*</td>
</tr>
<tr>
<td>63 - 75μm + 20% coarse glass beads*</td>
<td>68.7</td>
<td>84.4</td>
<td>183.5</td>
<td>1.36</td>
<td>0.93</td>
<td>0.91</td>
<td>spherical</td>
<td>2,500*</td>
</tr>
<tr>
<td>63 - 75μm + 10% fine glass beads**</td>
<td>41</td>
<td>70.1</td>
<td>99.7</td>
<td>0.84</td>
<td>-</td>
<td>-</td>
<td>spherical</td>
<td>2,500*</td>
</tr>
<tr>
<td>63 - 75μm + 20% fine glass beads***</td>
<td>9.8</td>
<td>67.5</td>
<td>97.5</td>
<td>1.30</td>
<td>-</td>
<td>-</td>
<td>spherical</td>
<td>2,500*</td>
</tr>
<tr>
<td>0 - 20μm glass beads***</td>
<td>0.8</td>
<td>3</td>
<td>10.6</td>
<td>3.30</td>
<td>-</td>
<td>-</td>
<td>spherical</td>
<td>2,500*</td>
</tr>
<tr>
<td>Alumina CT8005G####</td>
<td>0.3</td>
<td>3.4</td>
<td>8.6</td>
<td>2.44</td>
<td>-</td>
<td>-</td>
<td>plate-shaped</td>
<td>4,000*</td>
</tr>
<tr>
<td>Alumina Rapol 900 Batchground#####</td>
<td>0.4</td>
<td>2.9</td>
<td>23.1</td>
<td>7.83</td>
<td>-</td>
<td>-</td>
<td>rounded agglomerates</td>
<td>4,000*</td>
</tr>
<tr>
<td>Alumina Rapol 900 Conti. ground#####</td>
<td>0.4</td>
<td>2.8</td>
<td>13.9</td>
<td>4.82</td>
<td>-</td>
<td>-</td>
<td>irregular agglomerates</td>
<td>4,000*</td>
</tr>
<tr>
<td>Limestone#####</td>
<td>1.1</td>
<td>4.3</td>
<td>9</td>
<td>1.84</td>
<td>-</td>
<td>-</td>
<td>irregular</td>
<td>2,930*</td>
</tr>
<tr>
<td>Talc#####</td>
<td>3</td>
<td>7.5</td>
<td>17.6</td>
<td>1.95</td>
<td>-</td>
<td>-</td>
<td>plate-shaped</td>
<td>2,700***</td>
</tr>
<tr>
<td>Copper#####</td>
<td>10.4</td>
<td>18.3</td>
<td>30.7</td>
<td>1.11</td>
<td>0.83</td>
<td>0.6</td>
<td>dendritic</td>
<td>8,940*</td>
</tr>
<tr>
<td>Titania#####</td>
<td>0.092</td>
<td>0.148</td>
<td>0.293</td>
<td>1.36</td>
<td>-</td>
<td>-</td>
<td>irregular particles and agglomerates</td>
<td>4,200*</td>
</tr>
<tr>
<td>Maize starch#####</td>
<td>11.3</td>
<td>19.6</td>
<td>38.2</td>
<td>1.37</td>
<td>0.88</td>
<td>0.71</td>
<td>irregular</td>
<td>1,440**</td>
</tr>
<tr>
<td>Maltitol#####</td>
<td>11.5</td>
<td>30.8</td>
<td>92.4</td>
<td>2.63</td>
<td>0.87</td>
<td>0.67</td>
<td>irregular</td>
<td>1,450**</td>
</tr>
<tr>
<td>Pea protein#####</td>
<td>11.9</td>
<td>36.2</td>
<td>75.6</td>
<td>1.76</td>
<td>0.87</td>
<td>0.7</td>
<td>irregular</td>
<td>2,480**</td>
</tr>
</tbody>
</table>

* Size measurement by QICPIC (GRADIS)
** Size measurement by QICPIC (LIXELL)
*** Size measurement by Mastersizer
##### Size measurement by CILAS
#### Size measurement by Zetasizer Nano

* Taken from MSDS
" Measured using gas pycnometry
*** Reference: Yamamoto and Jiao, 1994
3.1.2 Particle size and shape characterisation

The QICPIC particle size and shape analyser (Sympatec GmbH, Germany) was used to characterise the particle size distribution and morphology of the majority of the powders. This dynamic image analysis device consists of a high speed camera (500 fps) which captures images of particles as they flow continuously past, either by gravitational dispersion (for free-flowing powders), or by wet dispersion (for cohesive powders). The provided 2D projections of the particles are obtained at random orientation, thus providing a more representative measure than may be given by dispersion onto a surface, which leads to particles usually sitting with their largest area, therefore leading to an overestimation of their size. Dynamic image analysis captures the size and shape information of each single particle, in contrast to laser diffraction which measures particle size distribution by the characteristic diffraction pattern of the sample. In the case of dry dispersion, the material was fed in the GRADIS gravitational dispersion unit using the vibratory feeder VIBRI (Figure 3.1), whilst for wet dispersion a peristaltic pump was utilised to circulate the solution in the LIXELL wet dispersion unit (Figure 3.2). The standard QICPIC M7 lens that captures a size range from 4.2 - 2,888 μm and the M4 lens that captures a size range of 1.1 - 750 μm were employed for dry and wet dispersion measurements, respectively. Dynamic image analysis measures the particle size distribution in the form of a number based distribution, which the software automatically converts and presents in the form of a volume based distribution. Measurements obtained using QICPIC give not only the particle size distribution of the sample, but also important information regarding the shape of the particles, presented as various shape descriptors, such as sphericity and aspect ratio. For each material, three repeats were made, and the average results are reported throughout the thesis. For the materials that were too fine to be analysed with either of the QICPIC modes, laser diffraction was used, except for titania which was exceptionally fine and thus dynamic light scattering was used. For all materials, particle shape was investigated with Scanning Electron Microscopy (SEM) using the JEOL JSM-7100F microscope, regardless of whether their shape was already analysed with QICPIC, or not.
Laser diffraction measurements were carried out to obtain the size distributions of the remaining powders using the Malvern Mastersizer 2000 (Malvern Panalytical, UK) in wet dispersion mode (Hydro 2000S cell), with water as a dispersant, at the University of Leeds (Figure 3.3). The Mastersizer 2000 is capable of measuring sizes ranging from 0.02 - 2,000 μm. In laser diffraction methods, particles are
assumed to be spherical, and the sizes are measured in the form of their volume equivalent sphere diameter, consequently the size distribution that is obtained is volume based. In this technique, the intensity of the light scattered as a laser beam passes through a dispersed powder is measured. The gathered data are then analysed to calculate the size distribution of the particles that created this scattering pattern, since a particle of a given size and shape creates its unique characteristic scattering pattern. For the data analysis, the Mie theory, which predicts the way light is scattered by spherical particles, and deals with the way light passes through or is absorbed by the particles, was employed. This theory requires optical properties to be known, namely the refractive index of both the solid and the dispersant, as well as the absorption index. For each measurement that was performed, ten repetitions were made to make sure that the sample is well dispersed during the measurement, while for each material three repeats were made, and the average results are reported throughout the thesis.

Specifically for the extremely fine titania nanopowder, the Zetasizer Nano S (Malvern Panalytical, UK) was used, which can measure particle sizes from 0.3 nm - 10 μm (Figure 3.4). This dynamic light scattering technique measures the diffusion of particles dispersed in a liquid (water in this case).
moving under Brownian motion as a laser beam illuminates them, and converts this to size distribution using the Stokes-Einstein relationship between diffusion speed and particle size. Small particles are known to diffuse more quickly in a liquid than larger ones, thus allowing the different sizes to be distinguished by the software. Also, Non-Invasive Back Scatter (NIBS) technology is incorporated in the instrument to give increased sensitivity simultaneously with the increased dynamic size and concentration range. The size measured for a particle with this method is the diameter of the sphere that diffuses at the same speed as the actual particle which is being measured. Prior to measuring, the samples were placed in an ultrasonic bath for 30 minutes in order to break agglomerates that this material has the tendency to form (Ku et al., 2015), and that could potentially be large enough to prevent measurement with the Zetasizer. For each measurement that was performed, ten repetitions were made to make sure that the sample is well dispersed during the measurement, while three repeats were made, and the average results are reported throughout the thesis.

Figure 3.4. Zetasizer Nano S

3.1.3 Adhesion characterisation

In this work, the surface energies of three samples of a mixture of 50 % w/w of the 53 - 63 μm glass beads and 50 % w/w of the 75 - 90 μm glass beads, one of which was uncoated, with the other two
being coated with Sigmacote® and Selectophore™, respectively, were measured using the drop test technique (Figure 3.5) in conjunction with the G3 S Morphologi instrument (Malvern Panalytical, UK) (Figure 3.6) at the University of Leeds (Zafar et al., 2014). The G3 Morphologi consists of an automated unit that is used for sample dispersion on a moving stage and an optical microscope equipped with lenses of different magnifications (2.5 - 50 x) that is used to scan the dispersed sample and provide 2D images of the scanned particles, therefore providing morphological data, along with size distribution data. The particle size operational range of the G3 is 0.5 - 3,000 μm.

Figure 3.5. Drop test setup (Zafar et al., 2014)
First, each sample was dispersed using the G3 Morphologi onto a 7 mm circular glass slide which had been treated (or not in the case of the uncoated glass beads) in order to have the same surface coating as the powder sample that would be dispersed onto it. The glass slides were glued to aluminium stubs which were placed on the G3 stage prior to the dispersion. The volume of the material, as well as the dispersion pressure, were tuned so that a sufficiently large number of particles is dispersed on the slide and simultaneously agglomeration is avoided. The substrate was then scanned using the G3 Morphologi, and images of all particles on the stub were taken. Then, the stub was dropped from different heights (10 cm for the uncoated samples; 40, 60 and 80 cm for the samples coated with Sigmacote®, and 60 and 80 cm for the Selectophore™ coated samples) accelerating under gravity inside a glass tube until it impacted against a stopper and rebounded, with the whole process being recorded using a Photron Fastcom SA5 high speed camera at 40,000 fps. The impact causes a number of particles to detach, with the number and size of the particles detaching depending on the balance between the detachment force and the adhesion of the sample. A critical particle size exists, above which particles are detached and below which they remain adhered, for a given impact velocity. Post-impact, the stubs were scanned again using the G3 Morphologi to determine which particles detached during the impact and which remained adhered to the glass slides. Finally, the 2D particle images and size data from the G3 Morphologi scans pre- and post-impact, and image processing of the high speed
camera recordings, were used to determine the relationship between the adhesive force given by the JKR theory (Johnson et al., 1971) and the detachment force given by Newton’s second law of motion, ultimately leading to the quantification of the surface energies of the samples. The surface energy value calculated is characteristic for a given material, independent of the particle size tested, therefore the drop test results can be used for the characterisation of the 0 - 20 μm samples which were used for the flowability tests (Zafar et al., 2014). The analytical procedure for estimating the surface energy from the drop test is reported in chapter 4, where the drop test results are discussed.

Finite Dilution Inverse Gas Chromatography (FD-IGC) experiments were also carried out using three 75 - 90 μm glass bead samples (one of which was uncoated, with the other two being coated with Sigmacote® and Selectophore™, respectively) at Imperial College London by Dr. Vikram Karde using a surface energy analyser (SEA, Surface Measurement Systems Ltd., UK) for surface energy heterogeneity characterisation. Approximately 1.3 g of each sample was packed in pre-silanised IGC columns (Surface Measurement Systems Ltd., UK). Prior to the experiments, each sample column was conditioned for 2 h at 30°C under Helium at a flow rate of 15 sccm. Methane gas was used to determine column dead time. After column conditioning, pulse injection measurements followed, using Helium as the carrier gas, at a flow rate of 10 sccm. Various non-polar alkane probe molecules; Heptane (C7), Octane (C8), Nonane (C9), and polar probes (Dichloromethane and Ethyl acetate), were injected at the same concentrations in order to achieve a certain range of target surface coverages, n/n_m, (< 1 % to 15 %) and determine the dispersive, γ_d, and non-dispersive (acid-base), γ_A/B, surface energies of the samples, respectively. The different surface energies of the samples were calculated using the methods mentioned by Shah et al. (2014). As with the drop test, the FD-IGC results can be used for the characterisation of the 0 - 20 μm samples which were used for the flowability tests. The theoretical principles of IGC and its variations are extensively discussed by Ho and Heng (2013).

3.1.4 Model material (glass beads)

In this study, glass beads supplied by Sigmund Lindner GmbH (Germany) were tested as a model material, due to their high sphericity and availability in a wide range of sizes. Two batches of ‘40 - 70 μm’ and ‘70 - 110 μm’ glass beads were sieved using British Standard sieves to produce five consecutive single sieve cuts of 45 - 53, 53 - 63, 63 - 75, 75 - 90 and 90 - 106 μm, for the study of the influence of particle size on the flow behaviour. An SEM micrograph of the 63 - 75 μm glass beads is shown in Figure 3.7. Furthermore, by mixing the above single sieve cuts, wider size distributions were created to study the influence of the width of the size distribution on flowability. A 53 - 90 μm mixture was created by mixing 50 % w/w of the 63 - 75 μm single sieve cut and 25 % w/w of each of the 53 - 63 and 75 - 90 μm single sieve cuts, while a 45 - 106 μm mixture was created by mixing 40 % w/w of
the 63 - 75 μm sieve cut, 20 % w/w of each of the 53 - 63 and 75 - 90 μm sieve cuts, and 10 % w/w of each of the 45 - 53 and 90 - 106 μm sieve cuts. Moreover, the median single sieve cut of 63 - 75 μm was mixed with fractions of fine and coarse particles to investigate the influence of the shift of \( d_{50} \) and \( d_{90} \), respectively, on powder flowability. In this case, the coarse particles came from a ‘100 - 200 μm’ batch, which was sieved to obtain a single sieve cut of 150 - 180 μm glass beads, with the fine particles coming from an as received ‘0 - 20 μm’ batch. Mixtures consisting of 90 % w/w 63 - 75 μm and 10 % w/w coarse/fine particles and others having 80 % w/w 63 - 75 μm and 20 % w/w coarse/fines were created. All mixtures were created by mixing in a TURBULA T2C Shaker-Mixer at 49 rpm for 45 mins each.

Particle characterisation of all aforementioned samples was conducted using the QICPIC (Sympatec, Germany) dry dispersion mode, except for the mixtures of 90 % w/w 63 - 75 μm with 10 % w/w fines and 80 % w/w 63 - 75 μm with 20 % w/w fines that were analysed using the Mastersizer 2000 (Malvern Panalytical, UK) at the University of Leeds, since the fines were too small to be analysed using the QICPIC. The size distributions of the consecutive single sieve cuts, the wider size distribution mixtures, the mixtures with coarse particles and the mixtures with fines are presented in Figures 3.8, 3.9, 3.10 and 3.11, respectively. Shape characterisation of the samples was carried out with the QICPIC, and is shown in Table 3.1.

Figure 3.7. SEM micrograph of 63 - 75 μm glass beads
Figure 3.8. Size distributions of glass bead single sieve cuts

Figure 3.9. Size distributions of glass bead wider distribution mixtures
**Silanisation**

After size and shape characterisation and prior to the flowability tests, all samples of glass beads were silanised in order to make them cohesive, because typically conventional glass beads are free-flowing, having very low surface energy (Bose *et al.*, 2005). The commercially available Sigmacote® silane solution supplied by Merck (Germany) was used for the surface treatment. Sigmacote® is 1,7-Dichloro-1,1,3,3,5,5,7,7-octamethyldisiloxane in Heptane solution. A 50 - 75 g sample of powder (depending on particle size) was submerged in Sigmacote® for 30 minutes, and the excess solution...
was removed by vacuum filtration for reuse. This step was repeated three times in total. Then, the solids were washed with de-ionised water in order to remove the hydrochloric acid by-product of the reaction. After that, the water was removed, and the coated samples were left overnight in the oven at 50 °C to dry. For another series of experiments, in which the effect of surface energy on flow behaviour is investigated, three samples of glass beads from the as received ‘0 - 20 μm’ batch were used. One of the samples was tested uncoated, since the particle size is sufficiently small to render it cohesive, with the other two samples being silanised. One of the latter was coated with Sigmacote®, whilst the other was coated with another commercially available silane solution, Selectophore™ (Merck, Germany). Selectophore™ is Dimethyldichlorosilane in Heptane solution. In all cases, the same coating protocol described above was followed. The same coatings were used for a mixture of 50 % w/w of the 53 - 63 μm glass beads and 50 % w/w of the 75 - 90 μm glass beads, and the 75 - 90 μm single sieve cut, which were used for the drop test and FD-IGC experiments, respectively. The size distribution of the ‘0 - 20 μm’ batch was provided by Sigmund Lindner, measured using the CILAS 1064 laser diffraction instrument, and is shown in Figure 3.12.

![Figure 3.12. Size distribution of 0 - 20 μm glass beads](image)

3.1.5 Inorganic materials

**Alumina**

Three grades of alumina (Al₂O₃), supplied by Almatis GmbH (Germany), were also used in this work; CT800SG, Rapol 900 Batchground and Rapol 900 Continuously ground, which are super-ground materials with tightly controlled \( d_{10}, d_{50} \) and \( d_{90} \), where the \( d_{10} \) and \( d_{50} \) are similar for all batches, as
can be seen in Table 3.1. The batchground and continuously ground Rapol 900 samples are stated by the supplier to have similar particle shape, but to form agglomerates of different shape, with the batchground agglomerate being more rounded and the continuously ground agglomerate being more irregular or ‘edge-rich’. The primary particles of the Rapol 900 samples are more rounded compared to the plate-shaped CT800SG single crystals. SEM images of the three batches of alumina are shown in Figure 3.13. The size distributions of these materials were provided by Almatis, measured using the CILAS 1064 laser diffraction instrument, and are shown in Figure 3.14.

Figure 3.13. SEM micrographs of the three alumina grades (a: CT800SG, b: Rapol 900 Batchground, c: Rapol 900 Conti. ground)
Another inorganic material used in this research is Limestone BCR 116, supplied by Merck (Germany), which is the certified reference material used for shear cell calibration. This is a fine, cohesive powder consisting of irregular, hard particles. An SEM micrograph of limestone is shown in Figure 3.15. The size distribution of limestone was measured using the Mastersizer 2000 at the University of Leeds by Dr. Selasi Dogbe, and is presented in Figure 3.16.
In addition, Talc TT8 was used, which is a macrocrystalline powder mined in Canada and supplied by Corning Inc. (USA). The particles are very thin plates which easily form loose agglomerates, as can be seen in the SEM micrograph in Figure 3.17. The size distribution of the talc sample was measured using the Mastersizer 2000 at the University of Leeds by Dr. Selasi Dogbe, and is shown in Figure 3.18.

Figure 3.16. Size distribution of limestone

Figure 3.17. SEM micrograph of talc
Pure copper powder is one of the most important products of powder metallurgy that is widely used in the electrical and the electronics industries, because of its excellent electrical and thermal conductivities. An electrolytic copper sample was used, supplied by William Rowland Ltd. (UK), which has a dendritic particle shape, as indicated by the SEM image in Figure 3.19. The size distribution of the copper sample was measured using the QICPIC wet dispersion mode, and is shown in Figure 3.20, while the powder’s shape descriptors can be found in Table 3.1.

Figure 3.19. SEM micrograph of electrolytic copper powder
Titania

Titania (TiO₂) Tiona AT-1, supplied by Cristal Global (Saudi Arabia), is another material investigated in this work. Tiona AT-1 is a technically pure, dry milled anatase pigment with crystal sizes of a few hundreds of nm, as shown in Table 3.1, however, it has a tendency to agglomerate to loose clusters of a few hundred microns up to a few millimeters (Ku et al., 2015), as can be seen from the SEM micrograph in Figure 3.21. This nanopowder is too fine for either QICPIC or Mastersizer 2000 analysis, therefore the Zetasizer Nano S was employed for its characterisation, with its size distribution shown in Figure 3.22.
In order to investigate the formed agglomerate size, the powder was analysed using the Malvern Morphologi G3 (Malvern Panalytical, UK). The samples were dispersed using pressures of 0.5 and 5 bar on a glass slide, and then scanned by a 20 x magnification microscope, as described in section 3.1.3. The size distributions of titania obtained at dispersion pressures of 0.5 and 5 bar are shown in Figures 3.23 and 3.24, respectively. Dispersion pressure has a significant effect on the measured particle size, therefore the size distribution of the dispersed titania is not expected to represent the cluster size distribution in the flowability measurements. However, since the clusters measured at the low dispersion pressure of 0.5 bar are significantly large in comparison to the individual particle size, this size is assumed to be more indicative of the agglomerates in the flowability measurements.
3.1.6 Organic materials

All three organic materials that were used in this research were food powders, supplied by Roquette (France). Maize starch, which is primarily used as a thickening agent, consists of granules separated from the grain of maize by a wet milling process. Maize starch has an irregular particle shape, with fairly smooth surfaces, as indicated by the SEM micrograph in Figure 3.25. Sweetpearl P35 D-maltitol is a sugar substitute used as a sweetener. This crystalline white powder has an irregular particle shape, and is prone to mild agglomeration, as can be seen in the SEM image of Figure 3.26. Nutralys XF pea
protein is a beige powder that is isolated from peas and is mostly used for texture improvement, or protein enrichment. This powder is an extra fine grade of pea protein with an irregular particle shape containing concave features, as indicated in Figure 3.27. The size distributions of all organic powders were measured using the QICPIC wet dispersion mode, and are presented in Figure 3.28, whereas their shape descriptors can be found in Table 3.1.

Figure 3.25. SEM micrograph of maize starch

Figure 3.26. SEM micrograph of maltitol
3.2 Powder flowability assessment methods

For all the experiments carried out in this research work the environmental conditions were not controlled, though they were recorded. Temperature was 20 - 25 °C and the relative humidity (RH) was 30 - 65 %.

