Experimental Study of the Segregation Tendency of Minor Ingredients in the Formulated Bulk Particulate Products

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Declaration

The candidate confirms that the work submitted is her own, except where work which has formed part of jointly authored publications has been included. The candidate confirms that appropriate credit has been given within the thesis where reference has been made to the work of others.

- A part of the work in Chapter 2 of the thesis has appeared in publication as follow:

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  I confirm here that this work has been completely done by myself including collation and assessment of the reviewed techniques and writing up the article, apart for the supervision role and directing the research.

- A part of the work in Chapter 3 of the thesis has appeared in publication as follow:

  Asachi, M., Hassanpour, A., Ghadiri, M., Bayly, A. (2017) Assessment of Near-Infrared (NIR) spectroscopy for segregation measurement of low content level ingredients. Powder Technology, 320, 143-154. https://doi.org/10.1016/j.powtec.2017.07.003.

  I confirm here that this work has been completely done by myself including writing up the manuscript and data analysis, apart for the supervision role and directing the research.

- A part of the work in Chapter 4 and Chapter 5 of the thesis has appeared in publication as follow:

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Asachi, M., Hassanpour, A., Ghadiri, M., Bayly, A. (2017) Analysis of Minor Component Segregation in Ternary Powder Mixtures, EPJ Web of Conferences, 140, 13013. https://doi.org/10.1051/epjconf/201714013013.

I confirm here that these works have been completely done by myself including writing up the manuscript and data analysis, apart for the supervision role and directing the research.

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Conference and seminar activities

- **Asachi, M.,** Hassanpour, A., Ghadiri, M., Bayly, A. (2015) “Evaluation of the effect of particle size on the segregation of powders mixture”, **Poster presentation** to Joint conference of the 5th UK-China and 13th UK Particle Technology Forum, Leeds, UK.

- **Asachi, M.,** Hassanpour, A., Ghadiri, M., Bayly, A. (2016) “Measurement of component fraction of laundry detergent powder using Near Infrared Spectroscopy”, **Poster presentation** to PARTEC, Nuremberg, Germany.

- **Asachi, M.,** Hassanpour, A., Ghadiri, M., Bayly, A. (2016) “Measurement of component fraction of laundry detergent powder using Near Infrared Spectroscopy”, **Poster presentation** to The joint IFPRI Robert Pfeffer symposium and UK Particle Technology Forum, University of Surrey, Guildford, UK.

- **Asachi, M.,** Hassanpour, A., Ghadiri, M., Bayly, A. (2017) “Evaluation of segregation of formulated powder mixtures using Near-Infrared spectroscopy”, **Poster presentation** to ChemEngDayUK, Birmingham, UK.

- **Asachi, M.,** Hassanpour, A., Ghadiri, M., Bayly, A. (2017) “Analysis of Minor Component Segregation in Ternary Powder Mixtures”, **Oral presentation** to Powders and Grains, Montpellier France.

Abstract

Segregation, the separation of particles during handling, transportation and storage of powders, is a phenomenon that nearly all industrial sectors dealing with powders encounter. A good example is detergent industry where segregation of the formulated powder mixtures and in particular the minor components such as enzyme granules could have significant economic as well as health and safety impacts. Most industrial processes aim to achieve a homogenous mixture as the inhomogeneities caused by segregation could contribute to significant effects on the economics of production.

In this research, a broad literature review on segregation of powders was carried out to understand the main segregation mechanisms and popular measurement techniques for the segregation evaluation. The literature review revealed that despite considerable reported research on particle segregation, there is a lack of in-depth work on the evaluation of segregation mechanisms and minimization of minor ingredients (less than 2 wt %), particularly in multicomponent powder mixtures during processes such as heap formation and vibration. In addition, robust measurement methods for quantifying the segregation of such ingredients must be investigated.

The aim of this research project is to investigate the segregation of the main constituents of laundry detergent powders (Blown Powder (BP), Tetraacetylethylenediamine (TAED) and enzyme granules). Specific attention is given to the segregation analysis of the minor ingredient enzyme granules as it is highly prone to segregate during heap formation and vibration. For the evaluation of the segregation propensity of minor ingredient, image processing technique is simple but it lacks the assessment of segregation in the mixture of powders with similar particle colours. On the other hand, differentiation of particles with similar colour could be achieved using spectroscopic techniques. In this work, two interesting areas of research are investigated: firstly, reliable measurement of the component fractions particularly for low level ingredients using both image processing and Near-Infrared spectroscopy technique is explored and secondly, segregation reduction approaches (by particle surface coating and modification) for the low-content level ingredient in the mixture of laundry detergent powders are examined.

The results have demonstrated that powder segregation analysis of the components can be successfully achieved using the proposed Near-Infrared spectroscopy instrument. In addition, different spectral pre-processing (to remove the effect of varying physical properties of the components) have been compared and the optimum spectral treatment technique is introduced for the accurate quantification of minor ingredient.

Study of the segregation of powder mixture during heap formation and vibration (representing the conditions encountered during box filling and transportation) has shown that enzyme granules are prone to extensive segregation towards the centre of the heap due to their higher density and the push-away effect as compared to other components. Segregation of enzyme granules in the ternary powder mixtures was shown to be reduced noticeably by applying a thin layer of a sticky liquid on the granules, due to the interlocking effect arising from the surface coverage of enzyme granules by fine particles. Optimum coating level has been found for this purpose to reduce the segregation of enzyme granules without compromising the flowability of the materials. Segregation of enzyme granules is further evaluated by modifying their surface properties to analyse its effects on density driven segregation. Granulation technique has been used for modifying the structural properties of enzyme granules. It is shown that surface modification of dense enzyme granules could hinder the push-away effect.

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Abbreviations and Acronyms

API	Active Pharmaceutical Ingredient
BP	Blown Powder
CLSM	Confocal Laser Scanning Microscope
ECT	Electrical Capacitance Tomography
EP granules	Enzyme Placebo Granules
FFC	Flow Function Coefficient
HME	Twin screw Hot-Melt Extrusion
HPLC	High Performance Liquid Chromatography
LVF	Linear Variable Filter
MAE	Mean Absolute Error
$MAE_{Overall}$	Mean Absolute Error (for total ingredients)
$MAE_{Placebo}$	Mean Absolute Error (for EP granules)
MAPE	Mean Absolute Percentage Error
MRI	Magnetic Resonance Imaging Tomography
NIR	Near-Infrared
N-W	Norris-Williams
PEG	Polyethylene Glycol
PEPT	Positron Emission Particle Tracking Tomography
SE	Specific Energy
SEM	Scanning Electron Microscope

S-G	Savitzky-Golay
SNV	Standard Normal Variate
TAED	Tetraacetylethylenediamine
UV	Ultra-Violet
XRT	X-ray Microtomography
μCT	X-ray Computed Tomography

Nomenclature

English Characters	
A	Fine fraction at the bottom of the powder bed
AB	Measured absorbance
b	Wavelength dependent absorptivity coefficient
C	Specimen concentration
C_0	Overall fine fraction
$\overline{CE}$	Mean circle equivalent diameter
CE_i	Circle equivalent diameter
C_s	Non-variance-based segregation index
D	Particle diameter
$\overline{FS}(\lambda)$	The average value of the sample spectrum
$FS'(\lambda_k)$	The corrected spectra after applying the first derivative
$FS''(\lambda_k)$	The corrected spectra after applying the second derivative
$FS_i(\lambda)$	Average intensity of pure components
$FS_{mix}(\lambda)$	Average intensity of the mixture
$FS_{SNV}(\lambda)$	Corrected spectra by SNV technique
I_s	Non-variance-based segregation index
M_1	Lacey index
M_2	Valentin index
M_3	Poole index

M_4	Kramer index
N	Number of particles in the mixture
n	Sample size
n_i	Number fraction
n_{comp}	Number of components
n_{grid}	Number of grids
P	The concentration of one component in the mixture
S	Standard deviation of the spectrum
SI	Segregation index
V	Velocity
W_B	Total weights of the bottom
w_B	Total weight of the large particles in the bottom
W_T	Total weights of the top
w_T	Total weight of the large particles in the top
X	The limiting travel distance
$X_{Image\ analysis,(i,j)}$	Fraction data of component j using the image processing
$X_{Method,,(i,j)}$	Fraction data of component j using NIR pre-processing method
x_i	ith element of the sample
$\bar{x}$	Mean of the sample

Greek Characters	
ρ_p	Particle density
μ	Viscosity of fluid
σ	Standard deviation of size distribution
ε	Path length
σ^2	Sample variance
σ_R^2	Variance for a randomly mixed binary mixture
σ_o^2	Variance for a fully segregated mixture

Chapter 1
Introduction

1.1 Background and challenges

In many industrial sectors involved in manufacturing and handling of granular materials, such as pharmaceutical, food, mining and cement (Remy et al., 2009; Badawy et al., 2000; Thakur et al., 2003; Hoornahad and Koenders, 2011), segregation phenomenon is encountered particularly during filling, transportation and storage of the product. Most processes aim to achieve a homogenous mixture as the inhomogeneities caused by segregation can contribute to significant effects on the economics of production. For instance, powder inhomogeneities resulting from segregation in laundry detergent powder products manufactured by P&G, costs over $20 million per year (Zafar et al., 2015). Other examples of segregation are active pharmaceutical ingredient content (API) variation of tablets in pharmaceutical industry or taste variation in a drink powder mixture. Therefore, segregation must be inhibited to ensure the quality of the end product (Prescott and Garcia, 2001; He et al., 2013).

Despite considerable reported research on particle segregation, there is a lack of in-depth work on the evaluation of segregation mechanisms and minimization of minor ingredients (less than 2 wt %), particularly in multicomponent powder mixtures. Segregation of minor components has a significant adverse impact on industries dealing with dry powders. For example, segregation of low content level enzyme granules in detergent industry should be closely monitored as it adversely impacts the quality of the final product. Using enzyme in detergent formulation, which acts like a catalyst, lower temperature and shorter time of cleaning could be achieved. However, because of the high cost of the enzyme granules as well as the safety issues, very small amount of enzymes is used in detergent formulation. The segregation of low content level enzyme granules in detergent industry could lead to some powder packages containing tiny amount of enzyme (which are low-quality) while few others with excessive enzymes (which further causes the health risks). Hence, an in-depth study of the segregation of this type of materials is crucial to be carried out.

To measure the segregation in the powder mixtures, the first required step is to determine each component fraction in the taken samples. The traditional methods are based on wet chemical analysis such as High Performance Liquid Chromatography (HPLC), which is very time-consuming and invasive. Moreover, they are not classified as green methods because the solid form is required to be dissolved into liquid for further analytical analysis (Baeten, 2002; Nkansah et al., 2015). Therefore, it is important to apply other segregation measurement techniques to facilitate a non-invasive and fast approach to assess the powder homogeneity (Gowen et al., 2008; Ambrose et al., 2016; Puchert et al., 2011; Scheibelhofer et al., 2013; Allan et al., 2013).

Non-cohesive particulate systems containing particles of different material properties are prone to segregation. Therefore, in-depth evaluation of the effect of material properties on the segregation behaviour of granular materials is crucial. In most studies conducted on the segregation of powders, the effects of particle size distribution and density variation have been investigated (Liao et al., 2016; Rodríguez et al., 2015; Jaklič et al., 2015; Hajra and Khakhar, 2011; Meier et al., 2008; Benito et al., 2013; Tai et al., 2010). Effects of operation parameters (Liao et al., 2015; Kingston and Heindel, 2014; Xiao et al., 2017), geometry and design (Marmur and Heindel, 2017; Windows-Yule and Parker, 2014) and material properties such as cohesion (Liao et al., 2016; Yang, 2006; Liao et al., 2016) have been also evaluated in other studies. By full understanding of the effect of the aforementioned material properties on the segregation of granular materials, reduction approaches of segregation could be found out. It should be noted that monitoring the segregation by manipulating the particle size distribution and/or density variation could not be feasible in most industrial cases. Moreover, optimising the equipment design for the segregation reduction of particles is less favourable in many industries due to the high level of capital investment. In addition, increasing the particle cohesion to hinder segregation could compromise the flowability of the materials. Desired property for segregation reduction of particles by finding the optimum particle cohesion, in such a way that material flowability is not affected, must be therefore addressed. Moreover, understanding the segregation behaviour of particles of varying surface properties, is a relatively new concept of research and has been identified as an area of great technological importance.

1.2 Research rationale

Quantifying powder segregation using a reliable and robust method is challenging, particularly for the case of low content level ingredients. One of the objectives of this research project is therefore to develop a simple method for characterising the uniformity of granular materials, with more emphasis on precise determination of low content level ingredients in a multi-component mixture. Literature review revealed that there is a lack of in-depth research on the evaluation of NIR technique for segregation evaluation of washing powders, particularly low content level ingredients of enzymes. Therefore, the application of a portable Near-Infrared based sensor (MicroNIR probe) will be investigated for the homogeneity evaluation of washing powder mixtures. This probe is cheap, transportable and easy to implement as compared to other spectroscopic instruments. In addition, spectral analysis is not affected by the material florescence like the other efficient spectroscopic instruments such as Raman. The results of NIR approach will then be compared to those of image processing technique.

Segregation mechanisms of the materials will be further investigated in granular piles, where they are generated by pouring the grains from a funnel fixed on top of a box (heap formation). The segregation reduction of the minor ingredient enzyme granules (the highly segregated material) will therefore be addressed by changing their surface cohesion. Incorporation of low level particulate ingredients into bulk products, whilst ensuring homogeneity without compromising other desirable physical properties such as flowability, is one of the main intentions of this approach. The concept of changing the structural properties of minor ingredient will also be tested by modifying the surface properties of the minor ingredient enzyme granules.

Overall, in this research two different aspects are considered, firstly, evaluation of the segregation of low content level ingredients using both image processing and spectroscopy techniques and secondly, investigation of their segregation reduction in the ternary mixture of laundry detergent powders together with the describing the relevant segregation mechanisms.

1.3 Thesis structure

A detailed outline of the thesis, including six main chapters, is summarized below:

Chapter two is mainly focused on conducting a comprehensive review of segregation mechanisms and reduction techniques as well as currently available techniques for the quantification of segregation of powder systems. Various types of analytical methods for the homogeneity evaluation of powder mixtures are discussed together with their advantages and disadvantages.

Chapter three contains evaluation of fast and accurate techniques for segregation assessment of a typical laundry detergent powder. First, precise analysis of component fractions, particularly the minor ingredient, using image processing is discussed. Then, application of an economic and portable NIR spectroscopic probe (MicroNIR1700® probe, manufactured by JDSU Ltd) for the estimation of the uniformity of ingredients in powder mixtures is highlighted.

Chapter four addresses the main segregation mechanisms in a multicomponent mixture of laundry detergent powders by in-depth investigation of the effect of material properties, notably size, shape and density, on the segregation of powders. The segregation of low-dose ingredient enzyme granules will be determined both during heap formation and vibration process and dominant segregation mechanisms of minor ingredient are discussed.

Chapter five investigates the effect of particle surface stickiness on the segregation of low content level enzyme granules by addressing the competing processes of flow and segregation propensity of minor particulate ingredients into the bulk mixtures. Moreover, the effect of modifying the surface properties of particles using granulation technique on the reduction of density driven segregation of low content level ingredients is demonstrated.

Chapter six summarises the general conclusions drawn from the current research.

Chapter 2
Literature Review

2.1 Introduction

Segregation is encountered by many powder handling industries, particularly during process such as handling, transportation and storage of the product. Segregation could have adverse impact on the quality as well as economics of the production. The end-used properties of powders that are produced nowadays are getting more complex. In some cases, a uniform mixture of up to 20 powder ingredients is necessary to meet acceptable quality standard of the final product. A batch of pharmaceutical powder tablets with thousands of dollars cost must be disposed due to powder in-homogeneities arising from segregation of active component (Prescott and Garcia, 2001). As another example, layer by layer deposition of segregated powders, before getting fused together by lasers, could adversely affect the quality of 3D printing manufacturing products (Aulton, 2007).

Over packing resulting from powder inhomogeneities and segregation in laundry detergent powder products could cause millions of dollars in losses per year. More importantly, segregation of low content level ingredients such as enzyme granules could influence the product performance efficiency leading to consumer dissatisfaction. There are several locations where segregation could happen in laundry detergent powder industry (Figure 2.1). As shown in Figure 2.1, segregation of granular materials, containing multicomponent ingredients of various properties, could take place during filling of the bins (where heaps are generated), discharge from silos and vibration caused during transportation (on conveyor belts).

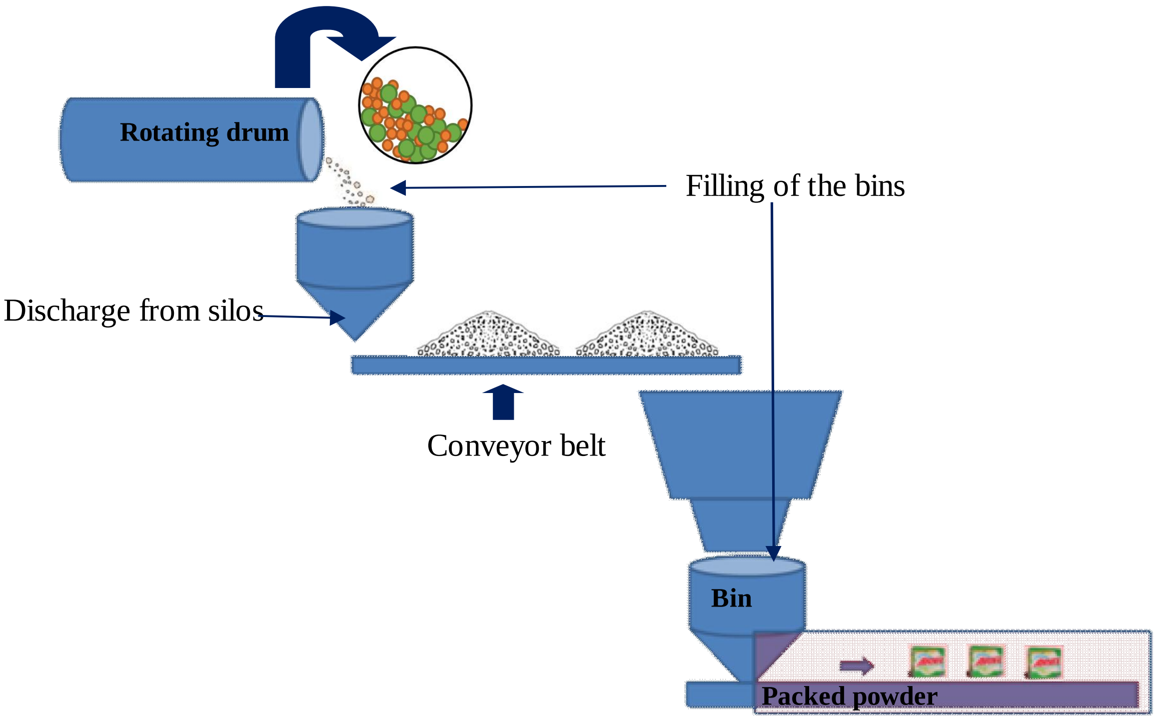


Figure 2.1: Simple schematic of segregation phenomenon in laundry detergent powder industry.

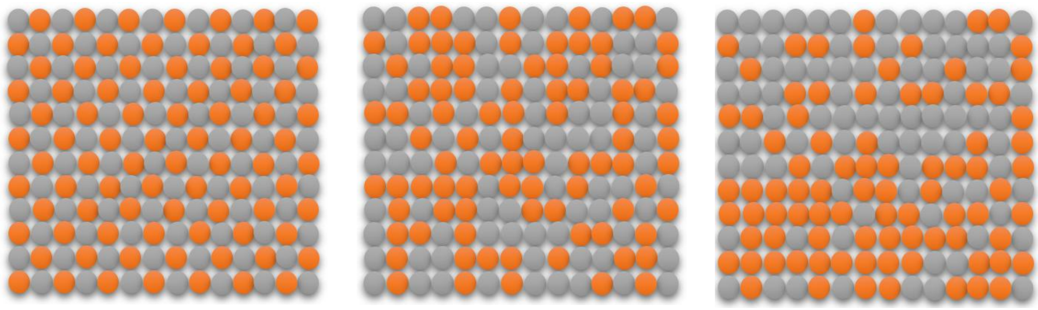
A typical laundry detergent powder product contains surface active agent (surfactants), builders, enzymes and bleaches to remove the fatty soils, improve the action of the surfactants, remove protein and other stains, respectively (Herman De Groot et al., 1995). The removal of fatty materials and dirt (particulate and greasy elements) from the fabrics and their disposal (without redeposition) can be carried out by surfactants, while calcium and magnesium ions (their main source is the water hardness) from the solution can be eliminated by builders. On the other hand, various reactions of biochemical nature could be accelerated using enzyme in detergent powders. They mainly help in the removal of stains including proteins such as gravy, blood, faeces and milk. Due to their severe impacts on human health, proper precautions in their used dosage, operating procedures and handling must be taken. The removal of organic colours from fabrics could be achieved using oxidizing agents of bleaches. Surfactant along with builders make up the majority of the formulation of laundry detergent powder (≥90 wt%). In contrast, the enzymes are used in minor ingredients (≤3 wt%) and bleaches in a range between (~6 to 10 wt%).

By proper understanding of the segregation mechanisms and segregation evaluation of powder formulation, it is possible to propose techniques to improve the powder homogeneity in the final product of laundry detergent powders. The aim of this chapter is to provide a general overview of the main concepts of this project. Firstly, segregation mechanisms and inhibition techniques are reviewed and then various analytical methods for segregation evaluation of dry powders are presented with an insight into advantages and drawbacks of all the techniques.

2.2 Segregation definition and main segregation mechanisms

Powder segregation, a phenomenon which is described as opposite of mixing or reverse mixing, takes place as a result of powder in-homogeneity during processes such as filling, discharge and blending (Poux et al., 1991; Enstad, 2001). In fact, it is the tendency of different particles to move to different directions. Some operations aim to segregate and separate powders of different properties, such as mining. However, most processes intend to achieve a more homogenous mixture (Huang and Kuo, 2014).

A perfect random mixture could be obtained when each particle of a component is next to a particle of another component to form a pattern like chessboard. This is the ultimate goal for the preparation of powder mixtures (Figure 2.2). However, the probability of obtaining such a mixture in industrial mixers is nearly zero (Poux et al., 1991). In a random mixture, the mixing of particles could be achieved by cluster movements, resulting in a possibility of the particles to appear at any place in any time and the formation of groups of equal particles next to each other. This is the best situation that can be reached for a non-segregated powder mixture. Segregation occurs when the powders with various physical properties are mixed. In a fully segregated mixture, the particles of one component can be mainly found in just one part of a mixture.



Perfect mixture **Random mixture** **Segregating mixture**

Figure 2.2: Powder illustration of different mixture types: perfect random mixture, random mixture and segregated mixture, (Rhodes, 2008).

Understanding the main segregation mechanisms in a mixture of powders facilitates finding solutions for the reduction of segregation. In general, segregation phenomenon is produced under the influence of two factors; particle to particle interactions based on physical properties of powders (such as size or density variation) and external forces based on the input energy (such as vibration or shear, Venables, 2001). Different segregation mechanisms (including percolation, angle of repose, floating and sinking, up-thrusting, trajectory, fluidization and avalanching) could be observed based on these interactions which are briefly reviewed below.

2.2.1. Percolation

Percolation is a phenomenon by which the coherent movement of particles through the static bed is possible particularly in the presence of vibration (Figure 2.3). In this mechanism, fine particles may find their way through a matrix of coarse particles provided that the void space between particles to be large enough to let the fines to penetrate. It is important to notice that no movement can occur through the void space between the same size particles. Many researchers have evaluated the percolation segregation of granular materials recently (Jha and Puri, 2010; Rahman et al., 2008; Jha and Puri, 2008) to investigate the effect of material properties on the percolation of particles. Wide particle size distribution, low internal friction, surface smoothness and agitation are shown to be effective for the penetration of smaller fractions through the bed of powders (Carson and Purutyan, 2007; Bates, 1997; Brown, 1939).

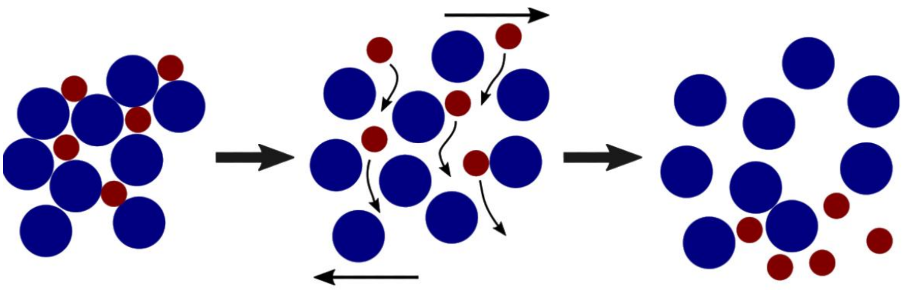
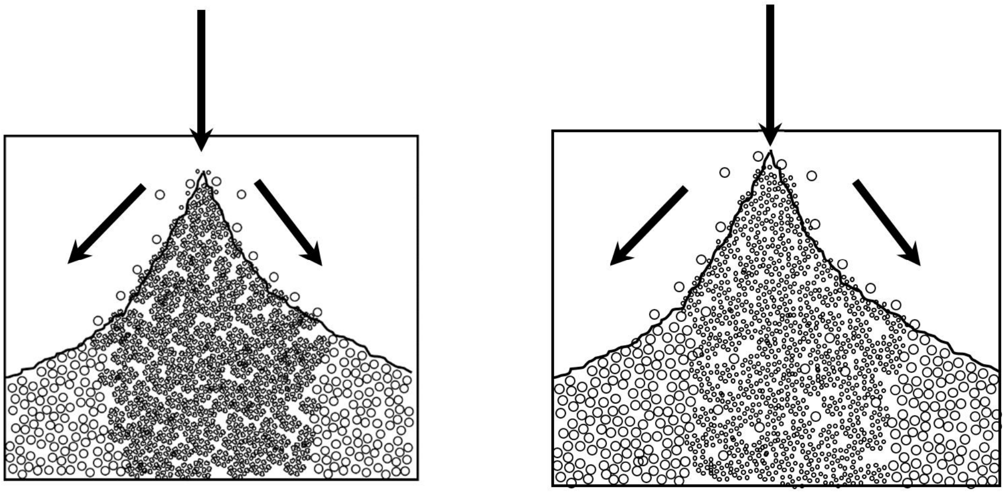


Figure 2.3: Percolation mechanism of segregation.

2.2.2. Angle of repose segregation

Powder separation in repose forming status is produced when differing materials form different repose inclinations (Figure 2.4). The angle of repose is an important factor affecting the internal friction behaviour of granules and therefore the stability of granular packing. For instance, rounded particles are reported to be less prone to stay together at steeper slopes as compared to the case of angular ones. Therefore, the top and the edge of most of piles are enriched with the material with the steepest and the flattest repose angle, respectively (Bates, 1997; McGlinchey, 1998; Mosby, 1996). In fact, the geometry and mass of particles could highly influence the movement and rest of particles (Bates, 1997). As compared to the smaller particles which could be easily arrested during bouncing, rolling and sliding down the slope of a pile, larger and heavier particles are prone to travel further. The effects of sliding and rolling frictions as well as particle size and shape were found to be significant on the angles of repose of granular materials (Li et al., 2017; Pohlman et al., 2006).



Difference in angle of repose (due to shape variation)

Difference in angle of repose (due to size variation)

Figure 2.4: Angle of repose segregation.

2.2.3. Floating and sinking

This process is almost similar to the percolation mechanism, but density variation is the influencing factor for particle separations, not size differences and finding holes and gaps for the case of percolation (Bates, 1997). In fact, dense particles behave as if they are small and could build up more into the centre of powder mixtures by means of a phenomenon called the push-away effect (Figure 2.5) (Tanaka, 1971). In fact, the push-away effect causes heavy granular materials to migrate towards the bottom of the flow. Using this mechanism, the light elements move towards the surface of the bulk and then a progressive change of particle density with depth could happen. In the study of F´elix and Thomas (2004), density variation of granular materials was experimentally shown to highly affect the push-away effect where dense particles mostly segregated in a circle close to the centre of a rotating drum, while the lightest large beads moved close to the periphery. In the study of F´elix and Thomas (2004), two segregation processes were therefore highlighted: a geometrical effect (dynamical sieving process) and a mass effect (push-away process) which is more attributed to size and density variation, respectively.

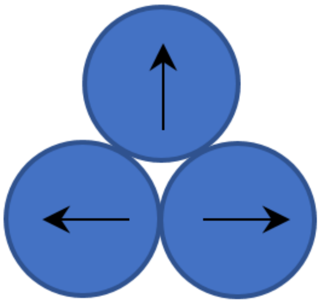


Figure 2.5: Push-away effect, (Mosby et al., 1996).

2.2.4. Up-Thrusting

The co-operative action of fines against the larger particles causes the larger particles to move upward. Small particles locate themselves inside of any gaps provided by the motion of larger particles, and therefore hinder the larger particles returning to their initial positions (Figure 2.6). It should be noted that the sufficient agitation of the bulk of powders and disordering of the structure of particles are prerequisites for the occurrence of unthrusting mechanism (Bates, 1997) which is also known as Brazil nut effect (Soterroni and Ramos, 2013). Further parameters such as size of the large particle and the vibration amplitude (Soterroni and Ramos, 2013), the number of species in the mixture (Metzger et al., 2011) and internal friction and elasticity (Liao et al., 2014) could also influence this phenomenon.

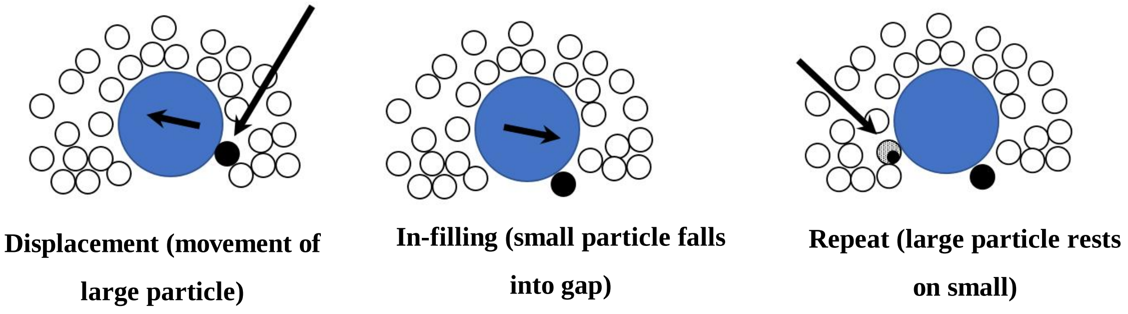


Figure 2.6: Displacement and in-filling processes in up-thrusting mechanism, (Bates, 1997).

2.2.5. Trajectory segregation

Gravity and drag forces could influence the movement of particles in free fall occasions. Particles in short vertical drops do not show remarkable segregation unless the fines are blown away by air. In the case of a high-speed belt conveyor, the material moves in an inclined direction. Therefore, the composition of the landing material at different positions could be affected by the combined gravity and air resistance forces (Bates, 1997). In inclined chute flow, larger particles could travel further than smaller particles by the trajectory segregation (Figure 2.7). The limiting distance that a small particle (diameter=D, density=ρ_p) could travel with a velocity of V into a fluid (viscosity=μ) can be obtained using Equation (2.1) (Enstad, 2001).

$$X = \frac{V\rho_P D^2}{18\mu} \qquad 2.1$$

In addition, segregation could happen across the section in an inclined chute by sliding or rolling of various fractions on the contact surface (sliding segregation).

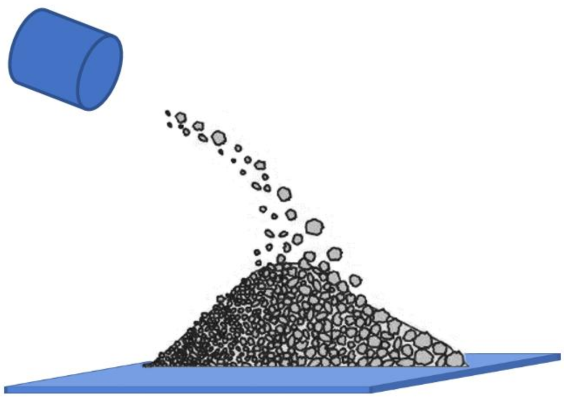


Figure 2.7: Trajectory segregation.

2.2.6. Fluidization segregation

When discharging from a height, dense particles could sink to the bottom while fine particles (lower density) become airborne for a long time by fluidisation segregation (Figure 2.8). The fluidised fine particles will then move towards to the edge of the heap after flowing down the slope (Enstad, 2001, Bates, 1997). For example, this phenomenon could be observed either during discharging from conveyor belt or when the powder is falling from a height. Past practice of tossing grain in the air to separate the chaff is also a good illustration of this mechanism. Elutriation, which is referred to particle entrainment, is one of the main issues of gas-solid fluidized reactors. This phenomenon is mainly observed when a gas-solid fluidized reactor is running at high gas velocities, causing the fine particles to entertain. The recovery of the elutriated particles needs the strict pollution control regulations which is costly (Briens et al., 1992; Alsmari et al., 2015). Inducing electrostatic charges on particles (Yang et al., 2017) and reducing the superficial gas velocities (Alsmari et al., 2015) were reported to suppress particle elutriation.

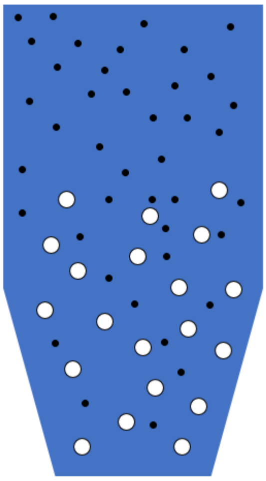


Figure 2.8: Fluidization segregation.

2.2.7. Rotating bed process

In a drum, a segregated ring pattern could be built where its position could continuously vary from the periphery to the center of drum depending on both size and density variation of particles (F´elix and Thomas, 2004). For instance, in a rotary drum mixer, pan granulator or rotary kiln, continuous repose flow of particles and the percolation of fines towards the downward direction cause the coarser fraction movement towards the boundary layer of the container, Figure 2.9 (Bates, 1997). Beside the effect of material properties, the operating condition of a rotating vessel and its geometry could affect the mixing of granular materials. Chand et al. (2012) found that the radial segregation is higher in the case of longer drums than shorter ones. They reported that the segregation greatly increased as the length of the drum was increased which could be due to insufficient energy injection to the system and therefore less inter-particular collisions. In fact, the diffusion flux which is resulting from inter-particle collisions, was increased for the case of shorter drums which further increased the mixing. In another study, the effect of rotational speed of a rotating drum was investigated by Xu et al. (2010). Avalanching segregation along the inclined surface layer was enhanced at lower rotational speeds. However, mixing was enhanced at larger rotational speeds due to dynamic features and inter-particle collisions.

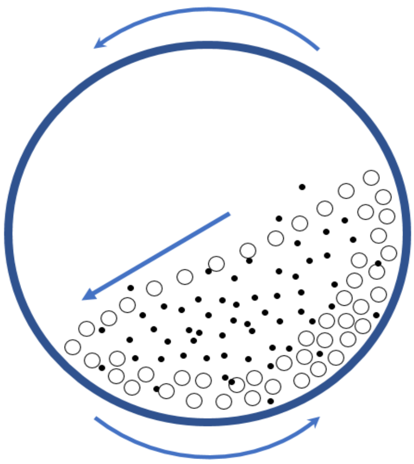


Figure 2.9: Concentration of fines into the central region caused by rotation.

2.2.8. Avalanching

The central region of a pile containing fine particles of steeper angle of repose becomes unstable and then collapses after material builds up. The repeated build up and avalanche mechanisms in central position could form a Christmas tree configuration, Figure 2.10 (Bates, 1997). In fact, an avalanche could occur during pile formation when a vessel is filled from a single point, making a velocity gradient through the bed of powders and shear deformation development. As a consequence, the smaller particles move towards the lower layers and generate the Christmas tree structure (Combarros et al., 2014).

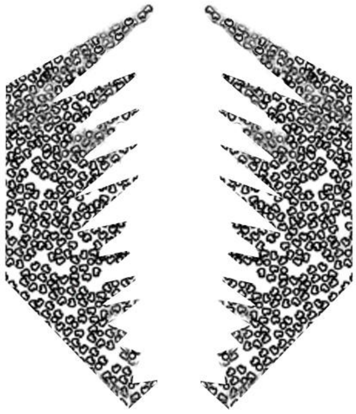


Figure 2.10: Christmas tree segregation generated by building-up and avalanching, (Bates, 1997).

Tang and Puri, 2004 simply divided the afore-mentioned mechanisms of segregation into four main categories as depicted in Figure 2.11. For instance, percolation and up-thrusting mechanisms could be included in sieving (top to bottom segregation) since the small particles move down relative to large particles. On the other hand, Rolling and trajectory could be considered as side to side segregation. Agglomeration segregation mainly occurs when particles are cohesive (e.g. in the presence of moisture). Based on this mechanism, fine particles could form large clusters and move towards the periphery of the bulk of mixture. In the next section, the main parameters affecting the segregation of granular materials are reviewed.

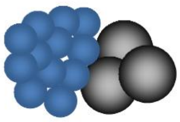
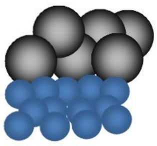
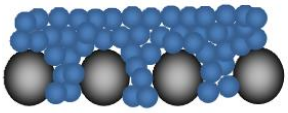
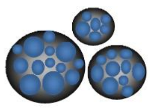
Trajectory segregation (side-to-side segregation) **Large particles**	**Sieving segregation (top-to-bottom segregation)** **small particles**	**Fluidization segregation (top-to-bottom segregation)** **Fine particles**	**Agglomeration segregation** **Cohesive fine particles**
			

Figure 2.11: Simplified segregation mechanisms based on particle size, (Tang and Puri, 2004).

2.3 Important parameters affecting the segregation of granular materials

The main factors affecting the segregation of granular materials are summarised in Figure 2.12. As illustrated in Figure 2.12, they are divided into two main categories: the effects of material properties and handling equipment which are explained in section 2.3.1 and section 2.3.2, respectively.

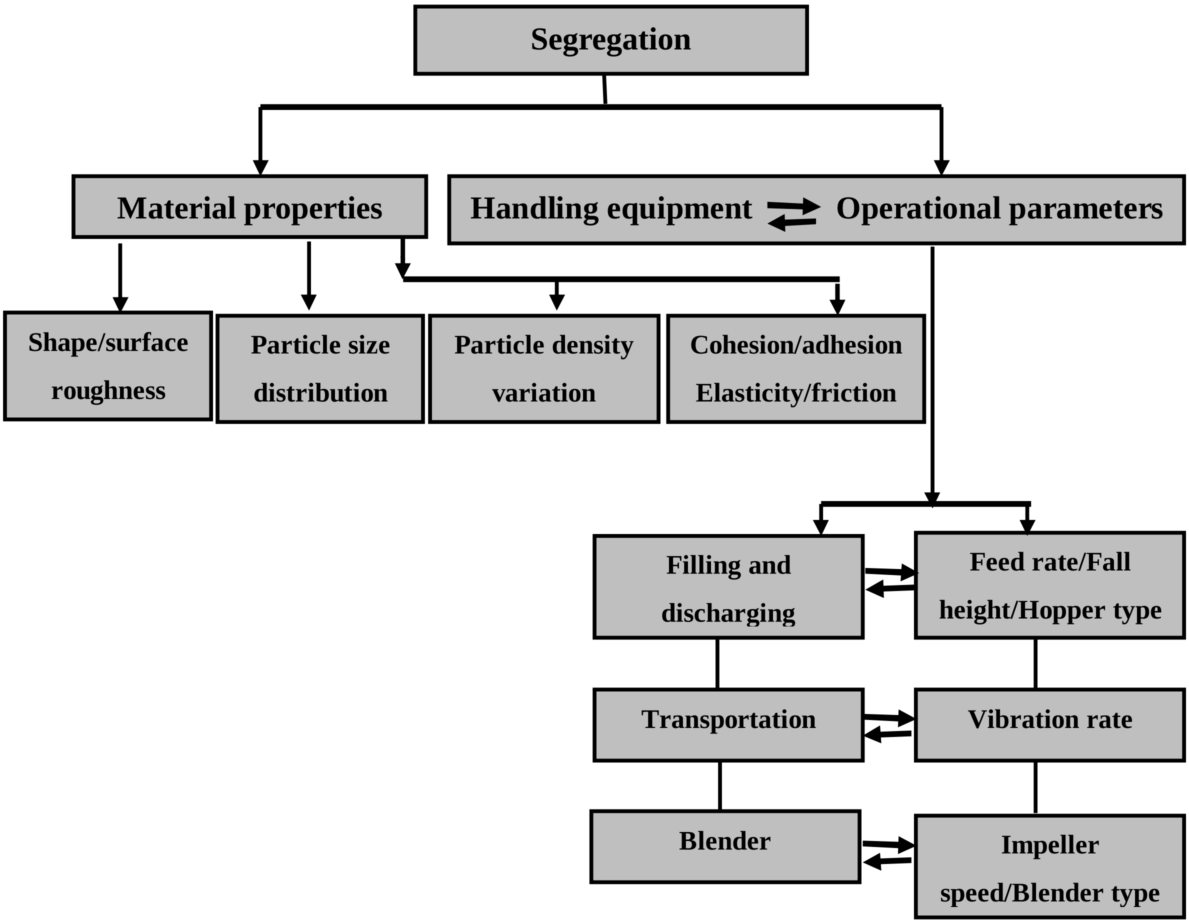


Figure 2.12: Important parameters affecting the segregation of powder mixtures.

2.3.1. The effect of material properties

Material properties are among important factors affecting the segregation of particles. Particles with identical properties do not tend to segregate, while, segregation may take place as soon as there are differences in the property of particles. Size distribution of particles in a bed of powders is a significant factor affecting their segregation. The wider the size distribution, the more possibility for segregation to happen. The concentration of fine particles could influence their segregation behaviours in such a way that the lower fine concentration could lead to improve the percolation mechanism and their higher amount could cause fluidization mechanism (Tang and Puri, 2004). Particle density variations improve the push-away effect. In this case, dense particles behave similar to the smaller particles and move towards the centre of the granular piles. In another word, dense particles are more likely to migrate to the bottom of a container than less dense particles if particles have the same size but different densities.

The effects of particle size and density on the segregation of granular materials have been widely investigated in the literature. Liao et al. (2015) studied the granule segregation in a rotating drum. They found that increasing the particle density led to an increase in mixing time as dense particles were gathered more into the centre of drum. Liu et al. (2013) investigated the segregation of granular samples of microcrystalline cellulose and starch during blending in a cylindrical container. They concluded that larger starch granules had more tendency to move to the top of the mixture. On the other hand, the smaller microcrystalline cellulose granules moved to the bottom of the mixture. In another research carried out by Cho et al. (2012), segregation of coloured glass beads was investigated in a double cone blender. They reported a better mixing of fines as compared to free-flowing large particles because of their cohesive nature arising from van der Waals forces.

Effects of shape and/or surface roughness of particles were however briefly explored experimentally by other researchers. Particle shape influences the segregation of granular materials in a complicated manner. Spherical particles almost behave as large particles in a heap of granular materials and when they are subjected to air currents. Non-spherical or needle shape particles tend to migrate to the centre of a heap. In addition, they get carried further away with air currents easier than the spherical ones (Enstad, 2001). Segregation of binary mixtures containing salt and other food seasoning powders was examined by Shenoy et al. (2015) in a paddle mixer. They concluded that particle size, shape and density could influence the segregation of binary powders. They showed that differences in bulk density and shape had a greater effect on particle segregation than differences in particle size. Remy et al. (2010) examined the effect of particle roughness of cohesionless glass beads on their kinematics in a bladed mixer by both experimental and numerical simulation methods, using particle image velocimetry and Discrete Element Method (DEM). Particles of various roughness with different friction coefficients were examined. They found that the amplitude of the velocity fluctuation of components increased as particle surface roughness was increased which led to the formation of less uniform flows inside of the mixer.

The other important property affecting the segregation of granular material is flowability of particles. Cohesive materials tend to less segregate than free flowing powder materials with wide size distribution since they move together in relatively mixed layers during discharge or sliding on a chute (Thomson, 1997).

Elasticity, friction and adhesion are other factors influencing the segregation of particles. Bouncing of elastic particles during filling the heaps could rise the separation and segregation of particles. On the other hand, particles of different friction coefficients could slide differently during sliding from a chute, increasing the segregation of components. Due to adhesion property, some particles tend to stick to the surfaces, for example on conveyor belts, giving rise to segregation (Enstad, 2001).

2.3.2. The effect of handling equipment and operational parameters

The operational parameters and handling equipment could also lead to intensify the segregation of granular materials (Tang and Puri, 2004). Operational parameters contributing to segregation during filling and discharge processes include feed rate, fall height and hopper type. It is reported that side to side segregation rises with an increase in the free-fall height for the case of granular materials having different particle sizes due to variation between the momentums of coarse and fine particles. Feed rate may also affect the segregation of granular materials in such a way that decreased segregation could be achieved at higher feed rates (Syskov and Lyan, 1960; Shinohara and Miyata, 1984; Peacock, 1938).

(First-in, first out) and (first-in, last out) flow patterns are referred to mass and funnel flow, respectively (Figure 2.13). Trajectory, percolation and fluidization segregation could be appeared during filling processes. Segregated materials inside of the bin could be re-mixed during discharging process in the case of mass flow. However, segregation remains intense in the case of discharging from funnel flow bin. Side to side segregation could be appeared after discharging process (Mosby et al., 1996).

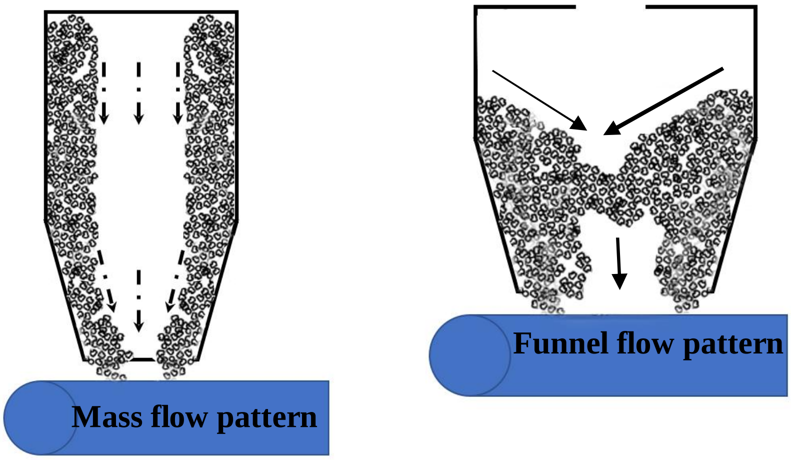


Figure 2.13: Flow patterns in mass and funnel flow, (Mosby et al., 1996).

During transportation on conveyor belts, size fractions could be separated by sieving due to the effects of acceleration and vibration. Many powder handling devices (such as hoppers and chutes) are affected by vibration leading to the elevation of large particles through a mass of fine particles (McGlinchey, 1998).

Segregation could also compromise the mixing and blending of granular materials. There are different types of blenders by which different mixing mechanisms of convection, diffusion and shear could be achieved (Bridgwater, 2012). Segregation may be reduced by applying a convective mixing, where homogenization can be reached by the motion of groups of particles. It should be noted that the high-speed impellers could give rise to the attrition segregation by reducing the particle size and generating the size distribution between particles, while tumbler mixers or low-speed convective mixers do not change the particle size distribution. However, mixing by tumbling could cause other types of segregation by rolling and sieving mechanisms (Enstad, 2001).

2.4 Inhibition of segregation

2.4.1. Minimization of segregation by changing the material properties

Changing the material properties to improve the uniformity of particles is an option to reduce segregation. One example is narrowing down the particle size distribution which further reduces the sieving segregation (Tang and Puri, 2004). This can be achieved by size enlargement processes. In addition, eliminating the irregularities between the shapes of particles (e.g. reducing the acicularities of particles by milling) could minimize the segregation. The flowability of the particles is another property to be controlled in order to enhance powder homogeneity, by adding a sticky liquid into the bed of powder mixtures (Mosby, 1996; Carson et al., 1986).

Several researches have been carried out to investigate the effects of manipulating particle properties (such as particle size distribution and/or bulk cohesion) to reduce the segregation (Oka et al., 2015; Jaklič et al., 2015). Jain et al. (2013) showed that the segregation of both binary and ternary mixtures of glass beads with different sizes could be reduced in vertically vibrated cylinders by slightly decreasing the size distribution of each species or by increasing the mass fraction of the intermediate size specie in the ternary mixture. In another work done by Chou and Hsiau (2010), the effect of wet granular material on the segregation reduction of particles in a rotating drum was investigated. They reported that at a higher liquid content, the segregation index could be reduced, presumably due to the formation of liquid bridge clumping the small particles forming larger particles. The formation of bigger particles could decrease the size ratio in the mixture and therefore could reduce the extent of segregation. Liao et al. (2016) examined the effect of adding a liquid on density-induced segregation of granular materials. In this study, they found that the extent of segregation could be reduced when the liquid content of the system was increased due to improving the cohesive force between particles. Following to this research, Liao (2018) found that density-induced segregation is hindered by adding liquid with larger liquid viscosity due to formation and rupturing of the liquid bridges causing the energy dissipation. The energy dissipation was reported to increase as liquid viscosity was increased mitigating the density-driven segregation. However, the addition of liquid into the bed of powders should be controlled in such a way that it does not compromise the flowability of the final product. Therefore, finding the optimum cohesivity must be further explored when modifying the surface cohesion is proposed as a segregation reduction technique.

2.4.2. Minimization of segregation by changing the handling equipment

The use of proper handling process is another approach for mitigating the segregation of granular materials. Trajectory and percolation segregation could be produced during heap formation, while fluidization is generated by free-fall height (Tang and Puri, 2004). Therefore, the best way to minimize segregation is reducing the free fall heights and heap size during filling processes. The reduction of the heap sizes could be achieved using different types of distributors and/or inserts. Non-powder-based and powder-based distributors are some typical examples of distributors used in the filling processes (Tang and Puri, 2004). Several small heaps, rings or flat layers instead of large-sized heap could be generated using non-powder-based distributors, while the generation of layers instead of large pile can be produced by movable or rotating feeders using powder-based distributors. The division of large heaps into several small heaps could be carried out by placing inserts into the hoppers, enabling the shifting of the centre of the heaps in some cases (Figure 2.14).

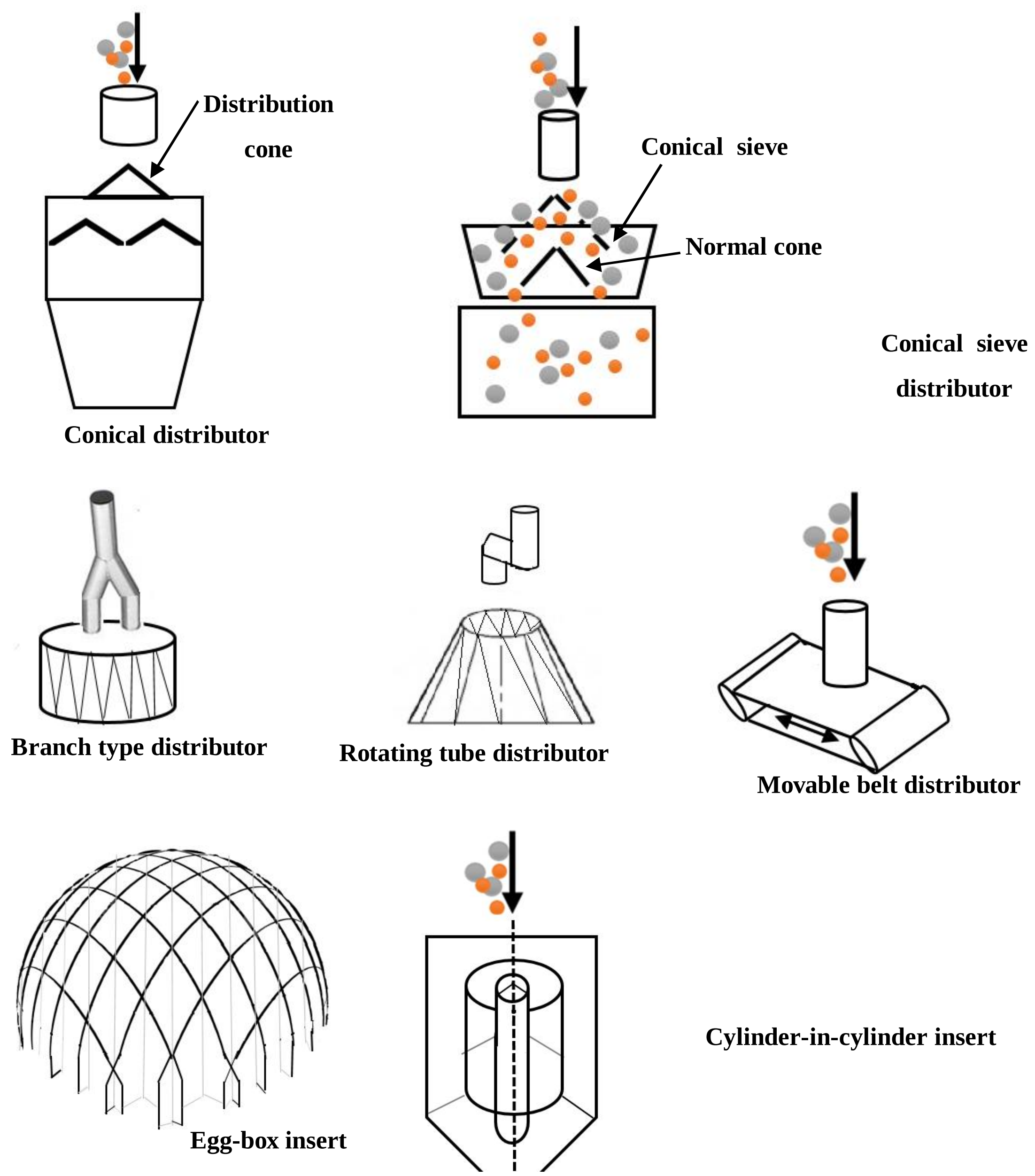


Figure 2.14: Different types of distributors or inserts, (Tang and Puri, 2004).

Discharging process (the reverse of filling process) intensifies the segregation by disturbing the well-mixed structure of particles inside of the container. It is recommended to use a mass flow instead of funnel type of hoppers to reduce the segregation during discharging processes (Mosby, 1996; Tang and Puri, 2004). However, it should be noted that using mass flow pattern of hoppers requires a steep hopper design which are mainly tall. A uniform velocity profile and constant flow rate could be maintained by applying a minimum size of hopper. In this case, using coupled funnel flow hopper with inserts is recommended (Tang and Puri, 2004).

Powder homogeneity should also be controlled during mixing of granular materials. Mixing processes of granular materials often aim at producing a product with a suitable degree of homogeneity. There are two main types of equipment available for the mixing of granular materials. In the first group, the shell rotates to blend the materials inside (dominant mixing mechanism: shear and diffusion). On the other hand, convection is the main mechanism in the second group in which shell is stationary and an internal rotor causes agitation (Bridgewater, 2012). For the mixing of granular materials, the choice of mixer type is of a significant value as the quality of mixtures highly depends on the mixer selection. Segregation of granular materials differing in particle size could be reduced using the blenders working based on convective mechanism rather than applying those working based on diffusive or shear mechanisms (Harnby, 2000).

It is also recommended to control the vibration segregation by eliminating or isolating the vibration sources. Optimising the geometrical design of mixers could be another approach for segregation reduction of granular materials (Hajra et al., 2010, Manickam et al., 2010). The effect of geometry design of a mixing process on particle segregation was investigated by Windows-Yule and Parker, (2014). In this study, they found that density-driven segregation could be controlled by manipulating the aspect ratio of the equipment without the need of changing particle material properties. In a work done by Vanarase and Muzzio, (2011), an optimum impeller configuration of a continuous mixer was reported to be when blades could push the powders backward (back mixing) to keep a relatively mixed state of the powders. Hajra et al. (2010) proposed a method to hinder density segregation using axially-located baffle. Effects of parameters such as length and location of the baffle were investigated on the segregation behaviour of particles. The maximum mixing performance was reported to be when the baffle (with size equal to the radius of the cylinder) was positioned within the shear layers. Nevertheless, optimising the equipment design for the segregation reduction of particles is less favourable in many industrial sectors due to the high level of capital investment.

2.5. Quantification of segregation

2.5.1. Mixing indices

Engineers and scientists mainly use mixing indexes to evaluate the status and quality of the final powder products (Huang and Kuo, 2014). Mixing indices could be measured either based on the variance or non-variance methods, where a complete review of them is provided by Poux et al., 1991 (some of which are briefly described below).

In a work done by Williams and Shields, (1967), segregation of a binary mixture containing different sizes of fertiliser granules was investigated in a vibrated channel using a non-variance-based segregation index (C_s) and dividing the discharging material into upper and lower sections. It was observed that the larger particles moved towards the upper area of the powder bed after vibration. However, sinking of particles to the lower section of the bed was reported for the smaller granules. The mass of large particles of each section was then used to estimate the mixing index according to the following equation:

$$C_s = \frac{\frac{w_T}{W_T} - \frac{w_B}{W_B}}{\frac{w_T}{W_T} + \frac{w_B}{W_B}} \times 100\% \qquad 2.2$$

where W_T, W_B, w_T and w_B are the total weights of the top, bottom and the total weight of the large particles in the top and bottom sections, respectively. A totally segregated and randomly mixed mixture was reported to have the value of C_s equal to 100% and 0%, respectively.

With a similar approach, Popplewell et al. (1989), used a non-variance-based index according to the fine fraction to measure the segregation index (I_s) as shown in the Equation (2.3):

$$I_s = \frac{A - C_0}{1 - C_0} \qquad 2.3$$

where A and C_0 are the fine fraction at the bottom of the powder bed and overall fine fraction, respectively. A totally segregated and randomly mixed mixture was reported to have the value of I_s equal to 1 and 0, respectively.

Several other researchers used statistical analysis based on estimation of σ^2, σ_o^2 and σ_R^2 for the measurement of mixing indices (Poux et al., 1991), where the sample variance σ^2 can be obtained using Equation (2.4). The variance for a fully segregated (σ_o^2) and randomly mixed binary mixture (σ_R^2) are shown in Equation (2.5) and (2.6), respectively.

$$\sigma^2 = \frac{\sum_{i=1}^{n}(x_i - \overline{x})^2}{n-1} \qquad 2.4$$

$$\sigma_0^2 = pq = p(1-p) \qquad 2.5$$

$$\sigma_R^2 = \frac{pq}{N} = \frac{p(1-p)}{N} \qquad 2.6$$

It should be noted that the sample variance is mainly in a range between σ_o^2 and σ_R^2.

Frequently used mixing indexes based on analysis of variance are provided in Table (2.1), (Huang and Kuo, 2014).

Table 2.1. Frequently used mixing indexes based on analysis of variance.

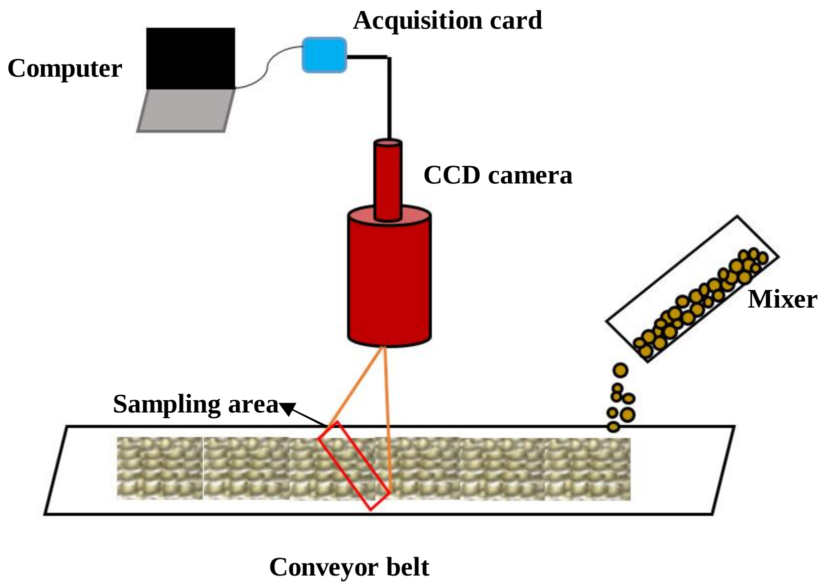
	Mixing index	Completely segregated	Fully randomized
Lacey	$M_1 = \frac{\sigma_0^2 - \sigma^2}{\sigma_0^2 - \sigma_R^2}$	0	1
Valentin	$M_2 = \frac{\log\sigma_0 - \log\sigma}{\log\sigma_0 - \log\sigma_R}$	0	1
Poole	$M_3 = \frac{\sigma}{\sigma_R}$	$\frac{\sigma_0}{\sigma_R}\rangle 1$	1
Kramer	$M_4 = \frac{\sigma_0 - \sigma}{\sigma_0 - \sigma_R}$	0	1

Without the use of the above-mentioned mixing indices, it could be possible to evaluate the mixing quality by plotting the concentration maps of different taken samples from a mixture (Standish, 1985; Xu et al., 2017). If the majority of a material is found towards the centre or the edge of a heap of powder mixture, the mixture is segregated. The coefficient of variance of fraction distribution of a component could then be used as a measure of segregation and mixing quality evaluation (Shenoy et al., 2015; Sudah et al., 2005), which can be estimated using the ratio between the standard deviation and the mean of samples (Equation 2.7). For a perfectly ordered mixture, Segregation Index (SI) is expected to be equal to zero.