3.2.1 Shear testing

In order to determine the unconfined yield strength of the materials, shear testing was carried out using the cylindrical shear cell attachment of the FT4 Powder Rheometer (Freeman Technology, UK).
The powder was poured through a funnel into the split cell chamber of 50 mm diameter to a bed height of approximately 50 mm. The 48 mm diameter FT4 blade was rotated clockwise and driven downwards into the bed at a helix angle of 5° and tip speed of -60 mm/s until it was 10 mm vertically above the base, after which the helix angle was reduced to 2° and the tip speed to -40 mm/s until it was 1 mm vertically above the base. The impeller was then driven clockwise upwards through the powder bed at a helix angle of -5° and tip speed of 60 mm/s until it exited the powder bed and was clear of the chamber. This step serves the purpose of preconditioning the powder bed, bringing it to a reproducible state, as mentioned in section 2.3.4.2.

Then, the blade was removed and replaced by the 48 mm vented piston, which is used to compact the powder at the desired pre-shear normal stress, allowing the entrained air to escape. The piston was driven downwards at a speed of 0.5 mm/s until the surface of the powder bed was detected and a selected small force, depending on the chosen pre-shear normal stress, was registered. Following this, the piston’s speed was reduced to 0.08 mm/s until the desired consolidation stress was reached. Once the desired stress was reached, the compaction force was held for 60 s before it was unloaded. The piston was then removed, and the chamber was split horizontally prior to shearing, leaving a bed height of approximately 43 mm.

After that, the 48 mm diameter shear head, with 18 radially aligned vanes of 3 mm depth, was attached to the device and driven downwards to the powder bed in exactly the same manner as the vented piston. The normal stress was maintained in order to remove any disturbances caused by the split, and to ensure that the powder bed surface was suitably consolidated, whilst the shear head was rotated at 0.05 rpm until steady-state flow was achieved. The pre-shearing protocol that was followed is the standard FT4 approach, which involves aspects of both the Jenike and Peschl protocols. According to this, multiple pre-shear steps are used in order to bring the powder to a critically consolidated state, with a maximum number of pre-shear steps being specified; between 2 and 16 steps were used in this work. Each pre-shear step is considered complete 20 seconds after the maximum shear stress has been established with no subsequent increase in shear stress. The pre-shear phase is considered complete when two consecutive pre-shear steps have maximum shear stresses which show a difference of less than 1 %. If this criterion is not achieved before the maximum number of pre-shears has been reached, then the test proceeds to shearing, regardless of the similarity between the pre-shear shear stresses, with the user not receiving any notification about this, therefore the user has to be cautious and manually discard the test results if this happens.

Once steady-state flow was attained, shearing was stopped, the normal stress was reduced to the normal stress intended for the actual measurement, and shearing at the same rotational speed was
performed until a point of incipient failure was obtained. Finally, shearing was stopped, and the shear stress was returned to zero by rotating the shear head in the reverse direction. This procedure of pre-shear followed by incipient failure measurement was repeated at different ranges of decreasing applied normal stress. At each pre-shear normal stress, the shear cell software takes the measured shear stress at each normal stress to generate a linear yield locus for this packing state. Application of Mohr circles, as described in section 2.1.1, allows the major principal stress, $\sigma_1$, and unconfined yield strength, $\sigma_c$, to be determined for each pre-shear normal stress. In addition to this, the flow factor, $ff_c$, is determined at each stress. For each material, three repeats were made at each pre-shear normal stress, and the average results are reported throughout the thesis, with the error bars indicating the standard deviation of the measurement. The overall procedure of the FT4 shear test is depicted in Figure 3.29.

Figure 3.29. FT4 shear test steps (a: conditioning, b: compaction, c: vessel splitting, d: shearing)
3.2.2 Ball indentation

The ball indentation method was applied to all materials assessed in the FT4 shear cell. The criteria for sample, die and indenter dimensions established by Zafar et al. (2017) were adhered to for this work. A 20 mm diameter stainless steel die, which was attached to a metal plate extending beyond the outer wall of the die, was filled by passing the powder through a sieve with an aperture approximately five times greater than \( d_{50} \) in the case of glass beads, and an aperture large enough to be able to break the large agglomerates and fill the die in a reasonable time (1 - 2 minutes) in the case of all other cohesive materials. The sieve was placed directly above a funnel, above the die. The die height was 20 mm, with a bed height of 15 - 20 mm generated in all cases, and the powder mass weighed. The die was placed below a stainless steel piston of 19.8 mm diameter attached to an Instron 1175 mechanical testing machine (Instron, USA) by a 1 N load cell, which has a resolution of 0.25 mN. Before each test was started, the metal plate to which the die was attached was driven towards the piston while the force was recorded (with the die offset to prevent contact with the die walls) until contact was made in order to determine the distance between the base of the die and the piston. After that, the plate was returned to its starting position, and the die was centred below the piston.

At the start of the actual test, the die was driven upwards, towards the piston, at a vertical speed of 1 mm/min, therefore testing in the quasi-static regime, until the desired consolidation stress was reached. The final displacement of consolidation, \( z_f \), was recorded and used along with the distance between the base of the die and the piston at the starting point, \( z_0 \), to determine the bed height, and consequently determine the packing fraction, \( \chi \), using Equation 3.1:

\[
\chi = \frac{\rho_b}{\rho_t} = \frac{M/V}{\rho_t} = \frac{4M}{\pi(z_0 - z_f)D_d^2} \tag{3.1}
\]

where \( \rho_t \) is the true density, \( V \) is the volume of the powder and \( D_d \) is the die diameter.

The sample was then unloaded at the same speed, and the piston was replaced by a 4 mm diameter, spherical, stainless steel indenter aligned centrally above the powder bed. The die was then driven upwards, towards the indenter, at the same speed as the consolidation step, until contact was detected, which was considered to be when a force of 2 or 3 mN (depending on the material) is registered. Following this, the penetration was continued until the desired penetration depth was reached, and the sample was then unloaded. The ball indentation setup is shown in Figure 3.30.
The bed hardness was calculated using Equation 2.16, with the projected area of the impression of the indenter determined using Equation 2.17. Equation 2.17 is valid as long as the penetration depth is equal to or less than the indenter radius. The penetration depth was non-dimensionalised using Equation 3.2, and dimensionless penetration depths, $h_d$, in the range of 0.1 - 0.7 were applied to each powder at consolidation stresses of 0.1 and 1 kPa.
\[ h_d = \frac{2h_c}{d_b} \quad (3.2) \]

If unloading has negligible effect on the material’s recovery, the penetration depth at maximum indentation load can be used in place of \( h_c \) in Equation 3.2.

Hardness measurements have to be independent of the indentation load/penetration depth in order to represent plastic yield stress (Zafar, 2013), therefore a dimensionless penetration depth determined to be in the stable hardness range was then applied in all experiments for the remaining consolidation stresses for a given powder. The ball indentation method was applied at the major principal stresses determined in the shear cell experiments at moderate to high pre-shear normal stresses, where it was assumed that the normal stress in the indentation process is equal to the major principal stress. The constraint factor was then determined at these major principal stresses. In addition, the ball indentation method was applied at low consolidation stresses of 0.1, 0.2, 0.4, 0.6, 0.8 and 1 kPa. The unconfined yield strength was then inferred at these stresses using Equation 2.18 and the established constraint factor for the powder. For each material, five repeats were made at each pre-shear normal stress, and the average results are reported throughout the thesis, with the error bars indicating the standard deviation of the measurement.
Chapter 4 Investigation of Powder Flowability at Low Stresses Using a Model Material: Influence of Particle Size, Size Distribution and Surface Energy

This chapter constitutes a study of the powder flow behaviour of model glass beads at both high and low stresses using shear testing and the ball indentation technique. Various samples are used that are different in either median particle size, width of size distribution, $d_{10}$, $d_{90}$, or surface energy. One property is isolated and studied at a time, and its influence on the constraint factor and flowability is assessed.

4.1 Introduction

The aim of this piece of research is to use shear testing and ball indentation following the procedures outlined in sections 3.2.1 and 3.2.2, respectively, in order to determine how powder flowability at low stresses ($\leq 1$ kPa) differs from that at high stresses, and to research the influence of various particle properties on powder flowability and the constraint factor. The influence of particle properties on bulk solid flow is well documented in the literature as presented in chapter 2, yet their influence on the constraint factor remains unknown. Furthermore, the reliability of the ball indentation technique is evaluated. For these purposes, model glass beads are used, as previously discussed in section 3.1.4. For each experimental series of this chapter, a set of glass bead samples was used, which varied by one parameter from the following: median particle size, width of size distribution, $d_{10}$, $d_{90}$, or surface energy. By doing this, the isolation of only one variable at a time was accomplished, rendering the study of its influence possible. Table 4.1 shows the glass bead samples that were used in the experiments of this chapter and the corresponding property that was investigated.
The particle characterisation of all samples presented in Table 4.1 has already been covered extensively in section 3.1. In addition to this, all samples were silanised using Sigmacote® as previously described in section 3.1.4, except the 0 - 20 μm glass bead samples, each of which has a different surface energy value, with one being uncoated, and the other two being silanised using Sigmacote® and Selectophore™, respectively, as also previously presented in section 3.1.4.

First, the flowability of all samples was measured by shear testing using the procedure outlined in section 3.2.1. For each sample, tests at four moderate to high pre-shear normal stresses were carried out, namely 2, 4, 6 and 8 kPa, with the exception of all the 0 - 20 μm samples that were found to be very cohesive, therefore higher pre-shear normal stresses were chosen in this case, namely 8, 10, 12 and 14 kPa. In addition to this, in the case of the 45 - 53 μm sample, additional shear tests were performed at low pre-shear normal stresses of 0.06, 0.1, 0.25, 0.5 and 1 kPa, which normally are not achievable with shear cells, in order to examine the reliability of the FT4 shear cell in this stress range. A pre-shear normal stress of 0.06 kPa represents the lowest possible stress in the FT4 that will allow five unique, lower values of target applied normal stress to be given. In each case, the target normal stresses were chosen by trial and error, so that they were distributed equidistantly, and the point of incipient flow at the lowest normal stress was not located either to the left of the tangency point of the yield locus to the failure Mohr circle (see Figure 4.1), or at a much greater normal stress than the point of tangency of the yield locus to the failure Mohr circle. The reason for the latter is that otherwise…

<table>
<thead>
<tr>
<th>Sieve size</th>
<th>Property investigated</th>
<th>Median particle size</th>
<th>Size distribution width</th>
<th>Surface energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>45 - 53 μm glass beads</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>53 - 63 μm glass beads</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>63 - 75 μm glass beads</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>75 - 90 μm glass beads</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>90 - 106 μm glass beads</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>63 - 75 μm glass beads</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>53 - 90 μm glass beads</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>45 - 106 μm glass beads</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>63 - 75 μm glass beads</td>
<td></td>
<td></td>
<td>d_{90}</td>
<td></td>
</tr>
<tr>
<td>63 - 75 μm + 10 % coarse glass beads</td>
<td></td>
<td></td>
<td></td>
<td>d_{10}</td>
</tr>
<tr>
<td>63 - 75 μm + 20 % coarse glass beads</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>63 - 75 μm glass beads</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>63 - 75 μm + 10 % fine glass beads</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>63 - 75 μm + 20 % fine glass beads</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 - 20 μm glass beads uncoated</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 - 20 μm glass beads coated with Sigmacote®</td>
<td></td>
<td></td>
<td></td>
<td>Surface energy</td>
</tr>
<tr>
<td>0 - 20 μm glass beads coated with Selectophore™</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
the yield locus has to be extrapolated too far towards lower stresses in order for the failure Mohr circle to be constructed, which would lead to increased uncertainty when determining the unconfined yield strength (Schulze, 2008). The desired range of normal stresses for shear to failure is shown in Figure 4.1, and is covered extensively by Schulze (2008).

![Figure 4.1. Desired range of normal stresses for shear to failure (Schulze, 2008)](image)

As a result of this approach, the target normal stresses that were chosen to be applied in the shear tests varied for each of the materials tested. The pre-shear normal stresses, as well as the target normal stresses at which the tests were conducted, are shown in Table 4.2 for the 45 - 53 μm, 53 - 63 μm, 63 - 75 μm, 75 - 90 μm, 90 - 106 μm, 53 - 90 μm, 45 - 106 μm, 63 - 75 μm + 10 % coarse and 63 - 75 μm + 20 % coarse samples, Table 4.3 for the 63 - 75 μm + 10 % fines sample, Table 4.4 for the 63 - 75 μm + 20 % fines sample, Table 4.5 for the 0 - 20 μm uncoated glass beads, Table 4.6 for the 0 - 20 μm glass beads coated with SigmaCote® and Table 4.7 for the 0 - 20 μm glass beads coated with Selectophore™.
Table 4.2. Normal stresses applied in the FT4 shear cell for all glass bead single sieve cuts, wider size distribution mixtures and mixtures with coarse particles

<table>
<thead>
<tr>
<th>Pre-shear normal stress, $\sigma_{\text{pre}}$ (kPa)</th>
<th>Target normal stresses, $\sigma$ (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.06*</td>
<td>0.05, 0.04, 0.03, 0.02, 0.01</td>
</tr>
<tr>
<td>0.10*</td>
<td>0.07, 0.06, 0.05, 0.04, 0.02</td>
</tr>
<tr>
<td>0.25*</td>
<td>0.18, 0.15, 0.13, 0.10, 0.05</td>
</tr>
<tr>
<td>0.50*</td>
<td>0.35, 0.30, 0.25, 0.20, 0.15</td>
</tr>
<tr>
<td>1.00*</td>
<td>0.70, 0.60, 0.50, 0.40, 0.30</td>
</tr>
<tr>
<td>2.00</td>
<td>1.80, 1.60, 1.40, 1.20, 1.00</td>
</tr>
<tr>
<td>4.00</td>
<td>3.40, 2.80, 2.20, 1.60, 1.00</td>
</tr>
<tr>
<td>6.00</td>
<td>5.00, 4.00, 3.00, 2.00, 1.00</td>
</tr>
<tr>
<td>8.00</td>
<td>6.60, 5.20, 3.80, 2.40, 1.00</td>
</tr>
</tbody>
</table>

* Only for the 45 - 53 μm glass beads

Table 4.3. Normal stresses applied in the FT4 shear cell for the 63 - 75 μm + 10 % fines sample

<table>
<thead>
<tr>
<th>Pre-shear normal stress, $\sigma_{\text{pre}}$ (kPa)</th>
<th>Target normal stresses, $\sigma$ (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.00</td>
<td>1.75, 1.50, 1.25, 1.00, 0.75</td>
</tr>
<tr>
<td>4.00</td>
<td>3.40, 2.80, 2.20, 1.60, 1.00</td>
</tr>
<tr>
<td>6.00</td>
<td>5.10, 4.20, 3.30, 2.40, 1.50</td>
</tr>
<tr>
<td>8.00</td>
<td>6.75, 5.50, 4.25, 3.00, 1.75</td>
</tr>
</tbody>
</table>

Table 4.4. Normal stresses applied in the FT4 shear cell for the 63 - 75 μm + 20 % fines sample

<table>
<thead>
<tr>
<th>Pre-shear normal stress, $\sigma_{\text{pre}}$ (kPa)</th>
<th>Target normal stresses, $\sigma$ (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.00</td>
<td>1.80, 1.60, 1.40, 1.20, 1.00</td>
</tr>
<tr>
<td>4.00</td>
<td>3.50, 3.00, 2.50, 2.00, 1.50</td>
</tr>
<tr>
<td>6.00</td>
<td>5.20, 4.40, 3.60, 2.80, 2.00</td>
</tr>
<tr>
<td>8.00</td>
<td>6.85, 5.70, 4.55, 3.40, 2.25</td>
</tr>
</tbody>
</table>

Table 4.5. Normal stresses applied in the FT4 shear cell for the 0 - 20 μm uncoated glass beads

<table>
<thead>
<tr>
<th>Pre-shear normal stress, $\sigma_{\text{pre}}$ (kPa)</th>
<th>Target normal stresses, $\sigma$ (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.00</td>
<td>6.00, 5.00, 4.00, 3.00</td>
</tr>
<tr>
<td>10.00</td>
<td>7.60, 6.40, 5.20, 4.00</td>
</tr>
<tr>
<td>12.00</td>
<td>9.00, 7.50, 6.00, 4.50</td>
</tr>
<tr>
<td>14.00</td>
<td>10.40, 8.60, 6.80, 5.00</td>
</tr>
</tbody>
</table>

Table 4.6. Normal stresses applied in the FT4 shear cell for the 0 - 20 μm glass beads coated with Sigmacote®

<table>
<thead>
<tr>
<th>Pre-shear normal stress, $\sigma_{\text{pre}}$ (kPa)</th>
<th>Target normal stresses, $\sigma$ (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.00</td>
<td>5.80, 4.70, 3.60, 2.50</td>
</tr>
<tr>
<td>10.00</td>
<td>7.60, 6.40, 5.20, 4.00</td>
</tr>
<tr>
<td>12.00</td>
<td>9.40, 8.10, 6.80, 5.50</td>
</tr>
<tr>
<td>14.00</td>
<td>11.20, 9.80, 8.40, 7.00</td>
</tr>
</tbody>
</table>
Table 4.7. Normal stresses applied in the FT4 shear cell for the 0 - 20 μm glass beads coated with Selectophore™

<table>
<thead>
<tr>
<th>Pre-shear normal stress, ( \sigma_{pre} ) (kPa)</th>
<th>Target normal stresses, ( \sigma ) (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.00</td>
<td>6.00, 5.00, 4.00, 3.00</td>
</tr>
<tr>
<td>10.00</td>
<td>7.80, 6.70, 5.60, 4.50</td>
</tr>
<tr>
<td>12.00</td>
<td>9.60, 8.40, 7.20, 6.00</td>
</tr>
<tr>
<td>14.00</td>
<td>11.40, 10.10, 8.80, 7.50</td>
</tr>
</tbody>
</table>

At each pre-shear normal stress, the shear cell software takes the measured shear stress at each normal stress to generate the yield locus for this packing state. By default the FT4 software applies a linear fit to the measured points, followed by application of Mohr circle analysis to allow \( \sigma_1, \sigma_c, \) and subsequently \( ff_c \) to be determined for each pre-shear normal stress. However, it was found that in many cases the measured yield locus was not tangent to the constructed failure Mohr circle, but cut through the circle, as shown in Figure 4.2, therefore the unconfined yield strength was overestimated.

![Figure 4.2. FT4 software’s measured yield locus that cuts through the failure Mohr circle](image)

In order to address this issue, the Warren Spring model (Ashton et al., 1965), which is described by Equation 2.2, introduced in section 2.1.2, was used for the characterisation of the yield locus. A MATLAB code provided by Dr. Massih Pasha (The Chemours Company, USA) was used for the Warren
Spring fitting of the experimental data. A representative example of the Warren Spring fit to the same experimental data as in Figure 4.2 is shown in Figure 4.3.

![Figure 4.3. Warren Spring fit to shear test data using Dr. Massih Pasha’s MATLAB code](image)

Following the determination of $\sigma_1$ and $\sigma_2$ at each pre-shear normal stress, the hardness values for all samples were measured at the major principal stresses derived from the FT4 shear cell tests, to allow comparison with shear cell measurements and the constraint factor to be computed using the approach outlined in section 3.2.2. Additionally, indentation tests were conducted at low consolidation stresses, namely 0.1, 0.2, 0.4, 0.6, 0.8 and 1 kPa, as previously discussed in section 3.2.2.