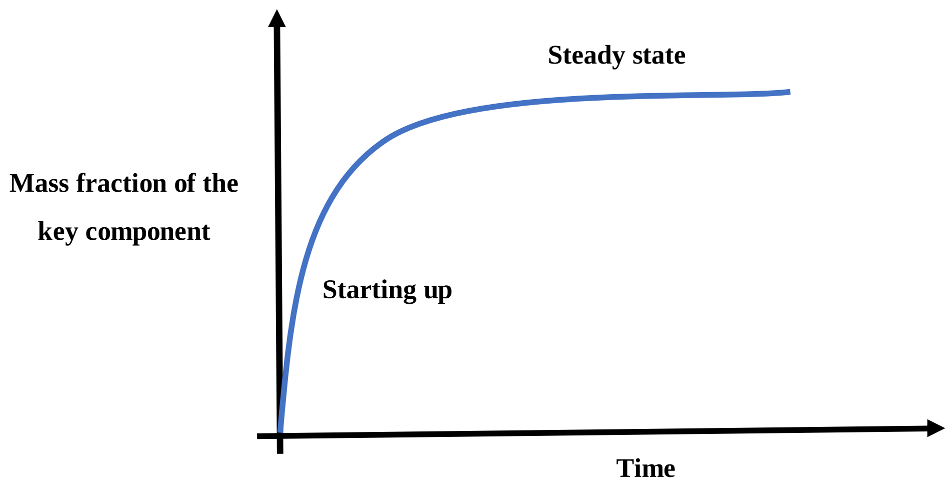
$$SI = \frac{\sigma_i}{\bar{x}} \tag{2.7}$$

In a work done by Ammarcha et al. (2017), mixing of segregating powder mixtures has been assessed by measuring the coefficient of variation for the key ingredient of mixtures. The discharging flow of the mixer was analysed by placing a camera on top of a conveyor belt, where the powder flow was passing. The quality of the mixing was examined by diagnosing the percolation segregation using the proposed device.

A simple schematic of the experimental set-up, sampling methodology and concentration map graph (based on the study of Ammarcha et al., 2017) for the evaluation of the segregation of the key ingredient is illustrated in Figure (2.15). Using this methodology approach, the onset of the powder mixing at different mixer's operational conditions was evaluated by finding the steady-state regime.



(A)



(B)

Figure 2.15: (A) The experimental set-up and (B) concentration map of the key ingredient during mixer's start and steady-state operation, Ammarcha et al., 2017).

Both concentration map and SI provide a simple and fast evaluation of powder uniformity, hence they will be used as segregation analysis techniques in this study.

To generate the concentration map and quantify segregation, the first step is to determine the component fraction of the taken samples from a mixture. Different analytical methods for the content measurement of powders are reviewed in section (2.5.2).

2.5.2. Analytical methods for the content measurement of granular materials

The bulk of granular materials must be divided into several segments to measure the SI and evaluate the powder homogeneities. The scale of scrutiny according to the product specification is mainly used to determine the ideal size of samples (Bridgwater, 2012). The extracted samples could then be analytically analysed using wet and/or dry based techniques which are briefly reviewed below. A simple flowchart of different analytical techniques is depicted in Figure (2.16).

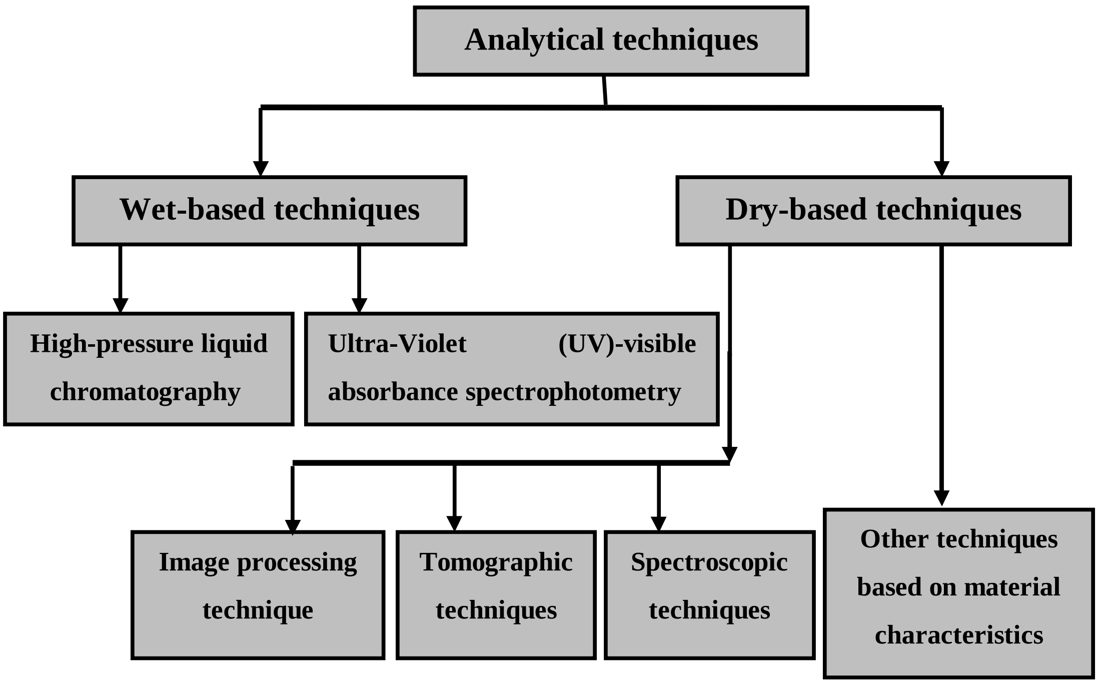


Figure 2.16: Flowchart of different analytical techniques for the content measurement of powder mixtures.

2.5.2.1. Wet based techniques

In this section, the frequently used wet based analytical technique for the measurement of the component concentration is introduced. Analytical techniques such as High-pressure liquid chromatography (HPLC) and Ultra-Violet (UV)-visible absorbance spectrophotometry are traditional off-line wet based techniques for the quantification of components in a mixture. In HPLC method, a solvent is first transformed to a mobile phase status using a high-pressure pump. The sample, injected to the mobile phase, is then transported to the HPLC column for content determination. The separation of components happens in a stationary phase, fixed inside of the HPLC column. The fraction of each component could then be measured using a detector such as UV (Gerber et al., 2004; Walash et al., 2011).

It should be noted that sample analysis using HPLC is relatively time consuming and the complete package of HPLC facilities is expensive. Moreover, the material is not recoverable by this method as the solid form needs to be dissolved into a solution. Hence, the material is lost utilising this technique. Lastly, this technique is not a green method as the solid needs to be dissolved into a solution, hence producing waste. Therefore, it is obvious that green methods for analysing powder content are required by which the powders are recoverable and no liquid waste is produced.

Ultra-Violet (UV)-visible absorbance spectrophotometry is another wet technique used for the measurement of the component fractions. With illuminating the ultraviolet radiation to the sample and obtaining the absorbance information, it is possible to estimate the concentration of a specimen. According to the Beer-Lambert law (Equation 2.8), the absorbance information has a linear correlation with the concentration data (Skoog, 2007; Harvey, 1999).

$$AB=\varepsilon bC \tag{2.8}$$

where AB, ε, b and C are the measured absorbance, path length, wavelength dependent absorptivity coefficient and specimen concentration, respectively.

For the sample analysis, the unknown sample is placed between a light source and a photodetector. The intensity of the beam of UV-visible light is then measured before and after passing the light through the sample to analyse the unknown concentration. The trend of the absorbance values versus different standard concentrations is necessary for the measurement of the unknown concentrations.

UV-visible spectrophotometer is widely used in different researches as it is simple to implement. However, absorption values could be influenced by parameters such as temperature and pH leading to inaccurate result analysis. In addition, the sensitivity of a spectrophotometer is often inadequate at low concentrations. Lastly, this technique is not a green method as the solid needs to be dissolved into a solution, hence producing waste similar to the HPLC technique.

2.5.2.2. Dry based techniques

In this section, different techniques which are classed as dry/green methods are reviewed; they are including: image processing, spectroscopy and tomography techniques as well as other methods based on material properties. Image processing is a fast and simple method for the quantification of component fraction in powder mixtures. With image processing of a captured photo of a powder mixture, it is possible to assess the uniformity of particles, provided that particles differ in colour. The 2D photo taken from a powder mixture can be divided into several sections, where a component of interest can be quantitatively analysed using an image processing software (Mizonov et al., 2017; Jung et al., 2012). Different stages for the evaluation of mixing quality of powder mixture's captured photo are illustrated in Figure 2.17 (Rosas and Blanco, 2012). The quality of the raw images is first improved by some pre-processing techniques. After obtaining the segmented images and splitting them into small subsections, the fraction of components could be estimated for each subsection to investigate the quality of the powder mixture.

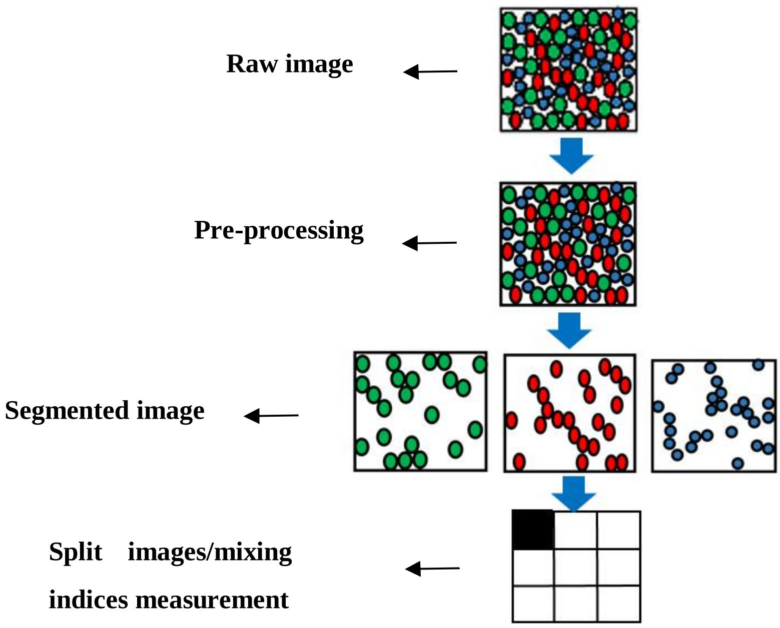


Figure 2.17: Different required steps for homogeneity assessment of mixtures, (Rosas and Blanco, 2012).

Using image processing technique, only the surface of a mixture could be scanned for homogeneity characterisation. Using solidification technique, more content information can be obtained from a discretized mixture (Realpe et al., 2015). By the addition of a binder (gelatin as solidifier) to the mixture and then refrigeration, the mixture could be solidified when it reaches to the homogeneity. After image processing of the captured pictures of the entire sliced samples, mixing quality of the mixture could be evaluated. Therefore, coupled solidification and image-processing technique should be beneficial for the uniformity assessment of powder mixtures. Based on solidification technique, more information of the internal structure of a mixture can be obtained. However, the binder could destroy the chemical structure of powders.

Tomographic techniques are among other well-known dry methods for the determination of component fractions. For instance, X-ray computed tomography (µCT) is a suitable non-invasive technique performed for the evaluation of powder homogeneity which could provide high resolution images (typically 50 microns or less, Paulus et al., 2000). By projecting an X-ray beam through the material and the

measurement of energy debilitation of the beam received on a detector, three-dimensional structure of an object could be constructed (Liu et al., 2013).
Surface imaging tools such as Scanning Electron Microscope (SEM) are only able to scan the outer surface and not the internal structure of objects and therefore they cannot be applied for full-scale evaluation of powder beds. On the other hand, µCT has a great potential for deep understanding of the structural properties of particulate materials (Poutiainen et al., 2011; Akseli et al., 2011). Precise data analysis could be provided from rendered high resolution images using this technique. However, material with similar structural properties cannot be easily differentiated using this technique. In addition, this method is an expensive tool for the evaluation of powder homogeneity. Moreover, limited amount of a powder mixture could be scanned at each run using this technique (due to the device's low spatial resolution), hence increasing the total time of analysis.

Electrical Capacitance Tomography (ECT), (Ehrhardt et al., 2005; Huang et al., 2017), Positron Emission Particle Tracking Tomography (PEPT, Marigo et al., 2013) and Magnetic Resonance Imaging Tomography (MRI, Hardy et al., 2007) are other tomographic techniques used for powder homogeneity analysis with relatively less spatial resolution than µCT.

Spectroscopic techniques have been developed based on analysis of the spectral information of powder samples and have already found a wide range of applications in industrial sectors (Gowen et al., 2008). Component composition of samples could be estimated using their spectral information to evaluate the final mixing performance.

NIR spectroscopy is a molecular vibrational spectroscopic method predicting vibrational transitions in the molecules. NIR analysis can be performed either by diffuse reflectance or transmission mode. The intensity ratio of the scattered light from the sample compared to the light reflected from a reference surface can be measured by diffuse reflectance mode. On the other hand, decrease in radiation intensity can be performed by transmission mode when radiation passes through the sample (Stuard, 2004).

In order to monitor the mixing of powders, a device entitled segregation tester, working based on a linear relationship between the mixture NIR spectral intensity and the spectral intensity of pure components was developed by Johanson, (2014). Using this method, local fractions could be determined by minimization of the difference between the computed intensity curve (Equation 2.9) and the experimental measured one obtained from spectroscopy tool as shown in Equation (2.10).

$$FS_{mix}(\lambda) = \sum_{i=1}^{n_{comp}} (x_i . FS_i(\lambda)) \tag{2.9}$$

$$Error = \sum_{k=1}^{n_{wave}} (FS_{mix}(\lambda_k) - F_{mix}(\lambda_k))^2 \tag{2.10}$$

where $FS_{mix}(\lambda)$, $FS_i(\lambda)$ and x_i are average intensity of the mixture, average intensity of pure components and fraction of components respectively.

The distribution of local component fractions through the mixture could then be used to evaluate the powder mixing uniformity. The expected error of this method was reported to be within 7% and 0.5% for a badly segregating and moderately segregating materials, respectively. Moreover, suitable range of particle size for this device was reported to be between 0.5 μm to 3 mm.

Other configurations of NIR set-ups have been applied to monitor greater quantities of samples. By placing several NIR probes at several positions of a blend (Figure 2.18), it is possible to monitor the entire blend (El-Hagrasy et al., 2001; Shi et al., 2008; Scheibelhofer et al., 2013).

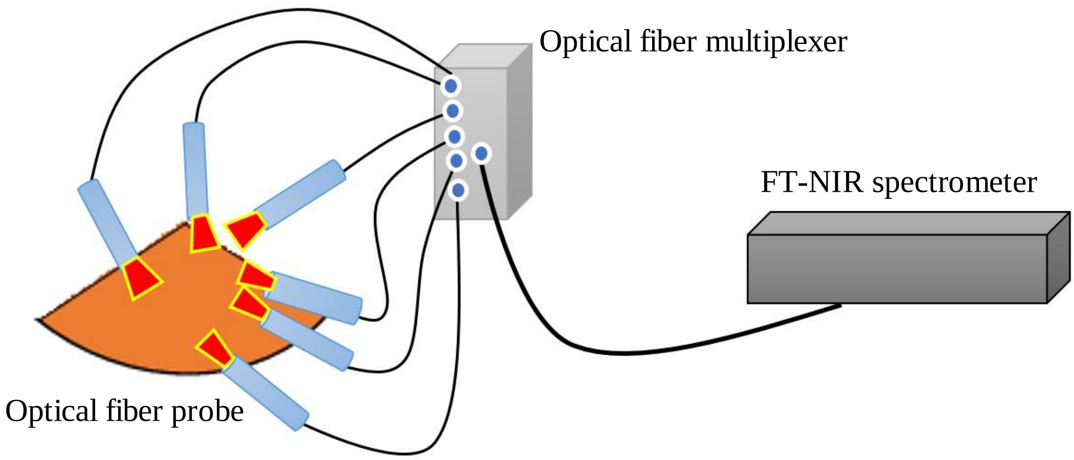


Figure 2.18: Schematic of multi-probe spectroscopy setup, (Scheibelhofer et al., 2013).

NIR technique offers a fast chemical analysis of multicomponent mixtures and continuous monitoring of samples at different modes of at-line, in-line and/or on-line (Zhang et al., 2005). However, it is difficult to obtain a very high-resolution visualization to the internal field of particulate systems using this method. Moreover, spectral analysis using this technique is influenced by the effect of physical properties of the materials, such as particle size variation.

The irradiation of materials causes different phenomena including scattering, absorption and fluorescence. The Raman effect is a scattering process that alters the frequency of an incoming monochromatic light beam, mainly from a laser in the visible, near infrared, or near ultraviolet range (Smith, 2005).

Wang et al. (2017) developed a custom-designed macro-Raman system for homogeneity analysis of multi-component bulk of pharmaceutical powders. This spectroscopy system was equipped with a motorized translational sample stage. For the quantitative analysis of component fraction, a correlation approach based on spectral information was applied. Larger sample volume scanning method was shown to be more suitable for bulk composition analysis of inhomogeneous samples, while large error was reported for single spot sampling method.

Raman imaging has less overlapped spectra and higher spatial resolution as compared to NIR and therefore it has a better sensitivity to detect minor components (Hudak et al., 2007; Amigo and Ravn, 2009). Thus, Raman technique eliminates the limitation of NIR in which the overlapped spectra make it difficult to perform low-dose quantitative analysis. However, this technique is more expensive than NIR. In addition, substantial interferences in Raman spectra can be produced by fluorescence when the molecule is excited to an elevated excited state (Svanberg, 2001).

Other powder properties, such as conductivity (Shenoy et al., 2015), interaction charges (Hao et al., 2013) or thermal behaviour (Mahmood et al., 2016; Bharvada et al., 2015) could also be a good indicator of powder homogeneity status. Using conductivity, interaction charges or thermal behaviour information of a system, segregation patterns can be predicted easily.

Electrical conductivity method is a simple, inexpensive tool to evaluate the uniformity of the whole volume of powder mixtures. This technique needs only a conductivity meter to measure the conductivity of samples in order to determine the mixing performance. The deficiency of this method is that it can only be applied for differentiation of a component with high conductivity which is mixed with other components of low conductivity (Shenoy et al., 2015). Therefore, this technique could be insufficient for the determination of the uniformity of multicomponent powder mixtures. In addition, this technique is relatively sensitive to the environmental conditions such as temperature and humidity.

Based on particle friction charges, it may be possible to evaluate powder blend uniformity. Contact friction between particles causes a phenomenon called tribo-electrification or particle charging. The tribo-electrification phenomenon is due to particle-particle and/or particle-surface interactions, usually creating bi-polar charging, which allows the creation of attractive or repulsive forces between individual particles (Hao et al., 2013). Measurement of the bulk electric charge of samples may offer a desirable and economical method for qualitatively assessing the blending uniformity of a mixture. However, it could be an unreliable tool for the evaluating the mixing performance because it is exposed to the variations of humidity, temperature and other environment factors (Hammond et al., 2009).

Moreover, sampling is usually required for the analysis of component concentration using this technique and therefore it is invasive.

Overall, spectroscopic approaches such as NIR and Raman have been broadly used for the assessment of powder mixture uniformity. These techniques attracted more attention as they could monitor the uniformity of several components either at-line, in-line and/or on-line. However, using tomography systems or methods based on material properties, such as conductivity meter, one or two ingredients could be monitored usually in an at-line mode. Among different spectroscopic tools, Raman showed a high sensitivity to detect minor components, therefore it can be applied for the evaluation of powder uniformity with higher accuracy. However, NIR spectroscopy is more commonly used for the evaluation of powder homogeneity due to its relatively low cost as compared to other spectroscopic instruments. In addition, this technique is not sensitive to the fluorescent materials like Raman. In general, the suitable technique must be chosen according to the application, material and device specifications, budget as well as the required precision and sensitivity. In this study, the image processing technique and NIR spectroscopy will be used for the uniformity assessment of powder mixture due to the simplicity, cost and functionality.

2.6. Segregation of low-dose ingredients

The uniformity of powder mixtures containing the low-dose ingredients is a significant attribute which must be addressed in many powder products. For example, excipient type and/or mixing device during formulation development of pharmaceutical products must be controlled for the production of homogenous low-dose drugs (Kukkar et al., 2008). Segregation of fine, low-dose powder ingredients in the final tablets has been examined by different researchers (Ende et al., 2007; Alyami et al., 2017; Park et al., 2013).

Alyami et al. (2017) investigated the effect of excipient process parameters on the homogeneity of low-dose drugs. Smaller API concentration was reported to highly experience segregation as a result of reduced interactions with the larger excipient particles and their appetite to produce agglomerates. In the work of Alyami et al.

(2017), a novel mixing device (dry powder hybrid mixer) was explored and reported to have a positive effect on the production of homogeneous powder mixtures due to enhancement of the adhesion forces between API and carrier particles than the cohesion forces between the drug particles. UV spectrophotometry and Relative Standard Deviation (RSD) concept were utilised for the measurement of API concentration (size<100 μm, maximum dose around 750±800 micrograms per tablet) of extracted samples from the mixer and uniformity index, respectively. Using the proposed mixing device, the homogeneity of low-dose API ingredient (1% and 0.5 wt %) was guaranteed.

In another research, Park et al. (2013) examined the uniformity of low-dose drugs (Limaprost, tamsulosin and glimepiride) in a twin screw Hot-Melt Extrusion (HME). The homogeneity of complexes of drug and polymer was assessed using a Confocal Laser Scanning Microscope (CLSM), HPLC method and RSD index. The proposed device helped in shearing the material under elevated temperature/pressure which further enhanced the polymer softening for homogeneous distribution of the low-dose drug. The results of CLSM imaging demonstrated a better uniformity of model drugs using the hot-melt extrudate, compared with simple physical mixtures.

The above-mentioned researches are particularly conducted for the segregation evaluation of pharmaceutical tablets containing the low-dose fine (size<100 μm) active ingredient, at which the adhesion between the fine particles and the carrier was mainly reported to affect the homogeneity of the product. However, detailed segregation mechanisms of low-dose ingredients, before and after uniformity enhancement approach, have not been properly hypothesized in these researches. Moreover, literature review revealed that segregation minimisation of low-dose ingredients in multicomponent powder mixtures has not been evaluated in other types of powder processes, such as filling and vibration. In fact, dense and large size minor ingredients (such as enzyme granules in laundry detergent powder mixtures) could highly segregate during the processes of heap formation and vibration. Therefore, further research is recommended to explore detailed segregation mechanisms of the minor ingredients in such systems. In the current research, the segregation of low-content level ingredient (size in a range of 600 μm) in mixture of laundry detergent powder will be examined after heap formation and vibration (resembling the processes of filling and transportation). For this purpose, robust segregation evaluation of low-dose ingredient will be first explored. Then, segregation mechanisms of low-dose ingredient before and after segregation reduction approaches will be evaluated and discussed.

2.7. Conclusion of the Literature Review

To obtain a high-end product quality, mixture of powders should be made with high content uniformity to reduce powder segregation and expensive product failure. Segregation could happen in many powder handling industries; one example is segregation during filling of the bins (where heaps are generated), discharge from silos and transportation in laundry detergent production industry, where segregation could affect the quality of the final product resulting in consumer complaints. More importantly, the uniformity of powder mixtures containing the low-dose ingredients is a significant attribute which must be addressed in this industry. Despite considerable reported research on particle segregation, there is a lack of in-depth work on the evaluation of segregation mechanisms and minimisation of low-dose ingredients (less than 2 wt %), particularly in multicomponent powder mixtures during heap formation and vibration (resampling the conditions of filling and transportation). Because of the high cost of the enzyme granules as well as the safety issues, very small amounts of enzymes are used in detergent formulation. Therefore, their segregation in detergent industry should be closely monitored as they could adversely impact the quality of the final product. In this research, the segregation mechanisms of components in laundry detergent powder mixtures will therefore be examined and the segregation of minor ingredient enzyme granules will be further explored (Chapter 4). Moreover, segregation reduction approaches will be investigated by hypothesizing the underling segregation mechanisms (Chapter 5).

To evaluate the uniformity of powder mixture, the first required step is to analytically determine the component fraction of the extracted samples. This review highlighted the importance of being able to robustly quantify the segregation of granular materials by introducing different assessment techniques of powder homogeneity. Many uniformity assessment methods of particulate systems have been developed and studied over the last few decades. Of a widely used non-invasive techniques for the determination of components fraction and powder mixture uniformity is the image analysis. Image analysis technique offers an accurate means of analysing component uniformity in powder mixtures, but this technique cannot be used for the mixture of components with similar colours. Same colour ingredients of many powder products make the determination of component fractions difficult using image processing. Therefore, it is suggested that future work be partly focused on finding alternative techniques for the determination of component fraction, particularly for accurate quantification of low-level ingredients. In this research, NIR spectroscopy is selected for the evaluation of homogeneity of minor ingredient due to its relatively low cost and functionality.

There is a lack of reported in-depth research on the evaluation of NIR technique for segregation evaluation of washing powders, particularly low content level ingredients of enzymes. Therefore, application of an economic and portable NIR spectroscopic probe (MicroNIR1700® probe, manufactured by JDSU Ltd) for the estimation of the component fraction of multicomponent washing powder mixtures will be addressed in Chapter 3 and the results are compared with those obtained by image processing.

Chapter 3
Evaluation of feasible techniques for segregation assessment of washing powders

3.1 Introduction

Quantifying powder segregation using a reliable and robust method is challenging, particularly for the low content level ingredients. In this chapter the application of both image processing and NIR spectral analysis for the determination of the segregation extent of components in a multi-component mixture is evaluated. Specific attention is given to accurate analysis of minor ingredient. As a model system, a typical laundry detergent formulation (containing BP, TAED and EP granules) is used.

The chapter is divided into two main sections:

1. Assessment of image processing technique for accurately quantifying the component fraction in powder mixtures.
2. Calibration of a NIR spectroscopic instrument (MicroNIR1700® probe, manufactured by JDSU Ltd) to determine the component fraction and therefore the homogeneity of powder mixtures.

The main objectives of this chapter are summarised at the following diagram:

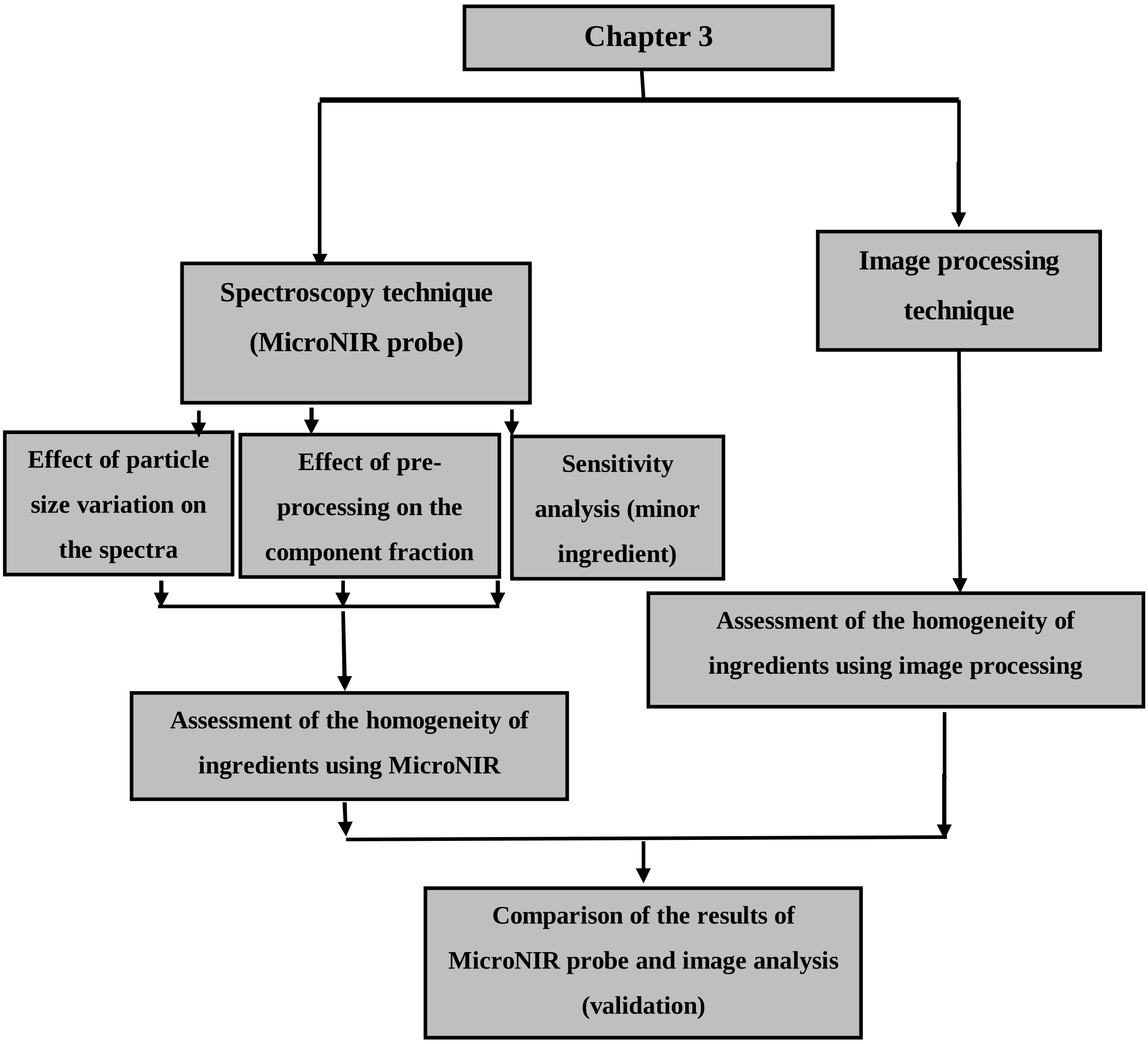


Figure 3.1: A summary of the objectives of chapter 3**.**

3.2 Materials

The mixture of components comprising Tetraacetylethylenediamine granules (TAED), spray-dried synthetic detergent powder (Arial LS Diamond), known as Blown Powder (BP) and Enzyme Placebo Granules (EP granules) are mainly used in this research. The reason for choosing these materials lay in the fact that they represent the main constituents of a typical washing powder mixture (surfactant, bleach and enzyme). BP and TAED were obtained from Procter and Gamble (P&G), Newcastle Innovation Centre, while EP granules were obtained from DuPont company, USA.

The process of spray drying of concentrated slurry of the raw materials produces a free-flowing base material called Blown powder, containing the most of required materials for washing. Blown Powder (BP) is a spray-dried synthetic detergent powder, containing surfactants, builders and other ingredients. Blown powder content in the finished product ranges from 40 to 99 wt %, therefore it is a key ingredient of a typical laundry detergent powder (Huntington, 2004). Some ingredients such as enzymes and bleaches cannot be added to the process of spray drying, hence they are added to the Blown powder afterward (Zoller, 2008).

Tetraacetylethylenediamine granules (TAED) is used as bleach activator in detergent formulation, where its main function is to remove the organic colours from fabrics using oxidizing agents. They are used in a range between (~5 to 10 wt %) in the finished product. Enzymes are used in minor ingredients (≤3 wt %) in detergent formulation (Herman De Groot et al., 1995). Due to the health and safety issues, Enzyme Placebo Granules (EP granules) representing the actual enzymes of washing powders, is applied in this study.

Figure 3.2 and Figure 3.3 shows the Scanning Electron Microscope (SEM) images of a number of BP, TAED and EP granules and their particle size distribution obtained by British standard sieve size analysis, respectively. It can be inferred from SEM images that the EP granules are more rounded in shape as compared to BP and TAED particles. It can be deduced from the particle size distribution of components that the EP granules has a narrower particle size distribution than other components. A relatively broad size distribution could be observed for BP and TAED. Detailed material properties of the afore-mentioned components and further characterisations will be presented in the section 4.2 along with their main segregation mechanisms.

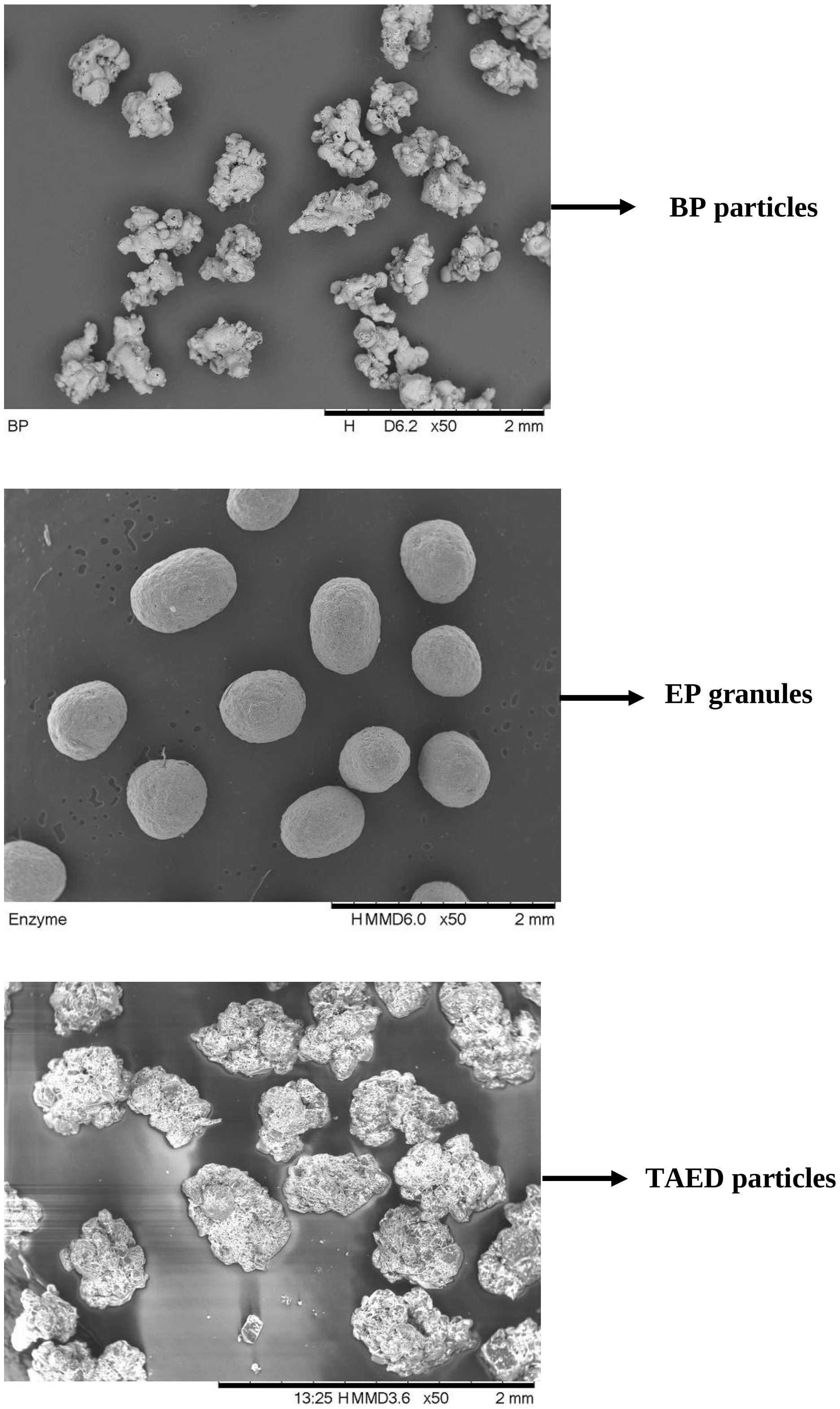


Figure 3.2: SEM images of a number of BP particle, EP granules and TAED bleach.

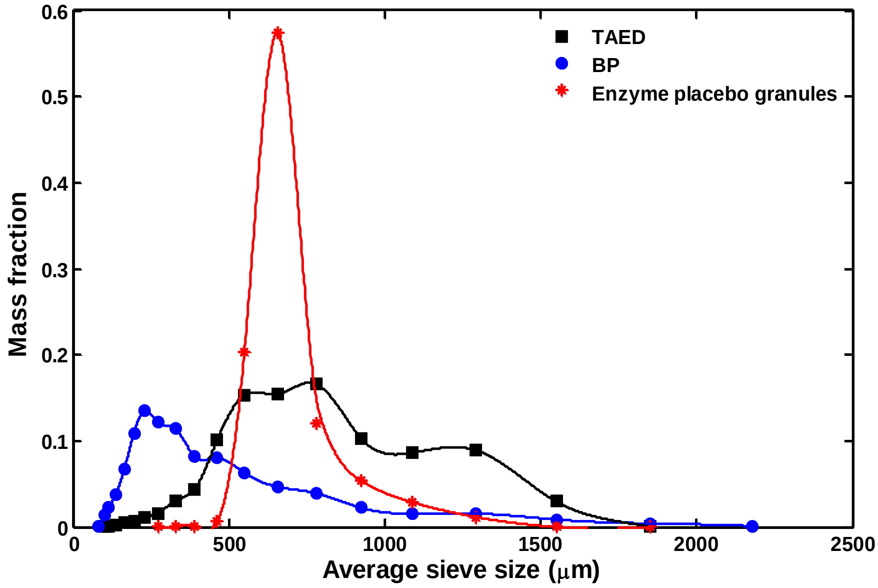


Figure 3.3: Particle size distribution of EP granules, BP and TAED.

3.3 Image analysis method

A method of performing some operations on a raw image to get useful information is named image processing. This method is a rapidly growing technology which has been broadly applied in many fields of engineering (Chen et al., 2004; Jung et al., 2012; Olaofe et al., 2013). By proper segmentation and area estimation of a specimen, it is possible to measure the component fraction. In fact, image segmentation is a method of partitioning a captured photo into several segments with the aim to facilitate further analysis on the images. For the image processing of a picture, the required steps are mainly as follow: 1) calibration of the image size, 2) gray scaling of the picture to reduce the noise and improve the quality of the image, 3) Thresholding the desired area for its segmentation and 4) looking into the histogram data to obtain the average pixel information of the specimen. For example, the afore-mentioned stages for the measurement of the fraction of water droplets are shown in Figure 3.4.

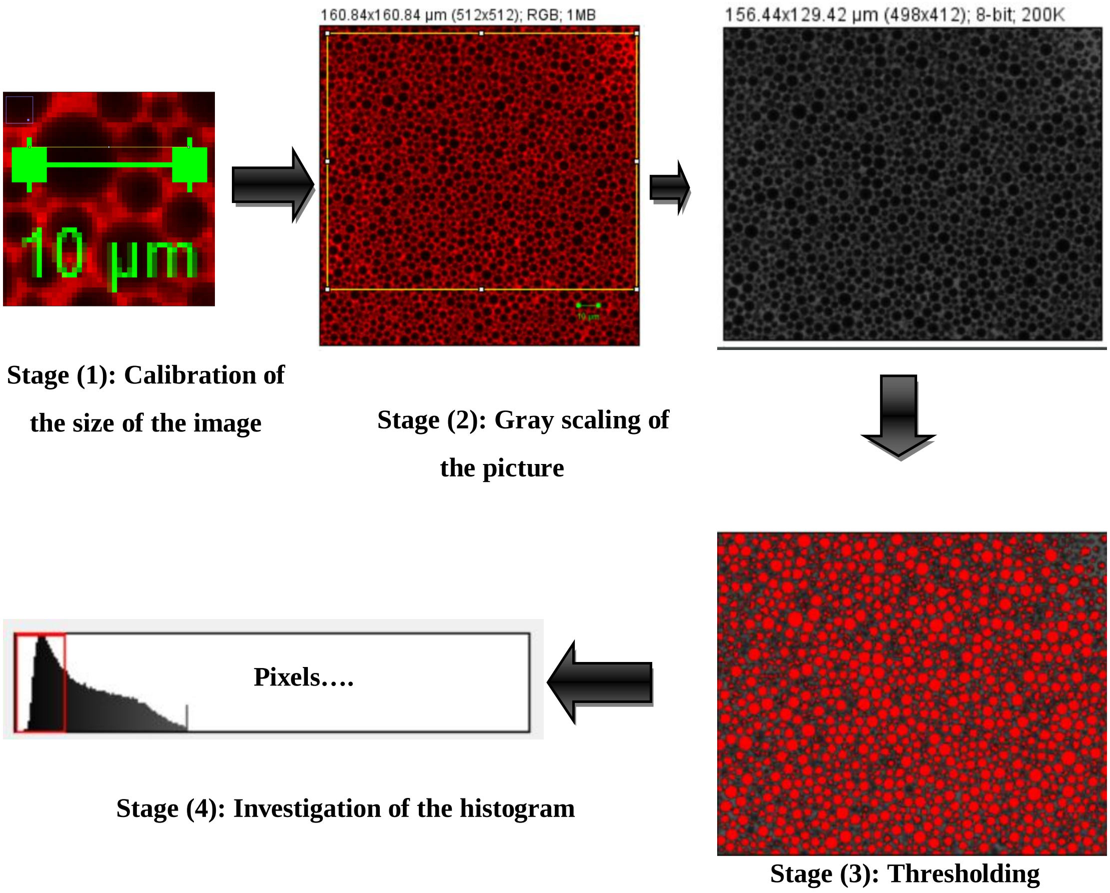


Figure 3.4: Different stages for the image processing of the droplets using ImageJ software.

In this section, simple methodologies for the image segmentation and therefore the concentration measurement of the main components of washing powders are described. Full description of the image segmentation and image splitting for the measurement of SI are provided in Figure 2.17 and Figure 3.4.

ImageJ is a simple open source application for the image processing of multidimensional images. Therefore, ImageJ was first evaluated to estimate the component fraction. For this purpose, a mixture of BP and TAED was randomly generated. The taken image of the mixture (by a Nikon camera, D3300-24 MP, Figure 3.5) was then processed using ImageJ software after dividing it into 4 different sections.

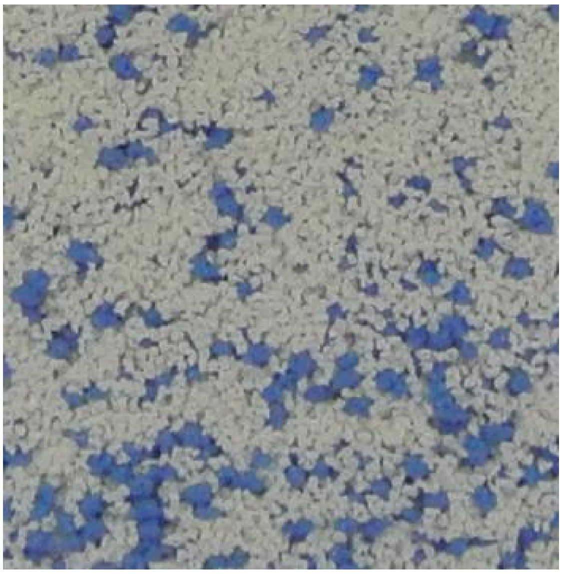


Figure 3.5: Randomly prepared mixture of BP and TAED.

For the measurement of the TAED component fraction, the desired boundary of particles was selected using threshold and binary tools of ImageJ software (Figure 3.6). The pixel information for the measurement of the fraction of TAED particles at each grid was then obtained using histogram tab. Table 3.1 summarises the fraction of TAED obtained for different grids using ImageJ software, where dividing the pixels of the desired TAED area to the total pixels of the figure was used for the measurement of the fraction. As illustrated in Figure 3.4, some dark areas of the mixture (voids between particles) are mistakenly included during thresholding of TAED particles. By decreasing the threshold sensitivity, less TAED particles could be diagnosed. Therefore, careful selection of the desired area must be made during image processing by ImageJ software.

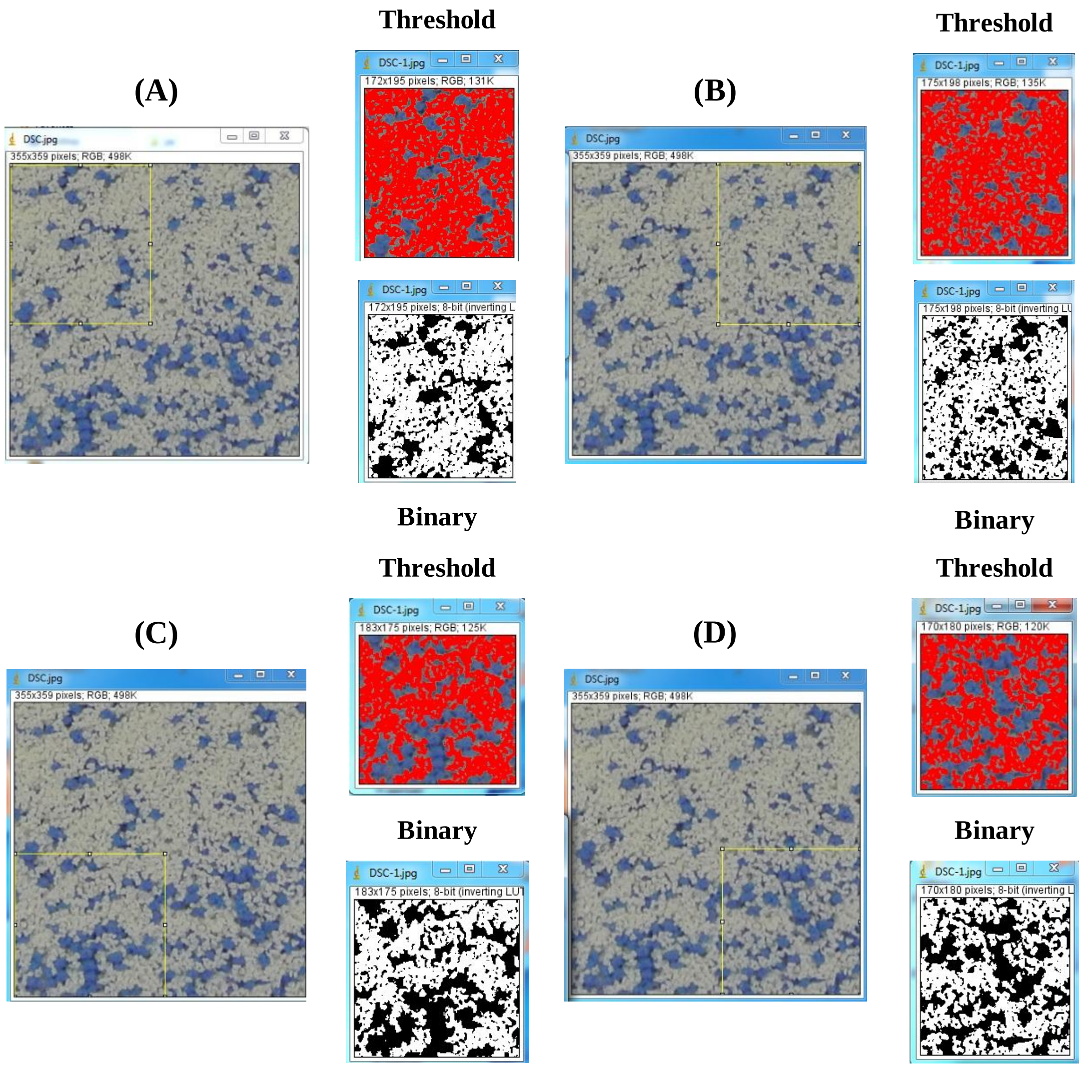


Figure 3.6: Different steps for TAED fraction analysis of Figure 3.5 using ImageJ software, grid (A) 1, (B) 2, (C) 3 and (D) 4.

Table 3.1: TAED fraction obtained by ImageJ software.

	Grid 1	Grid 2	Grid 3	Grid 4	SI (Eq. (2.7))
TAED fraction (Figure 3.5)	0.30	0.31	0.40	0.43	0.18

In this research, the application of Paintshop software (Corel PaintShop ® Pro X7) for quantifying the component fraction is further demonstrated. For this purpose, the picture of Figure 3.5 was first divided into 4 sections and then the desired area was segmented using sensitive selection tool of the software (TAED particles in this case,

Figure 3.7). The advantage of the selection tool of this software lays in the fact that only the particles could be segmented without the influence of the dark areas (such as voids). The fraction of TAED particles was then estimated using the pixel information (Table 3.2). As illustrated in Figure 3.7, better discrimination of TAED particles against voids and BP particles could be achieved using the sensitive tool of Paintshop software. In fact, the obtained average value of TAED using the mentioned approach is estimated as 22 %v/v which is close to the amount of the real value (25 %v/v).

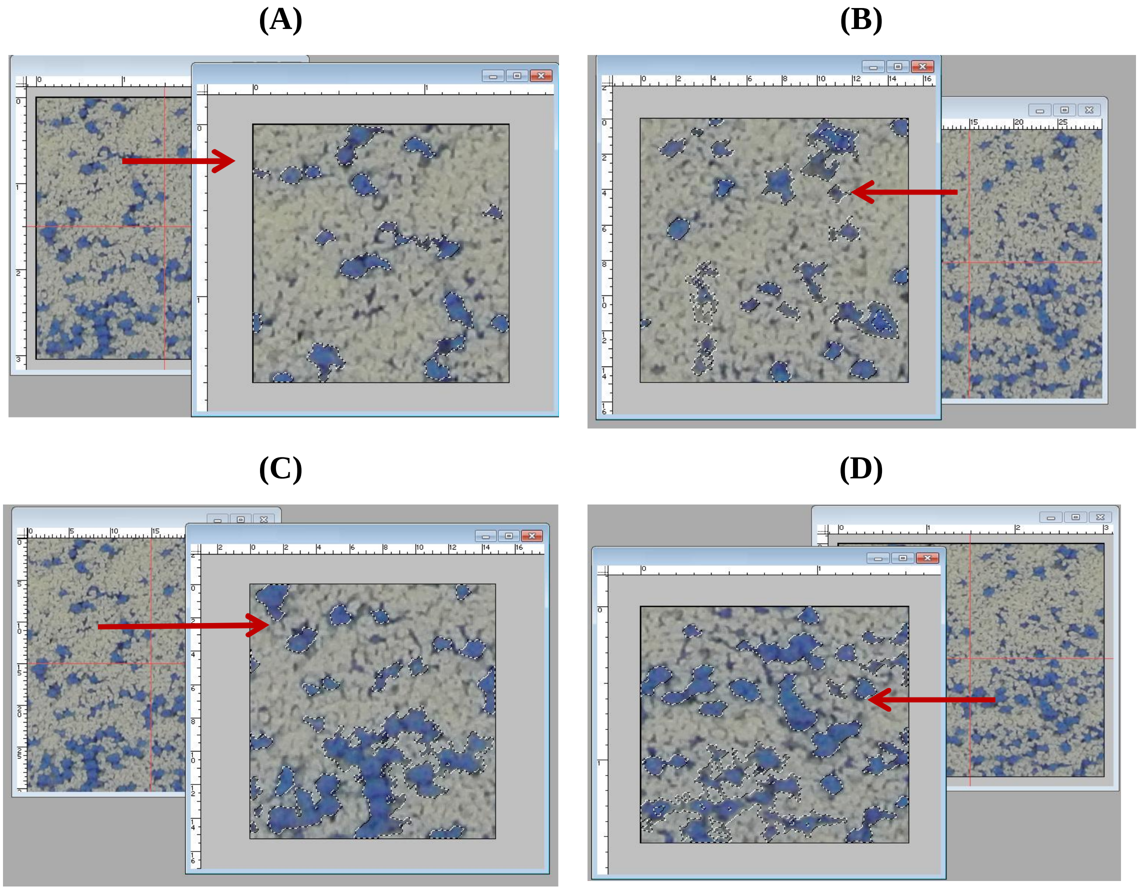


Figure 3.7: Selection of TAED particles using Paintshop software, grid (A) 1, (B) 2, (C) 3 and (D) 4.

Table 3.2: TAED fraction obtained by Paintshop software.

	Grid 1	Grid 2	Grid 3	Grid 4	SI (Eq. (2.7))
TAED fraction (Figure 3.5)	0.11	0.15	0.29	0.33	0.48

In many powder formulations, the particles have the same colour. Although image analysis technique offers a fast and accurate means of analysing component concentration in powder mixtures, this technique may not be applicable for the detection of components with similar colours. In the next section, the applicability of a Near-Infrared spectroscopy probe for the component fraction of laundry detergent powders is therefore investigated.

3.4 NIR spectroscopic technique

NIR technique has been widely used for the prediction of component concentration in powder mixtures. The objective of this section is to investigate application of an economic and portable NIR spectroscopic probe (MicroNIR1700® probe, manufactured by JDSU Ltd) to accurately estimate the component fraction distribution of washing powder mixtures.

3.4.1 MicroNIR1700® probe

The MicroNIR is a small model of NIR spectrometer platforms which is manufactured by JDSU Ltd (Viavi, Ltd). It could work with either reflectance or transmittance mode for the measurement of the absorption of a specimen. The reflectance mode is mainly used for the powder system, by which the illuminated Near-Infrared light to the sample is first reflected back from the surface of the specimen. Then, the reflected light is collected and analysed for the measurement of the absorption through the sample. Dispersing element of this system is called Linear Variable Filter (LVF) which is wedged in one direction at varying film thickness (Figure 3.8). Therefore, the light passed through the filter could be altered linearly towards the wedge direction, providing a specific wavelength range. Then, the transmitted light of different wavelengths could be detected by a linear detector array (128-pixel uncooled InGaAs photodiode array). The system is also equipped with integrated vacuum tungsten lamps as a light source and a 16 bit Analog-to-Digital Converter (ADC) as analog conversion. Other specification of the probe is listed below:

- Wavelength range: 900 – 1700 *nm*
- Spectrometer weight= 60 *g*
- Pixel to pixel interval (resolution)= 6.2 *nm*

Step by step software installation instructions as well as the running procedure are fully explained in the user guide and operational manual, provided by JDSU Ltd (Supplementary document, Folder name: MicroNIR™ Pro User Guide).

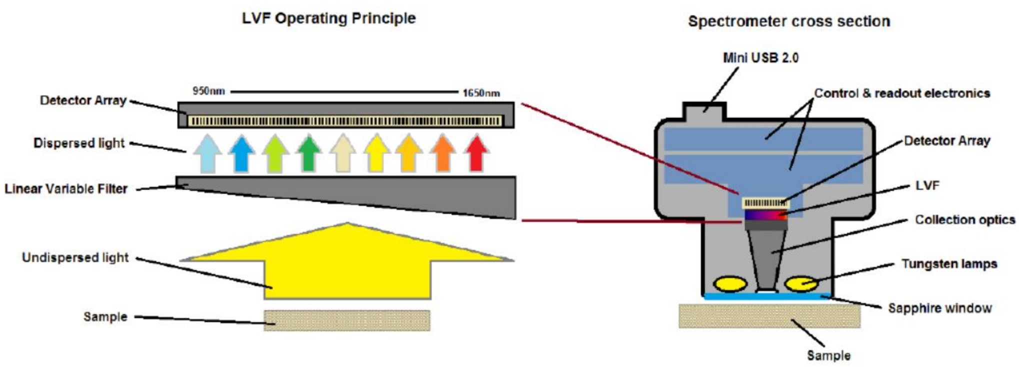


Figure 3.8: The operating principle and basic design of the MicroNIR, (Reprinted from MicroNIR™ Pro User Guide, JDSU Ltd (Viavi, Ltd)).

For the movement of the probe, a manual x-y positioner is used as shown in Figure 3.9. The automated mode of the set-up, for fast scanning the powder beds, is also developed and will be described later (section 3.4.7).

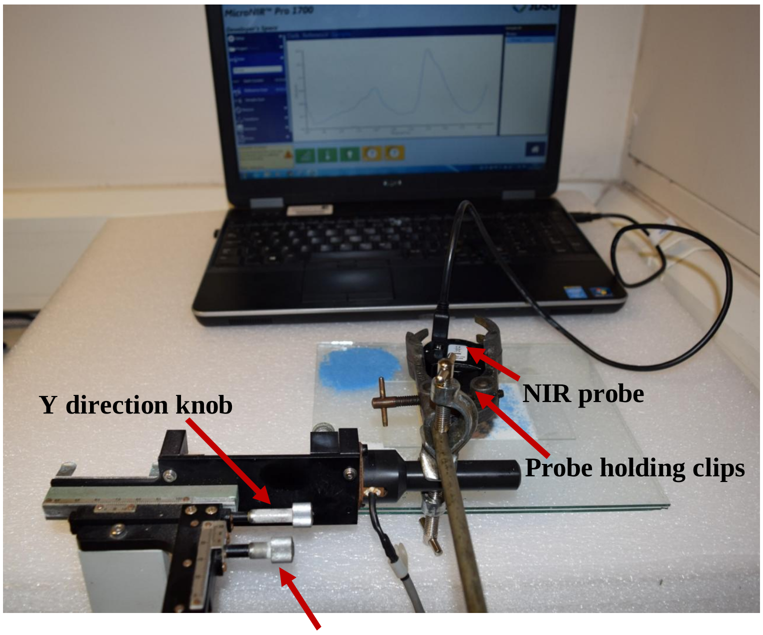


Figure 3.9: Coupled manual positioner and NIR probe for scanning the materials.

3.4.2 Absorbance spectra of pure materials

In vibrational spectroscopy approaches, such as NIR, the vibration at the molecular level will produce a spectral fingerprint of a specimen due to the dipole vibrations of O-H, C-H, and N-H bonds. The resulting spectra could be displayed in the form of absorption spectra. In this work, NIR spectra of individual components (at the full particle size distribution) were recorded by a single scan of the sample on the flat glass surface. Pure spectra of BP, TAED and EP granules are shown in Figure 3.10. A relatively clear difference between the pure spectra of components could be observed in Figure 3.10, particularly at wavelength range between 1350 to 1500 *nm*. However, the pure spectra shown in Figure 3.10 were obtained for full particle size distribution of components. It is recommended to investigate the effect of the particle size on the obtained raw absorbance spectra.

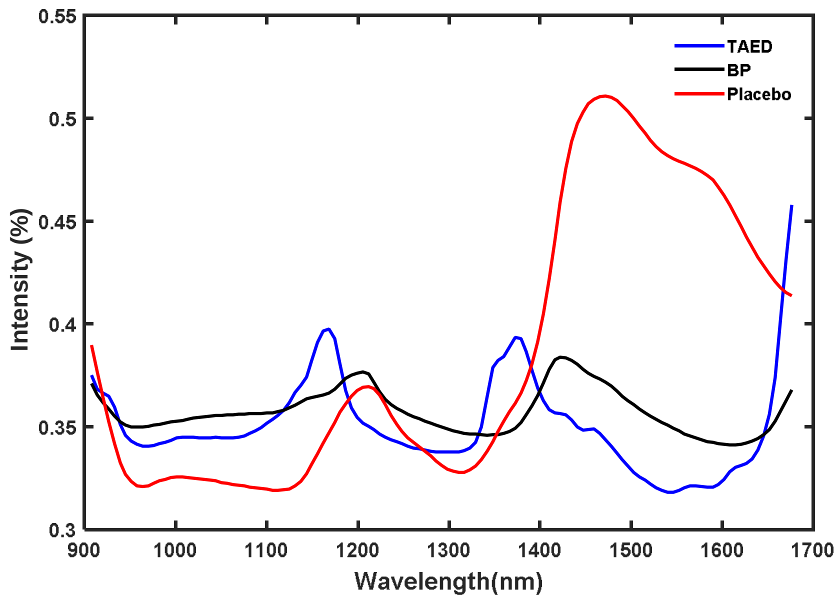


Figure 3.10: Pure spectra of BP, TAED and EP granules obtained for full particle size distribution.