### 4.2 Study of the flowability of consecutive single sieve cuts of silanised glass beads - Effect of varying particle size on constraint factor and flow behaviour

The measurements of unconfined yield strength at the corresponding major principal stresses determined for five consecutive single sieve cuts of glass beads silanised by Sigmacote® using the FT4 shear cell method outlined in section 3.2.1 are shown in Table 4.8. The size characterisation of all sieve cuts has already been shown in Table 3.1. For all sizes, the unconfined yield strength is found to increase approximately linearly with major principal stress, whilst decreasing with increasing particle size, as shown in Figure 4.4. For a given pre-shear normal stress, there is a clear increase in flowability with increasing particle size, as evidenced from the $ff_c$ values in Table 4.8. In addition to this, the flow factor increases with pre-shear normal stress and ranges from 1.6 - 4.2 for the 45 - 53 μm glass beads to 2.4 - 6.3 for the 90 - 106 μm glass beads.
Table 4.8. FT4 shear test data for five consecutive single sieve cuts of silanised glass beads

<table>
<thead>
<tr>
<th>45 - 53 μm</th>
<th>53 - 63 μm</th>
<th>63 - 75 μm</th>
<th>75 - 90 μm</th>
<th>90 - 106 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_{pre}$</td>
<td>$\sigma_1$</td>
<td>$\sigma_c$</td>
<td>$ff_c$</td>
<td>$\sigma_1$</td>
</tr>
<tr>
<td>2</td>
<td>3.2</td>
<td>2.0</td>
<td>1.6</td>
<td>3.2</td>
</tr>
<tr>
<td>4</td>
<td>5.7</td>
<td>2.2</td>
<td>2.6</td>
<td>5.8</td>
</tr>
<tr>
<td>6</td>
<td>8.2</td>
<td>2.3</td>
<td>3.5</td>
<td>8.3</td>
</tr>
<tr>
<td>8</td>
<td>10.8</td>
<td>2.6</td>
<td>4.2</td>
<td>10.9</td>
</tr>
</tbody>
</table>

Figure 4.4. Unconfined yield strength against major principal stress for five consecutive single sieve cuts of silanised glass beads

In order to use the ball indentation technique, first the suitable penetration depth range that can be applied to get reliable hardness measurements needs to be established, since hardness must be independent of the penetration depth in order to represent the true plastic yield stress (Zafar, 2013). For this purpose, hardness measurements at dimensionless penetration depths of 0.1, 0.3, 0.5 and 0.7 were performed on separate powder beds of 63 - 75 μm glass beads consolidated to 0.1 and 1 kPa, as shown in Figure 4.5. The dimensionless penetration depths were calculated using Equation 3.2 (section 3.2.2). It can be seen that for both tested consolidation stresses hardness is overestimated at a dimensionless penetration depth of 0.1, due to the fact that the indenter has only penetrated 0.2 mm into the bed (approximately 3 times the median particle size), and it is therefore in contact with only a few particles. However, beyond this point the hardness reaches a plateau, becoming constant for dimensionless penetration depths greater than 0.3. These findings are in agreement with the DEM
simulations of Pasha et al. (2013) and the experiments of Zafar et al. (2017). For all the aforementioned measurements, hardness was determined by considering the penetration depth at maximum indentation load rather than the elastically-recovered depth. Figure 4.6 shows the force-displacement profile for indentation up to a dimensionless penetration depth of 0.5 for a bed of 63 - 75 μm glass beads consolidated to 10.9 kPa. The hardness calculated at the highest major principal stress of 10.9 kPa for the 63 - 75 μm sample by considering the projected area of the impression of the indenter after unloading, was found to be almost identical (< 0.2 % difference) to the value computed by using the penetration depth at maximum indentation load to determine hardness, i.e. by ignoring unloading. The fact that unloading is negligible in hardness calculations for this particular material is also evidenced by the negligible curvature of the unloading part of the force-displacement profile. In addition to this, if the unloading effect is ignored, then hardness can be estimated at any penetration depth up to the depth tested. Figure 4.5 also shows this ‘continuous hardness’ calculated from indentation tests at a dimensionless penetration depth of 0.7. This estimate is shown to be almost identical to the direct measurement made at lower depths for both stresses, and hence confirms that unloading is negligible. The effect of unloading on hardness was also investigated at the highest major principal stresses for all other samples of glass beads tested in this chapter, and was found to be negligible. As a result, the use of the penetration depth at maximum indentation load in hardness calculations is justified for this material, it was therefore considered for all the hardness calculations in this chapter. Furthermore, as it is evident from Figure 4.5, the behaviour of hardness as a function of penetration depth is independent of the applied stress, therefore the obtained trends at higher stresses are qualitatively the same, with the same depth range providing valid measurements. Also, this behaviour is similar for all other sizes of glass beads investigated in this chapter, except for the very fine 0 - 20 μm particles, whose behaviour will be discussed in section 4.4.2. With the reliable range of hardness measurements established, the dimensionless penetration depth of 0.5 was chosen to be applied in all ball indentation measurements on silanised glass beads.
Figure 4.5. Hardness against dimensionless penetration depth for the 63 - 75 μm single sieve cut of silanised glass beads

Figure 4.6. Force against dimensionless penetration depth during indentation of a 63 - 75 μm glass beads bed at 10.9 kPa
In the ball indentation experiments, prior to the actual penetration, the die was driven towards the indenter until contact was detected in order to find the surface of the bed, which, in the case of glass beads was considered to be when a small force of 3 mN is registered. However, during this ‘pre-test’ step the target force was not instantaneously achieved when contact was made between the indenter and the powder bed, but the indenter penetrated the specimen slightly before the target force was reached, with this phenomenon being more pronounced for more weakly consolidated samples. This can be seen from the slope of the force-displacement curve during the ‘pre-test’ step in Figure 4.7. This ‘pre-test’ penetration, as well as the ‘pre-test’ force, were taken into account in hardness calculations. Consequently, even though the target dimensionless penetration depth for all hardness measurements was 0.5, the true dimensionless penetration depth was larger and varied between tests. However, this does not affect the validity of most of the hardness measurements (particularly at moderate to high stresses), since the true dimensionless penetration depth of 0.7 was not exceeded, and the measurements have already been shown to be independent of penetration depth for dimensionless penetration depths of 0.3 - 0.7. In some repeats at very low stresses though, the dimensionless penetration depth of 0.7 was exceeded, and hardness was overestimated, however in most cases this overestimation was within test error.

Figure 4.7. Force against displacement during indentation of a 63 - 75 μm glass beads bed
The ball indentation method was applied for all five consecutive single sieve cuts of silanised glass beads using the average major principal stress determined from the three shear cell tests for each sample at each pre-shear normal stress, with the results presented in Figure 4.8. At high stresses (> 1 kPa) the hardness values of the five sieve cuts are distinctively different, following the same trend as the shear cell results; increasing approximately linearly with major principal stress, and decreasing with an increase in particle size. At low stresses (≤ 1 kPa) the increase of hardness with stress is observed to be much steeper than at high stresses, a phenomenon also observed by Zafar (2013). Furthermore, in the case of weakly consolidated powder beds, hardness values are not distinctively different among the different particle sizes. In this range the error bars are somewhat larger, due to the difficulty of reproducing a uniformly flat powder bed surface, as well as creating a consistent packing structure. As the applied consolidation stress increases, the influence of bed surface asperities becomes less important. At all stress levels the standard deviation of five measurements (indicated by the error bars) is low; with the coefficient of variation being less than 10 % in most cases.

Figure 4.8. Hardness against major principal stress for five consecutive single sieve cuts of silanised glass beads

In order to investigate the cause of the discrepancy of the hardness increase against stress between high and low stresses, the packing fraction for all five sieve cuts was calculated using Equation 3.1 (section 3.2.2), and is shown against major principal stress in Figure 4.9.
Figure 4.9. Packing fraction against major principal stress for five consecutive single sieve cuts of silanised glass beads

As can be seen from Figure 4.9, all glass bead samples exhibit a dramatic increase of packing fraction with the increase of consolidation stress in the low stress region. A small increase of the applied stress leads to a much more compacted powder bed, which in turn provides a great increase of resistance to plastic deformation. On the other hand, in the high stress region, the packing state of the powder beds does not change considerably with the applied stress. The aforementioned behaviour leads to an approximately linear increase of hardness with packing fraction in the range 0.45 - 0.55, as shown in Figure 4.10. Generally hardness is greater for smaller particles at a given packing fraction, although this behaviour is clear only at high stresses. At low stresses the error bars of packing fraction are significant, and the difference in hardness among the different particle sizes is not clear.
The constraint factor was determined at each stress level for all sieve cuts of silanised glass beads using Equation 2.18 and the measurements of unconfined yield strength and hardness, and presented against major principal stress in Figure 4.11. The constraint factor is shown to be approximately constant for a given sieve cut across all tested major principal stresses. Moreover, $C$ is found to generally decrease with an increase in particle size. These findings agree with the work of Zafar (2013).
Since the constraint factor was found to be virtually independent of the major principal stress applied, it is assumed to remain constant at low stresses. This is assessed by DEM simulations in chapter 6. For all samples, the average constraint factor across all major principal stresses was used along with the ball indentation measurements at low consolidation stresses to determine the unconfined yield strength at such stresses via Equation 2.18. Figure 4.12 shows the inferred unconfined yield strength values from the ball indentation measurements at major principal stresses of 0.1, 0.2, 0.4, 0.6, 0.8 and 1.0 kPa, along with the unconfined yield strength measurements carried out in the shear cell at pre-shear normal stresses of 2, 4, 6 and 8 kPa shown in Figure 4.4. The indentation technique suggests a significant reduction in unconfined yield strength at lower consolidation levels in comparison to values that would be linearly extrapolated from the shear tests.
Measurement of unconfined yield strength at low stresses is often not reliable, or even possible, using a shear cell, however the shear cell is more likely to achieve steady-state failure, and therefore generate a result, for more cohesive powders. Since the 45 - 53 μm were the most cohesive glass beads used here, shear cell measurements were made at pre-shear normal stresses of 0.06, 0.1, 0.25, 0.5 and 1 kPa for this sample, and are shown compared to the indentation measurements in Figure 4.13. The trends of unconfined yield strength against major principal stress are remarkably similar in this low stress range for both techniques.
Figure 4.13. Unconfined yield strength at low stresses determined from the shear cell and ball indentation for the 45-53 μm single sieve cut of silanised glass beads

In order to further investigate the shear cell measurements, the measured shear stresses and applied normal stresses of three repeats of the FT4 shear cell measurements at the pre-shear normal stresses of 0.06, 0.25, 1, 4 and 8 kPa, are shown in Figure 4.14. At pre-shear normal stresses of 0.06 and 0.25 kPa the data show great variation among repeats, with the generated yield loci not consistently showing a monotonic increase in shear stress with normal stress. In addition to this, in both cases there is notable discrepancy between the target normal stresses and the actual applied stresses. The nature of the FT4 shear cell protocol, which leads to shearing from the highest to the lowest chosen target stress, can lead to data points that exceed the pre-shear point when the applied stress is greater than the target stress, which invalidates the measurement. This phenomenon is observed in the case of tests at 0.06 kPa, where stresses beyond 0.06 kPa have been applied during the shear test, and leads to an overestimation of the unconfined yield strength, however this is not observed at higher stresses. At a pre-shear normal stress of 1 kPa the generated test data are highly reproducible, although the applied stresses are still not equidistant, and deviate notably from the target normal stresses, but less so than at lower pre-shear normal stresses. At a pre-shear normal stress of 4 kPa, the shear tests are highly reproducible and the achieved stresses are equidistant, though deviate slightly from the target normal stresses. At 8 kPa, not only are the tests highly reproducible, but the target stresses have been virtually achieved, with the test points also being equidistant. Therefore, a
general trend of increasing reliability and reproducibility of shear testing is observed as the pre-shear normal stress is increased. As a result of the above discussion, even if it is possible to perform shear tests using certain shear cells and shearing protocols, caution should be taken and detailed analysis is required before trusting the obtained data, since the shear cell user has limited control over the applied stresses, particularly at low pre-shear normal stresses (for weight-driven shear cells this problem does not occur). Consequently, this highlights the need for ball indentation as a much more accurate alternative to extrapolation of shear cell data.
Figure 4.14. Measured shear and applied normal stresses for 45 - 53 μm silanised glass beads at pre-shear normal stresses of a) 0.06 kPa, b) 0.25 kPa, c) 1.00 kPa, d) 4.00 kPa and e) 8.00 kPa
4.3 Study of the flowability of silanised glass bead mixtures of varying particle size distribution

4.3.1 Effect of the width of particle size distribution on constraint factor and flow behaviour

The FT4 shear cell measurements of unconfined yield strength at the corresponding major principal stresses are shown in Table 4.9 for the medium 63 - 75 μm single sieve cut, along with two mixtures of 53 - 90 μm and 45 - 106 μm of silanised glass beads. The two mixtures have essentially the same \( d_{50} \) as the single sieve cut, but wider size distributions, as reported in Table 3.1. As the size distribution is widened, the \( d_{10} \) and \( d_{90} \) reduce and increase, respectively, by about 3 - 4 μm with each additional sieve cut. The unconfined yield strength against major principal stress is shown in Figure 4.15. Unconfined yield strength increases approximately linearly with major principal stress, as with the single sieve cuts in section 4.2. It can be seen from both Table 4.9 and Figure 4.15 that at a given pre-shear normal stress there is a slight increase in unconfined yield strength as the size distribution is widened. Moreover, \( ff_c \) is found to increase with the pre-shear normal stress applied and decrease as the size distribution is widened.

<table>
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<th>( \sigma_c )</th>
<th>( ff_c )</th>
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</table>

Table 4.9. FT4 shear test data for three samples of silanised glass beads with varying width of size distribution
Figure 4.15. Unconfined yield strength against major principal stress for three samples of silanised glass beads with varying width of size distribution

Figure 4.16 shows the hardness measurements made at all major principal stresses for all three size distributions of silanised glass beads. As with the unconfined yield strength from the shear tests above, hardness is observed to marginally increase when widening the size distribution at higher stresses, whereas no notable difference can be seen at low stresses. As with Figure 4.8, indentation tests indicate a more rapid increase of hardness with major principal stress for weakly consolidated powder beds, which is explained by the packing fraction trend presented in Figure 4.17.
Figure 4.16. Hardness against major principal stress for three samples of silanised glass beads with varying width of size distribution.

Figure 4.17. Packing fraction against major principal stress for three samples of silanised glass beads with varying width of size distribution.
The constraint factor determined from the ball indentation and shear cell measurements for all size distributions is shown in Figure 4.18. Once again, constraint factor is found to remain constant throughout the range of consolidation stresses applied. In addition to this, a slight reduction in constraint factor is observed with an increase in the span of the sample, however this effect may not be statistically significant.

![Figure 4.18. Constraint factor against major principal stress for three samples of silanised glass beads with varying width of size distribution](image)

Figure 4.19 shows the unconfined yield strength values inferred from the ball indentation method at low stresses, along with the measurements made in the shear cell at higher stresses. As in the case of the consecutive single sieve cuts, the increase of the unconfined yield strength is estimated to be sharper with increasing major principal stress at lower stresses. At lower stresses the inferred values of unconfined yield strength are not distinctively different among the samples.
Figure 4.19. Unconfined yield strength shear cell measurements and inferred values from ball indentation for three samples of silanised glass beads with varying width of size distribution

4.3.2 Effect of $d_{10}$ and $d_{90}$ on constraint factor and flow behaviour

The FT4 shear testing data of 63 - 75 μm silanised glass beads mixed with 10 % and 20 % w/w coarse and fine particles are reported in Table 4.10, along with the data for the 63 - 75 μm single sieve cut for comparative purposes. The size analysis of all size distributions is reported in Table 3.1. The unconfined yield strength against major principal stress is shown in Figure 4.20. The addition of coarse particles is found to have negligible effect on the unconfined yield strength regardless of the quantity added, whilst the addition of fines substantially increases the unconfined yield strength, with a further increase observed as the quantity added increases. This is in agreement with the finding of Molerus and Nwylt (1984) that unconfined yield strength increases with fines content up to 30 % w/w, beyond which it becomes equal to the strength of the fines alone. The addition of 20 and 10 % w/w coarse particles can be viewed as 80 and 90 % w/w 63 - 75 μm added, respectively, to the 150 - 180 μm sample, and so the yield strength of the mixtures is essentially equal to the yield strength of the 63 - 75 μm sample in this case. Adding 10 % w/w coarse particles leads in most cases to a slight reduction in $ff_c$, with an increase in coarse content to 20 % w/w coarse particles causing the flow factor to slightly increase again. The flow factor decreases with the addition of fines, as shown in Table 4.10.
Table 4.10. FT4 shear test data for 63 - 75 μm silanised glass beads mixed with varying amounts of coarse and fine particles, along with the 63 - 75 μm single sieve cut

<table>
<thead>
<tr>
<th></th>
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<th>63 - 75 μm + 10 % fines</th>
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Figure 4.20. Unconfined yield strength against major principal stress for 63 - 75 μm silanised glass beads mixed with varying amounts of coarse and fine particles, along with the 63 - 75 μm single sieve cut

Figure 4.21 shows the hardness against major principal stress for the same mixtures of glass beads. A reduction of $d_{10}$ (addition of fines) leads to an increase in hardness, as in the case of unconfined yield strength. In contrast to the shear tests though, an increase in the $d_{90}$ (addition of coarse particles) leads to a reduction in hardness. Though the influence that the addition of coarse particles has on the hardness of the mixture is less significant than the effect of an addition of fine particles. The packing fraction data, shown in Figure 4.22, partially explain the increased resistance to plastic deformation with the addition of fines. However, when the quantity of fines added increases, the packing fraction is not greatly increased, whereas hardness is significantly affected. The mixture that has 20 % w/w
fines has more contacts between fine particles, hence being more resistant to flow. In the case of the mixtures with coarse particles, the large error bars mean that firm conclusions cannot be drawn.

Figure 4.21. Hardness against major principal stress for 63 - 75 μm silanised glass beads mixed with varying amounts of coarse and fine particles, along with the 63 - 75 μm single sieve cut.
Figure 4.22. Packing fraction against major principal stress for 63 - 75 μm silanised glass beads mixed with varying amounts of coarse and fine particles, along with the 63 - 75 μm single sieve cut

The constraint factor values for the same samples with added coarse particles or fines are plotted in Figure 4.23, and are shown to be relatively constant regardless of stress. Moreover, as a result of the trends observed in Figures 4.20 and 4.21, $C$ is found to decrease as the quantity of coarse particles in the mixture is increased, while it increases as the quantity of fines in the mixture increases. Regarding the glass bead mixtures studied in section 4.3.1, as size distribution is widened the $d_{10}$ is reduced and $d_{50}$ is increased by similar amounts, so the two competing effects seen in Figure 4.23 cancel each other out, hence leading to only slight differences in the constraint factor between the narrow and wide size distributions (see Figure 4.18).
Figure 4.23. Constraint factor against major principal stress for 63 - 75 μm silanised glass beads mixed with varying amounts of coarse and fine particles, along with the 63 - 75 μm single sieve cut

In order to clearly illustrate the effect of the addition of coarse and fine particles on the constraint factor, the average constraint factor values are shown for samples with added fines against $d_{10}$ in Figure 4.24, and with added coarse particles against $d_{90}$ in Figure 4.25. It can be seen that $C$ increases as either $d_{10}$ or $d_{90}$ are reduced.
Figure 4.24. Average constraint factor against $d_{10}$

Figure 4.25. Average constraint factor against $d_{90}$
4.4 Effect of surface energy on constraint factor and flow behaviour

In this section, the flowability of three samples of 0 - 20 μm glass beads, each of which has a different surface energy value, with one being uncoated, and the other two being silanised using Sigmacote® and Selectophore™, respectively, is studied. Prior to flowability testing, the surface energies of all three samples were determined using both the drop test and the FD-IGC techniques, as outlined in section 3.1.3.

4.4.1 Surface energy measurements

The surface energy measurements of the drop test technique are based on the balance between the adhesion force, $f_{ce}$, and the detachment force, $F_{det}$, during the impact. The adhesion force between two bodies is given by the JKR theory (Johnson et al., 1971) from Equation 4.1:

$$f_{ce} = \frac{3}{2} \pi R^* \Gamma$$  \hspace{1cm} (4.1)

where $\Gamma$ is the interface energy and $R^*$ is the reduced radius computed from Equation 4.2:

$$R^* = \left( \frac{1}{R_1} + \frac{1}{R_2} \right)^{-1}$$  \hspace{1cm} (4.2)

where $R_1$ and $R_2$ are the radii of the two elements in contact. In case one of the elements in contact is a wall and not a particle, its radius is considered to be infinite ($\infty$).

The detachment force, $F_{det}$, is derived from Newton’s second law of motion and is given by Equation 4.3 (Zafar et al., 2014):

$$F_{det} = \frac{mv}{t_{cont}/2}$$  \hspace{1cm} (4.3)

where $m$ is the mass of the particle, $v$ is the impact velocity and $t_{cont}$ is the contact time between the stub and the stopper. Both $v$ and $t_{cont}$ are calculated using image processing of the high speed camera recordings.

The post-impact size distributions of the particles on the glass slides are analysed using the G3 S Morphologi, as mentioned in section 3.1.3. For a given impact velocity (or drop height), the critical radius, $R_{crit}$, above which a particle detaches ($F_{det} \geq f_{ce}$) and below which it remains adhered to the stub ($F_{det} < f_{ce}$), is estimated by taking the arithmetic number mean of the largest particle which remained adhered on the stub after the impact and the smallest particle which detached during the impact. Since the particles of this study are near-spherical, the mass of the particle is given by Equation 4.4:
\[ m = \frac{4}{3} \pi \rho_p R_{\text{crit}}^3 \quad (4.4) \]

The interface energy is estimated by taking \( F_{\text{det}} = f_{\text{ce}} \) for \( R^* = R_{\text{crit}} \), and is subsequently given by Equation 4.5:

\[ \Gamma = \frac{16 \rho_p v R_{\text{crit}}^2}{9 t_{\text{cont}}} \quad (4.5) \]

Finally, the interface energy is divided by two to obtain the surface energy.

The results of the drop test measurements are presented in Figure 4.26. The average surface energy was calculated to be 23, 66 and 108 mJ/m², for the uncoated, Sigmacote® coated and Selectophore™ coated samples, respectively. The measurements for the uncoated and the Sigmacote® coated samples are based on an average of five repeats, while the measurement for the Selectophore™ coated sample is based on an average of three repeats. The uncoated sample is found to have the lowest surface energy, followed by the sample coated with Sigmacote®, while Selectophore™ results in the highest value of surface energy, though the error bar is much larger compared to the other samples.

![Figure 4.26. Surface energy of the coated and uncoated glass beads measured by the drop test](image)
The FD-IGC was employed to further investigate the surface energies of these samples and attempt to decouple the contribution of the dispersive, $\gamma^d$, and acid-base, $\gamma^{AB}$, components of surface energy to the flowability of the samples. Figure 4.27 shows the dispersive surface energies measured by Inverse Gas Chromatography as a function of probe surface coverage. The uncoated sample showed variation of $\gamma^d$ with surface coverage, which indicates that the uncoated glass beads are energetically heterogeneous. However, both coated glass bead samples showed almost homogeneous energy distribution at different coverages. For surface energy measurements to be representative of the entire material surface properties, typical fractional coverages used for analysis range from $n/n_m = 0.02$ to 0.05, therefore a value of 0.04 was chosen for the analysis of this study’s samples (Shah et al., 2014). At $n/n_m = 0.04$, the value of the dispersive component of surface energy was found to be 44 mJ/m$^2$ for the uncoated sample, while the experiments with the two samples coated with Sigmacote® and Selectophore™ gave very similar values, 40.5 and 41.4 mJ/m$^2$, respectively. These findings agree with the work of Shah et al. (2014) who showed that for milled mefenamic acid powder, silanisation leads to lower dispersive surface energy, with the values depending on the silane used.

![Figure 4.27. Dispersive surface energy against surface coverage of the coated and uncoated glass beads measured by FD-IGC](image)

The acid-base surface energies of all three samples are presented as a function of surface coverage in Figure 4.28. As can be seen, the Selectophore™ coated sample showed the highest acid-base
component of surface energy (3.5 mJ/m$^2$), as compared to the uncoated (3.2 mJ/m$^2$) and the Sigmacote® coated samples (2.8 mJ/m$^2$). The total surface energies of the samples are given as the sum of the dispersive and the acid-base components against surface coverage in Figure 4.29, and are observed to follow the same order as the dispersive component among samples, due to the fact that the values of the dispersive component are much greater in comparison to the acid-base component.