3.4.3 The effect of particle size on the absorbance spectra

NIR spectroscopy gives information on reflected light from samples which consists of both chemical composition of samples as well as scattering effect arising from physical phenomena such as variation in particle size. For component fraction data analysis, only the information on chemical composition of samples is required, while that associated with size variation needs to be eliminated (Rinnan et al., 2009).

In order to investigate the effect of particle size on the pure spectra, different sieve cuts of components have been analysed separately. Particles were carefully sieved (in a range between: 355-425, 425-500, 500-600, 600-710, 710-850, 850-1000, 1000-1180 and 1180-1400 μm) using British standard size sieves and the absorbance spectra of single sieve cuts were obtained using MicroNIR1700® probe. The absorbance spectra of components for different sieve cut sizes are presented in Figure 3.11, where the mean of each sieve cut size is displayed on each plot.

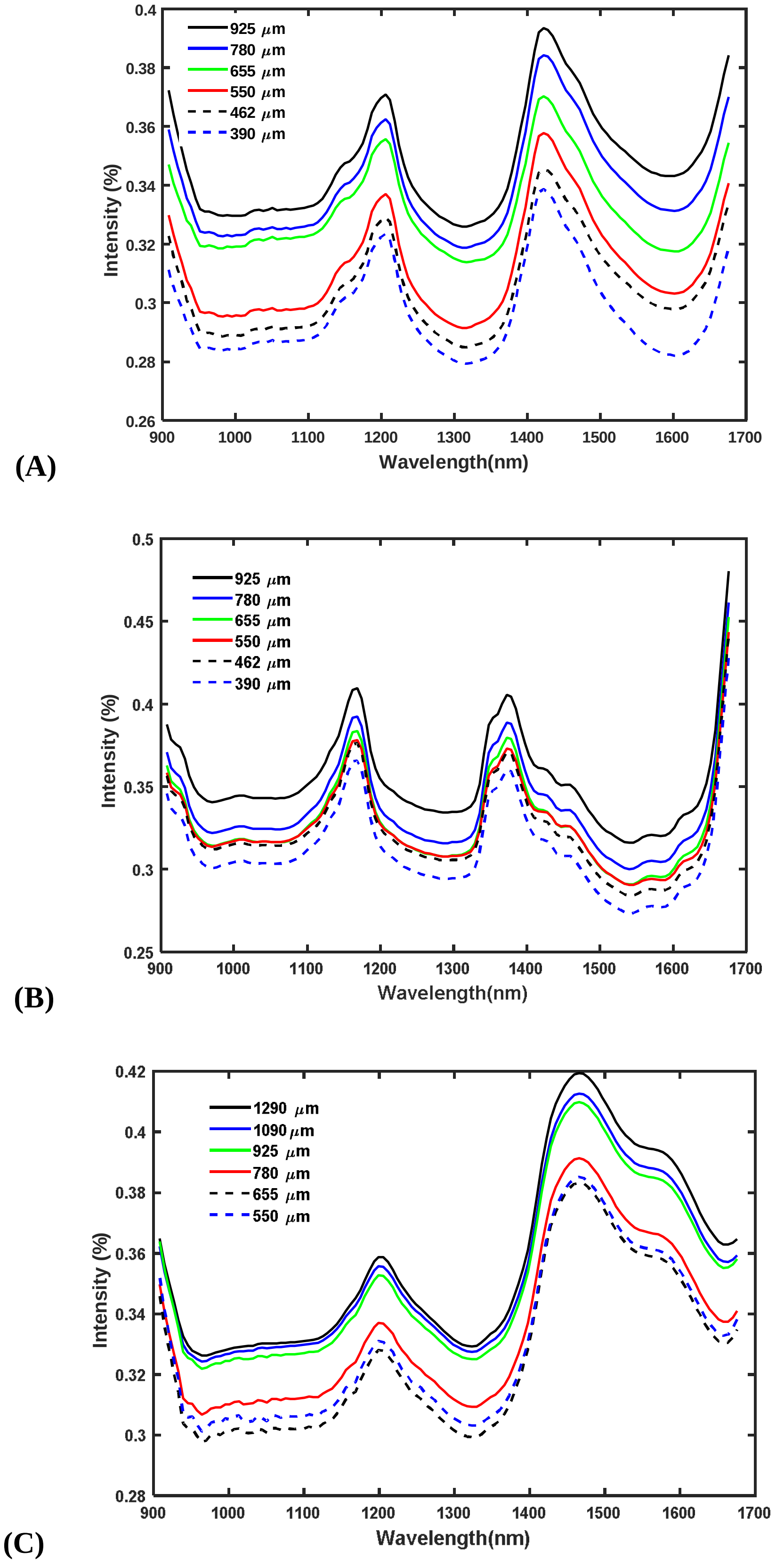


Figure 3.11: Raw absorbance spectra of (A) BP, (B) TAED and (C) EP granules at different sizes.

It could be seen from the absorbance curves that the spectra shift downward as the particle size is decreased, suggesting that different particle sizes in a mixture could influence the spectra acquisition. For an accurate data analysis, the effects of baseline shift and non-linearities resulting from size variations must be further eliminated. This could be done by applying different pre-processing techniques which will be described in the next section.

3.4.4 The effect of pre-processing on the absorbance spectra

For improving the multivariate regressions, it is first required to apply pre-processing methods to eliminate the physical phenomena of the spectra. The scatter effects could be eliminated using spectral pre-processing methods, which are divided into two main categories of scatter correction and spectral derivatives methods. Scatter correction is mainly applied for adjusting the baseline shifts, whilst using derivatives both baseline shifts and non-linearities could be corrected (Rinnan et al., 2009). In this section, most frequently used pre-processing techniques are investigated for improving the spectral information of powders and then the results are compared.

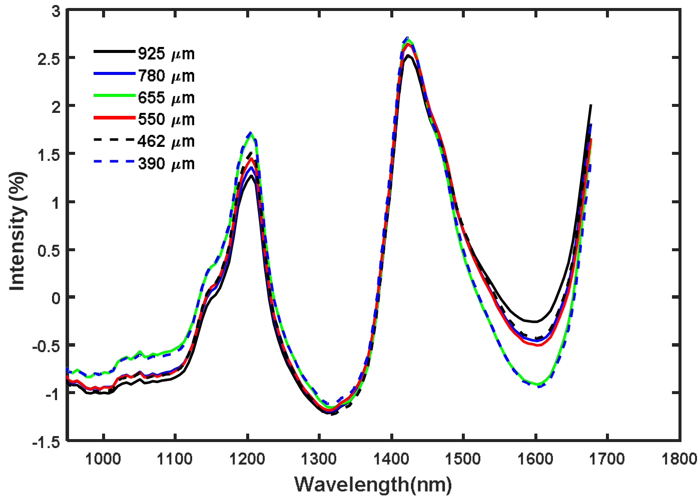
3.4.4.1 Scatter correction

Standard Normal Variate (SNV) is a simple scatter correction pre-processing technique used for enhancing the spectral information. This technique is mainly used for removing scatter differences of sample spectra having baseline changes (Barnes et al., 1989).

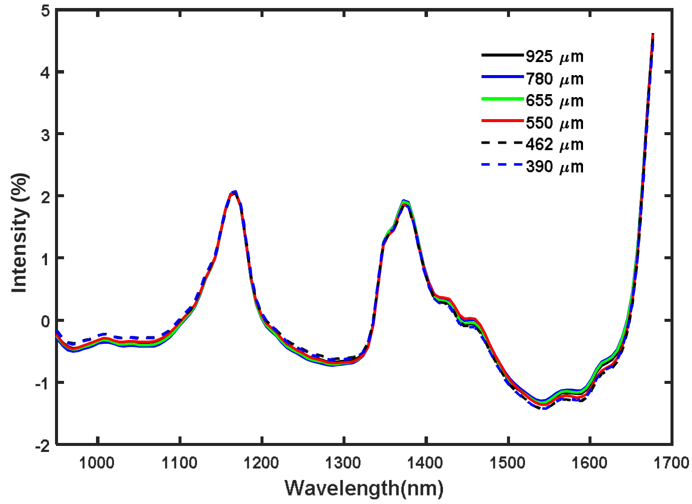
$$FS_{SNV}(\lambda) = \left(\frac{FS(\lambda) - \overline{FS}(\lambda)}{S}\right) \qquad 3.1$$

where $FS_{SNV}(\lambda)$, $\overline{FS}(\lambda)$ and S are the corrected spectra by SNV technique, the average value of the sample spectrum and standard deviation of the spectrum, respectively.

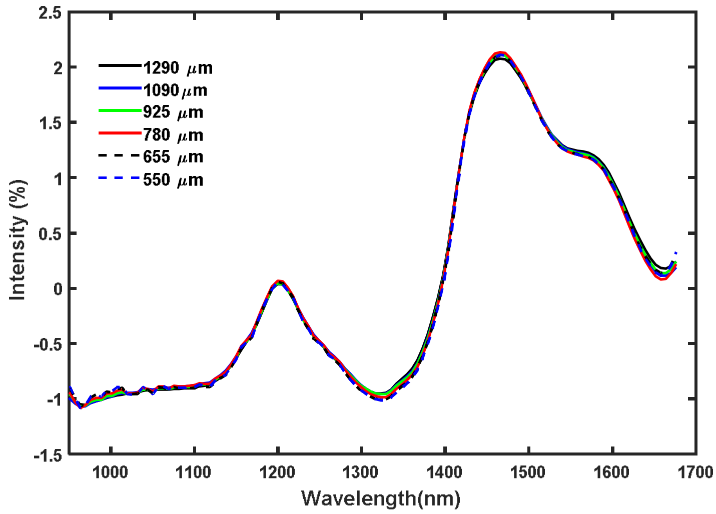
The SNV correction of the original absorbance spectra (Figure 3.11) is shown in Figure 3.12 for different components of BP, TAED and EP granules. It can be observed from Figure 3.12 that the baseline shifts could be treated by applying the SNV method. However, some non-linearities still exist between the spectra trends, particularly for BP. Therefore, the effects of derivatives on spectra treatment are further evaluated.



(A)



(B)



(C)

Figure 3.12: SNV correction of absorbance spectra (A) BP, (B) TAED and (C) EP granules at different sizes.

3.4.4.2 Derivatives

First and second derivatives are calculated numerically using the original reflectance spectral data according to the following equations:

$$FS'(\lambda_k) = \frac{FS(\lambda_{k+1}) - FS(\lambda_k)}{\lambda_{k+1} - \lambda_k} \tag{3.2}$$

$$FS''(\lambda_k) = \frac{FS(\lambda_{k+1}) - 2FS(\lambda_k) + FS(\lambda_{k-1})}{(\lambda_{k+1} - \lambda_k)^2} \tag{3.3}$$

where $FS'(\lambda_k)$ and $FS''(\lambda_k)$ are the corrected spectra after applying the first and second derivative modes, respectively.

The first and second derivative corrections of the original absorbance spectra of BP, TAED and EP granules (Figure 3.11) is shown in Figure 3.13 and Figure 3.14. A better uniformity of the spectra is observed after pre-processing using derivatives, particularly for second derivative, which could be due to the treatment of both baseline shifts and non-linearities.

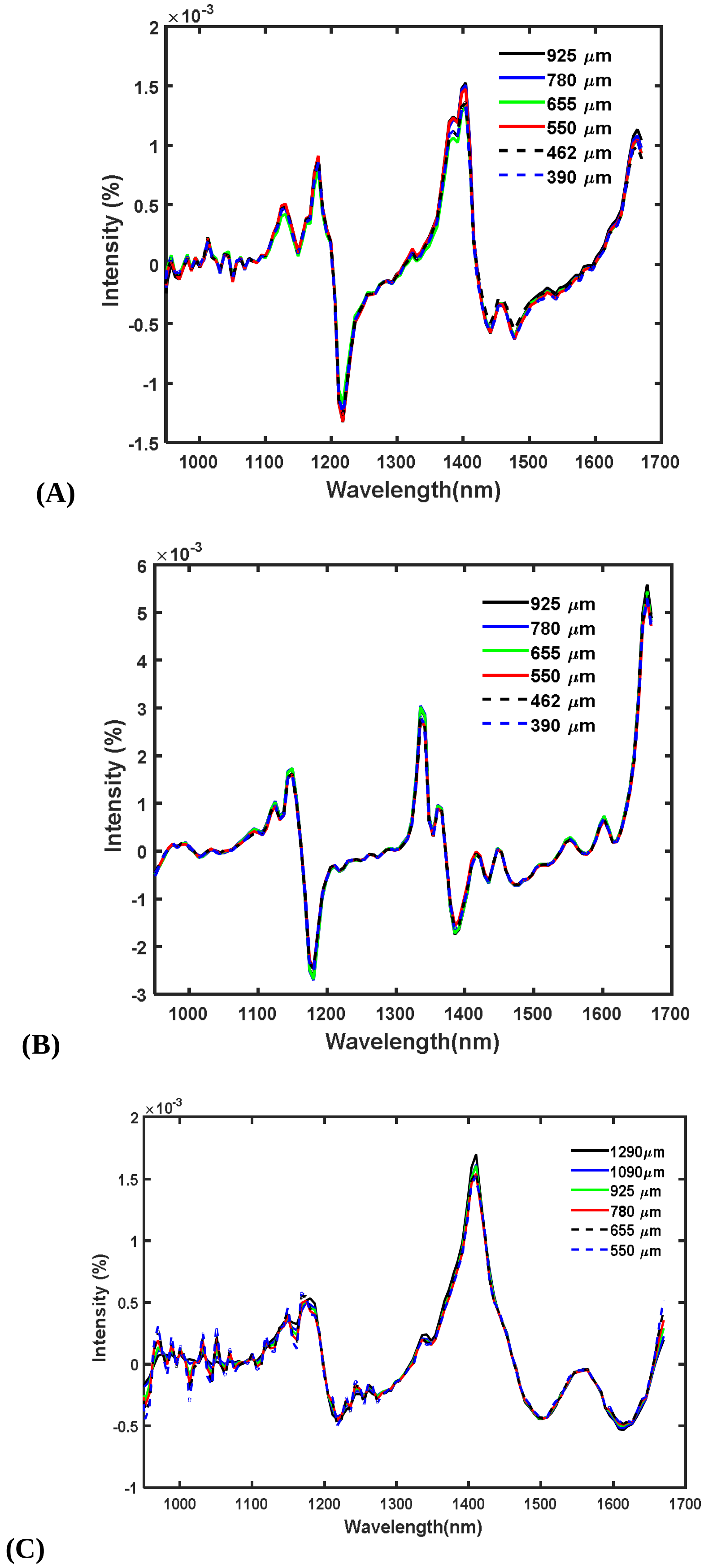
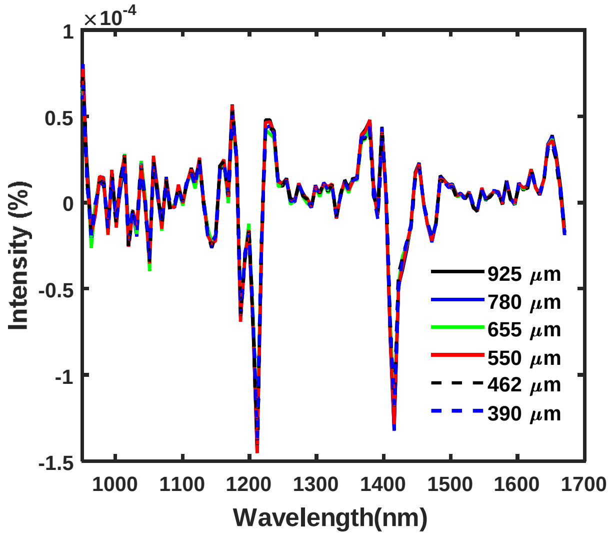
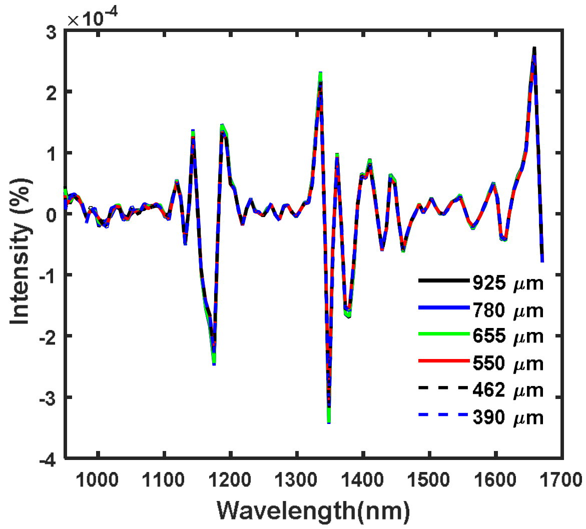


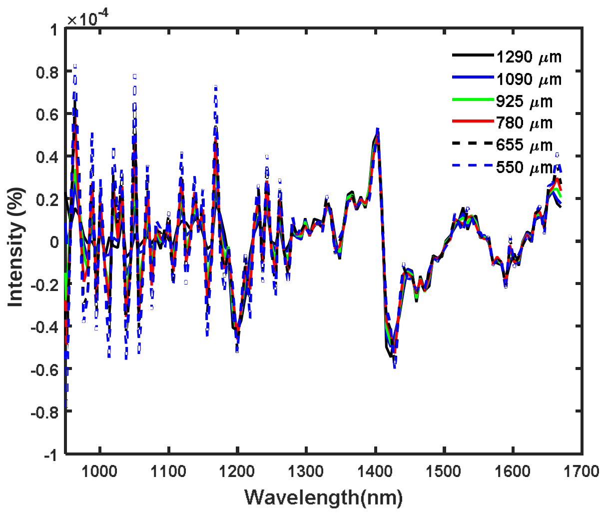
Figure 3.13: First derivative correction of absorbance spectra (A) BP, (B) TAED and (C) EP granules at different sizes.



(A)



(B)



(C)

Figure 3.14: Second derivative correction of absorbance spectra (A) BP, (B) TAED and (C) EP granules at different sizes.

First and second derivative methods are very simple; however they may cause some detrimental effects on the signal-to-noise ratio (Rinnan et al., 2009). Derivation techniques based on Norris-Williams and Savitzky-Golay are based on a smoothing method to reduce the detrimental effects on the signal-to-noise ratio (Norris and Williams, 1984; Savitzky and Golay, 1964). Therefore, it is recommended to use smoothing technique before applying the derivatives as pre-processing technique.

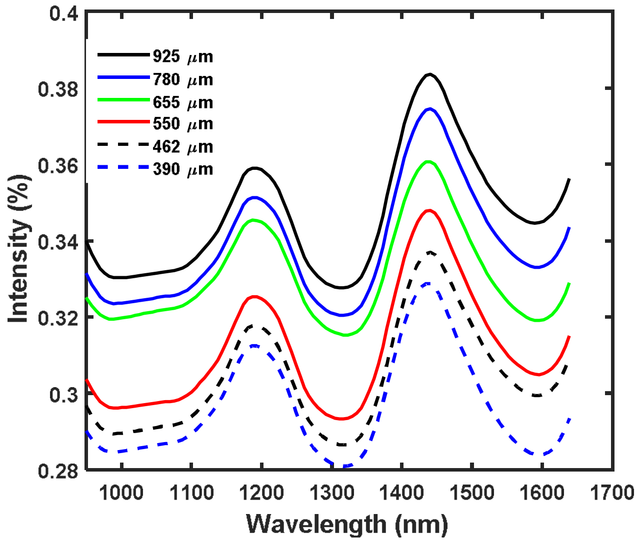
3.4.4.3 Smoothing techniques

Smoothing of the spectra prior to converting the raw spectra to the derivatives can be applied by Norris-Williams (N-W) and/or Savitzky-Golay (S-G) polynomial techniques (Norris and Williams, 1984; Savitzky and Golay, 1964). In Norris-Williams pre-processing technique, the smoothing of original reflectance spectra can be obtained by Equation 3.4:

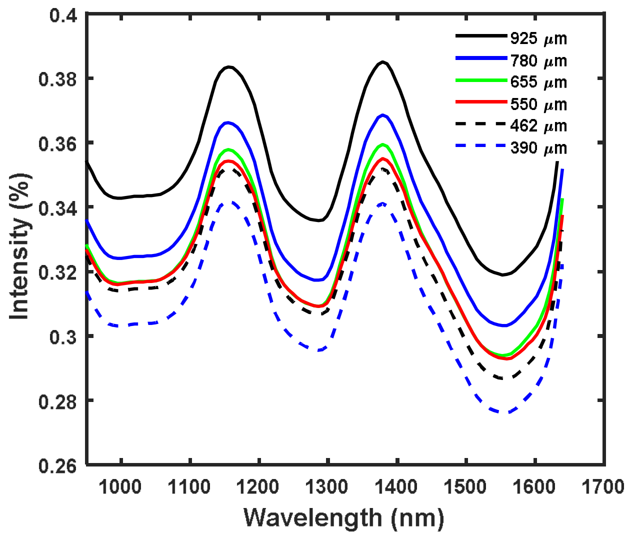
$$FS_{smooth}(\lambda)_k = \frac{\sum_{l=-m}^{m} FS\ (\lambda)_{k+l}}{2m+1} \tag{3.4}$$

where m is the number of points around the measurement point of k. The first and second derivatives of the smoothed spectra can then be obtained.

In the Savitzky-Golay method, a polynomial curve is fit to a specific number of points of the original reflectance spectra. The first and second derivatives of the smoothed spectra can then be obtained and used in post-processing data analysis. The smoothing of the original absorbance spectra of BP, TAED and EP granules (Figure 3.11) is shown in Figure 3.15 and 3.16. As illustrated in Figure 3.15 and 3.16, relatively smoothed spectra could be obtained after applying the N-W and S-G methods.



(A)



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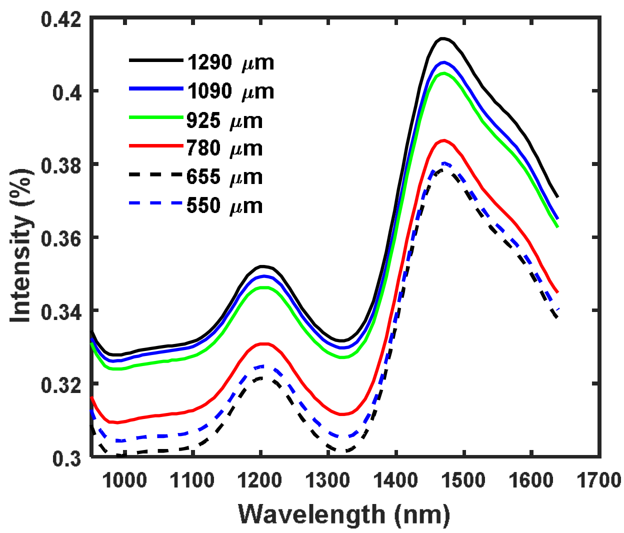
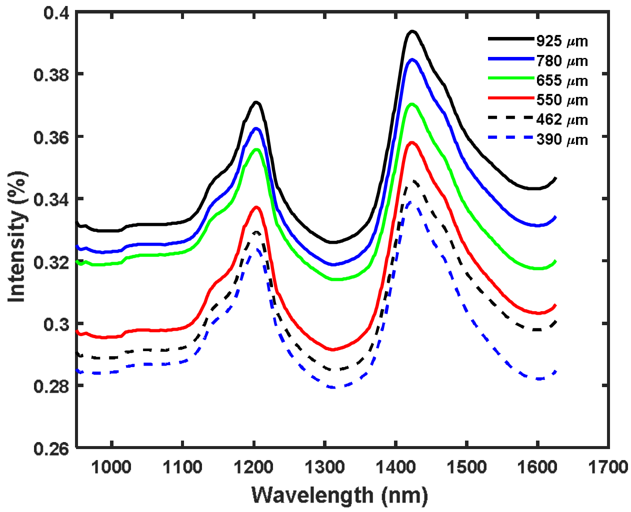
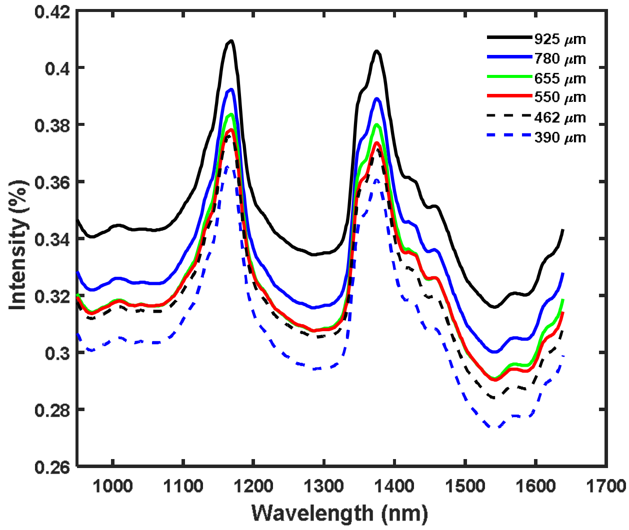


(C)

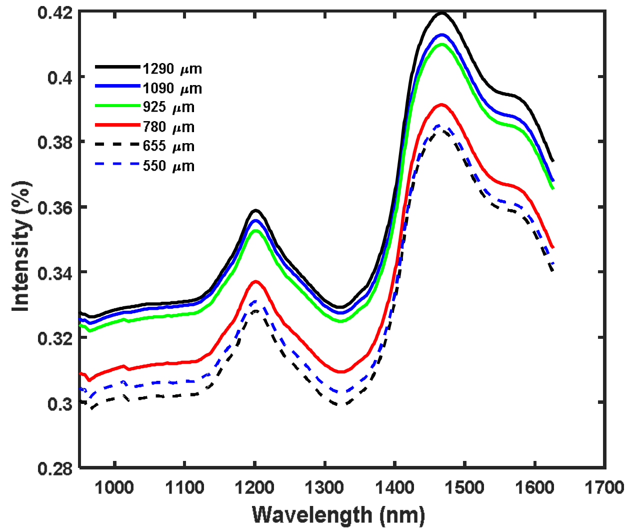
Figure 3.15: Smoothing of the absorbance raw spectra (A) BP, (B) TAED and (C) EP granules at different sizes, using N-W methods (m=6).



(A)



(B)



(C)

Figure 3.16: Smoothing of the absorbance raw spectra (A) BP, (B) TAED and (C) EP granules at different sizes, using S-G methods (P=6 and m=7).

3.4.5 Component fraction measurement using MicroNIR1700® probe

For validation of the results of NIR probe, a thin layer of washing powder mixture, containing BP, TAED and EP granules, was prepared on a flat glass surfaces (Figure 3.17). Different amounts of EP granules were added intentionally at specific areas on the ternary mixture. This enabled to accurately analyse the spatial distribution of the enzyme's component fraction in the mixture using image processing. The area of interest of the mixture was divided into 28 different grids, each equal to the area of detection of the probe. The absorbance spectra in each grid was obtained using the MicroNIR1700® probe. The probe was set up on an X-Y stepper (Figure 3.9) for an accurate scan of the mixture area. Using the proposed approach, large quantities of powder mixture could be analysed using spectroscopy technique.

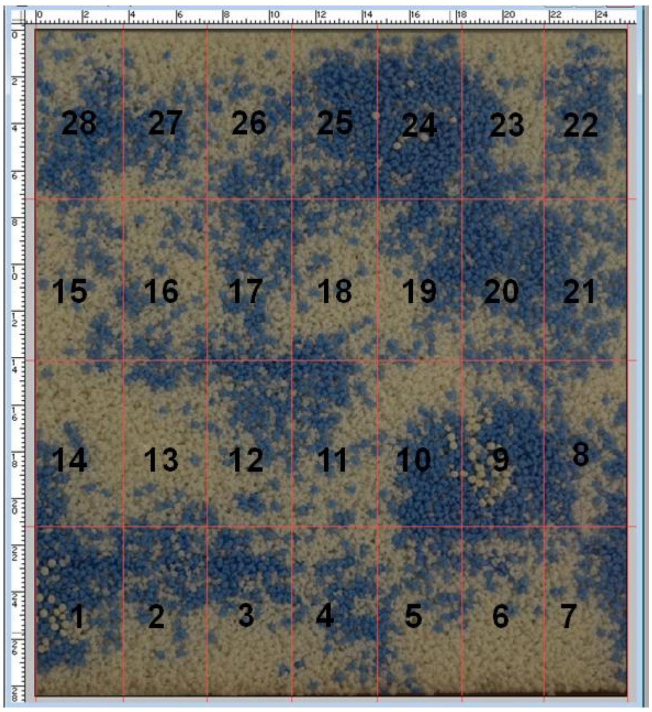


Figure 3.17: A washing powder mixture containing TAED, BP and EP granules.

The mixture spectral intensity was simulated by a linear combination of the spectral intensity of the pure components based on the local fraction (x_j) of each component (Equation 2.9 and 2.10). The least squares method was selected as the optimisation technique to minimise the sum of residual differences between the observed NIR intensity of the mixture and the average simulated intensity of the mixture. All programming and optimisation were done using Matlab R2014a software.

The effect of both pre-processed and raw absorbance spectra was investigated on the validation of the NIR results. The efficiency of the different pre-processing methods was evaluated by comparing the components fraction difference obtained from the NIR technique and the image processing. In this study, optical image processing was carried out using the approach explained in section 3.3.2. The value of Mean Absolute Error (MAE) and Mean Absolute Percentage Error (MAPE) could show the efficiency of the pre-processing method for the estimation of components fraction according to the Equation 3.5-3.7.

$$MAE_{overall} = \frac{1}{n_{grid}} \sum_{i=1}^{n_{grid}} \sum_{j=1}^{n_{comp}} \left| X_{Image\ analysis,(i,j)} - X_{Method,(i,j)} \right| \tag{3.5}$$

$$MAPE = \frac{100}{n_{grid}} \sum_{i=1}^{n_{grid}} \left| \frac{X_{Image\ analysis,(i)} - X_{Method,(i)}}{X_{Image\ analysis,(i)}} \right| \tag{3.6}$$

$$MAE_{placebo} = \frac{1}{n_{grid}} \sum_{i=1}^{n_{grid}} \left| X_{Image\ analysis,(i)} - X_{Method,(i)} \right| \tag{3.7}$$

where $X_{Image\ analysis,(i,j)}$ and $X_{Method,,(i,j)}$ are fraction data of component j using the image processing and NIR pre-processing method, respectively in grid i. n_{comp} is the number of components and n_{grid} is the number of grids.