![Graph showing acid-base surface energy against surface coverage of coated and uncoated glass beads measured by FD-IGC](image)

**Figure 4.28.** Acid-base surface energy against surface coverage of the coated and uncoated glass beads measured by FD-IGC
The results of shear testing for three samples of 0 - 20 μm glass beads, each of which has a different value of surface energy, with one being uncoated, and the other two being silanised using Sigmacote® and Selectophore™, respectively, are shown in Table 4.11, while the unconfined yield strength measured for each sample is presented against major principal stress in Figure 4.30. At a given stress, the unconfined yield strength of each of two coated samples is clearly greater compared to the uncoated sample, whilst the behaviour of the two coated samples is similar, with the Selectophore™ coated sample exhibiting a slightly steeper trend. The aforementioned order of unconfined yield strength corresponds to the order of surface energy values found from the drop test experiments (Figure 4.26). In addition to this, the higher acid-base surface energy of the Selectophore™ coated sample might account for it being the worse flowing powder. This finding is in agreement with the work of Shah et al. (2014) who performed IGC measurements, and showed that the cohesion of milled mefenamic acid powder increased linearly as the surface energy increased, with the increase in cohesion being 11.7 times higher due to the contribution of the acid-base component compared to the dispersive one. In contrast to this, the Sigmacote® coated sample was found to have the lowest value of $\gamma_{AB}$ among the three glass bead samples, but significantly worse flow behaviour than the

![Figure 4.29. Total surface energy against surface coverage of the coated and uncoated glass beads measured by FD-IGC](image-url)
uncoated beads. Therefore, the relationship between the flow behaviour of the three samples cannot be fully explained by the acid-base surface energy. As for the flow factor values of the samples, they are found to fluctuate across the pre-shear normal stress range applied, remaining essentially constant, a phenomenon characteristic of very cohesive powders, the shear testing of which leads to very shallow yield loci slopes (Schulze, 2008).

Table 4.11. FT4 shear test data for 0 - 20 μm coated and uncoated glass beads

<table>
<thead>
<tr>
<th></th>
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<th>0 - 20 μm (Sigmacote)</th>
<th>0 - 20 μm (Selectophore)</th>
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Figure 4.30. Unconfined yield strength against major principal stress for 0 - 20 μm coated and uncoated glass beads

Indentation tests at a dimensionless penetration depth of 0.5 were also used for all three 0 - 20 μm glass bead samples at the major principal stresses shown in Table 4.11. Figures 4.31, 4.32 and 4.33 show ‘continuous’ hardness against dimensionless penetration depth for the uncoated, the Sigmacote® coated and the Selectophore™ coated sample, respectively. In the case of all 0 - 20 μm
samples, it was found that hardness increases slightly with penetration depth (up to the dimensionless penetration of 0.5 that was applied), in contrast to all other sizes of glass beads that were investigated in this chapter (Figure 4.5). This could be caused by local consolidation by the indenter, and may result in $H$ being overestimated, and subsequently $C$ being overestimated. However, the increase of hardness with penetration depth was found to be virtually independent of the applied consolidation stress, as evidenced from the slopes of ‘continuous’ hardness in Figures 4.31, 4.32 and 4.33. In addition to this, the hardness against depth slopes are very similar for all materials. Based on the two aforementioned findings, $H$ and $C$ will still be representative of the materials, and therefore the use of ball indentation for powder flow determination is still justified.

![Figure 4.31. Hardness against dimensionless penetration depth for 0 - 20 μm uncoated glass beads](image-url)
Figure 4.32. Hardness against dimensionless penetration depth for 0 - 20 μm glass beads coated with Sigmacote®

Figure 4.33. Hardness against dimensionless penetration depth for 0 - 20 μm glass beads coated with Selectophore™
The ball indentation results of the same samples are shown in Figure 4.34. As with the unconfined yield strength results, hardness is found to be noticeably greater in the case of the coated samples, compared to the uncoated one, though the trends of the two coated samples are remarkably similar. As shown from the drop test and FD-IGC results, the surface energy values of the two coated samples are distinctively different, therefore it seems that the contribution of surface energy to the flow resistance of the samples is negligible. For all samples, the hardness trends correspond to their packing behaviour (Figure 4.35), but hardness increases much more sharply with stress as compared to packing fraction, which could be attributed to individual particles undergoing plastic deformation.

![Figure 4.34. Hardness against major principal stress for 0 - 20 μm coated and uncoated glass beads](image-url)
The constraint factor quantified for the same glass bead samples is shown in Figure 4.36. C appears to generally increase with the increase of surface energy, as measured by the drop test technique. However, the error bars are large, especially for the two coated samples, due to the shear testing data variation, while C also shows notable variation with major principal stress. Taking into consideration the aforementioned observations, along with the error bars of the drop test measurements, it is rather difficult to draw strong conclusions on the basis of these experiments on the influence of surface energy on the constraint factor, hence it is further explored by DEM simulations in chapter 6.
Figure 4.36. Constraint factor against major principal stress for 0 - 20 μm coated and uncoated glass beads

4.5 Concluding remarks

The ball indentation technique was employed along with shear testing on a wide variety of glass bead samples in order to investigate the difference between powder flow behaviour at low and high stresses, and the influence of a number of parameters (median particle size, width of size distribution, $d_{10}$, $d_{90}$, surface energy) on the constraint factor and flowability.

Both unconfined yield strength and hardness were found to increase with an increase in the major principal stress applied, due to an increased packing fraction and interparticle contact area. At low stresses the increase in packing fraction with stress is more pronounced than at higher stresses, and likewise so are the hardness and unconfined yield strength measurements. Hardness was shown to be independent of penetration depth for dimensionless penetration depths between 0.3 - 0.7, except for the case of very fine glass beads, for which it was found that the increase of hardness with depth is independent of the consolidation stress applied and similar for all three samples. The constraint factor determined from indentation and shear cell tests was virtually independent of the stress applied for all samples, except for the case of 0 - 20 μm samples, where its variation was noticeable. As a result, the inferred unconfined yield strength from ball indentation at low stresses followed a similarly
steep trend as hardness. This sharp change in behaviour at low stresses suggests that an extrapolation of shear cell results from higher stresses would overestimate the yield strength.

An increase of median particle size led to an increase in powder flowability and decrease of the constraint factor. In addition to this, widening the size distribution, while maintaining the same median size, resulted in a slight decrease of both flowability and constraint factor. The addition of fines caused a great decrease of powder flowability and an increase of constraint factor, while the addition of coarse particles appeared to only decrease the material’s resistance to plastic deformation, with the unconfined yield strength being unchanged. As a result, the increase of coarse particle content led to a decrease of constraint factor. As for the influence of surface energy, both the yield strength and hardness of the silanised samples were greater than the uncoated, with the trends of the former not being clearly distinguishable. No significant influence of surface energy on the constraint factor could be determined with the samples investigated due to the error bars.

Overall, ball indentation showed good reproducibility down to consolidation stresses of 0.1 kPa. Whereas shear cell measurements in the low stress region produced inconsistent results for this material, rendering the stress control of the user rather poor. This highlights the need for a reliable technique like ball indentation for powder flowability determination at low stresses.
Chapter 5  Investigation of Powder Flowability of ‘Real’ Materials at Low Stresses

In this chapter, the flow behaviour of a wide range of inorganic and organic materials is experimentally studied at both high and low consolidation stresses utilising shear testing and the ball indentation technique. For all the ‘real’ powders under investigation, the operational range and reliability of the ball indentation technique are established, along with the repeatability and reliability of the FT4 shear cell down to very low stresses (0.1 kPa). In addition to this, potential factors that can influence the constraint factor are explored. Furthermore, the influence of single crystal and agglomerate shape on the constraint factor and flowability is studied, as well as the stick-slip phenomenon that occurs during the testing of some organic powders.

5.1 Introduction

The objectives of this experimental series are manifold. Firstly, in all sections of this chapter, the suitability and applicability of the ball indentation technique on a wide range of ‘real’ powders are investigated at both high and low stresses. Also, the reproducibility and reliability of the FT4 shear cell are assessed at both high and low stresses. Moreover, in section 5.2, the influence of single crystal and agglomerate shape on the constraint factor and flow behaviour is studied using a set of alumina powders. In section 5.3, possible properties that could influence the constraint factor and powder flowability of a group of inorganic materials are explored. Lastly, in section 5.4, the stick-slip behaviour of some food powders and its influence on the indentation measurements are investigated.

For all the aforementioned purposes, both shear testing and ball indentation were employed following the methods outlined in sections 3.2.1 and 3.2.2, respectively. In this chapter, the default FT4 software linear fit to the measured shear test points, followed by application of Mohr circle analysis, was used to determine $\sigma_1$, $\sigma_c$, and subsequently $ff$, for each pre-shear normal stress applied. For each material, tests at four moderate to high pre-shear normal stresses were performed, namely 2, 4, 6 and 8 kPa, with the exception of two alumina samples; 900 Rapol Batchground and 900 Rapol Continuously ground. For these samples, measurements at the aforementioned stresses were unreliable, with the generated failure Mohr circle intercepting the normal stress axis at a negative value in some cases, therefore higher pre-shear normal stresses were chosen in this case, namely 8, 10, 12 and 14 kPa. Additionally, for all powders except the aforementioned alumina samples, shear tests at low pre-shear

normal stresses in the range of 0.06 - 1 kPa were carried out. The reason behind the choice of the target normal stresses applied in the shear tests has already been covered in section 4.1. Regarding the hardness measurements, indentation tests at the major principal stresses obtained from shear testing were conducted in order for the constraint factor to be quantified, along with measurements at stresses ≤ 1 kPa. The size and shape analysis of all ‘real’ materials is shown in Table 3.1, with their characterisation being extensively discussed in sections 3.1.5 and 3.1.6 for all inorganic and organic materials, respectively.

5.2 Study of the flowability of a set of alumina powders - Effect of single crystal and agglomerate shape on constraint factor and flow behaviour

In this section, the materials under study are three grades of alumina; CT800SG, Rapol 900 Batchground and Rapol 900 Continuously ground. As mentioned in section 3.1.5 and shown in Table 3.1, the $d_{10}$ and $d_{50}$ are similar for all three batches. According to the supplier, the two Rapol 900 samples have similar particle shape, but form agglomerates of different shape, with the batchground agglomerate being more round and the continuously ground being more ‘edge-rich’, as shown in Figure 3.13. In addition to this, the single crystals of the two Rapol 900 samples are more round than the CT800SG crystals, which are plate-like, as shown in Figure 3.13.

The normal stresses that were chosen for shear testing of the CT800SG grade and the two Rapol 900 grades are shown in Tables 5.1 and 5.2, respectively. The results of the shear cell experiments at moderate to high pre-shear normal stresses are reported in Table 5.3 for the CT800SG sample and in Table 5.4 for the two Rapol 900 samples. All three samples are either cohesive or very cohesive throughout the measured range. Table 5.3 shows that the flow factor of alumina CT800SG increases with the increase of the consolidation stress applied, whereas the flow factors of the two Rapol 900 batches remain constant throughout the range of stresses applied, as can be seen from Table 5.4. Both Rapol 900 batches are shown to be very cohesive, with the continuously ground one exhibiting slightly more cohesive behaviour ($ff_c = 1.5$) compared to the batchground sample ($ff_c = 1.7$). Compared to the Rapol 900 grades, CT800SG is better flowing, giving larger flow factor values ($1.9 \leq ff_c \leq 2.6$), even though it was tested at lower pre-shear normal stresses.
Table 5.1. Normal stresses applied in the FT4 shear cell for alumina CT800SG

<table>
<thead>
<tr>
<th>Pre-shear normal stress, ( \sigma_{\text{pre}} ) (kPa)</th>
<th>Target normal stresses, ( \sigma ) (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>0.18, 0.15, 0.13, 0.10, 0.05</td>
</tr>
<tr>
<td>0.50</td>
<td>0.35, 0.30, 0.25, 0.20, 0.15</td>
</tr>
<tr>
<td>1.00</td>
<td>0.70, 0.60, 0.50, 0.40, 0.30</td>
</tr>
<tr>
<td>2.00</td>
<td>1.50, 1.25, 1.00, 0.75</td>
</tr>
<tr>
<td>4.00</td>
<td>3.40, 2.80, 2.20, 1.60, 1.00</td>
</tr>
<tr>
<td>6.00</td>
<td>5.00, 4.00, 3.00, 2.00, 1.00</td>
</tr>
<tr>
<td>8.00</td>
<td>6.76, 5.52, 4.28, 3.04, 1.80</td>
</tr>
</tbody>
</table>

Table 5.2. Normal stresses applied in the FT4 shear cell for the two Rapol 900 alumina grades

<table>
<thead>
<tr>
<th>Pre-shear normal stress, ( \sigma_{\text{pre}} ) (kPa)</th>
<th>Target normal stresses, ( \sigma ) (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.00</td>
<td>3.50, 3.00, 2.50, 2.00, 1.50</td>
</tr>
<tr>
<td>10.00</td>
<td>3.90, 3.30, 2.70, 2.10, 1.50</td>
</tr>
<tr>
<td>12.00</td>
<td>4.40, 3.80, 3.20, 2.60, 2.00</td>
</tr>
<tr>
<td>14.00</td>
<td>4.80, 4.10, 3.40, 2.70, 2.00</td>
</tr>
</tbody>
</table>

Table 5.3. FT4 shear test data for alumina CT800SG

| | CT800SG |  |
|---|---|---|---|---|
| \( \sigma_{\text{pre}} \) | \( \sigma_1 \) | \( \sigma_c \) | \( f_{\text{fc}} \) |
| 2 | 4.9 | 2.6 | 1.9 |
| 4 | 9.7 | 4.6 | 2.1 |
| 6 | 13.6 | 5.3 | 2.6 |
| 8 | 17.7 | 6.9 | 2.6 |

Table 5.4. FT4 shear test data for the two Rapol 900 alumina grades

| | Rapol 900 Batchground | Rapol 900 Conti. ground |
|---|---|---|---|---|---|
| \( \sigma_{\text{pre}} \) | \( \sigma_1 \) | \( \sigma_c \) | \( f_{\text{fc}} \) | \( \sigma_1 \) | \( \sigma_c \) | \( f_{\text{fc}} \) |
| 8 | 20.4 | 11.5 | 1.7 | 18.5 | 12.6 | 1.5 |
| 10 | 24.6 | 14.8 | 1.7 | 22.4 | 15.0 | 1.5 |
| 12 | 28.6 | 16.8 | 1.7 | 26.9 | 17.6 | 1.5 |
| 14 | 33.1 | 20.0 | 1.7 | 30.7 | 20.0 | 1.5 |

For the three alumina grades, the unconfined yield strength is plotted against major principal stress and presented in Figure 5.1, showing that the slope of the increase of unconfined yield strength with stress is much steeper for the two Rapol 900 samples, which seem to have very similar trends considering the error bars.
As previously discussed, before proceeding with employing the ball indentation technique, the behaviour of hardness when varying the penetration depth had to be investigated for all materials. For this purpose, separate indentation tests in the range of dimensionless penetration depths of 0.1 - 0.7 at consolidation stresses of 0.1 and 1 kPa were carried out for all three grades of alumina, and are shown alongside ‘continuous hardness’ calculated from indentation tests at a dimensionless penetration depth of 0.7 in Figures 5.2, 5.3 and 5.4. For all three materials, hardness is found to overshoot at very low depths, before reaching a minimum at a dimensionless penetration depth of around 0.1, from which point onwards it starts to gradually increase with the increase of depth. The effect of unloading on hardness was found to be negligible for all three materials and the ‘continuous hardness’ curves agree well with the direct measurements in almost all cases, therefore the penetration depth at maximum indentation load was used in the calculation of hardness. The only notable discrepancy between the direct tests and the ‘continuous hardness’ curves was observed in the case of alumina CT800SG consolidated at 1 kPa at small dimensionless penetration depths (0.1, 0.3), due to the difficulty of reproducing a uniformly flat powder bed surface, as well as creating a consistent packing structure for these particular tests.

Figure 5.1. Unconfined yield strength against major principal stress for the three alumina grades
Figure 5.2. Hardness against dimensionless penetration depth at 0.1 and 1 kPa for alumina CT800SG

Figure 5.3. Hardness against dimensionless penetration depth at 0.1 and 1 kPa for alumina Rapol 900 Batchground
Figures 5.5, 5.6 and 5.7 show the ‘continuous hardness’ against dimensionless penetration depth at the major principal stresses from Tables 5.3 and 5.4 for alumina CT800SG, Rapol 900 Batchground and Rapol 900 Continuously ground, respectively. It is observed that the increase of hardness with depth, which could be caused by local consolidation by the indenter, as previously discussed in chapter 4, is independent of the applied consolidation stress and similar for all three samples. The aforementioned findings were not clear at low stresses (Figures 5.2, 5.3 and 5.4), due to the larger error present in tests in this region because of the difficulty of reproducing a uniformly flat powder bed surface, as well as creating a consistent packing structure, hence the need for the ‘continuous’ hardness curves at higher stresses. The consistent increase of hardness with stress in the depicted depth range validates the application of any penetration depth in this range. For the indentation tests on all alumina grades, the dimensionless penetration depth of 0.5 was applied.

Figure 5.4. Hardness against dimensionless penetration depth at 0.1 and 1 kPa for alumina Rapol 900 Conti. ground
Figure 5.5. Hardness against dimensionless penetration depth at high stresses for alumina CT800SG

Figure 5.6. Hardness against dimensionless penetration depth at high stresses for alumina Rapol 900 Batchground
Figure 5.7. Hardness against dimensionless penetration depth at high stresses for alumina Rapol 900 Conti. ground

Hardness is presented against major principal stress for all three alumina batches in Figure 5.8. Due to the very high major principal stresses generated in the shear cell at pre-shear normal stresses of 8, 10, 12 and 14 kPa for the batchground and continuously ground grades, additional indentation measurements were carried out at major principal stresses of 5, 10 and 15 kPa for these batches. The measurements are found to be highly reproducible across the whole range of applied stresses, with the coefficient of variation being around 5 % at high stresses and less than 15 % at low stresses in almost all cases. For all materials, hardness increases linearly with stress, with the trends of the two Rapol 900 samples being virtually identical, and the gradient of the CT800SG sample being reduced compared to the other two. In addition to this, the slopes of the increase of hardness for the two Rapol 900 aluminas are very similar both at low and high stresses, whereas in the case of CT800SG the trend is steeper at low stresses. Moreover, although CT800SG exhibits the lowest resistance to plastic deformation, it packs better than the other two batches, probably because of its plate-shaped particles which pile up on each other during consolidation, as shown in Figure 5.9. In contrast, the continuously ground sample, whose particles form ‘edge-rich’ agglomerates, forms the loosest packed beds.
Figure 5.8. Hardness against major principal stress for the three alumina grades

Figure 5.9. Packing fraction against major principal stress for the three alumina grades
The constraint factor of all samples was quantified using the unconfined yield strength and hardness measurements determined at each of the moderate to high major principal stresses using Equation 2.18, and presented against major principal stress in Figure 5.10. C is found to be approximately constant throughout this range of stresses for all three alumina grades, with the fluctuations being marginal. The error bars of the constraint factor are noticeable, mainly because of the error present in the shear cell measurements. If particle size distribution was the only factor affecting the constraint factor, and considering that all grades have very similar $d_{10}$ and $d_{50}$, it would be expected that the constraint factor would follow the reverse order of the $d_{90}$ among these materials, based on the findings of section 4.3.2. As such, CT800SG would have the highest constraint factor, as it has the lowest $d_{90}$, followed by Rapol 900 Conti. ground and then Rapol 900 Batchground. Indeed, CT800SG exhibits the highest C, but the batchground Rapol 900 sample has a slightly higher constraint factor than the continuously ground one. It could be the case that the ‘edge-rich’ agglomerate shape of the continuously ground batch is the reason for a lower C, compared to the batchground material which forms more round agglomerates. In addition to this, it is possible that the plate-shaped single crystals of the CT800SG are the cause of a greater C, compared to the more round single particles of the Rapol 900 grades. Furthermore, it is noteworthy that the order of constraint factor is the same as the packing fraction (Figure 5.9), thus it may be the case that an increased packing fraction leads to an increased constraint factor. Surface energy is not expected to have any effect on the differentiation of the constraint factor value among these samples, since all samples are aluminium oxide.
As previously shown in chapter 4, since the constraint factor is found to be almost constant in the tested range of stresses, it can be assumed that it remains constant at low stresses as well, and by using the average value of $C$ across the applied stresses together with the hardness values at low stresses, the unconfined yield strength of all three alumina grades at low stresses was determined via Equation 2.18. Figure 5.11 shows the inferred unconfined yield strength values from the ball indentation measurements at low stresses, along with the unconfined yield strength measurements carried out in the shear cell at higher stresses shown in Figure 5.1. The results show that for all materials, the behaviour of the yield strength in the low stress regime is similar to their hardness trends in this range, as expected.
Figure 5.11. Unconfined yield strength shear cell measurements and inferred values from ball indentation for the three alumina grades

Next, the reliability and repeatability of shear testing of all three alumina powders are investigated by determining the difference between the achieved stresses and the target normal stresses, and the variation among three repeats at pre-shears in the range of 0.25 - 8 kPa for Alumina CT800SG (Figure 5.12) and at 10 and 14 kPa for the two Rapol 900 grades (Figure 5.13). Alumina CT800SG tests are highly reproducible both at 4 and 8 kPa, with the applied stresses evenly distributed. It is noted though that at 4 kPa there is a discrepancy between the target and the actual applied normal stresses. At 1 kPa, the tests are somewhat reproducible, but the target stresses are not achieved, while at 0.25 kPa the resulting yield loci are not reliable as they do not exhibit a monotonic increase. As for the two Rapol 900 aluminas, the continuously ground grade gives more reproducible results at both pre-shear stresses depicted in Figure 5.13, with the target stresses being achieved, while in the case of the batchground grade the accuracy of achieving the target stresses is noticeably reduced.
Figure 5.12. Measured shear and applied normal stresses for alumina CT800SG at pre-shear normal stresses of a) 0.25 kPa, b) 1.00 kPa, c) 4.00 kPa and d) 8.00 kPa
Figure 5.13. Measured shear and applied normal stresses for alumina Rapol 900 Batchground at pre-shear normal stresses of a) 10.00 kPa and b) 14.00 kPa and alumina Rapol 900 Conti. ground at pre-shear normal stresses of c) 10.00 kPa and d) 14.00 kPa

Moreover, in Figure 5.14, the unconfined yield strength values inferred from ball indentation measurements for Alumina CT800SG are plotted alongside the FT4 shear cell measurements at low pre-shear normal stresses against major principal stress. It can be seen that the slope of the increase of unconfined yield strength with stress is steeper for the shear cell measurements. Also, the FT4 shear cell is found to possibly overestimate the unconfined yield strength, due to the lack of accuracy of its measurements in this stress range.
Study of the flowability of a set of inorganic powders -
Decoupling the effect of different properties on constraint factor and flow behaviour

In this section, the flowability of a set of inorganic materials - limestone, talc, copper and titania - is investigated. These powders have a wide range of particle size distributions and particle shapes, as evidenced by Table 3.1. An attempt is made to decouple the effects of different properties on the constraint factor which is associated with powder flowability.

The target stresses in shear cell experiments for limestone, talc, copper and titania are presented in Tables 5.5, 5.6, 5.7 and 5.8, respectively. The shear testing data at moderate to high pre-shear normal stresses are reported in Table 5.9, whilst, for all materials, the unconfined yield strength derived from the shear tests is plotted against major principal stress in Figure 5.15. Titania is found to be the most cohesive among the materials tested with a virtually constant flow factor of 1.1 - 1.2, followed by limestone with $2.1 \leq ff_c \leq 3.5$, for the range of pre-shear normal stresses applied. This is explained by the fact that titania has by far the smallest particle size, which is in the nanometre range, followed by...
limestone with a $d_{50}$ of 4.3 μm, while both powders have irregular particles. In the range of stresses applied, talc and copper are cohesive to easy-flowing with flow factors of 3.2 - 5.3 and 2.6 - 6.3, respectively, with copper being the more cohesive of the two at lower stresses and talc being more cohesive at higher stresses. Talc and copper have more irregular particles than titania and limestone with their shape being plate-like and dendritic, respectively, nevertheless they flow better, likely due to their larger particle size.

**Table 5.5. Normal stresses applied in the FT4 shear cell for limestone**

<table>
<thead>
<tr>
<th>Pre-shear normal stress, $\sigma_{\text{pre}}$ (kPa)</th>
<th>Target normal stresses, $\sigma$ (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.06</td>
<td>0.05, 0.04, 0.03, 0.02, 0.01</td>
</tr>
<tr>
<td>0.10</td>
<td>0.07, 0.06, 0.05, 0.04, 0.02</td>
</tr>
<tr>
<td>0.25</td>
<td>0.18, 0.15, 0.13, 0.10, 0.05</td>
</tr>
<tr>
<td>0.50</td>
<td>0.35, 0.30, 0.25, 0.20, 0.15</td>
</tr>
<tr>
<td>1.00</td>
<td>0.70, 0.60, 0.50, 0.40, 0.30</td>
</tr>
<tr>
<td>2.00</td>
<td>1.25, 1.05, 0.85, 0.65, 0.45</td>
</tr>
<tr>
<td>4.00</td>
<td>3.40, 2.80, 2.20, 1.60, 1.00</td>
</tr>
<tr>
<td>6.00</td>
<td>5.00, 4.00, 3.00, 2.00, 1.00</td>
</tr>
<tr>
<td>8.00</td>
<td>6.60, 5.20, 3.80, 2.40, 1.00</td>
</tr>
</tbody>
</table>

**Table 5.6. Normal stresses applied in the FT4 shear cell for talc**

<table>
<thead>
<tr>
<th>Pre-shear normal stress, $\sigma_{\text{pre}}$ (kPa)</th>
<th>Target normal stresses, $\sigma$ (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.06</td>
<td>0.05, 0.04, 0.03, 0.02, 0.01</td>
</tr>
<tr>
<td>0.10</td>
<td>0.07, 0.06, 0.05, 0.04, 0.02</td>
</tr>
<tr>
<td>0.25</td>
<td>0.18, 0.15, 0.13, 0.10, 0.05</td>
</tr>
<tr>
<td>0.50</td>
<td>0.35, 0.30, 0.25, 0.20, 0.15</td>
</tr>
<tr>
<td>1.00</td>
<td>0.70, 0.60, 0.50, 0.40, 0.30</td>
</tr>
<tr>
<td>2.00</td>
<td>1.67, 1.34, 1.01, 0.68, 0.35</td>
</tr>
<tr>
<td>4.00</td>
<td>3.32, 2.64, 1.96, 1.28, 0.60</td>
</tr>
<tr>
<td>6.00</td>
<td>4.95, 3.90, 2.85, 1.80, 0.75</td>
</tr>
<tr>
<td>8.00</td>
<td>6.62, 5.24, 3.86, 2.48, 1.10</td>
</tr>
</tbody>
</table>

**Table 5.7. Normal stresses applied in the FT4 shear cell for copper**

<table>
<thead>
<tr>
<th>Pre-shear normal stress, $\sigma_{\text{pre}}$ (kPa)</th>
<th>Target normal stresses, $\sigma$ (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>0.18, 0.15, 0.13, 0.10, 0.05</td>
</tr>
<tr>
<td>0.50</td>
<td>0.35, 0.30, 0.25, 0.20, 0.15</td>
</tr>
<tr>
<td>1.00</td>
<td>0.70, 0.60, 0.50, 0.40, 0.30</td>
</tr>
<tr>
<td>2.00</td>
<td>1.66, 1.32, 0.98, 0.64, 0.30</td>
</tr>
<tr>
<td>4.00</td>
<td>3.27, 2.54, 1.81, 1.08, 0.35</td>
</tr>
<tr>
<td>6.00</td>
<td>4.90, 3.80, 2.70, 1.60, 0.50</td>
</tr>
<tr>
<td>8.00</td>
<td>6.50, 5.00, 3.50, 2.00, 0.50</td>
</tr>
</tbody>
</table>
Table 5.8. Normal stresses applied in the FT4 shear cell for titania

<table>
<thead>
<tr>
<th>Pre-shear normal stress, $\sigma_{\text{pre}}$ (kPa)</th>
<th>Target normal stresses, $\sigma$ (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>0.35, 0.30, 0.25, 0.20, 0.15</td>
</tr>
<tr>
<td>1.00</td>
<td>0.70, 0.60, 0.50, 0.40, 0.30</td>
</tr>
<tr>
<td>2.00</td>
<td>1.60, 1.40, 1.20, 1.00</td>
</tr>
<tr>
<td>4.00</td>
<td>2.80, 2.20, 1.60, 1.00</td>
</tr>
<tr>
<td>6.00</td>
<td>4.00, 3.00, 2.00, 1.00</td>
</tr>
<tr>
<td>8.00</td>
<td>5.20, 3.80, 2.40, 1.00</td>
</tr>
</tbody>
</table>

Table 5.9. FT4 shear test data for the four inorganic powders

<table>
<thead>
<tr>
<th>Limestone</th>
<th>Talc</th>
<th>Copper</th>
<th>Titania</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_{\text{pre}}$</td>
<td>$\sigma_1$</td>
<td>$\sigma_c$</td>
<td>$ff_c$</td>
</tr>
<tr>
<td>2</td>
<td>3.9</td>
<td>1.8</td>
<td>2.1</td>
</tr>
<tr>
<td>4</td>
<td>8.0</td>
<td>3.2</td>
<td>2.5</td>
</tr>
<tr>
<td>6</td>
<td>11.7</td>
<td>3.9</td>
<td>3.0</td>
</tr>
<tr>
<td>8</td>
<td>15.4</td>
<td>4.4</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Figure 5.15. Unconfined yield strength against major principal stress for the four inorganic powders

As in section 5.2, the trend of hardness against dimensionless penetration depth was investigated prior to carrying out indentation tests at various stresses. Figures 5.16, 5.17, 5.18 and 5.19 show separate indentation tests for limestone, talc, copper and titania, respectively, in the range of dimensionless penetration depths of 0.1 - 0.7 at 0.1 and 1 kPa consolidation stress, and ‘continuous
hardness’ plotted from ball indentation tests at a dimensionless penetration depth of 0.7. The observed behaviour is the same as in section 5.2, with hardness reaching a maximum when the indenter is in contact with a few particles, after which it reaches a minimum at a dimensionless penetration depth of around 0.1, and then increasing until 0.7. The separate tests are in agreement with the ‘continuous hardness’ trends. Unloading was found to have a significant effect on the measured hardness values only in the case of talc, for which hardness is underestimated by 7 - 12 % in the range of applied major principal stresses if the bed recovery during unloading is not considered in the measurement, and as such it was taken into account by calculating hardness using the elastically-recovered depth. For all other materials, the underestimation falls within test error, hence was not considered, and the penetration depth at maximum indentation load was used to determine hardness.

Figure 5.16. Hardness against dimensionless penetration depth at 0.1 and 1 kPa for limestone
Figure 5.17. Hardness against dimensionless penetration depth at 1 kPa for talc

Figure 5.18. Hardness against dimensionless penetration depth at 0.1 and 1 kPa for copper
Also, once again, as in the case of the alumina grades in section 5.2, the increase of hardness with penetration depth is observed to be independent of the applied stress, and similar for all materials, as evidenced by Figures 5.20, 5.21, 5.22 and 5.23, which depict ‘continuous hardness’ against dimensionless penetration depth at moderate to high stresses for all four materials investigated in these experiments. For this series of experiments, the dimensionless penetration depth of 0.2 was applied in all indentation tests, since this tended to represent the most stable hardness region.
Figure 5.20. Hardness against dimensionless penetration depth at high stresses for limestone

Figure 5.21. Hardness against dimensionless penetration depth at high stresses for talc
Figure 5.22. Hardness against dimensionless penetration depth at high stresses for copper

Figure 5.23. Hardness against dimensionless penetration depth at high stresses for titania
For all four inorganic materials, hardness is plotted against major principal stress and shown in Figure 5.24. The error of the measurements is small, as evidenced by the error bars, with a coefficient of variation typically less than 5% at high stresses and less than 15% at low stresses. Hardness increases with stress, due to an increased packing fraction (Figure 5.25), with the order of hardness values among materials being the same as in the case of the shear tests. However, compared to the unconfined yield strength measurements determined in the FT4 shear cell, the hardness of limestone and titania are closer, with this occurrence indicating a difference in constraint factor between these two powders. The order of resistance to plastic deformation of the materials does not correspond to the order of packing fraction, which is shown in Figure 5.25. Furthermore, for all materials, hardness increases more rapidly with major principal stress for weakly consolidated powder beds, except for the case of titania, which has the same gradient throughout the range of the applied stresses. It is interesting to point out here that the only materials so far that exhibit the same slope of hardness against major principal stress at both high and low stresses are the materials that are very cohesive in the range of stresses applied; titania and the two alumina Rapol 900 grades (Figure 5.8) which were investigated in section 5.2.
Figure 5.25. Packing fraction against major principal stress for the four inorganic powders

The constraint factor of all four materials is shown in Figure 5.26 and is observed to be almost constant, regardless of the consolidation level. Surprisingly, titania has the lowest $C$, even though its particle size is by far the smallest, as it was found in section 4.2 that a decrease in particle size leads to an increase in the constraint factor. There is a possibility though, that titania is in the form of agglomerates which are larger than the particles of all other inorganics (Figure 3.23), due to its tendency to auto-agglomerate (Ku et al., 2015), and this results in such a low constraint factor. Also, in contrast to the finding in section 4.2, limestone, which has the second smallest particle size, shows the greatest values of $C$, together with talc. Limestone is finer than talc, with both having similar spans of size distribution, but talc’s single crystal shape is plate-like, whereas limestone particles are irregular, but more rounded. This suggests that non-sphericity of the single particle shape increases $C$, a finding also observed in the study of the alumina powders in section 5.2. In the cases of limestone and talc, particle size and shape may counterbalance each other, therefore leading to a similar $C$ for both materials. Also, copper exhibits a higher constraint factor than titania, despite having the largest particles among the four materials tested, thus indicating that its more irregular dendritic shape could be the reason for this. Furthermore, it was suggested in section 5.2 that $C$ could depend more on the packing state of the powder bed (Figures 5.9, 5.10). In this series of experiments, the order of $C$ follows the packing fraction order for limestone, copper and titania. It can be seen in Figure 5.25 that copper packs a little better than titania, corresponding to an increased constraint factor of around 2.5,
compared to titania’s constraint factor of 2. Limestone’s packing fraction is noticeably greater than that of the aforementioned powders, hence the substantially greater average $C$ of around 4.5. However, in contrast to the above, talc, with the thin, plate-like particles, shows by far the worst packing behaviour, nevertheless having the largest average constraint factor value of approximately 4.5, like the best packing material, limestone. Packing is directly linked to both the particle size, width of size distribution and shape of the powders, with complex geometries promoting mechanical interlocking, which are all believed to have an effect on $C$, however other unknown factors might also come into play influencing $C$.

![Figure 5.26. Constraint factor against major principal stress for the four inorganic powders](image)

Figure 5.26. Constraint factor against major principal stress for the four inorganic powders

Figure 5.27 shows for all four inorganic materials the inferred unconfined yield strength values from indentation measurements at low stresses, along with the unconfined yield strength values from shear cell measurements at moderate to high stresses shown in Figure 5.15. It can be seen that for all materials, except for titania, the extrapolation of shear data from high to low stresses leads to an overestimation of unconfined yield strength.
The accuracy and repeatability of the shear tests at a range of low to high pre-shear normal stresses are studied for all materials by plotting the target normal stresses alongside the achieved stresses for limestone, talc, copper and titania in Figures 5.28, 5.29, 5.30 and 5.31, respectively. As can be seen, tests at 8 kPa provide very repeatable results with the achieved stresses almost coinciding with the target stresses, except for titania, in which case there is a difference between the exerted and the target normal stresses. Reducing the pre-shear to 4 kPa leads to equally repeatable tests, though now the difference between the desirable stresses and the actual applied stresses is more pronounced. In the case of titania, this behaviour is significantly more pronounced, whilst the test points are not equidistant like for the other powders. At a pre-shear of 1 kPa, the repeatability is still good for limestone and talc, even though the target stresses aren’t achieved and the test points aren’t equidistant. In the case of copper and titania, the generated yield loci do not increase monotonically, rendering the shear tests unreliable. This occurrence is also present in tests below 1 kPa for these materials, suggesting that the determination of the flow behaviour of these materials in the low stress range is not possible with the FT4 shear cell. For limestone, the reproducibility and accuracy are greatly decreased at 0.25 kPa, while at 0.06 kPa the yield loci are not acceptable, and stresses beyond the pre-shear stress have been exerted. Talc is the only powder that gives highly reproducible data even down to a pre-shear normal stress of 0.06 kPa, despite the fact that the applied stresses deviate
heavily from the target ones. Overall, the shear tests of these ‘real’ materials were found to be both reliable and repeatable only in the moderate to high stress range, illustrating the need for alternative low stress flowability techniques.
Figure 5.28. Measured shear and applied normal stresses for limestone at pre-shear normal stresses of a) 0.06 kPa, b) 0.25 kPa, c) 1.00 kPa, d) 4.00 kPa and e) 8.00 kPa
Figure 5.29. Measured shear and applied normal stresses for talc at pre-shear normal stresses of a) 0.06 kPa, b) 0.25 kPa, c) 1.00 kPa, d) 4.00 kPa and e) 8.00 kPa
Figure 5.30. Measured shear and applied normal stresses for copper at pre-shear normal stresses of a) 0.25 kPa, b) 1.00 kPa, c) 4.00 kPa and d) 8.00 kPa
Figure 5.31. Measured shear and applied normal stresses for titania at pre-shear normal stresses of a) 0.50 kPa, b) 1.00 kPa, c) 4.00 kPa and d) 8.00 kPa

In Figure 5.32, the unconfined yield strength inferred from ball indentation, together with the values measured with the shear cell at low stresses, are presented for all four inorganic powders. In the case of limestone, ball indentation predicts a much shallower slope of unconfined yield strength against stress in comparison with the shear tests, whereas for the other three powders the trends are not very different.
5.4 Study of the flowability of a set of organic powders - Effect of stick-slip on flow behaviour

In this study, the tested materials are a set of brittle food powders; maize starch, maltitol and pea protein. The normal stresses applied in the FT4 for maize starch, maltitol and pea protein are reported in Tables 5.10, 5.11 and 5.12, respectively, while the results of the FT4 shear cell measurements for all materials are shown in Table 5.13. In addition to this, for all three organic powders, the unconfined yield strength at moderate to high stresses is presented against the applied stress in Figure 5.33. Maltitol is clearly the most cohesive powder among all, ranging from very cohesive to cohesive in the applied stress range ($1.4 \leq ff_c \leq 2.1$). Maize starch and pea protein exhibit a cohesive to easy-flowing behaviour with $2.0 \leq ff_c \leq 4.6$ and $3.0 \leq ff_c \leq 6.8$, respectively. Moreover, the unconfined yield strength is observed to increase linearly with major principal stress for all powders.
Table 5.10. Normal stresses applied in the FT4 shear cell for maize starch

<table>
<thead>
<tr>
<th>Pre-shear normal stress, $\sigma_{pre}$ (kPa)</th>
<th>Target normal stresses, $\sigma$ (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.06</td>
<td>0.05, 0.04, 0.03, 0.02, 0.01</td>
</tr>
<tr>
<td>0.10</td>
<td>0.07, 0.06, 0.05, 0.04, 0.02</td>
</tr>
<tr>
<td>0.25</td>
<td>0.18, 0.15, 0.13, 0.10, 0.05</td>
</tr>
<tr>
<td>0.50</td>
<td>0.35, 0.30, 0.25, 0.20, 0.15</td>
</tr>
<tr>
<td>1.00</td>
<td>0.70, 0.60, 0.50, 0.40, 0.30</td>
</tr>
<tr>
<td>2.00</td>
<td>1.40, 1.20, 1.00</td>
</tr>
<tr>
<td>4.00</td>
<td>3.40, 2.80, 2.20, 1.60, 1.00</td>
</tr>
<tr>
<td>6.00</td>
<td>5.00, 4.00, 3.00, 2.00, 1.00</td>
</tr>
<tr>
<td>8.00</td>
<td>6.60, 5.20, 3.80, 2.40, 1.00</td>
</tr>
</tbody>
</table>

Table 5.11. Normal stresses applied in the FT4 shear cell for maltitol

<table>
<thead>
<tr>
<th>Pre-shear normal stress, $\sigma_{pre}$ (kPa)</th>
<th>Target normal stresses, $\sigma$ (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>0.35, 0.30, 0.25, 0.20, 0.15</td>
</tr>
<tr>
<td>1.00</td>
<td>0.70, 0.60, 0.50, 0.40, 0.30</td>
</tr>
<tr>
<td>2.00</td>
<td>1.80, 1.60, 1.40, 1.20, 1.00</td>
</tr>
<tr>
<td>4.00</td>
<td>3.40, 2.80, 2.20, 1.60, 1.00</td>
</tr>
<tr>
<td>6.00</td>
<td>5.16, 4.32, 3.48, 2.64, 1.80</td>
</tr>
<tr>
<td>8.00</td>
<td>6.80, 5.60, 4.40, 3.20, 2.00</td>
</tr>
</tbody>
</table>

Table 5.12. Normal stresses applied in the FT4 shear cell for pea protein

<table>
<thead>
<tr>
<th>Pre-shear normal stress, $\sigma_{pre}$ (kPa)</th>
<th>Target normal stresses, $\sigma$ (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>0.07, 0.06, 0.05, 0.04, 0.02</td>
</tr>
<tr>
<td>0.25</td>
<td>0.18, 0.15, 0.13, 0.10, 0.05</td>
</tr>
<tr>
<td>0.50</td>
<td>0.35, 0.30, 0.25, 0.20, 0.15</td>
</tr>
<tr>
<td>1.00</td>
<td>0.70, 0.60, 0.50, 0.40, 0.30</td>
</tr>
<tr>
<td>2.00</td>
<td>1.36, 1.04, 0.72, 0.40</td>
</tr>
<tr>
<td>4.00</td>
<td>3.30, 2.60, 1.90, 1.20, 0.50</td>
</tr>
<tr>
<td>6.00</td>
<td>4.90, 3.80, 2.70, 1.60, 0.50</td>
</tr>
<tr>
<td>8.00</td>
<td>6.60, 5.20, 3.80, 2.40, 1.00</td>
</tr>
</tbody>
</table>

Table 5.13. FT4 shear test data for the three organic powders

<table>
<thead>
<tr>
<th>$\sigma_{pre}$</th>
<th>$\sigma_1$</th>
<th>$\sigma_c$</th>
<th>$\sigma_{ff}$</th>
<th>$\sigma_1$</th>
<th>$\sigma_c$</th>
<th>$\sigma_{ff}$</th>
<th>$\sigma_1$</th>
<th>$\sigma_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>3.2</td>
<td>1.6</td>
<td>2.0</td>
<td>4.6</td>
<td>3.3</td>
<td>1.4</td>
<td>2.9</td>
<td>1.0</td>
</tr>
<tr>
<td>4</td>
<td>6.4</td>
<td>2.3</td>
<td>2.8</td>
<td>8.8</td>
<td>4.9</td>
<td>1.8</td>
<td>5.6</td>
<td>1.2</td>
</tr>
<tr>
<td>6</td>
<td>9.4</td>
<td>2.5</td>
<td>3.8</td>
<td>12.8</td>
<td>6.6</td>
<td>1.9</td>
<td>8.2</td>
<td>1.3</td>
</tr>
<tr>
<td>8</td>
<td>12.4</td>
<td>2.7</td>
<td>4.6</td>
<td>16.8</td>
<td>8.1</td>
<td>2.1</td>
<td>11.0</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Maize starch | Maltitol | Pea protein
Figure 5.33. Unconfined yield strength against major principal stress for the three organic powders

As with all other materials in the previous sections of this chapter, the behaviour of hardness as a function of dimensionless penetration depth at low stresses is presented in Figures 5.34, 5.35 and 5.36 for the three food powders, with the observed trend being the same as in the case of the rest of the materials investigated in this chapter. It is noteworthy that in the case of pea protein, hardness error bars of direct tests at 1 kPa consolidation stress are substantially greater as compared to the other two food powders. In addition to this, the effect of bed recovery for all three organic materials falls within test error and is not influential on the measurement, therefore the penetration depth at maximum indentation load was used for the calculation of hardness.
Figure 5.34. Hardness against dimensionless penetration depth at 0.1 and 1 kPa for maize starch

Figure 5.35. Hardness against dimensionless penetration depth at 0.1 and 1 kPa for maltitol
For all three organic powders, ‘continuous hardness’ is shown against dimensionless penetration depth at moderate to high consolidation stresses in Figures 5.37, 5.38 and 5.39. In the case of maltitol, the increase of hardness with depth is independent of the applied penetration depth (Figure 5.38) like with all other materials in this chapter, while for maize starch (Figure 5.37) and pea protein (Figure 5.39) this is not clear, due to the occurrence of notable fluctuations during indentation. These fluctuations are present in tests on maize starch only at the two highest applied stresses, whilst in the case of pea protein they are more erratic and appear at all tested high stresses. These trends are a result of the instability in the force measurement during indentation. Figure 5.40 shows ‘continuous hardness’ against dimensionless penetration depth for maize starch, pea protein and limestone and titania that were tested as part of section 5.3. It can be seen that for the two inorganic materials the force-displacement follows a near constant gradient, in contrast to maize starch and pea protein. The behaviour of the two food powders is believed to correspond to stick-slip phenomenon around the indentation zone. As the indenter descends and contacts the bed, the particles initially stick to each other resisting flow under shear with the exerted shear stress increasing, before they overcome this resistance and slip at the point when static friction is overcome, thus leading to a decrease in shear stress when they are mobilised. The local maximum points of the ‘continuous hardness’ curves depict the sticking, while the minimum points the slipping motion.
Figure 5.37. Hardness against dimensionless penetration depth at high stresses for maize starch

Figure 5.38. Hardness against dimensionless penetration depth at high stresses for maltitol
Figure 5.39. Hardness against dimensionless penetration depth at high stresses for pea protein

Figure 5.40. Force against dimensionless penetration depth for four materials
Further evidence of stick-slip behaviour is the bed surface profile after unloading the indenter. Typically indentation tests result in a ‘sink in’ surface profile, which is not the case for maize starch and pea protein, as can be seen from Figure 5.41. These two stick-slip powders exhibited a ‘pile-up’ surface profile around the indentation zone, which appears to arise as the material flows towards the bed surface boundary along a slip plane as the indentation force suddenly reduces, followed by further penetration before a further slip plane arises lower down in the bed, resulting in material rising to the surface at a greater radial position. The pile-up behaviour was observed only at consolidation stresses greater than 1 kPa, and was more pronounced as the exerted stress increased, with additional pile-up layers forming around the indentation zone. In the case of maize starch, the pile-up is less pronounced than for pea protein, and the slip planes appear to be more consistent, therefore explaining the much more moderate fluctuations during measurement (Figures 5.37, 5.40).