3.4.5.1 Effect of raw absorbance spectra, SNV and derivatives

Overall error analysis results using original reflectance spectra, SNV as well as the first and second derivative pre-processing methods based on $MAE_{overall}$ are listed in Table 3.3 for the ternary mixture depicted in Figure 3.17. For comparison, the minimum value of MAE error is highlighted in bold, which relates to the suitable pre-processing method for the estimation of components fraction. Spectra were acquired for three time to measure the coefficient of variation between the measurements. According to the $MAE_{overall}$ results in Table 3.3, the minimum value of overall error could be achieved using the second derivative method. It can be deduced from the Table 3.3 that the component fraction obtained using derivatives is more in agreement with those obtained by the image processing as compared to the raw original reflectance mode. Good repeatability of the experimental results could also be observed in Table 3.3. As mentioned before, derivatives could correct the effect of baseline shifts and non-linearities arising from physical characteristic of particles such as size, improving the the multivariate regressions. As shown in Table 3.3, SNV method could not effectively estimate the component fractions, as this technique probably could not remove the spectra nonlinearities.

Table 3.3: $MAE_{overall}$ results using original reflectance, SNV, first and second derivative methods.

Mode	**Original Reflectance**	**SNV**	**First Derivative**	**Second Derivative**
$MAE_{overall}$	0.9194±0.04	0.6049±0.02	0.1830±0.02	**0.1731±0.01**

3.4.5.2 Effect of smoothing techniques

$MAE_{overall}$ results based on Norris-Williams derivation pre-processing method for different *m* values (according to Equation 3.4) are presented in Table 3.4 for the ternary mixture depicted in Figure 3.17. It can be concluded that $MAE_{overall}$ results using the second derivative of Norris-Williams method have the minimum value for the ternary mixture at m=6.

Table 3.4: $MAE_{overall}$ results based on Norris-Williams method.

	Mode	m						
		1	**2**	**3**	**4**	**5**	**6**	**7**
$MAE_{overall}$	**First Derivative**	0.1822 ±0.04	0.1818 ±0.02	0.1845 ±0.02	0.1942 ±0.01	0.2195 0.03	0.2587 ±0.03	0.3107 ±0.03
	Second Derivative	0.1749 ±0.01	0.1774 ±0.01	0.1760 ±0.03	0.1736 ±0.01	0.1713 ±0.03	**0.1673 ±0.03**	0.1721 ±0.03

$MAE_{overall}$ results of Savitzky-Golay pre-processing method using different polynomial orders and different spectral points are presented in Table 3.5 for the ternary mixture depicted in Figure 3.17. The least $MAE_{overall}$ value is achieved by the second derivative and the polynomial order of 6 for the ternary mixture (7 points). From the overall MAE error results so far, it can be concluded that the pre-processing method based on the second derivative of Savitzky-Golay is the optimum approach for the estimation of components fraction in the ternary mixtures studied here.

Table 3.5: $MAE_{overall}$ results based on Savitzky-Golay method.

Polynomial order (P)	**Number of points (m)**	**$MAE_{overall}$**	
		First Derivative	**Second Derivative**
2	**3**	0.2481±0.03	0.1909±0.02
	5	0.2501±0.02	0.1898±0.01
	7	0.2499±0.04	0.1725±0.04
	9	0.2473±0.05	0.2133±0.03
3	**5**	0.2506±0.02	0.1906±0.03
	7	0.2493±0.03	0.1743±0.01
	9	0.2487±0.04	0.2594±0.03
4	**5**	0.2505±0.02	0.1902±0.05
	7	0.2506±0.01	0.1713±0.02
	9	0.2492±0.03	0.2525±0.02
5	**7**	0.2513±0.01	0.1719±0.02
	9	0.2487±0.03	0.2541±0.02
6	**7**	0.2510±0.01	**0.1643±0.03**
	9	0.2497±0.04	0.2557±0.01

It could be seen from raw absorbance spectra (Figure 3.11) that the spectra shift downward as the particle size is decreased, suggesting that different sizes in a mixture could influence the optimisation differently using original absorbance mode. The baseline shifts caused by the particle size of the component could be corrected by derivatives approaches of original reflectance spectra making the spectral to be more identical. However, a better treatment could be made by smoothing as they could reduce the detrimental effect of derivative pre-processing alone on the signal-to-noise ratio (Figure 3.15 and 3.16).

3.4.5.3 Combination of scatter correction and derivative techniques

In a number of studies, the combined derivative and scatter correction method is reported as the optimum method for pre-processing of spectra (Wu et al., 2012; Ziémons et al., 2011; Michelle and Alan, 2013). For example, Karande et al. (2010) used SNV followed by the first derivative Savitzky–Golay method using nine points technique for eliminating NIR spectral scattering of blend components. In our work, the results of combined SNV with different derivative approaches for the estimation of component fractions of washing powders are shown in Table 3.6. It can be observed that the combined approaches could not reduce $MAE_{overall}$ of the component fraction results as compared to the derivatives method alone. According to the Tables 3.3 and 3.6, the scatter correction based on SNV method is not suitable for the pre-processing of the spectra analysed here.

Table 3.6: Effect of SNV method followed by different derivatives.

	Ternary mixture			
	SNV+first derivative	**SNV+second derivative**	**SNV+ Norris-Williams derivative**	**SNV+ Savitzky-Golay derivative**
$MAE_{overall}$	0.4488±0.02	0.2943±0.02	0.2785±0.02	0.3186±0.04

3.4.5.4 Accurate quantification of low content level ingredient of enzyme granules

MAPE (Equation 3.6) results of individual components using original raw reflectance, derivatives based on first and second derivatives as well as optimum points using Norris-Williams and Savitzky-Golay methods are reported in Table 3.7 for the ternary mixture depicted in Figure 3.17. It should be noted that MAPE works well when there are no zero data. The error on zero data can be extremely high, making a false estimation using MAPE. For this reason, MAPE is not reported for low content level EP granules as they produced zero data in the ternary mixture studied here. $MAE_{Placebo}$ instead of MAPE is reported for EP granules as shown in Table 3.7.

It should be noted that for the ternary system, the minimum overall $MAE_{overall}$ is obtained using the Savitzky-Golay method, (Table 3.5). However, $MAE_{Placebo}$ and fraction results of the EP granules (as presented in Table 3.7) show that the Norris-Williams method based on the second derivative gives the smallest error for EP granules. Thus, good care must be taken in choosing a good pre-processing method for the low-level ingredient by taking account of the error result of the mixture as well as the individual components. According to the results of Table 3.7 and Figure 3.18, the second derivative mode of Norris-Williams pre-processing method gives a good estimation of the enzyme fraction, the component being a low content level ingredient in the ternary mixture.

Table 3.7: Error results of individual components.

Error	**Components**	**Mode**				
		Original Reflectance	**First Derivative**	**Second Derivative**	**N-W, Second derivative**	**S-G, Second derivative**
MAPE	**TAED**	55.01	13.98	15.46	14.68	13.89
	BP	46.27	12.00	13.93	13.82	13.53
$MAE_{Placebo}$	**Placebo**	0.1436	0.0322	0.0065	**0.0047**	0.0092

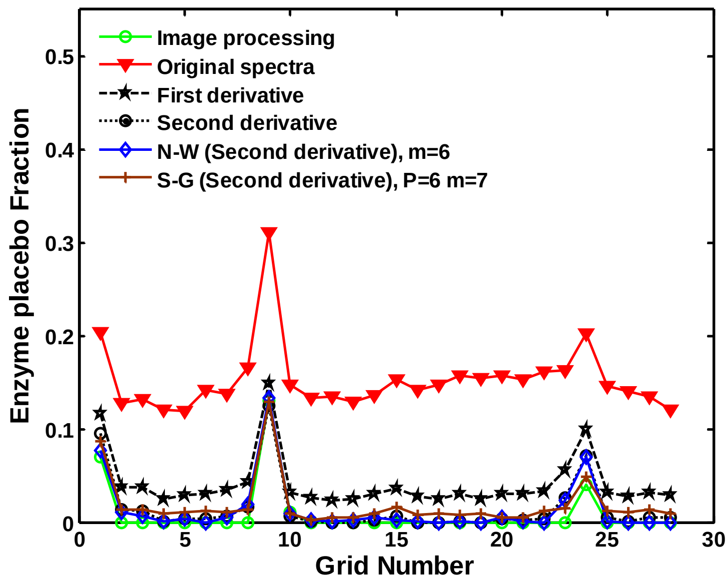


Figure 3.18: EP granule's fraction in ternary mixture obtained by image analysis, original reflectance and different pre-processing methods.

In fact, according to the nature of raw spectra data of each component, specific pre-processing methods could be beneficial for different spectra treatment (Xu et al., 2008). Depending on the composition of powders and particle size distribution of each species, samples show different spectra patterns with baseline shifts and/or non-linearities (Rinnan et al., 2009). Good care must be taken for applying the best pre-treatment method, as they could negatively affect the signal quality. Thus for each powder system, it is important to select the appropriate pre-processing method. According to the above-mentioned results, the pre-processing technique that uses derivative works better than the scatter correction method for the samples studied here. This treatment could be further improved by spectral smoothing. As previously mentioned, derivatives alone could have some detrimental effect on the signal-to-noise ratio. However, the most appropriate smoothing technique should also be investigated as some techniques could worsen the treatment. Savitzky-Golay method has broadly been used as a robust smoothing technique in many cases (Sankaran et al., 2010; Preisner et al., 2008; He et al., 2007; Luginbühl et al., 2006). However, it does not always offer the best spectra pre-treatment. For example, in the case of Kokalj et al. (2011) it is shown that among different smoothing techniques, pre-processing using Savitzky-Golay method could not be appropriate for spectral treatment of biological samples as important information of spectra could be lost by this technique. In our case, the prediction of low content level ingredient of EP granules is found to be more accurate using smoothing technique of Norris-Williams, as shown in Table 3.7. Some spectral information of EP granules, which enables its differentiation from the spectra of BP and TAED during optimisation, could be eliminated using Savitzky-Golay method whilst preserved using Norris-Williams method.

3.4.6 Sensitivity of MicroNIR1700 to the minor ingredient

In this section, the sensitivity of the MicroNIR to the minor ingredient enzyme granules is first studied where different ternary mixtures having different amounts of EP granules were analysed (Figure 3.19). As illustrated in Figure 3.19, EP granules are added individually to the mixture of BP and TAED to make five different ternary mixtures. The acquired spectra of the ternary mixture were then analysed (according to the optimum pre-processing method reported for EP granules, section 3.4.5.4) to estimate the fraction of EP granules.

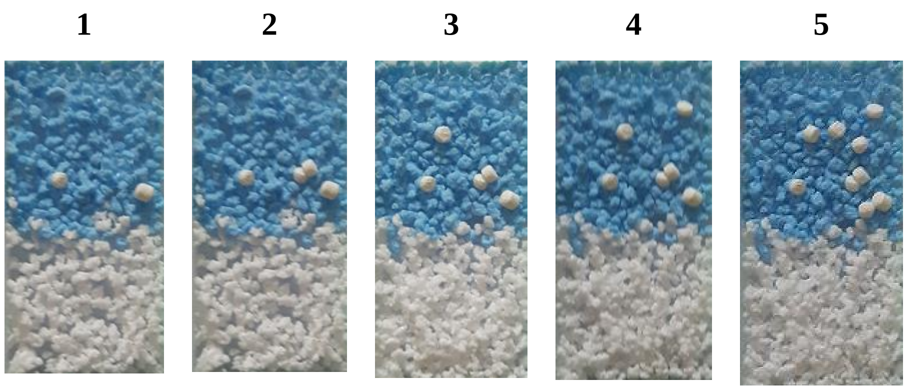


Figure 3.19: Gradual addition of EP granules on the bed of TAED and BP.

The obtained fraction of EP granules using the proposed optimisation technique is presented in Figure 3.20-A. As shown in Figure 3.20-A, the proposed technique could successfully spot the addition of single enzyme granules to the mixture. The spectral shifting of the mixture to the spectra of pure EP granules, after gradually adding the EP granules to the mixture, could be observed in (Figure 3.20-B).

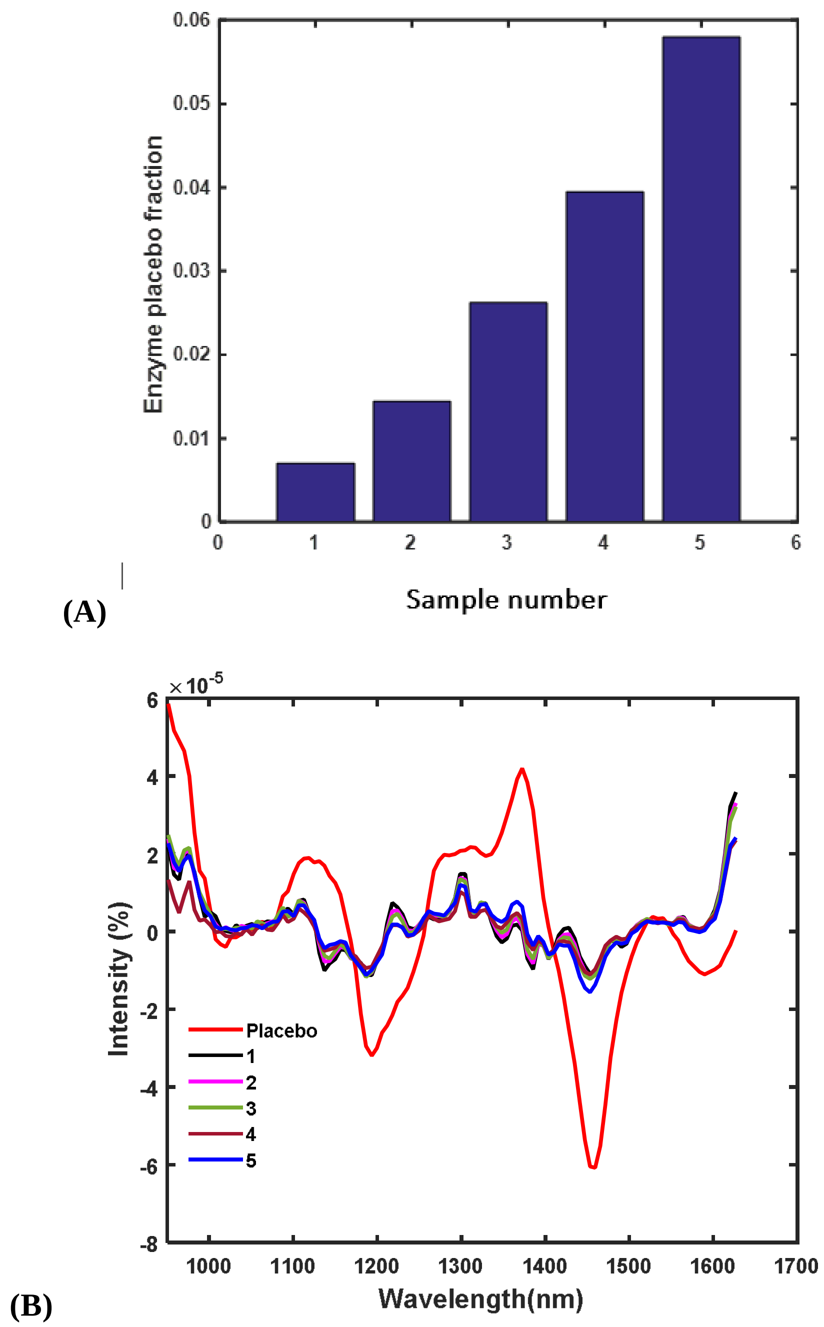
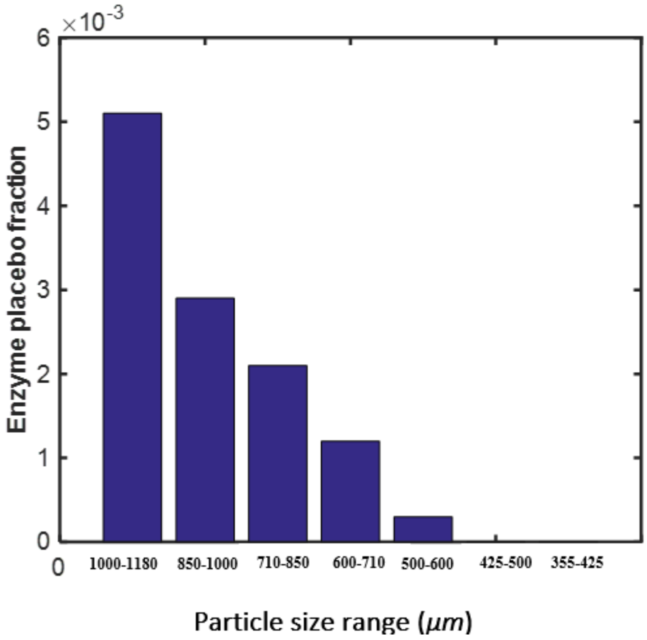


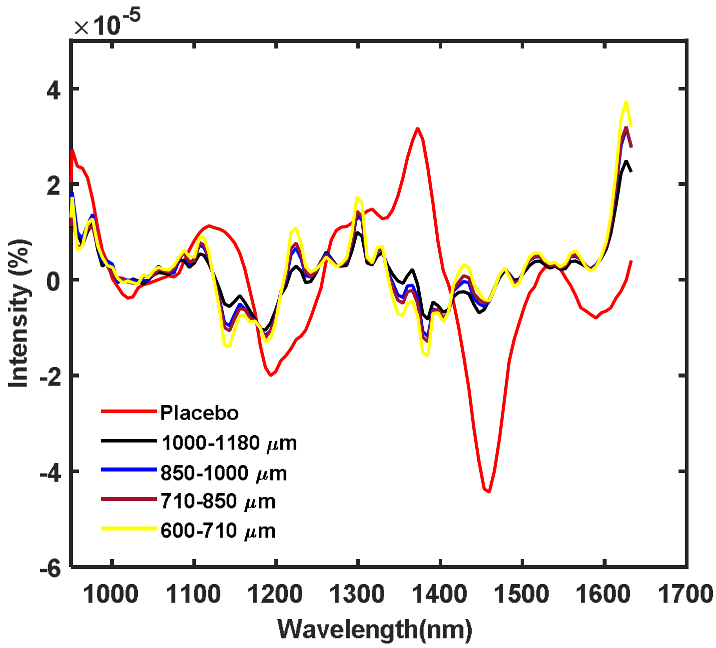
Figure 3.20: (A) EP granule's fraction measured for the mixtures shown in Figure 3.19 and (B) spectra viarition between different samples.

In another study, sensitivity of the MicroNIR probe for the detection of minor ingredient is analysed. For this purpose, EP granules at different sieve cut size ranges (355-425, 425-500, 500-600, 600-710, 710-850, 850-1000, 1000-1180 μm) was placed into the interface between the beds of BP and TAED. The sensor was placed on top of the ternary mixture in such a way that the centre of the probe was adjusted on top of the EP granules. The acquired spectra of the ternary mixture were then analysed (according to the optimum pre-processing method obtained for EP granules, reported in section 3.4.5.4) to estimate the fraction of EP granules. Figure 3.21-A illustrates the fraction of EP granules at different size ranges. As shown in the Figure 3.19-A, MicroNIR could successfully detect the minor ingredient at sieve cut size range more than 500-600 μm.

The spectra variation of the ternary mixture containing different sizes of EP granules (using the second derivative of Norris-Williams method (m=6)) is shown in Figure 3.21-B. It can be observed in Figure 3.21-B that the spectrum of mixture is gradually shifting to the spectrum of pure EP granules by increasing the size of enzyme in the ternary mixture.



(A)



(B)

Figure 3.21: (A) EP granule's detection by MicroNIR probe at different size ranges and (B) spectra variation of the ternary mixture containing different size ranges of enzyme granules.

3.4.7 Development of a NIR set-up for fast scanning of the surface of powders

An automated stepper device, equipped with MicroNIR1700® probe, was developed for fast scanning of the powders bed. The representative map of the developed X-Y positioner is shown in Figure 3.22, which consists of a central controller, two sets of motion drivers, two stepper motors, two power supplies and two actuators (X-Y table).

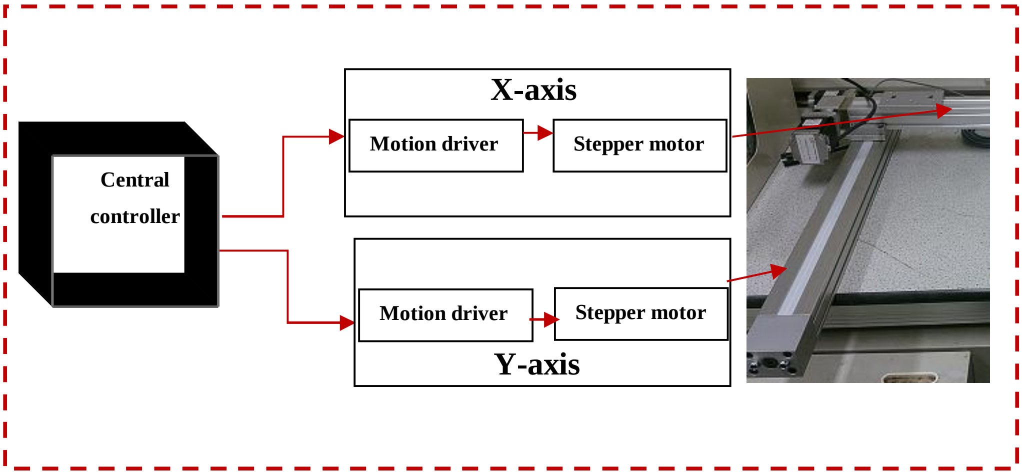


Figure 3.22: Representative map of the positioner set-up.

The central controller performs the function of motion trajectory and data communication with motion drivers, via user program execution on PC (perfect motioner software, Ver. 3, in this case). Each motion driver is applied for adjusting the position, speed and acceleration of each stepper motor. The stepper motors are located on the actuators, enabling the movement of the NIR probe in X-Y directions.

The developed MicroNIR-positioner set-up is illustrated in Figure 3.23, for which the power supply, central controller, motion drivers and stepper motors, (manufactured by SmartDrive Ltd), are connected all together. As illustrated in Figure 3.23, the probe is set up on the automated X-Y stepper where the accurate scan of the mixture area could be performed by programming. The NIR set-up developed in this study can enable analysing large quantities of samples and can significantly reduce the sample preparation time. Further information, including the free version software, programming instructions and related documents are provided in Supplementary document (Folder name: X-Y positioner).

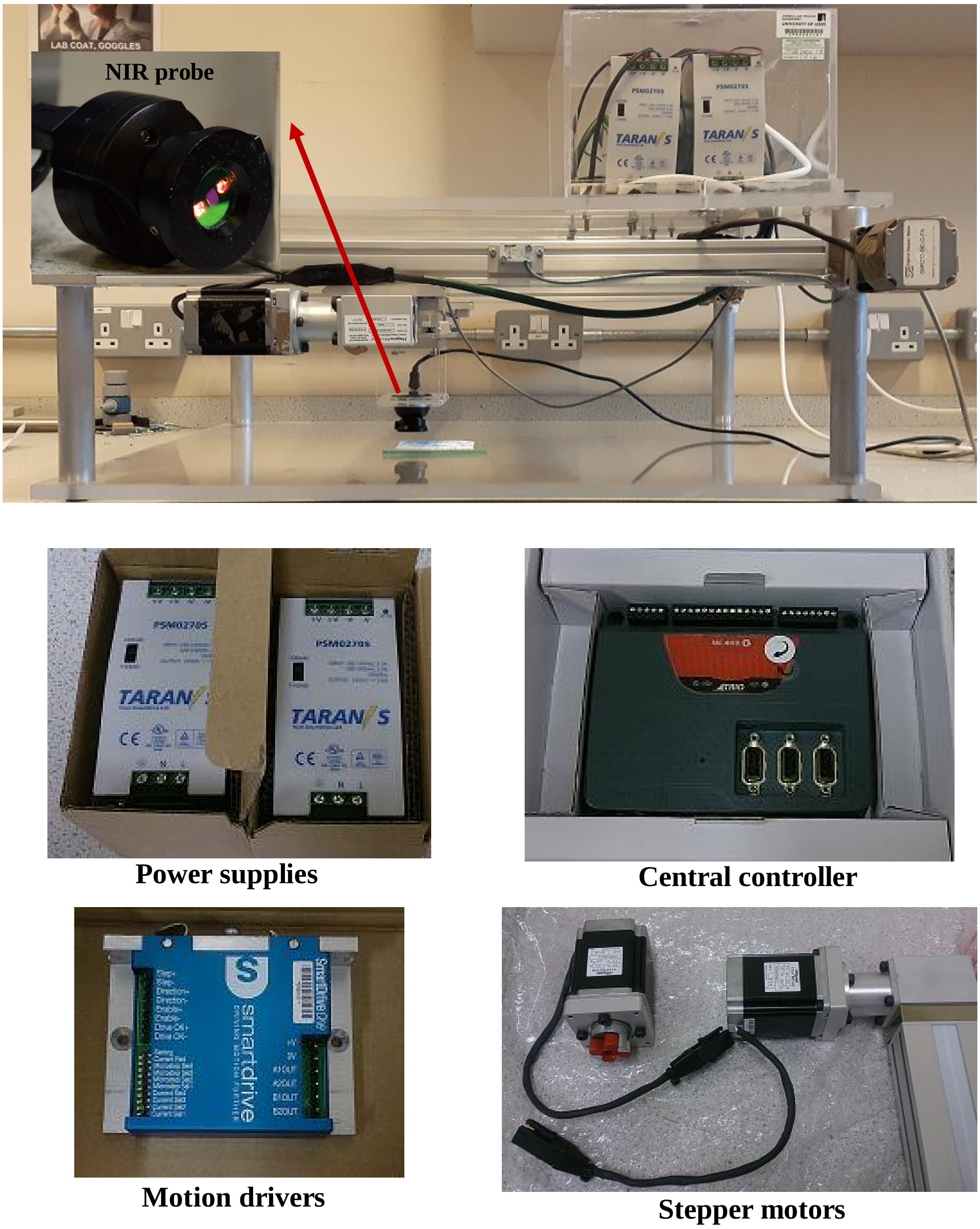


Figure 3.23: MicroNIR-positioner set-up consists of: power supplies, central controller, motion drivers and stepper motors.

3.5 Segregation analysis of minor ingredient in heaps

Segregation of components can be observed using heap formation of blended powder mixtures as particles of differing material properties can separate from each other during the pouring process (Harris and Hildon, 1970; Benito et al., 2013). As a case study, segregation of minor ingredient EP granules in a ternary mixture heap comprising BP, TAED and EP granules with 93/6/1 wt% (exact composition ratio used in detergent formulation) is analysed. Heap formation and the extraction of samples from the formed heap (dimension: 0.2× 0.2× 0.015 *m*) have been performed in a 3D grid box (Figure 3.24). For this purpose, a heap of powder was generated by pouring the primarily mixed powders through a funnel into the box. The box used in this study has dividing blades, enabling the extraction of samples from different regions within the whole mixture. In fact, three stages are required for extracting the materials from the heap box: 1) the heap of powders is generated using the funnel, 2) the vertical blades are gently inserted into the bed of the material to divide the mixture into different parallel subsections, 3) the horizontal blades are pushed into the bed of powders to subdivide the mixture into smaller subsections and 4) finally, each subsection could be extracted individually, starting from the corner of the heap.

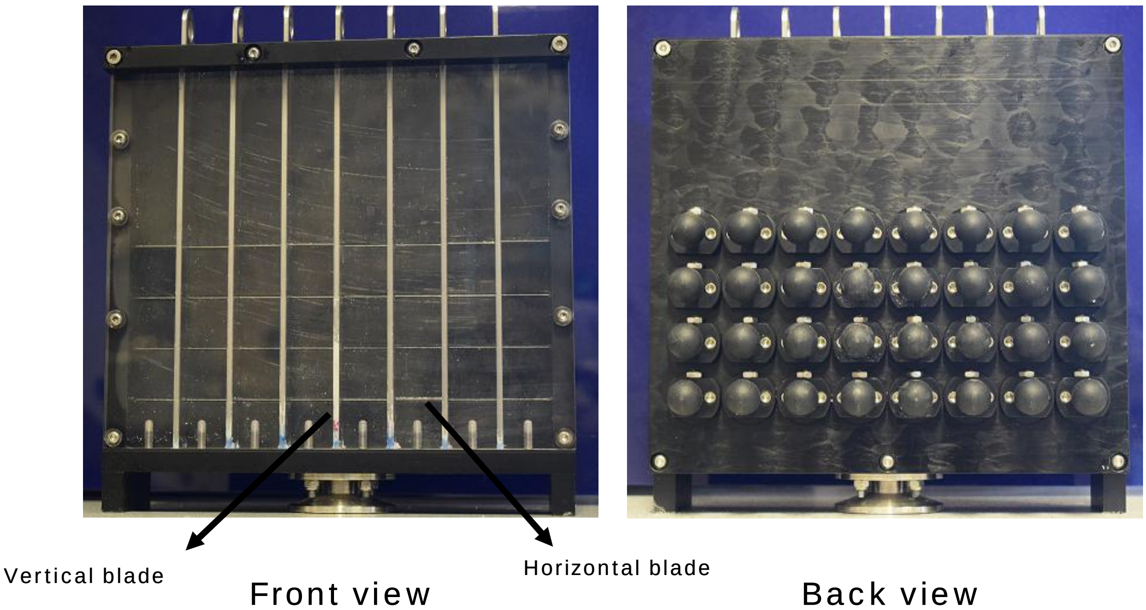


Figure 3.24: The grid box used for making a heap.

Different stages required for the extraction of samples within the ternary mixture heap are shown in Figure 3.25-A. To estimate the average fraction of EP granules in each extracted sample, thin layers of them were spread on a glass slide and scanned by NIR probe and image processing method, according to the procedure described in section 3.3 and 3.4. The optimum pre-processing method for EP granules (reported in section 3.4.5.4) has been used for the measurement of enzyme fraction using NIR technique. Enzyme's fraction measured for a number of extracted powder mixtures (highlighted in red in Figure 3.25-B) using the proposed NIR technique are shown in Figure 3.26 and compared with the image analysis results. A relatively good agreement between the results of NIR technique and image processing is observed.

(A)

1-Unsegmented heap **2-Inserting vertical blades** **3-Inserting horizontal blades**

(B)

Figure 3.25: (A) Different stages of sample extraction in ternary heap (B) grid marked heap.