![Figure 5.41. Powder bed surface profiles after indentation (a: maltitol, b: maize starch, c: pea protein)](image)

As a result of the above discussion, the potential similarity among the hardness against dimensionless penetration depth trends for all materials is not possible to be assessed for the whole range of dimensionless penetration depths. The dimensionless penetration depth of 0.5 that has been applied for most materials in this work was chosen to also be applied in all indentation measurements on the three organic powders.

For the three organic materials tested, hardness is reported against major principal stress in Figure 5.42, which shows that hardness increases with stress for all materials, with the trend being sharper at low stresses. The order of resistance to plastic deformation and the slopes of the curves closely resemble the unconfined yield strength results from shear testing (Figure 5.33). Tests on maltitol are very reproducible, with an average coefficient of variation of around 5% at high stresses. In the high stress range, the coefficient of variation is 7% and 16% for maize starch and pea protein, respectively, therefore suggesting that the reproducibility drops as stick-slip behaviour becomes more pronounced.
At lower consolidation levels, the stick-slip phenomenon is not that pronounced due to the weaker exerted force, thus test reproducibility is similar for all three materials with a coefficient of variation less than 15 %. As for the packing of these food powders, the least free-flowing maltitol packs the best, followed by maize starch and pea protein (Figure 5.43).

Figure 5.42. Hardness against major principal stress for the three organic powders
It is known that shear resistance is independent of indentation speed in the quasi-static regime (Tardos et al., 2003). In agreement with the previous statement, the work of Zafar (2013) and Pasha (2013) showed that hardness is independent of indentation speed in the quasi-static regime. However, in a side investigation, the speed of the indentation test was reduced from the speed of 1 mm/min that is used for all measurements throughout this thesis to 0.1 mm/min, and tests were conducted using limestone and titania from section 5.3, along with maize starch and pea protein at the highest consolidation stress that is applied to each of the materials in the thesis, with the results reported in Figure 5.44. Both indentation speeds are well within the quasi-static regime, as defined by Tardos et al. (2003), with the dimensionless shear strain rates per indentation speed for each material shown in Table 5.14. The findings agree with Zafar (2013) for the two inorganic materials, limestone and titania, which aren’t prone to stick-slip, whilst this isn’t the case for the two food powders that are prone to stick-slip. A tenfold decrease of indentation speed results in substantially greater hardness values for both materials, with the increase being more pronounced for pea protein, which is more prone to stick-slip. Consequently, the shear resistance of powders prone to stick-slip is found to be dependent on strain rate, even under such slow conditions. Furthermore, the fluctuations in force are much more noticeable at slower speeds (Figure 5.45).
Figure 5.44. Hardness against indentation speed for four materials

Table 5.14. Dimensionless shear strain rates at two indentation speeds for four materials

<table>
<thead>
<tr>
<th>Indentation speed</th>
<th>Limestone</th>
<th>Titania</th>
<th>Maize starch</th>
<th>Pea protein</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 mm/min</td>
<td>5.52E-06</td>
<td>1.02E-06</td>
<td>1.18E-05</td>
<td>1.60E-05</td>
</tr>
<tr>
<td>0.1 mm/min</td>
<td>5.52E-07</td>
<td>1.02E-07</td>
<td>1.18E-06</td>
<td>1.60E-06</td>
</tr>
</tbody>
</table>
Figure 5.45. Influence of indentation speed on force response for pea protein at 11.04 kPa

The constraint factor for all three organic powders is presented in Figure 5.46. For maize starch and maltitol, \( C \) is constant throughout the range of applied major principal stresses, whereas in the case of pea protein it fluctuates, with the error bars being significant, which is attributed to the deviation in hardness measurements caused by stick-slip. As evidenced by Table 3.1, all powders consist of irregular particles with similar sphericity and aspect ratio, therefore particle shape is expected to have a similar effect on \( C \) for all three materials. Pea protein has the greatest constraint factor, despite the fact that it has the largest particle size among the three powders, which all have relatively comparable particle sizes. This is probably because of the large error present in hardness measurements for this material. Maize starch, which is the finest among the three powders, has the second greatest constraint factor, while maltitol has the lowest constraint factor, perhaps due to its size distribution, which is wider in comparison with the other powders. The order of the constraint factor among the three materials is seen to be the opposite of the order of packing fraction (Figure 5.43).
Figure 5.46. Constraint factor against major principal stress for the three organic powders

Figure 5.47 shows for the three food powders the inferred unconfined yield strength values from hardness measurements at low stresses, along with the unconfined yield strength values determined from shear tests at higher stresses shown in Figure 5.33. It is clear for all materials that once again the unconfined yield strength increases more rapidly in the low stress regime, just like hardness (Figure 5.42), suggesting that the extrapolation of shear test results from higher stresses towards low stresses leads to an overestimation of unconfined yield strength. In the case of pea protein, the results are not expected to be reliable, due to the fluctuations in C.
The measured shear stresses and applied normal stresses, along with the target normal stresses for FT4 shear cell measurements of maize starch, maltitol and pea protein at pre-shear normal stresses in the range of 0.06 - 8 kPa are shown in Figures 5.48, 5.49 and 5.50, respectively. The results at 8 kPa pre-shear stress for all materials show that the tests are highly reproducible and the achieved normal stresses equidistant, with the target normal stresses having been virtually achieved, especially in the cases of maize starch and pea protein. At 4 kPa, the data are also reproducible, but there is a discrepancy between the target normal stresses and the actual applied stresses, particularly in the case of maltitol. Moreover, at 1 kPa, there is a notable difference between the target and the actual applied stresses for maltitol and pea protein, whilst for maize starch the deviation is not significant. At this stress, the tests are still reproducible in the case of maize starch, despite the fact that the stresses achieved are not the desired ones. At stresses lower than 1 kPa, the resulting yield loci are usually not monotonic, and in some cases the pre-shear normal stress has been exceeded, for example for maize starch at 0.06 kPa and for pea protein at 0.25 kPa. As a result, it is suggested that only maize starch can be tested down to 1 kPa pre-shear, demonstrating the unreliability of shear cells in the low stress region.
Figure 5.48. Measured shear and applied normal stresses for maize starch at pre-shear normal stresses of a) 0.06 kPa, b) 0.25 kPa, c) 1.00 kPa, d) 4.00 kPa and e) 8.00 kPa
Figure 5.49. Measured shear and applied normal stresses for maltitol at pre-shear normal stresses of a) 0.50 kPa, b) 1.00 kPa, c) 4.00 kPa and d) 8.00 kPa
Figure 5.50. Measured shear and applied normal stresses for pea protein at pre-shear normal stresses of a) 0.25 kPa, b) 1.00 kPa, c) 4.00 kPa and d) 8.00 kPa

For all three organic powders, the inferred unconfined yield strength from indentation, as well as the measured unconfined yield strength at low stresses by the FT4 shear cell, are plotted against major principal stress in Figure 5.51. As can be seen, even though some measurements from both techniques cannot be trusted for reasons that were previously explained, the two techniques give very similar results in the low stress range for all three organic materials.
5.5 Concluding remarks

The flowability of a broad class of cohesive powders was assessed by ball indentation and shear cell methods. The ball indentation technique is shown to be highly reproducible down to consolidation stresses of 0.1 kPa, with a typical coefficient of variation being around 5 % at high stresses and 15 % at low stresses. Only pea protein, which was found to be prone to stick-slip, showed greater deviation. In contrast, analysis of the accuracy and reproducibility of shear testing data at a wide range of pre-shear normal stresses down to 0.06 kPa, led to the conclusion that for most materials the FT4 shear cell cannot provide reliable flow measurements at stresses from 1 kPa and below. In addition to this, there is no clear conclusion as to how the results of the two techniques compare at low stresses.

Hardness was investigated as a function of penetration depth at a wide range of consolidation stresses, with the findings for all materials showing that it first rises significantly when the indenter first comes into contact with the powder bed, therefore touching a few particles, before falling and reaching a minimum at a dimensionless penetration depth of around 0.1, from which point onwards it starts increasing, at least until the dimensionless penetration depth of 0.7, which was the highest that was applied. The increase of hardness with depth was found to be independent of the
consolidation stress and similar for all materials tested, except for the stick-slip-prone maize starch and pea protein, in which case fluctuations were observed. Moreover, hardness was studied as a function of applied stress, with the results showing that seven out of ten powders tested exhibited a sharper increase in hardness in the low stress region. Interestingly, the three materials that had a consistent gradient of increase in hardness with stress, the two alumina Rapol 900 grades and titania, were the only ones classified as very cohesive (flow factor of 1 - 2) across the whole range of stresses applied.

Indentation measurements along with the unconfined yield strength derived from shear tests were used to compute the constraint factor, which was found to be virtually constant regardless of the applied stress for all materials, with the exception of pea protein which exhibited fluctuations and notable error bars, due to stick-slip. The series of experiments using a set of alumina powders suggests that an increase in the irregularity of the single crystal shape may result in an increase of $C$, whereas an increase in the irregularity of the agglomerate shape might result in a decrease of the constraint factor, though this conclusion should be treated with caution, because of the error bars of the constraint factor of the two Rapol 900 alumina grades and the difficulty of classifying relevant shape factors. Also, it was observed that the order of the constraint factor values follows the order of packing fraction values among these materials, indicating that an increased packing fraction may result in an increased $C$. On the other hand, the exact opposite trend was observed in the case of the organic powders.

Furthermore, the powder flow experiments on the food powders revealed that stick-slip results in fluctuating force-displacement response of the powder bed during indentation and a ‘pile-up’ bed surface profile after unloading, whereas materials not prone to stick-slip exhibit a smooth force-displacement response and a ‘sink-in’ indentation profile. Last but not least, it was found that for stick-slip powders, the shear resistance is not independent of strain rate in the quasi-static regime, but increases with the decrease of strain rate, as do the fluctuations of the force-displacement response of the powder bed.
Chapter 6  Investigation of Powder Flowability at Low Stresses by DEM Modelling

This chapter is dedicated to the computational part of this thesis. First, the Distinct Element Method (DEM) is introduced, and some of the most widely used contact models in DEM simulations are presented, including the one employed in this research. Following this, the setup of the ball indentation simulations is described. By DEM modelling, the behaviour of the constraint factor throughout a wide range of low and high pre-consolidation stresses is investigated. Moreover, the influence of a number of particle properties (interface energy, static friction, rolling friction, plastic yield stress) on the constraint factor and subsequently powder flowability is studied.

6.1 Distinct Element Method (DEM)

The behaviour of granular materials is complex and depends on the interactions between the distinct elements, the particles, which they consist of. The study of the interactions at a microscopic level is a challenging task, which is not usually experimentally feasible, at least not in a time- and cost-efficient way. To address this issue, several numerical simulation methods for granular modelling have been developed, rendering it possible to investigate the particle interactions within a bulk solid in an efficient way. The Distinct Element Method (DEM) (also known as Discrete Element Method) constitutes the most well-established and widely used computational technique capable of describing the mechanical behaviour of particles, since it takes into account the physical and mechanical properties of each individual particle within a system. This can provide fundamental understanding of powder behaviour, with a characteristic example being the determination of the internal stresses exerted in a powder bed, which typically cannot be determined experimentally. Initially intended for rock mechanics’ studies, DEM was first introduced by Cundall (1971) and further developed by Cundall and Strack (1979), and is based on the study of the motion of each individual particle in an assembly and the forces exerted on it. In this method, an assembly of particles is considered a set of distinct rigid bodies. Under the assumption that within a short time-interval (time-step), the velocity of the particles does not change, the calculations follow a two-step cycle: first, Newton’s second law is applied to characterise the motion of each particle (both translation and rotation are considered), which is monitored, and then a force-displacement model is used to determine the contact forces between neighbouring particles, resulting from their deformation, which is represented by allowing
them to overlap whilst maintaining their fixed shape. The greater the overlap, which is usually not more than a few % of the particle radius, the larger the subsequent contact force is. At each time-step, the position of each particle is updated and its interactions are re-assessed, with a complete description of each individual particle’s behaviour being obtained over the course of the simulation.

In reality, the movement of a particle within an assembly is not only influenced by the normal and rotational forces that arise when it comes into contact with neighbouring particles, but also from disturbance propagation from particles that are far away from its position. A short enough time-step to ensure that these disturbance waves do not travel beyond neighbouring particles is considered, resulting in the disturbances propagating through successive time-steps (Cundall and Strack, 1979). The speed of the disturbance waves is approximated by Rayleigh surface wave propagation based on the properties of the simulated material. The time-step must be sufficiently smaller than the Rayleigh time-step, else the disturbances can potentially cause instability in the simulated system and jeopardise the depiction of the true behaviour of the particles. The Rayleigh time-step, \( T_R \), is given by Equation 6.1 (EDEM User Guide):

\[
T_R = \frac{\pi R \left( \frac{\rho_p}{G} \right)^{1/2}}{0.1631 \nu + 0.8766} \tag{6.1}
\]

where \( G \) is the shear modulus of the particles. If the system consists of particles that have different properties, the smallest time-step among all should be considered for safety purposes (Ning and Ghadiri, 2006). A time-step close to \( 0.2T_R \) is typically used in DEM simulations (EDEM User Guide).

In recent years, the continuous improvement of computer performance and development of rigorous models more accurately representing the true contact mechanics between particles have resulted in a substantial increase in DEM use as a research tool. This has also translated in the field of powder flow, with Hare and Ghadiri (2013), Pasha et al. (2013) and Höhner et al. (2014) being examples of researchers that have employed DEM simulations on powder flow studies.

### 6.2 DEM contact force models

When two particles collide, the resulting forces, both normal (translational) and tangential, lead to a degree of elastic and possibly plastic deformation at the point of contact, which corresponds to an extent of overlap in DEM simulations. In addition to this, in reality, adhesive forces, such as van der Waals forces, exist between contacting particles. As mentioned in section 6.1, in DEM, the forces acting between particles are determined with the use of a force-displacement model. Over the years, several contact models have been developed for the representation of the contact mechanics between the individual elements in a particulate system, some of which can also depict the adhesive
behaviour of the particles. Continuous work is carried out in academia in order to improve the computational efficiency and accuracy of existing models and develop new models which can represent the behaviour of particular particle assemblies even more realistically, since the model used should depend on the material. Most commonly, these physical models use perfect spheres, since they are the easiest to simulate. In a DEM simulation, at each time-step, the chosen contact force model is applied at each contact of each particle, and the overall contact force acting on a given particle is determined as the vectorial sum of the forces acting at each contact point it shares with a neighbouring one (Cundall and Strack, 1979). A review of some of the most widely used DEM contact models is presented below. Extensive reviews have been carried out by Zhu et al. (2007) and Pasha (2013).

6.2.1 Linear spring-dashpot contact model
The linear spring-dashpot is a rather simple contact model which was introduced by Cundall and Strack (1979). In this model, the deformation corresponds to a linear spring, and the contact force between two perfectly elastic spheres is resolved into normal and tangential (shear) components with respect to the contact plane. The normal contact force, $F_n$, is given by Equation 6.2:

$$F_n = F'_n + \Delta F_n \quad (6.2)$$

where $F'_n$ is the previous normal force and $\Delta F_n$ is the increment of the normal force, which is quantified based on the overlap of the particles in contact from Hooke’s law (Equation 6.3):

$$\Delta F_n = k_n \Delta a \quad (6.3)$$

where $\Delta a$ is the increment of the normal displacement (overlap) of the contact and $k_n$ is the normal stiffness at the contact, which is given by Equation 6.4:

$$k_n = \frac{k_n^1 k_n^2}{k_n^1 + k_n^2} \quad (6.4)$$

where $k_n^1$ and $k_n^2$ are the normal stiffness values of the elements in contact.

The tangential force, $F_t$, is quantified from Equation 6.5:

$$F_t = F'_t + \Delta F_t \quad (6.5)$$

where $F'_t$ is the previous tangential force and $\Delta F_t$ is the increment of the tangential force, which is calculated from Equation 6.6:

$$\Delta F_t = k_t \Delta a_t \quad (6.6)$$
where $\Delta \alpha_t$ is the increment of the tangential displacement of the contact and $k_t$ is the tangential stiffness at the contact, which is given by Equation 6.7:

$$k_t = \frac{k_t^1 k_t^2}{k_t^1 + k_t^2} \quad (6.7)$$

where $k_t^1$ and $k_t^2$ are the tangential stiffness values of the elements in contact.

### 6.2.2 Hertzian contact model

The Hertzian normal contact model (Hertz, 1882) is a non-linear model, in which the normal contact force between two perfectly elastic spheres in contact is calculated from Equation 6.8:

$$F_n = \frac{4}{3} E^* R^{1/2} a^{3/2} \quad (6.8)$$

where $a$ is the normal overlap and $E^*$ is the reduced Young’s modulus given by Equation 6.9:

$$E^* = \left( \frac{1 - \nu_1^2}{E_1} + \frac{1 - \nu_2^2}{E_2} \right)^{-1} \quad (6.9)$$

where $E_1$ and $E_2$, and $\nu_1$ and $\nu_2$ are the Young’s moduli and the Poisson’s ratios of the two elements in contact, respectively.

### 6.2.3 Mindlin’s tangential contact model

Perhaps the most widely used model for the determination of tangential displacement is the tangential contact model proposed by Mindlin and Deresiewicz (1953), and in particular its simplified version, known as Mindlin’s ‘no-slip’ model, which is based on Mindlin’s theory of ‘no-slip’ in the tangential direction (Mindlin, 1949). The initial version of the model takes into account the tangential slip at the contact, due to which the tangential force-displacement depends on the loading history of the contact and the rate of change of both the normal and tangential force. The simplified version disregards the hysteretic behaviour accounting for the micro-slip in the original model, and both loading and unloading follow the same curve, with the tangential force given by Equation 6.10:

$$F_t = -k_t a_t \quad (6.10)$$

where $a_t$ is the tangential overlap. The tangential stiffness is calculated from Equation 6.11:

$$k_t = 8 G^* \sqrt{R' a} \quad (6.11)$$

where $G^*$ is the reduced shear modulus given by Equation 6.12:

$$G^* = \left( \frac{1 - \nu_1^2}{G_1} + \frac{1 - \nu_2^2}{G_2} \right)^{-1} \quad (6.12)$$
where $G_1$ and $G_2$ are the shear moduli of the two elements in contact.

### 6.2.4 JKR contact model

As aforementioned in chapter 2, according to JKR theory (Johnson et al., 1971), van der Waals forces only act within the area of contact between particles. The adhesion force, also known as the pull-off force, is a function of the interface energy of the particles, as described from Equation 4.1 (section 4.4.1). In this model, the contact area between two perfectly elastic and adhesive spheres comprises an inner circular Hertzian contact area and an outer annular area that surrounds this, in which tensile stress is exerted because of the acting adhesive force, therefore the overall contact area is larger as compared to the Hertzian one (Thornton and Yin, 1991). The model is shown in Figure 6.1.