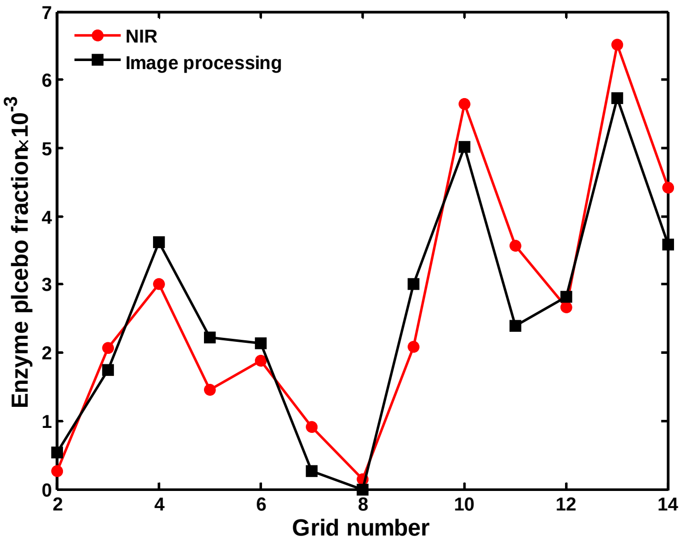


Figure 3.26: EP granule's fraction for the ternary heap of laundry detergent powders obtained by the proposed NIR technique and image processing.

The segregation index of the EP granules could then be measured using Equation 2.7. Segregation index of enzyme granules obtained from NIR analysis (calculated for filled cells highlighted in red in Figure 3.25-B) is found to be 0.71 which is close to that obtained using image processing (0.64). Relatively high segregation index measured for EP granules in the ternary mixture studied here could be due to presence of less enzyme granules towards the surface of the heap (grid 2, 7 and 8) than the centre of the heap (grid 10, 11, 13 and 14). The segregation mechanisms of the studied powder formulation will therefore be discussed in the next chapter.

3.6 Concluding remarks

Image processing and spectroscopy techniques (using MicroNIR1700® probe) has been examined for the investigation of segregation in the mixture of laundry detergent powders. NIR spectroscopy using MicroNIR1700® probe and the concept of classical least square method based on the analysis of mixture and pure component spectra was used for the quantification of components fraction. Raw reflectance data as well as data obtained by different pre-processing methods were used for the spectral analysis. The comparison of segregation index obtained by MicroNIR1700® probe and image analysis showed that there was a relatively good agreement between the results obtained by these methods. It is found that spectral pre-processing using derivatives can be used to correct both baseline shift and non-linearities arising from differing physical properties of the components such as particle size. The second derivative of Norris-Williams pre-processing method showed the best optimisation technique for the quantification of low content level EP granules in the ternary mixture of detergent powder. The findings of this research demonstrate that the suitable pre-processing technique for the accurate quantification of the desired ingredient must be investigated separately, while different researchers only utilized one pre-processing technique for the component analysis of the entire sample (Bittner et al., 2016; Luginbühl et al., 2006; Karande et al., 2010). Moreover, accurate component analysis of the main constituents of laundry detergent powder mixtures using NIR technique has not been fully addressed before. The results of this investigation evaluate the robust techniques for the measurement of the main constituents of laundry detergent powder mixtures. As a case study, segregation of minor ingredient enzyme granules in a ternary mixture heap, containing the exact component composition ratio used in detergent formulation, was analysed. The results have demonstrated that powder segregation analysis of low content level ingredients can be successfully achieved using the proposed NIR technique. It should be noted that the key methodology for the assessment of the extent of segregation of multi-component powder mixture using the segregation tester, proposed by Johanson (2014), is by scanning the surface of the heaps, where segregated powder pattern was produced during discharging process. The methodology for the current study proposes an alternative approach, where the scanning of thin layers of extracted powder materials (from gridded heap box) enables evaluating the concentration of larger amounts of the material which could be a better representation of the entire powder mixture. In addition, the results of this research study highlights the importance of carrying out a sensitivity analysis in order to find out the minimum possible size of particle detectable by the sensor and the proposed analytical analysis, which is very important for the segregation analysis of low content level ingredients. Moreover, the major advantage of the utilized portable NIR probe in this research is that it could be used for in-line measurement of the critical quality attributes in process. Overall, the NIR approach used in this research study enabled more content of segments taken from the heap to be analysed. Using this technique, it is concluded that the minor ingredient EP granules is highly segregated towards the centre of the heap. Therefore, main segregation mechanisms of the components in laundry detergent powders and segregation reduction approach must be explored which are described in the chapter 4 and chapter 5, respectively.

Chapter 4
Segregation mechanisms in washing powder mixtures

4.1 Introduction

As shown in the previous chapter (section 3.5), the low content level ingredient enzyme granules were prone to extensive segregation towards the centre of the heap of washing powder mixtures. Segregation of components, especially the low content level of a highly active substance, has serious deleterious effects on the final product quality. This chapter investigates the effect of particle properties, particularly size, shape and density, on the segregation of laundry detergent powders. The main segregation mechanisms in multicomponent mixture of laundry detergent powders are then discussed. Like the previous chapter, Tetraacetylethylenediamine (TAED), Blown Powder (BP) and Enzyme Placebo Granules (EP granules) are used as a model formulation. First, the segregation mechanisms will be investigated for the binary mixture and then the investigation will be extended to the ternary mixture.

4.2 Segregation mechanisms during filling

The phenomenon of particle segregation during heap formation is well known and has been an active area of research for several decades. During heap formation of blended powder mixtures, segregation of components happens as particles of differing material properties can separate from each other (Harris and Hildon, 1970; Benito et al., 2013). The experimental set-up used here, equipped with a two-dimensional (2D) heap box, mainly represents the granular pile building up in the form of heap which could expose the materials to a high extent of segregation (Figure 4.1). The produced heap of powders could also be subjected to a vertical vibration, by a defined frequency and amplitude using a vibration system as shown in Figure 4.1, which is controlled by an electrometer, TG315 function generator (AIM-TTI instruments, Cambridgeshire).

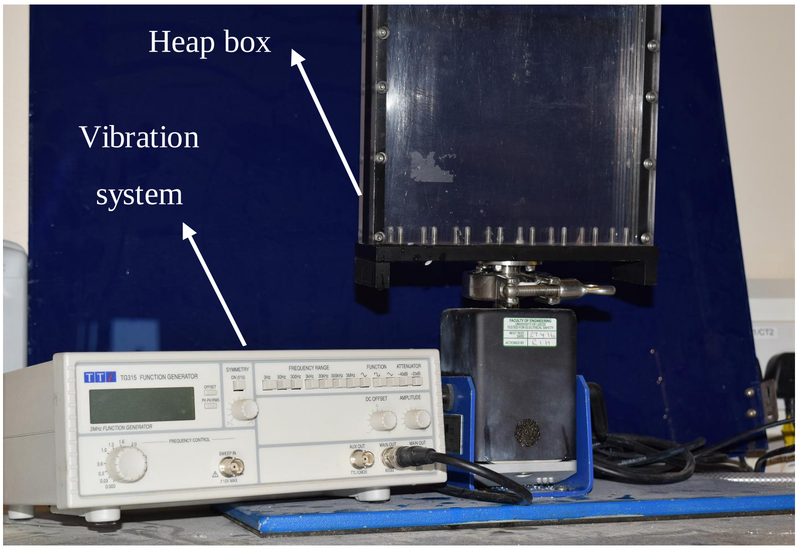


Figure 4.1: Schematic of segregation set-up.

The mixture of powders is poured through a funnel fixed to the top side of the heap box to form a heap. The funnel has an inclusive half angle of ~40° and the downcomer pipe of 30 *mm* long with 7 *mm* ID. When fixed to the top of the rig, the tip of the downcomer is at 150 *mm* distance from the base of the container. A Nikon camera (D3300, 24 MP) was used for taking the photos of the heap of powders. For generating the concentration map of components, the image is first divided into several grids and the component fraction of each grid is estimated using image-processing (as explained in section 3.3). For the estimation of component fraction of each grid, the coverage area of particles is determined, the pixels of the defined area are measured and converted to the fraction data using image processing. In this section, the main segregation mechanisms of laundry detergent powder mixtures are discussed. They are first evaluated for a binary mixture comprising BP and TAED and then the evaluation is extended to a ternary mixture comprising BP, TAED and EP granules.

4.2.1 Segregation in the binary mixtures

4.2.1.1. The effect of particle size variation on the segregation of binary mixtures

As described earlier, a typical laundry detergent powders mainly contains builders, having the active agent (surfactants) and bleaches. Therefore, the main segregation mechanisms are first explored for a binary mixture containing BP and TAED. Binary mixtures with different size ratios were first prepared and poured to form heaps as illustrated in Figure 4.2. The mixture mass was 40 g and had a 50/50 ratio (by mass) of TAED/BP. The sieve cut size of BP was kept constant (425-500 μm) while that of TAED was changed at different sieve cut size ranges, (425-500), (500-600), (600-710), (710-850) and (850-1000) μm. As illustrated in Figure 4.2, TAED particles segregate towards the corners of the heap as their size is increased.

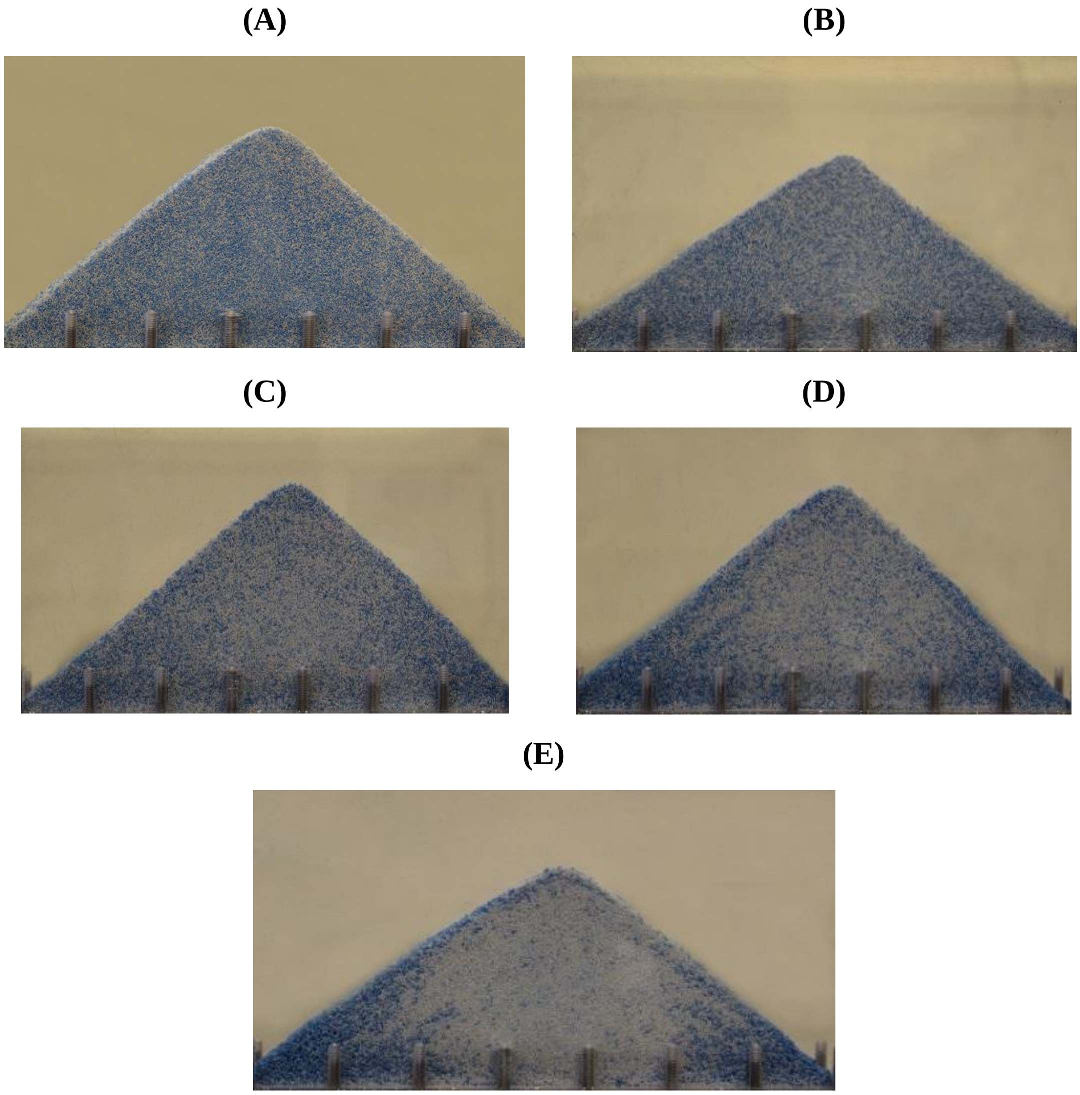
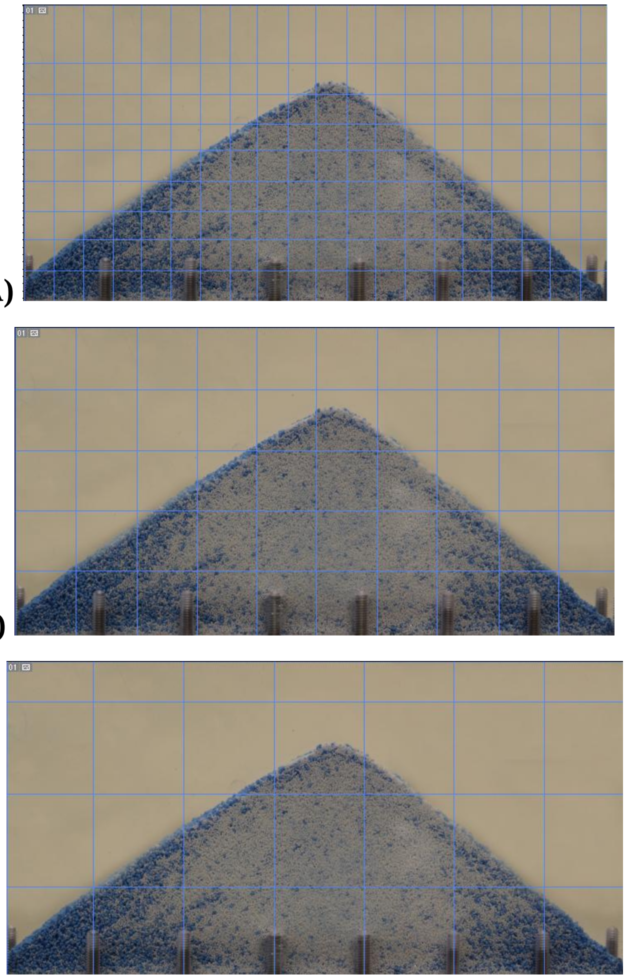


Figure 4.2: Binary mixtures of TAED and BP with different mean sieve cut size ratios of TAED over BP, (A): 1, (B): 1.18, (C): 1.41, (D): 1.68 and (E): 2.

The SI of TAED (obtained from Equation 2.7, measured for 3 bin sizes; small, medium and large, Figure 4.3) is presented in Table 4.1, where it can be observed that the SI increases as the size ratio of components is increased for all bin sizes.



(A) (B) (C)

Figure 4.3: Different bin sizes used for the measurement of SI, (A) small, (B) medium and (C) large.

Table 4.1. SI of TAED with different arithmetic mean size ratios of TAED over BP, obtained at different bin sizes.

	Bin size	Arithmetic mean size ratio				
		1	**1.18**	**1.41**	**1.68**	**2**
SI	**Small**	0.30	0.34	0.42	0.50	0.72
	Medium	0.27	0.32	0.39	0.47	0.68
	Large	0.25	0.30	0.32	0.40	0.58

The concentration map of the TAED particles, (for the heaps shown in Figure 4.2 and for the larger bin size shown in Figure 4.3), is depicted in Figure 4.4. A better uniformity of the TAED fractions could be obtained when the size ratio of components is reduced. Therefore, it can be deduced from Figure 4.2 and 4.4 that unity mean sieve size ratio of components results in a better mixing in binary mixture of BP and TAED particles. However, segregation increases as the size ratio is increased.

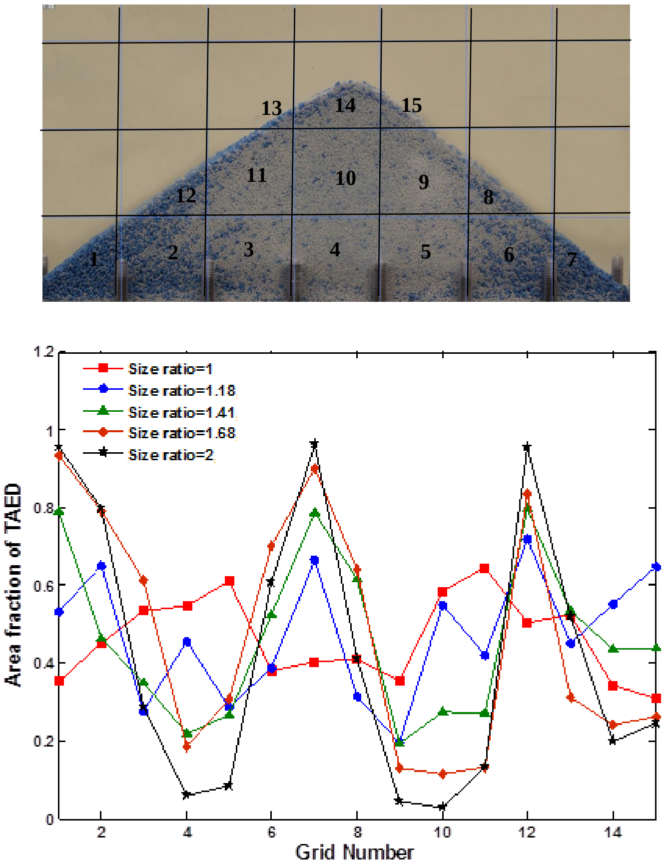


Figure 4.4: Concentration map of TAED particles for the heaps shown in Figure 4.2.

Percolation of smaller particles of BP could take place if the size ratio is such that they can get into the interstices of larger particles of TAED. This process continues to the extent that they can fill the void fraction. According to Savage and Lun (1988), Arteaga and Tüzün (1990) and Lacey (1954), a size ratio typically greater than ~3:1 is needed for the unhindered percolation to happen. Increasing trend of SI as the size ratio is increased could be due to the angle of repose variation between BP (at size range of 425-500 μm) and TAED particles at different sizes (Table 4.2). Angle of repose of the generated powder piles was measured using image processing tool as shown in Figure 4.5. Due to the lower angle of repose of larger sizes of TAED particles, they prefer to migrate towards the corners of the heap during the pouring process. Therefore in this case, the effect of percolation of fine BP is negligible compared to the effect of angles of repose of larger particles of TAED.

Table 4.2: Angle of repose of BP and TAED particles.

	BP	TAED				
Sieve cut size (μm)	**425-500**	**425-500**	**500-600**	**600-710**	**710-850**	**850-1000**
Angle of repose, ^{O}	36.06±1.63	33.43±1.13	32.91±2.91	31.93±1.17	28.80±0.75	26.28±1.90

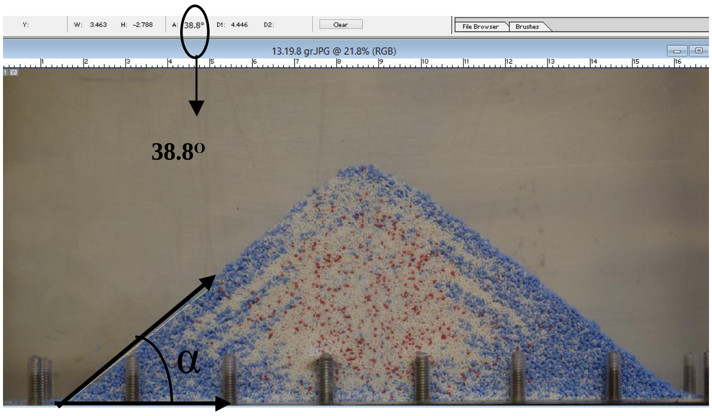
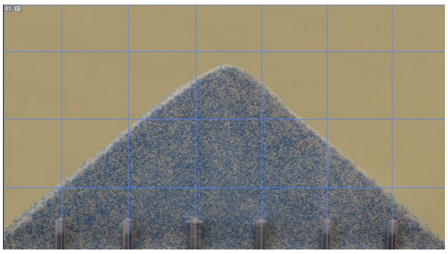


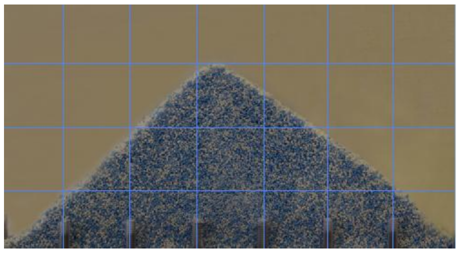
Figure 4.5: Angle of repose measurement using image processing tool.

4.2.1.2. The effect of particle shape variation on the segregation of binary mixtures

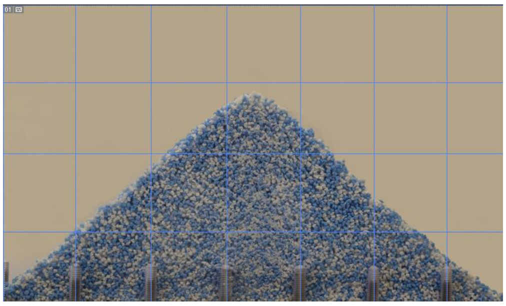
The unity sieve cut size ratio of components was found to be the mixed status for a binary mixture of BP and TAED (section 4.2.1.1). In this section, the segregation of different binary mixtures at different size ranges, having the unity component sieve cut size ratio, was investigated. For this purpose, binary mixtures (40 *g*, 50/50 ratio by mass of TAED/BP) with different size ranges (425-500, 850-1000 and 1180-1400 μm) were mixed and poured to form heaps as illustrated in Figure 4.6. Concentration maps and the SI of TAED (measured for different heap forms illustrated in Figure 4.6-A to Figure 4.6-C) are shown in Figure 4.6-D. The larger bin size (Figure 4.3) was chosen for the measurement of SI as it better represents the required scale of scrutiny (based on the regular scoop size in laundry detergent). In fact, the suitable bin size was chosen based on the minimum amount of laundry detergent powder required for washing (in this work=2 cm * 2 cm *1.5 cm). From decreasing pattern of SI and better concentration map uniformities (Figure 4.6-D), it can be concluded that the segregation of TAED particles decreases as their sieve size are increased.

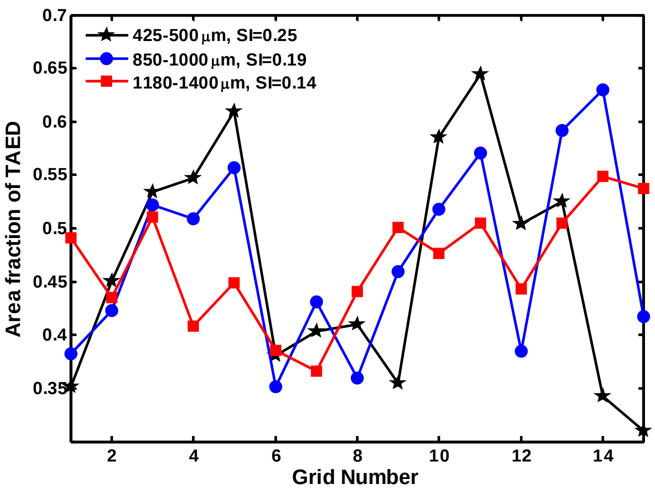
(A) **(B)**





(C)





(D)

Figure 4.6: Binary mixtures of BP and TAED with unity mean sieve cut size ratio; (A) 425-500, (B) 850-1000, (C) 1180-1400 μm and (D) concentration map/SI of TAED particles.

Variation between physical properties of different sieve cut sizes of components could influence the segregation pattern shown in Figure 4.6-D. Thus, size homogeneity and shape characteristics of a number of TAED and BP particles with different sieve sizes have been further evaluated. Size uniformity of particles of each sieve cut of the binary mixture has been first evaluated. For this purpose, particles with sieve cut sizes of 425-500, 850-1000 and 1180-1400 μm extracted from a representative full size distribution BP and TAED samples have been examined using Malvern Morphology G3 to determine the size variation of particles. Size uniformity of the particles at the mentioned sieve cut sizes are then evaluated using polydispersity index obtained by equation (4.1 to 4.3) and the results are shown in Table 4.3. Polydispersity index is a good indicator of size uniformity of particles (Allen, 1997; Shi et al., 2015).

$$PDI = \left(\frac{\sigma}{\overline{CE}}\right)^2 \qquad 4.1$$

$$\sigma = \sqrt{\frac{\sum(\overline{CE} - CE_i)^2 n_i}{\sum n_i}} \qquad 4.2$$

$$\overline{CE} = \frac{\sum n_i CE_i}{\sum n_i} \qquad 4.3$$

where CE_i, $\overline{CE}$, n_i and σ are circle equivalent diameter, mean circle equivalent diameter, number fraction and standard deviation of size distribution, respectively.

Table 4.3: Polydispersity index of particles obtained for the binary mixtures at sieve cut sizes of 425-500, 850-1000 and 1180-1400 μm.

	Sieve cut size (μm)		
	425-500	**850-1000**	**1180-1400**
Polydispersity index	0.0133±0.10	0.010±0.12	0.006±0.15

As can be seen in Table 4.3, by increasing the sieve cut size the polydispersity index is decreased. Better size uniformity between particles of larger sieve cut sizes might reduce the segregation in a binary mixture with unity size ratio. Size uniformity of particles of each sieve cut size could be affected by the particle shape characteristics. A sieve cut range with more spherical particles could have a better particle size uniformity. SEM photos of some TAED and BP particles with sieve cut sizes of 425-500 and 1180-1400 μm are presented in Figure 4.7 together with X-ray tomography images. The sphericity of one single particle of each sieve cut size, obtained using image-processing of X-ray tomograms, is also provided on the top of X-ray images.

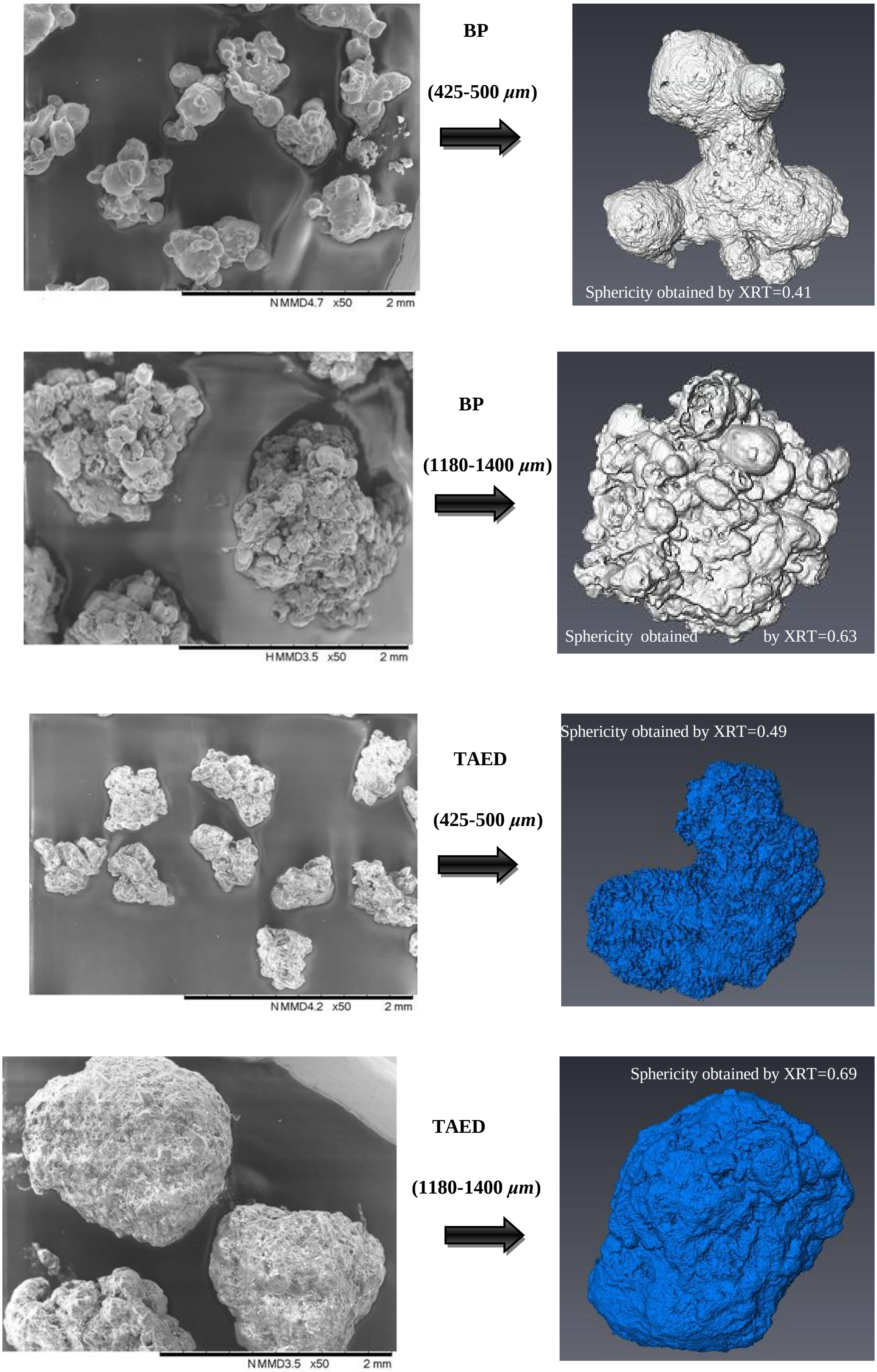


Figure 4.7: SEM and XRT pictures of BP and TAED particles at sieve cut sizes of 425-500 and 1180-1400 μm.

According to the Figure 4.7, the sphericity of both TAED and BP particles is increased by increasing their sieve cut sizes. However, images illustrated in Figure 4.7 could not adequately represent the accurate shape characteristic of the components. Hence, the shape characteristics of a number of TAED and BP particles (around 100 particles of each sieve cut) are also analysed using Malvern Morphology G3 and their average aspect ratio (the ratio of Feret's minimum length to the maximum length), solidity (ratio of image area to the convex hull area), circularity (degree to which the particle is close to a circle shape) and elongation (the ratio of the length of bounding box around the particle to the width of box) have been evaluated and reported in Figure 4.8. A high aspect ratio, solidity, circularity and a low elongation indicate a more rounded characteristic for an object (Olson, 2011). An increased solidity, circularity and aspect ratio and a decreased elongation of BP and TAED particles at higher mean sieve cut sizes is observed in Figure 4.8. This suggests particles have more circularity/shape uniformity when their sizes are increased. In fact, Figures 4.7 and 4.8 reveal that there is more shape uniformity between particles with larger sieve cut size as compared to the smaller sizes. More shape uniformity of particles at larger sieve cut size could contribute to the decreasing trend of segregation as seen in Figure 4.6-D.