![Figure 6.1. JKR contact model (Pasha, 2013)](image)

When two spherical particles come into contact at an overlap equal to zero, the normal force will instantly drop to a negative force equal to $8/9$ of the pull-off force, due to van der Waals forces (Thornton and Ning, 1998). At this point, the velocity of a given particle, and therefore its kinetic energy, starts decreasing until it becomes zero when the contact force has reached a maximum value and loading is finished. The kinetic energy lost has been transferred to its neighbouring particles in the form of elastic waves. During unloading, the elastic energy gathered by the neighbouring particles is released in the form of kinetic energy, resulting in the particles moving in opposite directions. Unloading is completed when all the work done during loading has been recovered at zero overlap, however the contact isn’t broken yet due to the adhesive force, with additional work needed in order
for the particles to separate, which is known as the work of adhesion. The contact breaks at a negative overlap, \( \alpha_n \), with the normal contact force at this point being 5/9 times the pull-off force, which corresponds to the maximum tensile stress exerted on the contact (Ning, 1995). The normal contact force is given by Equation 6.13, with the overlap calculated from Equation 6.14 (Johnson, 1985):

\[
F_n = \frac{4E^*a^3}{3R^*} - \left(8\pi E^*a^3\right)^{1/2} \tag{6.13}
\]

\[
a = \frac{a^2}{R^*} - \left(\frac{2\pi a}{E^*}\right)^{1/2} \tag{6.14}
\]

### 6.2.5 Luding’s contact model

Luding’s model (Luding, 2008) constitutes a simplified version of the elasto-plastic and adhesive model developed by Tomas (Tomas, 2007). The normal force-overlap response of the model is depicted in Figure 6.2.

![Figure 6.2. Luding’s contact model (Luding, 2008)](image)

In this model, the normal force will instantly decrease to a negative value, \( f_0 \), when two spherical particles come into contact, due to van der Waals forces. At first, the contact deformation is plastic, with the normal force increasing linearly with a plastic stiffness, \( k_p \), until a maximum overlap, \( \alpha_{\text{max}} \), has been achieved. The unloading stage is governed by an elastic stiffness, \( k_e \). With the unloading of the contact, the normal force becomes zero at an overlap of \( \alpha_p \), which represents the plastic contact deformation. Loading is reversible, with reloading following the elastic stiffness, \( k_e \), until the previous
maximum force is reached. If the overlap during reloading becomes greater than \( \alpha_{\text{max}} \) though, the normal force is once more governed by the plastic stiffness, \( k_p \), and \( \alpha_{\text{max}} \) is re-calculated. Regarding the unloading, if an overlap below \( \alpha_p \) is reached, an adhesive force (pull-off force) arises, which reaches a maximum value, \( f_{cp} \), at an overlap of \( \alpha_{cp} \). The greater \( \alpha_{\text{max}} \) is, the larger the negative value of \( f_{cp} \) is. Beyond this point (\( \alpha_{cp} \)), additional unloading results in a decreasing pull-off force following a negative stiffness -\( k_c \), where \( k_c \) is the cohesive stiffness. If the overlap reduces below \( \alpha_{cp} \) during unloading and then reloading occurs, it follows a linear line parallel to the initial unloading line. Furthermore, in this model, up to a certain overlap, the greater the maximum overlap is, the greater the elastic stiffness is. This threshold is the plastic flow limit overlap, \( \alpha^* \), defined by Equation 6.15:

\[
\alpha^* = \frac{\hat{k}_e}{\hat{k}_e - k_p} \phi_f 2R^* \quad \text{(6.15)}
\]

where \( \hat{k}_e \) is the maximum value of the elastic stiffness and \( \phi_f \) is the dimensionless plasticity depth. For maximum overlaps until this limit, the elastic stiffness is given by Equation 6.16:

\[
k_e = k_p + (\hat{k}_e - k_p) \frac{\alpha_{\text{max}}}{\alpha^*} \quad \text{(6.16)}
\]

Beyond \( \alpha^* \), the elastic stiffness is considered to be equal to \( \hat{k}_e \) and independent of the maximum overlap.

Moreover, the tangential force of the model follows a linear tangential stiffness similar to the linear spring-dashpot model.

Although Luding’s model is elasto-plastic and adhesive, it suffers from two significant drawbacks. The contact breaks at zero overlap, disregarding loading and unloading history, which translates to plastic deformation not being permanent, which of course is not the case in reality. Secondly, at overlaps smaller than \( \alpha_{cp} \), unloading is supposed to be elastic, hence reloading until the maximum overlap is reached should be possible, beyond which the plastic stiffness is followed, but this is not the case.

### 6.2.6 Thornton and Ning’s contact model

Thornton and Ning’s elasto-plastic and adhesive model (Thornton and Ning, 1998) is based on the model developed by Thornton (1997) for elastic-perfectly plastic spheres. The model’s force-overlap response is presented in Figure 6.3:
In this model, the assumption is made that the pressure distribution over the contact area is Hertzian with a cut-off at the limiting contact pressure, based on which Equation 6.17 is derived for the contact yield pressure, $p_y$:

$$p_y = \frac{2E^*a_y}{\pi R^*} - \left( \frac{2\Gamma E^*}{\pi a_y} \right)^{1/2} \quad (6.17)$$

where $a_y$ is the overlap at which the plastic yield occurs. The elastic deformation prior to the plastic yield follows Hertz (Equation 6.8), whilst plastic deformation linearly follows the stiffness given by Equation 6.18:

$$k_n = \frac{3\pi R^*\sigma_y - 2E^*a_y \left( \frac{a_c}{a} \right)^{3/2}}{3 - \left( \frac{a_c}{a} \right)^{3/2}} \quad (6.18)$$

where $\sigma_y$ is the plastic yield stress, $a$ is the JKR overlap in Equation 6.14, from which the normal overlap is calculated, and $a_c$ is the overlap at the pull-off force (not shown in Figure 6.3) computed from Equation 6.19:

$$a_c = \left( \frac{3R^*f_{ce}}{4E^*} \right)^{1/3} \quad (6.19)$$

where $f_{ce}$ is the JKR pull-off force.

If plastic deformation is initiated during loading, the contact curvature during unloading is less than that of elastic unloading, due to permanent contact deformation. During unloading, the force-overlap
response is elastic-adhesive and is described by the JKR model equations, but with a curvature of $R^*_p$ at the maximum force during plastic deformation, $F_{\text{max},p}$, which is given by Equation 6.20:

$$R^*_p = \frac{R^*F^*_{\text{max}}}{F_{\text{max},p} + \sqrt{4f_{ce}F^*_{\text{max}}}}$$  (6.20)

where $F^*_{\text{max}}$ is the equivalent JKR force of $F_{\text{max},p}$.

Furthermore, in this model, the plastic pull-off force, $F_{cp}$, is quantified from Equation 6.21:

$$F_{cp} = \frac{3}{2} \pi R^*_p \Gamma$$  (6.21)

The contact breaks at $\alpha_{fp}$ overlap, at which point the contact force is equal to 5/9 times the plastic pull-off force. It can be re-established though, if the particles contact again, at a greater overlap, $\alpha_{co}$, where the contact force is equal to 8/9 times $F_{cp}$ (Ning, 1995).

### 6.2.7 Pasha et al. contact model

The linear elasto-plastic and adhesive contact model of Pasha et al. (Pasha et al., 2014) is a simplified version of the model by Thornton and Ning (1998), but is less computationally costly. Also, it considers aspects of Tomas (Tomas, 2007), Luding (Luding, 2008) and Walton and Johnson’s (Walton and Johnson, 2009) models. The force-displacement behaviour of the model is shown in Figure 6.4.

![Figure 6.4. Pasha et al. contact model (Pasha et al., 2014)](image-url)
At first, when two spherical particles come into contact at an overlap, \( \alpha \), equal to zero, the contact force immediately reduces to a negative force, \( f_0 \), to represent van der Waals forces. The deformation is initially elastic, with an elastic stiffness, \( k_e \). The elastic deformation at the beginning follows a linear version of JKR theory with the tensile force at the contact, \( f_0 \), being equal to \( \frac{8}{9} \) times the JKR elastic pull-off force given by Equation 4.1, and depicted as \( f_{ce} \) in Figure 6.4 (point B). For the BC line of the graph, the normal contact force is given by Equation 6.22:

\[
F_n = k_e a + \frac{8}{9} f_{ce} \tag{6.22}
\]

While the deformation is elastic, the unloading curve follows the same elastic stiffness, \( k_e \), first reaching an overlap, \( a_0 \), at which the unloading force becomes zero, and then continues until point B. Further unloading, beyond point B, follows a ‘stiffness’ equal to -\( k_e \), with contact breakage occurring at a negative overlap, \( a_{fe} \) (point A), at which the contact force is equal to \( \frac{5}{9} \) times the JKR elastic pull-off force. During loading, after a certain load has been applied, an overlap equal to \( \alpha_y \) (point C) is achieved, beyond which the deformation is plastic until point D, with a plastic stiffness, \( k_p \). The transition point from elastic to plastic behaviour, \( \alpha_y \), is governed by the plastic yield stress of the simulated material, \( \sigma_y \). The deformation on the CD line is computed from Equation 6.23:

\[
F_n = k_p (a - a_{op}) \tag{6.23}
\]

where \( a_{op} \) is the overlap at which the extrapolated plastic loading curve CD intercepts the x-axis.

Once the deformation has transitioned to plastic, unloading proceeds after reaching \( a_{max} \) (point D) with elastic stiffness (\( k_e \)), reaching first an overlap, \( a_p \), at which the unloading force becomes zero, with the contact force in this part of the graph given by Equation 6.24:

\[
F_n = k_e (a - a_p) \tag{6.24}
\]

Then, unloading continues until the maximum tensile force, known as the pull-off force, \( f_{cp} \), is reached (point E), at an overlap of \( a_{cp} \). Unloading beyond this point is governed by a ‘stiffness’ equal to -\( k_e \) until the contact breaks at an overlap of \( \alpha_{fp} \), with the force being \( \frac{5}{9} \) times the pull-off force, \( f_{cp} \) (point F). On the EF line the contact force is calculated from Equation 6.25:

\[
F_n = -k_e (a - 2a_{cp} + a_p) \tag{6.25}
\]

The plastic deformation described by this model is reversible. If the two particles come towards each other again after the contact has been broken, the contact is re-established at an overlap of \( a_{a0} \), which is slightly larger than \( \alpha_{cp} \), because the particles relax after contact breakage, with the contact force being \( \frac{8}{9} \) times the pull-off force, \( f_{cp} \). The pull-off force, \( f_{cp} \), and the overlap at contact breakage, \( \alpha_{fp} \),
are determined based on the interface energy, $\Gamma$, and the maximum contact force, $f_{max}$, which is achieved at the maximum overlap, $a_{max}$ (point D). As the degree of plastic deformation, $\alpha_{cp}$, increases, so does the pull-off force. For computational cost-efficiency purposes, the linearised version of the contact model's pull-off force curve, which is shown in Figure 6.5, is used in this work, where the pull-off force is given by Equation 6.26:

$$f_{cp} = -k_{cp}a_{cp} + f_{op} \quad (6.26)$$

where $k_{cp}$ is the slope of the linear fit to the pull-off force curve and $f_{op}$ is the intercept of the fit with the force axis.

![Figure 6.5. Pull-off force as a function of $\alpha_{cp}$ (Pasha et al., 2014)](image)

For tangential displacement, the tangential stiffness is taken to be linear, like in the cases of the linear spring-dashpot and Mindlin’s models, and is given by Equation 6.27:

$$F_t = k_t a_t \quad (6.27)$$

For all DEM simulations in this thesis, the linear elasto-plastic and adhesive contact model of Pasha et al. (Pasha et al., 2014) was used.

### 6.3 Ball indentation simulations setup

In this work, the ball indentation method is simulated using DEM to determine the constraint factor throughout a wide range of low and high pre-consolidation stresses, and to investigate the effects of various particle properties on the constraint factor and subsequently powder flowability. EDEM® DEM software provided by DEM Solutions (Edinburgh, UK) was used to simulate the ball indentation system,
which is shown in Figure 6.6. The criteria for sample, die and indenter dimensions established by Pasha (2013) and Zafar (2013) were adhered to for the simulation work carried out. The indenter velocity was set to 0.057 m/s during loading and unloading, which resulted in a strain rate of 2 s⁻¹, assuming strain rate is equal to indenter velocity divided by indenter radius. This corresponds to a dimensionless strain rate of around 0.03, therefore testing in the slow, frictional regime (Tardos et al., 2003). For computational efficiency a particle size greater than the experimental materials was used, however these particles were made cohesive using the Pasha et al. model (Pasha et al., 2014). The contact model captures the attractive forces brought about by van der Waals interactions, but does not consider adhesive forces caused by electrostatics and capillary interactions. Around 68,000 spherical particles of 33.3 % w/w 1 mm, 33.3 % w/w 1.43 mm and 33.3 % w/w 1.86 mm radius were generated inside a cylindrical die of 65 mm radius and 500 mm height, with an initial downward velocity of 0.5 m/s, and allowed to settle under gravity, so that a powder bed height of approximately 72 mm was obtained. The particles created were given a size distribution in order to avoid ordered packing. Once the particles had settled, which was indicated by their average velocity having reached a negligible value (≈ 0.001 m/s), a cylindrical piston of 65 mm radius was generated above the powder bed, and driven downwards at a velocity of 0.057 m/s, as aforementioned, until contact was made, at which point a servo-control mechanism modified the piston velocity until the target vertical stress was achieved. The target stress was maintained for a short period (0.2 - 0.3 s), before unloading the piston at the same velocity until the vertical stress was zero, and finally removing it from the simulation. Following this consolidation step, a 28.5 mm radius spherical indenter, which is a mesh geometry designed in CAD, was imported in EDEM® above the consolidated powder bed, and driven downwards at the same velocity as the piston until a penetration depth of approximately 26 mm ($h_d = 0.9$) was obtained.

![Figure 6.6. Ball indentation in EDEM® (a: simulated ball indentation system, b: stress measurement cell)](image-url)
All the particles simulated were given properties similar to nylon, having a particle density of 1,000 kg/m$^3$, a Young’s modulus of 2 GPa and a Poisson’s ratio of 0.25. The properties of both particle-particle and particle-wall interactions that were used for all simulations throughout the thesis are shown in Table 6.1, with the particle-particle and particle-wall values reported referring to the values given for the interactions between two mid-sized particles, and a mid-sized particle and the geometries, respectively.

<table>
<thead>
<tr>
<th>Property</th>
<th>Particle-Particle</th>
<th>Particle-Wall</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_e$ (kN/m)</td>
<td>165</td>
<td>165</td>
</tr>
<tr>
<td>$k_p$ (kN/m)</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>$k_t$ (kN/m)</td>
<td>165</td>
<td>165</td>
</tr>
<tr>
<td>$k_{cp}$ (kN/m)</td>
<td>1.43</td>
<td>0</td>
</tr>
<tr>
<td>$f_0$ (N)</td>
<td>-0.117</td>
<td>0</td>
</tr>
<tr>
<td>$f_{0p}$ (N)</td>
<td>-0.0148</td>
<td>0</td>
</tr>
<tr>
<td>$e$ (-)</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>$\mu_s$ (-)</td>
<td>0.1, 0.3, 0.5</td>
<td>0.1</td>
</tr>
<tr>
<td>$\mu_r$ (-)</td>
<td>0.01, 0.05, 0.1</td>
<td>0.01</td>
</tr>
<tr>
<td>$\Gamma$ (J/m$^2$)</td>
<td>1, 2, 5, 10, 20</td>
<td>0</td>
</tr>
<tr>
<td>$\sigma_y$ (MPa)</td>
<td>11.25, 22.5, 45</td>
<td>-</td>
</tr>
</tbody>
</table>

$e$, $\mu_s$, and $\mu_r$ in Table 6.1 are the coefficients of restitution, static friction (also known as sliding friction) and rolling friction, respectively. The coefficient of restitution is the ratio of speed of separation to speed of approach in a collision (EDEM User Guide). The coefficient of static friction is a scalar value used to determine how much force is required before an inert object, of a given material, at rest on another known substance, can be put into motion, whilst the coefficient of rolling friction is a scalar value used to determine how much torque is needed to be applied to an object of a given material at rest on a flat surface to put it into motion, and represents non-sphericity. In the case of interparticle interactions, both the object and the surface on which is at rest are the simulation particles. The default values for the coefficients of restitution, static friction and rolling friction were chosen to be close to the ones used in the work of Pasha (2013). The radii, Young’s moduli and Poisson’s ratios of the two particles in contact, along with the interface energy and the plastic yield stress, are direct inputs for a MATLAB code provided by Dr. Massih Pasha (The Chemours Company, USA) that was used to compute $k_e$, $k_p$, $k_t$, $k_{cp}$, $f_0$ and $f_{0p}$, which in turn are inputs for the contact model used. Since each simulation contained a range of particle sizes, the different interface energy values between particles of different radii needed to be considered. In this regard, the interface energy of particles of different size was scaled following the recommendation of Thakur et al. (2016) using Equation 6.28:

$$\frac{\Gamma_{p2}}{\Gamma_{p1}} = \left(\frac{R_{p2}}{R_{p1}}\right)^2 \quad (6.28)$$
where $\Gamma_{p1}$, $\Gamma_{p2}$ and $R_{p1}$, $R_{p2}$ are the values of interface energy and the radii of particle size 1 and particle size 2, respectively. Subsequently, the stiffness values, $f_0$ and $f_{op}$ changed with size.

In each simulation, the integration time-step, $t_{sim}$, was computed based on a mass-spring system by Equation 6.29 (Pasha, 2013):

$$t_{sim} = 0.2 \sqrt{\frac{m_{\text{smallest}}}{k_{\text{largest}}}} \quad (6.29)$$

where $m_{\text{smallest}}$ is the mass of the smallest particle in the system and $k_{\text{largest}}$ is the largest stiffness in the system.

The particle flow field at the dimensionless penetration depth of 0.5 is shown in Figure 6.7 for the simulation with the default values from Table 6.1, with the particles coloured based on their magnitude of velocity. It can be seen that the flowing portion of the bed is confined to a narrow region (approximately 3 - 5 particle diameters wide) surrounding the indenter.

![Figure 6.7. Visualisation of the particle flow field around the indenter at $h_d = 0.5$ (a: the assembly is clipped by a plane y-direction, b: -Z plane view)](image)

In all simulations carried out throughout this work, hardness was calculated using Equation 2.16. For the calculation of the projected area of the impression of the indenter (Equation 2.17), the penetration depth at maximum indentation load was considered, assuming unloading has negligible effect on the simulated material’s bed recovery. The region of interest is the plastically deformed area right beneath the indenter, therefore a 13.5 mm length cubic measurement cell (containing approximately 90 - 590 particles) was created directly beneath and centrally aligned with the indenter, and its position was
fixed relative to the indenter (Figure 6.6). The forces acting on every particle whose centre was within the measurement cell were calculated, and the $ij$-component of the stress tensor in the measurement cell, $\sigma_{ij}$, was determined following the approach of Bagi (1996) via Equation 6.30:

$$\sigma_{ij} = -\frac{1}{V_m} \sum_{N_p} \sum_{N_c} |x^c_i - x^p_i| n_i F_j \quad (6.30)$$

where $V_m$ is the volume of the measurement cell, $N_p$ is the number of particles in the measurement cell, $N_c$ is the number of contacts around particle $p$, $x^c_i$, $x^p_i$ and $n_i$ are the $i$-components of contact location, particle centre location and normal vector directed from a particle centroid to its contact, respectively, and $F_j$ is the $j$-component of the contact force. The term $|x^c_i - x^p_i|$ is approximately equal to the particle radius, therefore was replaced by particle radius in Equation 6.30. This stress calculation is implemented as a subroutine for EDEM® software.

The deviatoric stress, $\tau_D$, corresponding to the shear stress was calculated using Equation 6.31:

$$\tau_D = \sqrt{\left(\frac{\sigma_1 - \sigma_2}{2}\right)^2 + \left(\frac{\sigma_1 - \sigma_3}{2}\right)^2 + \left(\frac{\sigma_2 - \sigma_3}{2}\right)^2} \quad (6.31)$$

where $\sigma_3$ is the intermediate principal stress. The three principal stresses were determined from the nine components of the stress tensor.

In order to determine the constraint factor, it is necessary to know the hardness and the unconfined yield strength. The hardness can be determined in the DEM simulations using Equation 2.16, however the unconfined yield strength cannot be determined in the ball indentation simulations. As such, an alternative method is needed. Considering a set of experimental shear cell data of 63 - 75 \(\mu\)m silanised glass beads (S), alumina CT800SG (A), limestone (L) and maize starch (M) from those reported in chapters 4 and 5, a strong, approximately linear relationship is found between the shear stress and the unconfined yield strength, particularly at the lower applied stress of 1 kPa, which is closer to the failure Mohr circle, as shown in Figure 6.8. Therefore, the term $C'$ is used instead of the constraint factor, by using the deviatoric (shear) stress in place of the unconfined yield strength, as shown in Equation 6.32:

$$C' = \frac{H}{\tau_D} \quad (6.32)$$

It is noted that $C'$ will be larger than $C$, since deviatoric stress close to the failure Mohr circle (1 kPa in Figure 6.8) is smaller than unconfined yield strength, however it is proportional to $C$. Therefore, any trends observed for $C'$ also apply to $C$. 
Figure 6.8. Shear stress against unconfined yield strength at a pre-shear normal stress of 6 kPa, showing steady-state and three points of incipient failure (first, third and fifth point)

6.4 Investigation of the behaviour of constraint factor as a function of applied stress

In this series of simulations, five different stresses, namely 0.1, 0.5, 1, 5 and 10 kPa, were applied to consolidate the powder bed prior to indentation, so that the behaviour of the constraint factor as a function of the applied stress can be studied. The default values of particle-particle and particle-wall interactions, which are highlighted in bold in Table 6.1, were used for the setup of all five simulations.

Figure 6.9 shows hardness against dimensionless penetration depth in the range of 0.2 - 0.9, at all five pre-consolidation stresses. Hardness was overestimated at very shallow depths due to the limited number of contacts and therefore inaccuracy in estimating the projected area of the impression, hence the dimensionless penetration depth of 0.2 was considered as the minimum depth for data analysis. Hardness is found to increase with applied stress, and is virtually independent of penetration depth beyond a dimensionless penetration depth of 0.4, though some fluctuations are present. Greater pre-consolidation stresses lead to more tightly packed powder beds, hence hardness increases due to an increased packing fraction, as shown in Figure 6.10, where the packing fraction at maximum compression is plotted against pre-consolidation stress. Also, it can be seen that as the pre-
consolidation stress is increased, the minimum depth required to reach the stable hardness region increases, with the threshold being a dimensionless penetration depth of about 0.2 and 0.4 in the cases of beds compressed at 0.1 and 10 kPa, respectively.

Figure 6.9. Hardness against dimensionless penetration depth at five pre-consolidation stresses
Figure 6.10. Packing fraction against pre-consolidation stress

Figure 6.11 shows the deviatoric stress against dimensionless penetration depth for the five pre-consolidation stresses. There is a general increase in deviatoric stress with pre-consolidation stress, while it does not exhibit any general increases or decreases with penetration depth. It is noteworthy that significant fluctuations occur, which are more significant than the fluctuations of hardness.
Using Equation 6.32, $C'$ was quantified, and is plotted as a function of dimensionless penetration depth at all five pre-consolidation stresses in Figure 6.12. $C'$ is found to fluctuate around a fixed value for a given pre-consolidation stress, being virtually constant and independent of the pre-consolidation stress applied. In addition to this, the average $C'$ was calculated through the dimensionless penetration depth range of 0.4 - 0.8, and is presented against pre-consolidation stress in Figure 6.13, with error bars showing the standard deviation throughout this penetration depth range. Figure 6.13 confirms that the average $C'$ remains relatively constant throughout the range of pre-consolidation stresses. Previously, in chapters 4 and 5, it wasn’t possible to compute $C$ at low stresses, due to the inability of shear cells to give reliable and repeatable results in this stress range. Therefore, in order to infer the yield strength of powders at low stresses, $C$ was determined at moderate to high stresses, and since it was constant in this range, it was assumed that it would remain constant in the low stress range. The data from Figures 6.12 and 6.13 suggest that the aforementioned assumption is valid. The fact that the constraint factor remains constant at low stresses means that it is possible to determine the constraint factor from hardness and unconfined yield strength measurements at moderate to high stresses by performing ball indentation and shear cell experiments, respectively, and use the same value of constraint factor in order to infer the unconfined yield strength of powders from ball indentation measurements at low stresses.
Figure 6.12. $C'$ against dimensionless penetration depth at five pre-consolidation stresses

Figure 6.13. Average $C'$ in the depth range of 0.4 - 0.8 against pre-consolidation stress
6.5 Study of the influence of various particle properties on
constraint factor and powder flow behaviour

6.5.1 Effect of interface energy

In this series of simulations, powder beds of five different values of interparticle interface energy, namely 1, 2, 5, 10 and 20 J/m$^2$, were consolidated at 1 kPa and penetrated by the indenter. All five simulations were carried out with the default values given in Table 6.1 (indicated in bold), except for the interparticle interface energy which was the only property varied with the aim of studying its influence on the constraint factor. In Figure 6.14 hardness is shown against dimensionless penetration depth for all five values of interface energy. In the cases of the two powder beds with the lowest values of interface energy, hardness increases continually with depth. This indicates that for these relatively cohesionless powders the bed was consolidated during the indentation test, rendering the measurement unreliable. For the middle value of interparticle interface energy, hardness is constant across the whole range of penetration depths, while for the two higher values of interface energy it exhibits the same behaviour beyond a dimensionless penetration depth of around 0.25. An increased interface energy results in greater cohesion, and therefore greater resistance to plastic deformation. The deviatoric stress variation with depth is shown for each interface energy value in Figure 6.15. Although notable fluctuations exist, there is an increase of deviatoric stress with increasing interface energy. Qualitatively similar findings have been reported in the work of Pasha (2013).
Figure 6.14. Hardness against dimensionless penetration depth for five different values of interface energy

Figure 6.15. Deviatoric stress against dimensionless penetration depth for five different values of interface energy
Figure 6.16 shows $C'$ against dimensionless penetration depth, where for a given value of interface energy, $C'$ fluctuates around a fixed value beyond a dimensionless penetration depth of 0.4. There is a general increase of $C'$ with interface energy, as the interface energy is increased from 2 to 5 J/m$^2$. This behaviour is seen more clearly in Figure 6.17, where the average value of $C'$ in the dimensionless penetration depth range of 0.4 - 0.8 is presented against interface energy. An increase in interface energy from 1 to 2 J/m$^2$ leads to a slight increase of $C'$, while a further increase to 5 J/m$^2$ results in a substantial increase in $C'$, from around 2.5 to around 3.8. It should be noted that 5 J/m$^2$ is the lowest value of interface energy applied for which the powder bed does not appear to be consolidated during indentation. A further increase of interface energy from 5 to 20 J/m$^2$ leads to no significant change in the value of $C'$. This suggests that for powder beds that are sufficiently cohesive to be tested by ball indentation, interface energy does not influence the constraint factor. The influence of surface energy on $C$ was also experimentally investigated using coated and uncoated fine glass beads, with the findings reported in section 4.4.2. As it is evidenced from Figure 4.36, the experimental work resulted in constraint factor values with large error bars, hence it wasn’t possible to draw clear conclusions. However, the DEM work helped elucidate the influence of interface energy on $C'$ and subsequently $C$, a fact highlighting its importance as a research tool.

![Figure 6.16. $C'$ against dimensionless penetration depth for five different values of interface energy](image-url)
6.5.2 Effect of static friction

Three simulations of ball indentation at 1 kPa pre-consolidation stress were run using different values of the coefficient of static friction for interparticle interactions. All the other simulation parameters were given the default values from Table 6.1, with the aim to isolate and study the influence of interparticle static friction on the constraint factor. Figure 6.18 shows the hardness variation with penetration depth for the different values of static friction coefficient. It can be seen that \( \mu_s \) values of 0.1 and 0.3 lead to a constant hardness throughout the range of dimensionless penetration depths presented, whereas when the interparticle friction is further increased to 0.5 the hardness is relatively constant in the depth range of 0.3 - 0.5, but then increases notably at a depth of around 0.5, from which point onwards it remains relatively constant. In contrast to this, it can be seen in Figure 6.19 that the deviatoric stress fluctuates around a relatively constant value until a dimensionless penetration depth of 0.8, beyond which it increases for all coefficient of static friction values. Also, increasing the static friction coefficient from 0.1 to 0.3 leads to an increase of deviatoric stress, whilst increasing \( \mu_s \) to 0.5 leads to no further increase. It is expected that increased friction will result in a greater internal resistance to shear deformation, but after a certain level of static friction (\( \mu_s = 0.3 \) in this case), Coulomb’s sliding criterion is not met by the particle’s tangential force in certain contacts, and as such contact sliding does not take place. For these non-sliding contacts, a further increase in

![Figure 6.17. Average \( C' \) in the depth range of 0.4 - 0.8 against interface energy](image)
The coefficient of static friction does not lead to any increase in the shear stress, since these contacts remain in a non-sliding condition. This finding agrees with the work of Gröger and Katterfeld (2006) and Pasha (2013), who also showed a limiting \( \mu_s \) beyond which the shear stress does not increase.

**Figure 6.18.** Hardness against dimensionless penetration depth for three different values of coefficient of static friction

\( s.f.=0.1 \)
\( s.f.=0.3 \)
\( s.f.=0.5 \)
As can be seen, $C'$ is relatively constant regardless of the applied penetration depth, but it is not clear whether static friction has any influence on $C'$, since it fluctuates around a similar value for all values of the coefficient of static friction. Figure 6.21 shows the average $C'$ in the dimensionless penetration depth range of 0.2 - 0.8, which displays a slight reduction with an increase of the coefficient of static friction. However, since the error bars are large, this result is considered to be statistically insignificant.
Figure 6.20. $C'$ against dimensionless penetration depth for three different values of coefficient of static friction

Figure 6.21. Average $C'$ in the depth range of 0.2 - 0.8 against coefficient of static friction
6.5.3 Effect of rolling friction

Ball indentation simulations at 1 kPa pre-consolidation stress were carried out for three different values of coefficient of interparticle rolling friction, whilst the default values from Table 6.1 were used for the other simulation parameters. Figure 6.22 shows that an increase in $\mu_r$ from 0.01 to 0.05 leads to an increased hardness, whilst further increase to a value of 0.1 leads to an almost negligible reduction of hardness. In all cases, hardness remains constant beyond a dimensionless penetration depth of 0.4. Figure 6.23 shows that the deviatoric stress exhibits the same behaviour against penetration depth as hardness, whilst it shows that increasing the rolling friction coefficient from 0.01 to 0.05 results in a slight increase of the shear stress, but further increasing it to 0.1 results in a clear reduction of shear stress. This reduction in shear stress could be due to a decrease in packing fraction, which translates to a smaller force required for shearing.

![Figure 6.22. Hardness against dimensionless penetration depth for three different values of coefficient of rolling friction](image-url)
For all values of coefficient of rolling friction, $C'$ is observed to fluctuate around a fixed value throughout the range of applied penetration depths, with the fluctuations being larger for $\mu_r = 0.1$ (Figure 6.24). The average $C'$ value in the range of 0.4 - 0.8 dimensionless penetration depth is found to be independent of the coefficient of rolling friction as it is increased from 0.01 to 0.05, and then to substantially increase from around 3.5 to around 4.5 with a further increase of $\mu_r$ to a value of 0.1 (Figure 6.25).

Figure 6.23. Deviatoric stress against dimensionless penetration depth for three different values of coefficient of rolling friction
Figure 6.24. $C'$ against dimensionless penetration depth for three different values of coefficient of rolling friction

Figure 6.25. Average $C'$ in the depth range of 0.4 - 0.8 against coefficient of rolling friction

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6.5.4 Effect of plastic yield stress

Ball indentation simulations at 1 kPa pre-consolidation stress were carried out for three different values of plastic yield stress ($\sigma_y$), while all other parameters were given the default values from Table 6.1. The hardness variation with penetration depth is shown for the different values of $\sigma_y$ in Figure 6.26. Figure 6.26 shows that as the plastic yield stress is increased the hardness decreases, which can be explained as follows. Since a higher plastic yield stress means that a greater stress needs to be overcome in order for plastic deformation to initiate, then the number of particles which plastically deform, and therefore create cohesive contacts, decreases. Therefore, since fewer cohesive contacts exist for higher plastic yield stress, then the hardness of the bed is lower. In addition to this, hardness is seen to remain relatively constant with depth for all values of $\sigma_y$. In contrast to hardness, the exerted shear stresses do not seem to be influenced by the plastic yield stress, as indicated in Figure 6.27.

![Figure 6.26. Hardness against dimensionless penetration depth for three different values of plastic yield stress](image-url)
Figure 6.27. Deviatoric stress against dimensionless penetration depth for three different values of plastic yield stress

$C'$ is plotted against dimensionless penetration depth in Figure 6.28, and is shown to be relatively constant across the whole range of penetration depths, regardless of the plastic yield stress. Furthermore, in Figure 6.29 the average $C'$ in the range of 0.2 - 0.8 dimensionless penetration depth is depicted against plastic yield stress, and is found to decrease with the increase of plastic yield stress, though noticeable error is present.
Figure 6.28. $C'$ against dimensionless penetration depth for three different values of plastic yield stress

Figure 6.29. Average $C'$ in the depth range of 0.2 - 0.8 against plastic yield stress
In both DEM and experiments, fluctuations always arise due to constant rearrangement and deformation of the particle contacts. Throughout all the simulations using the range of properties defined in Table 6.1, the fluctuations in $C'$, which are predominantly caused by fluctuations in deviatoric stress (e.g. Figure 6.27), are of similar magnitude. The increased fluctuations in DEM simulations, as compared to experiments, are attributed to the sampling frequency in DEM, 100 Hz in this work, whereas most experimental equipment only provide data at much lower frequencies. Furthermore, real materials usually behave in a more ductile manner than represented in DEM, and hence reduced fluctuations would be expected.

6.6 Concluding remarks

The ball indentation method was simulated using DEM modelling. Hardness and localised shear stresses directly beneath the indenter were calculated, and $C'$, which is representative of the constraint factor, was determined. Ball indentation simulations at different pre-consolidation stresses in the range of 0.1 - 10 kPa showed that both hardness and the shear stress increased with an increase in pre-consolidation stress, whilst $C'$ was found to be independent of the applied pre-consolidation stress. This finding is in agreement with trends previously determined experimentally, however these results demonstrate that this remains the case down to very low stresses, beyond the range that could be determined experimentally. In addition to this, the influence of a number of particle properties on the exerted stresses and the constraint factor was studied by independently varying each property. An increase in interparticle interface energy was shown to lead to an increase in hardness and deviatoric stress, and an increase in $C'$ for relatively cohesionless particles, however $C'$ was found to be independent of interface energy for cohesive particles. DEM modelling helped to explain the effect of the interface energy on the constraint factor, which wasn’t clear from the experimental work, due to the notable error bars. As for the interparticle friction coefficients, an increase in static friction resulted in an increase in hardness and shear stress, up to a certain point ($\mu_r = 0.3$), after which they remained relatively constant, whilst an increased interparticle rolling friction coefficient from 0.01 to 0.05 led to increases in both hardness and deviatoric stress, with a further increase causing them to reduce. $C'$ steadily decreased with increased static friction, although the error bars are noticeable, while it significantly increased when $\mu_r$ was increased from 0.05 to 0.1. Lastly, an increase in the plastic yield stress led to a decrease in hardness, though did not influence the deviatoric stress, hence $C'$ was reduced.
Chapter 7  Conclusions and Recommended Future Work

In this chapter, an overview of the main conclusions of this thesis is given, followed by suggestions for further research in the field, which were inspired from the work carried out in this thesis.

7.1 Conclusions

The overall aim of this PhD was to enhance the understanding of powder flowability at low consolidation stresses (≤ 1 kPa), which is of significant industrial interest for many processes, such as flow in small scale hoppers, filling and dosing of powders in capsules, feeding powders for packing and tableting machines, and dispersion in dry powder inhalers (DPI). For this purpose, the ball indentation technique developed by Hassanpour and Ghadiri (2007) was employed, with its operational range, reliability and repeatability being investigated. Alongside ball indentation, shear testing was used, whose reliability and repeatability were also assessed, in order for the constraint factor to be established. The influence of stress level and various powder properties on the constraint factor and subsequently powder flow behaviour were experimentally evaluated for a wide range of powders. This study was assisted by simulating the ball indentation method using DEM, which allowed for the powder bed internal failure stresses to be realised.

As part of this study, a comprehensive literature review was undertaken with the goal of better understanding powder flowability. In this, basic principles of powder flow and the most dominant factors that can influence it were discussed. Furthermore, the most notable powder flowability assessment techniques were presented, and evaluated based on some proposed criteria.

For the experiments of this work, at first, a wide variety of glass bead samples were tested to study powder flowability in a wide range of both low and moderate to high stresses, and the effects of a variety of properties (median particle size, width of size distribution, $d_{10}$, $d_{50}$, surface energy) on the constraint factor and flow behaviour were assessed. For all glass beads, both indentation measurements and shear testing showed an increase of hardness and unconfined yield strength, respectively, with the increase of applied stress, due to an increase in packing fraction and interparticle contact area. For most of the glass bead samples measured by indentation, hardness was found to be independent of depth for dimensionless penetration depths greater than 0.3 (tested up to 0.7). The only exception were the 0 - 20 μm samples, which exhibited an increase of hardness with depth, which was independent of the applied stress and similar for all these samples. Moreover, at
low stresses, the increase of hardness with stress was observed to be much steeper than at moderate to high stresses, due to a more significant change in packing fraction. For all samples, the constraint factor was quantified from indentation and shear cell tests at moderate to high stresses, and was shown to be independent of the applied stress, with the exception of the 0 - 20 μm glass bead samples, which displayed notable variation. C was assumed to remain constant at low stresses as well, with the hardness measurements at low stresses being used to infer the unconfined yield strength of the materials in this stress range. Ball indentation is able to measure at low stresses which cannot be reliably achieved with the shear cell. However, it should be noted that at low stresses it is very challenging to reproduce a uniformly flat powder bed surface, as well as to create a consistent packing structure, therefore bed surface asperities are particularly influential to the measurement. The results suggested that extrapolation of shear testing data from higher stresses would have led to an overestimation of yield strength at low stresses.

The increase of median particle size resulted in improved flow behaviour and a decrease in the constraint factor, whilst widening the size distribution of a sample (keeping $d_{50}$ constant) led to slightly worse flow behaviour and a decrease in C. Adding fines to a mixture decreased the flowability and increased the constraint factor, whilst adding coarse particles did not affect the unconfined yield strength, though led to a reduced hardness and a decrease in constraint factor. In addition to this, silanised glass beads showed greater yield strength and resistance to plastic deformation, as compared to uncoated glass beads. The surface energy of both coated and uncoated samples was measured by the drop test and inverse gas chromatography, but its effect on C was not clear.

A broad class of ‘real’ cohesive powders were also tested utilising both ball indentation and the FT4 shear cell. For all ‘real’ materials tested, in the applied dimensionless penetration depth range of 0.1 - 0.7, hardness was found to continually increase with the increase of the applied depth. The gradient of this increase was observed to be independent of the applied stress and similar for all materials tested, except for maize starch and pea protein powders which are prone to stick-slip and exhibited a fluctuating force response. At low stresses, alumina CT800SG, limestone, talc, copper, maize starch, maltitol and pea protein indicated a more rapid increase of hardness with stress, whereas the three powders classified as very cohesive; the two alumina Rapol 900 grades and titania, showed a consistent gradient of hardness against stress throughout the whole range of applied stresses. The constraint factor of all ‘real’ powders was found to be independent of the applied stress in the stress range tested, as in the case of glass beads, with the exception of pea protein due to the error present in indentation tests caused by stick-slip.
Testing of three alumina grades of different particle and agglomerate shape revealed that an increase in the irregularity of the single crystal shape may lead to greater values of constraint factor, whereas an increase in irregularity of the agglomerate shape might result in reduced $C$. The experimental series on three organic powders showed that stick-slip is responsible for force-displacement fluctuations during indentation and a different bed surface profile than the one exhibited by powders not prone to stick-slip. Furthermore, in the case of materials prone to stick-slip, both the shear resistance and force-displacement fluctuations were found to increase with a reduction of strain rate in the slow, frictional regime.

The reliability and repeatability of both ball indentation and the FT4 shear cell were assessed at low to high stresses, with the overall results showing that, in almost all cases, hardness measurements are highly reliable and reproducible down to very low consolidation stresses ($0.1$ kPa). In contrast, the accuracy and reproducibility of shear testing were found to decrease with the decrease of the applied pre-shear normal stress, providing inconsistent and unreliable results at low stresses ($\leq 1$ kPa) for almost all materials tested. Moreover, no explicit correlation was found as to how the results of the two techniques compare at low stresses. The conclusions drawn expose the need for reliable powder flowability assessment techniques in the low stress range, such as ball indentation.

DEM simulations were also considered for the investigation of the behaviour of the constraint factor in the low stress regime, which cannot be studied experimentally. The effects of interface energy, static and rolling friction, and plastic yield stress on $C$, and subsequently powder flow, were also investigated. Ball indentation simulations of powder beds consolidated at $0.1 - 10$ kPa showed that the constraint factor is independent of the applied stress throughout the applied stress range. An increase in interparticle interface energy caused an increase of both hardness, deviatoric stress and the constraint factor for relatively cohesionless powders, however $C$ was found to be independent of interface energy for cohesive powders. Increasing the coefficient of interparticle static friction led to an increase of both hardness and deviatoric stress, up to a certain point ($\mu_s = 0.3$), beyond which they both remained relatively stable. Increasing the coefficient of interparticle rolling friction from $0.01$ to $0.05$ resulted in increased hardness and shear stress, whilst a further increase to $0.1$ led to reduced hardness and shear stress. $C$ decreased with the increase of static friction, whereas it substantially increased with the increase of the rolling friction coefficient from $0.05$ to $0.1$. Last but not least, an increase of plastic yield stress indicated a decrease in hardness, however did not affect the deviatoric stress, therefore a reduced constraint factor was obtained.

It is important to highlight that although trends have been shown between particle properties and constraint factor, for a new material to be tested by indentation it would be necessary to determine
the constraint factor by measuring the material’s hardness and unconfined yield strength at moderate
to high stresses. For most materials studied in this work $C$ was found to be independent of stress,
however in case it is not found to be constant, the hardness measurement cannot be used to reliably
determine the unconfined yield strength at low stresses.

7.2 Recommended future work

Based on the work carried out in this PhD, a number of recommendations for the advancement of
research in the field of powder flowability, and powder technology in general, are made below:

- Comparative testing between ball indentation and other low stress powder flowability
  assessment techniques, such as the SSSpin Tester, could be carried out to further explore the
  reliability of ball indentation.
- The influence of more single particle properties, such as particle hardness, Young’s modulus
  and interparticle friction, on the constraint factor and powder flow could be experimentally
  investigated.
- Confocal Laser Scanning Microscopy (CLSM) could be used to study the surface roughness of
  consolidated powder beds in order to quantitatively evaluate its influence on the indentation
  measurements.
- The relative humidity and temperature during indentation testing could be controlled rather
  than monitored, so that the influence of environmental factors on hardness measurements
  can be eliminated during testing. The effects of humidity and temperature on the constraint
  factor and powder flowability could also be investigated. Furthermore, the effect of
  environmental factors on the flowability of powder mixtures, and its relationship to the flow
  behaviour of individual constituents, could be studied.
- Dynamic indentation experiments could be carried out to investigate how an increase in strain
  rate influences the constraint factor, and whether the influence of various particle properties
  on constraint factor are affected. Moreover, the flow behaviour of materials prone to stick-
  slip could be explored in the dynamic regime.
- It would be a great addition to the knowledge in powder flowability for new methods to
  manipulate various particle properties individually to be devised.
- X-ray Microtomography (XRMT) could also be employed to obtain the shape of real particles
  and replicate them in DEM simulations. In addition to this, contact models, which more
  accurately represent the deformation of non-spherical particles, could be developed, so that
  it is rendered possible to study the effects of single particle and agglomerate shape on the
  constraint factor and flow behaviour of cohesive powders. It would also be very useful for
other computationally efficient contact models that can represent very fine cohesive materials, like titania, to be developed.
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BS EN ISO 4490:2008


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