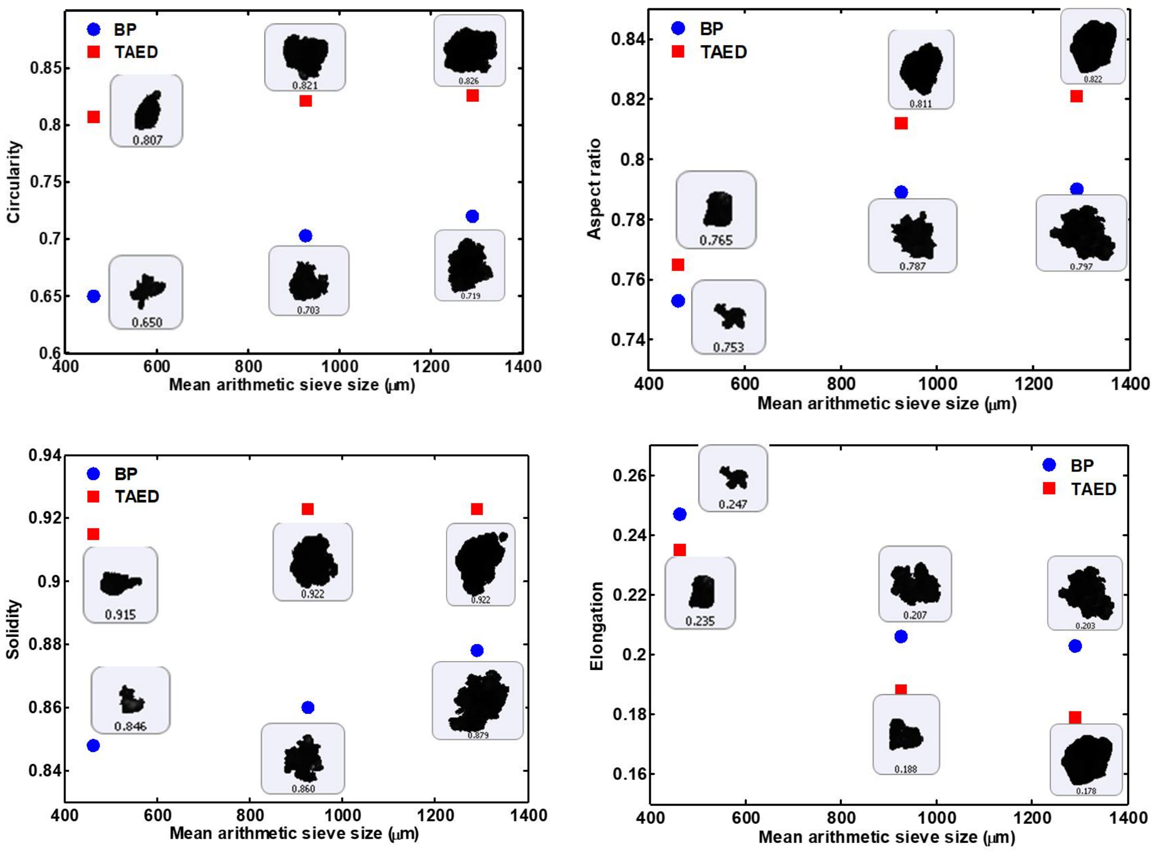


Figure 4.8: Circularity, aspect ratio, solidity and elongation of BP and TAED particles obtained using G3 morphology instrument.

Physical properties of particles, such as size, shape and/or density, are important factors affecting the segregation of powders. According to the above-mentioned results, the particle shapes of BP and TAED, are more similar at larger sieve cut sizes and thus less segregation takes place. The physical properties of particles depend on the formation during the manufacturing process. For example, for spray dried particles, atomization and droplet drying affect the properties of the dried particles (Vehring, 2008), whilst for granulated material, the granulation process such as the impeller speed and the rate of addition of binder (Levin, 2006) could affect the particle characteristics.

4.2.2 Segregation in the ternary mixtures

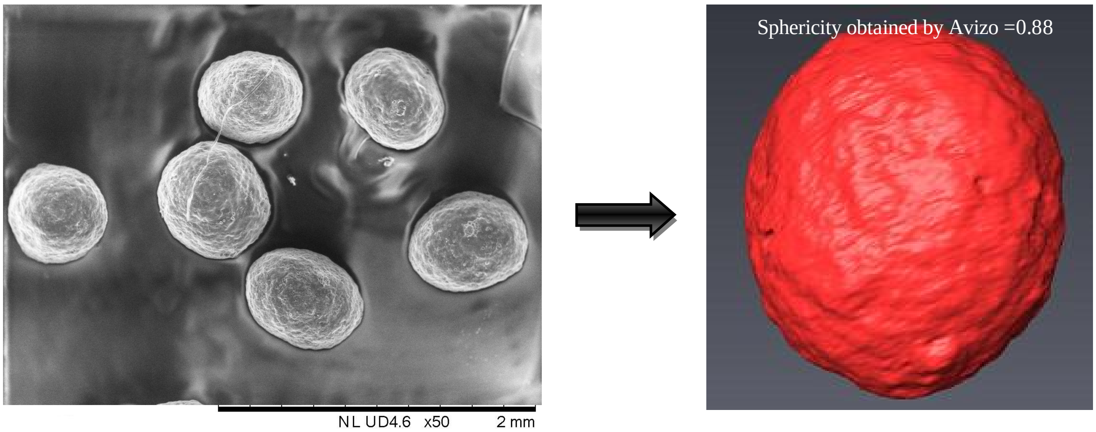
In a typical laundry detergent powder formulation, some fillers such as enzyme granules are mainly added with the aim of improving the product quality. However, due to the variation in particle properties, they could be also prone to segregate in mixture of different powder ingredients. In this section, the segregation in ternary powder mixture containing BP, TAED and enzyme granules are investigated. The red EP granules were used to visually observe the segregation pattern in the produced heaps. Before discussing the main segregation mechanisms in the ternary mixture (section 4.2.2.2), the material properties of a number of EP granules are characterised and compared to those obtained for BP and TAED (section 4.2.1.2), as summarised in the next section (section 4.2.2.1).

4.2.2.1 Material properties of EP granules

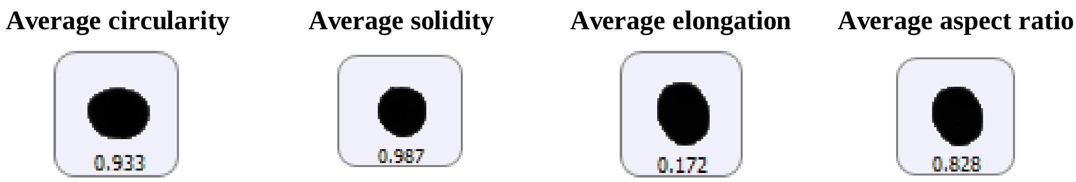
Some particle characteristics of EP granules are first evaluated and compared to those of BP and TAED particles. It can be inferred from SEM image, G3 morphology and XRT structural analysis of a number of particles that the EP granules are more spherical in shape as compared to BP and TAED particles (Figure 4.9 and Figure 4.7). Also, the bulk tapped density of EP granules is estimated as 1450 $kg.m^{-3}$ which is nearly three times higher than those measured for TAED (530 $kg.m^{-3}$) and BP (400 $kg.m^{-3}$). This could be due to higher solid density (Table 4.4) and the less particle voidage of individual EP granules than BP and TAED (Figure 4.10). Bulk tapped density measurement was done by pouring the mixture of powders in a graduated cylinder and tapping the poured powders until the pack reached an equilibrium. The mass and the volume of the equilibrated pack was then used to measure the bulk tapped density. The material solid density was measured using a Micromeritics Acupyc 1330 pycnometer system. Internal structure characteristics of particles were evaluated by X-ray microtomography (XRT) using a Nanotom X-ray computed tomography instrument (GE Phoenix, Wunstorf, Germany). VGStudio software and Avizo Fire software were then used for the reconstruction of the images and the post-processing analysis, respectively.

Table 4.4: Solid density of components obtained by Pycnometer.

	TAED	**BP**	**EP granules**
Solid density ($kg.m^{-3}$)	1.36	1.5	2.46



(A)



(B)

Figure 4.9: (A) SEM photo and X-ray tomograms of EP granules (mode size: 600-710 μm) and (B) average circularity, aspect ratio, solidity and elongation of EP granules obtained by G3 morphology.

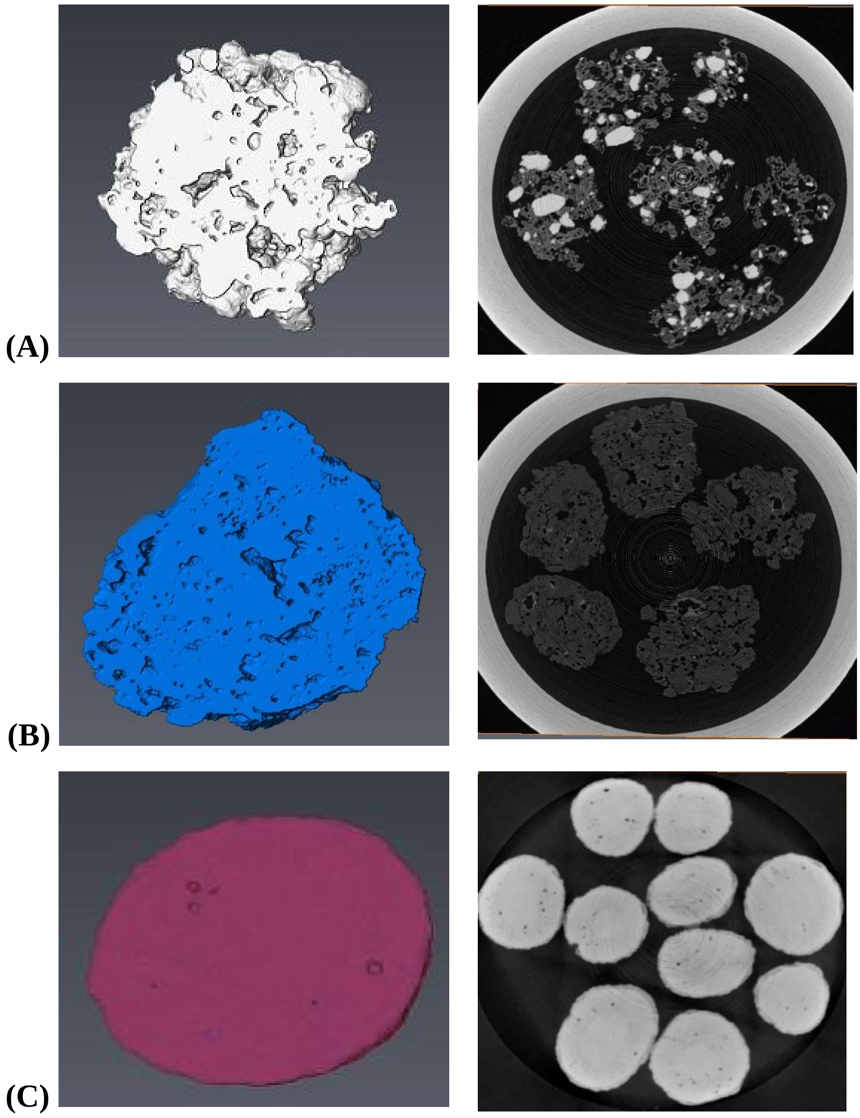
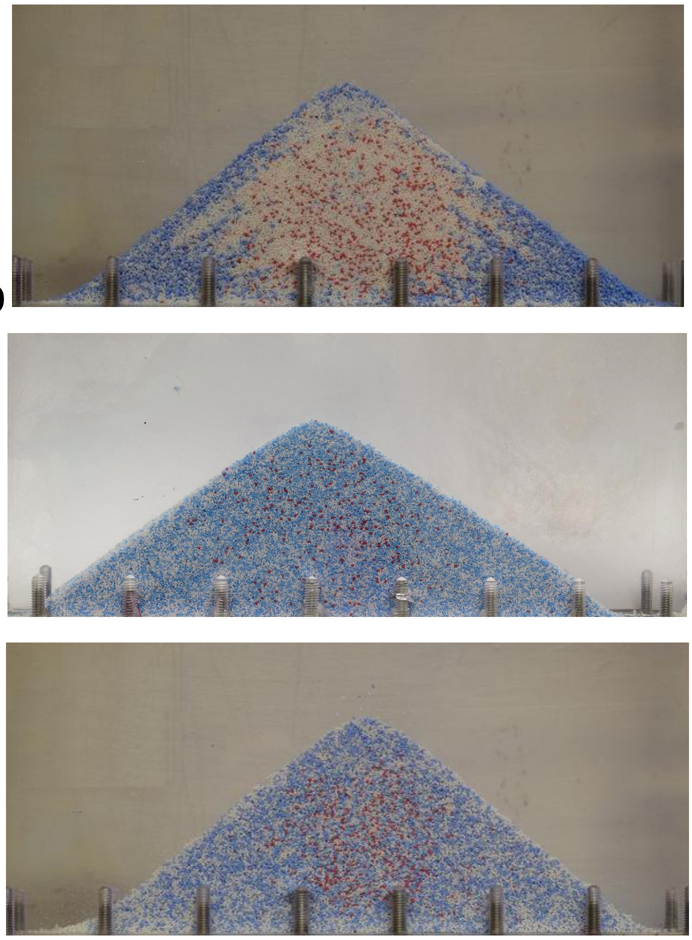


Figure 4.10: Internal cross-sectional view of individual particle (resolution=2 μm) and bulk (resolution=4 μm) of (A) BP, (B) TAED and (C) EP granules.

4.2.2.2 Segregation of EP granules in the ternary mixture

The segregation behaviour of components in the ternary mixture are investigated by adding the EP granules into binary mixtures. 40 *g* ternary mixtures (with equal mass of TAED, BP and EP granules) are then formed by the addition of EP granules into both relatively mixed (with unity size ratio) and segregated binary mixtures of BP and TAED particles (size ratio of TAED over BP=2, Figure 4.2-E) as shown in Figure

4.11. For this purpose, the mode of the narrow size distribution of EP granules (600-710 μm) is used as their representative because it contains majority of the EP granules. As shown in Figure 4.11, it can be observed that the EP granules are accumulated towards the centre of both segregated and mixed binary mixtures after pouring process due to presumably their higher bulk density (section 4.2.2.1). Although unity size ratio is ideal for a mixed binary mixture (section 4.2.1), Figure 4.11-C reveals that this condition is not favourable to achieve a mixed ternary system in this study, presumably to the higher density of EP granules as compared to the BP and TAED granules.



(A) **(B)** **(C)**

Figure 4.11: Addition of EP granules into (A) segregated and relatively mixed binary mixtures in sieve cut size range of (B) 425-500 and (C) 600-710 μm.

In separate experiment, 40 g ternary mixture heap with equal mass of TAED, BP and EP granules but with full particle size distribution of components was prepared as shown in Figure 4.12. The enzyme granules are mostly accumulated in the centre of the heap in the case of full particle size distribution of components. From the SI and concentration map results of components in the case of full particle size distribution (Figure 4.13), it could be deduced that the segregation is not very intense for the case of BP and TAED particles, presumably due to their wide particle size distribution (Figure 3.3) and the same density. However, SI of EP granules reveals that this component is prone to extensive segregation. Therefore, it is recommended to separately explore the main mechanisms for the EP granules in the mixture of BP and TAED particles which is described in the next section.

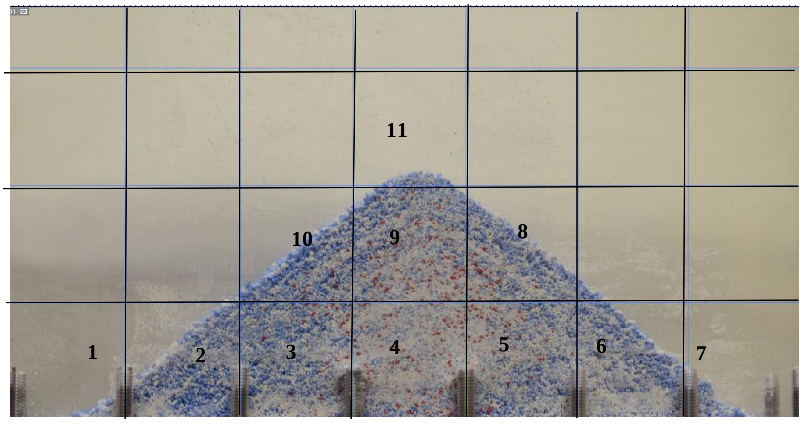


Figure 4.12: Ternary mixture containing equal mass of TAED, BP, EP granules with full particle size distribution.

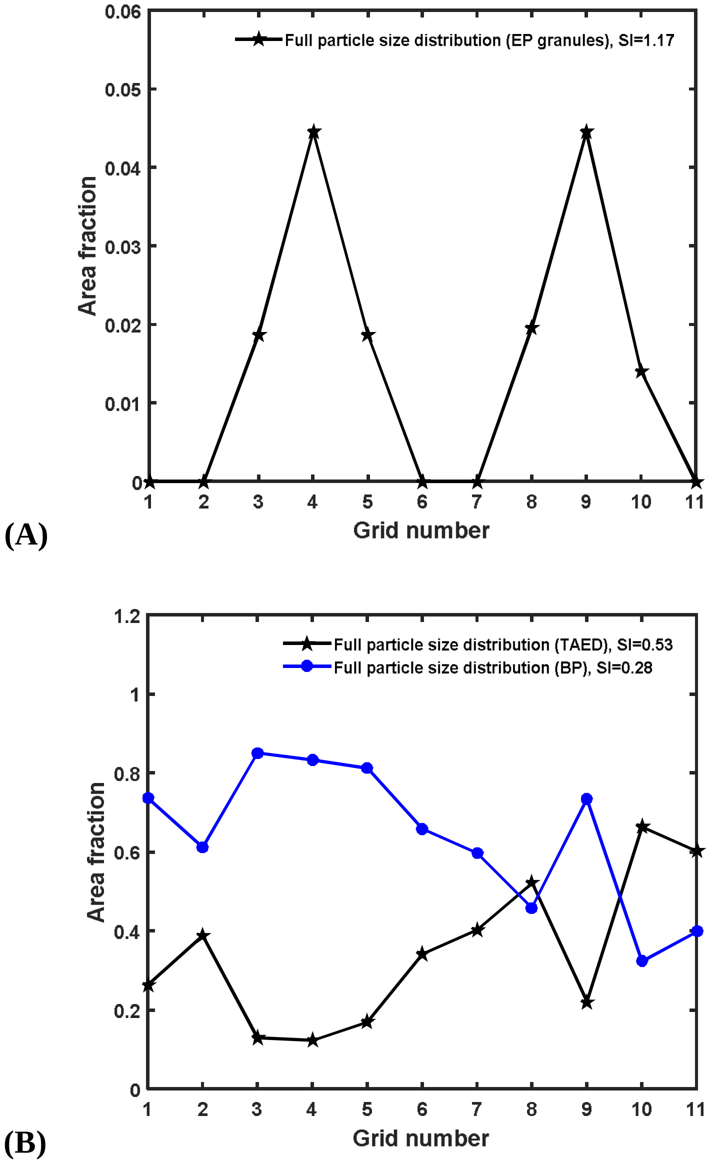
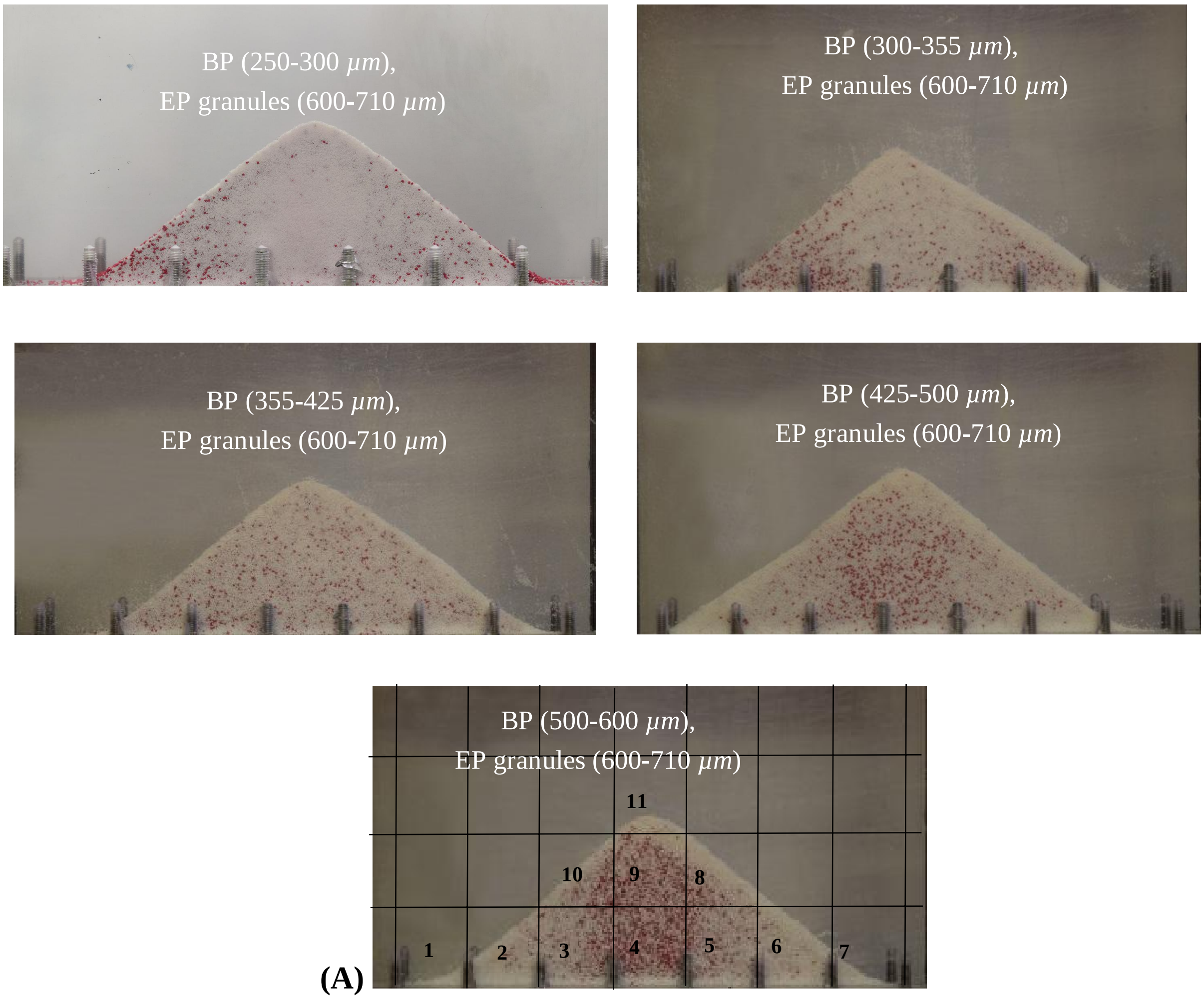


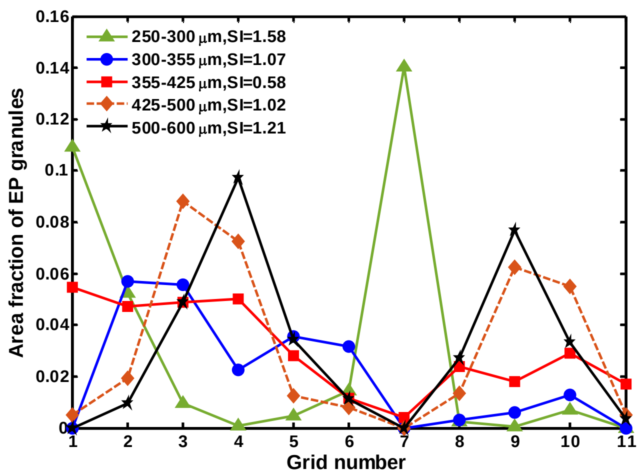
Figure 4.13: Concentration map and SI information of (A) EP granules and (B) TAED and BP in the ternary mixtures with full particle size distribution of components.

4.2.2.3 Well-mixed ternary mixture

To further analyse the segregation mechanisms of EP granules, series of experiments have been carried out using binary mixtures of BP/EP and TAED/EP granules. For this purpose, EP granules with their mode size have been added to different sieve cut sizes of BP and TAED particles, individually. Figure 4.14 shows 50/50 weight percentage ratio binary mixtures (40 g), comprising different sieve cut sizes of BP (sieve cut sizes between 300-500 μm) and the mode size of distribution of EP granules. It can be seen in Figure 4.14 that the binary mixtures of BP-EP granules with sieve cut sizes of (250-300 μm), (300-355 μm), (425-500 μm) and (500-600 μm) have undergone more segregation as compared to the case of 355-425 μm. In can be inferred that, there is a competition between the segregation of small particles of BP and the segregation of dense particles of EP granules during the heap formation. In general, both small and dense particles are prone to move towards the centre of the pile. Fine BP particles with sieve cut size of less than or equal to 300-355 μm overcame the density segregation of EP granules. On the other hand, density segregation of EP granules (due to push-away effect) could dominate the size segregation of BP particles with sieve cut size of greater than or equal to 425-500 μm. The same behaviour has also been observed for the mixture of TAED/EP granules (Figure 4.15).



(A)



(B)

Figure 4.14: (A) Binary mixture containing equal weight percentage of BP/EP granules and (B) concentration maps of EP granules.

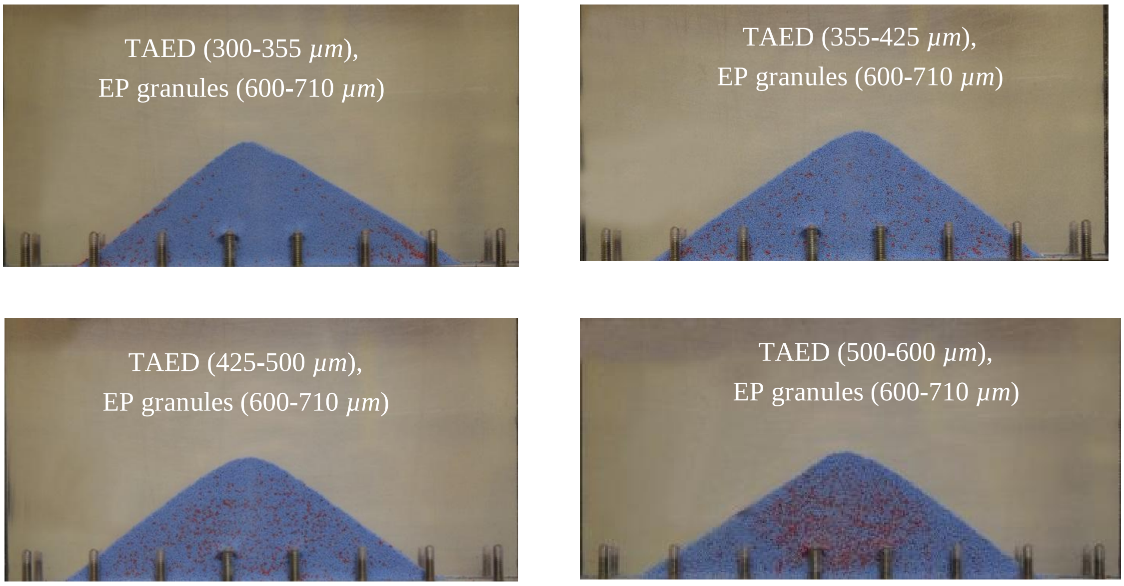
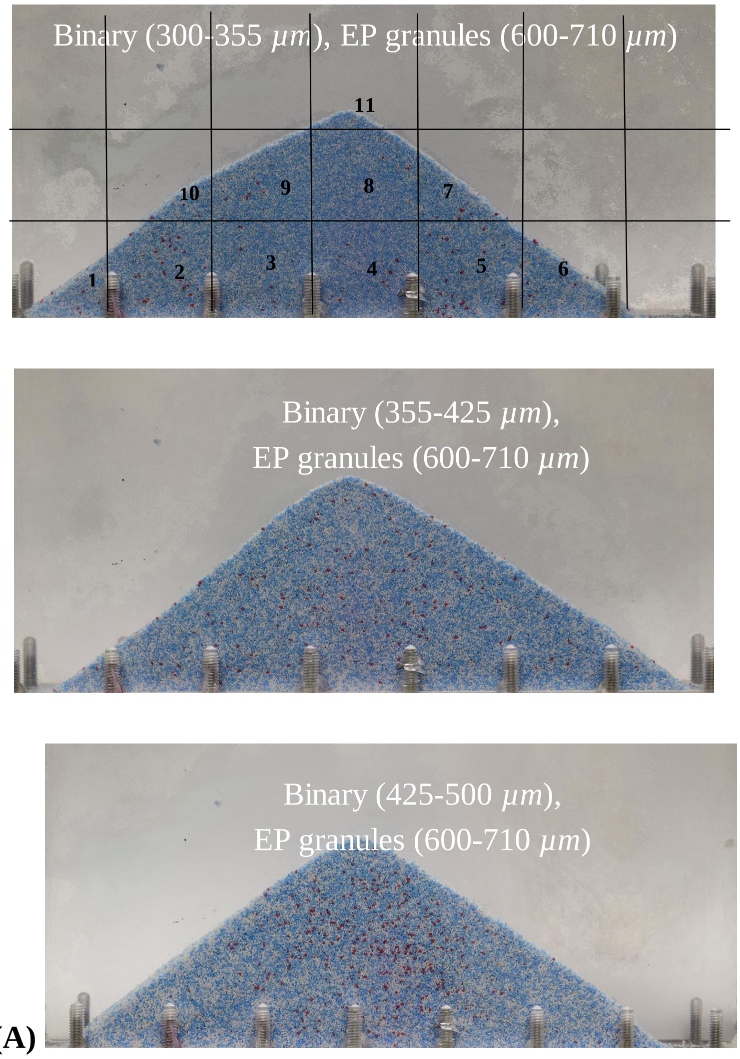
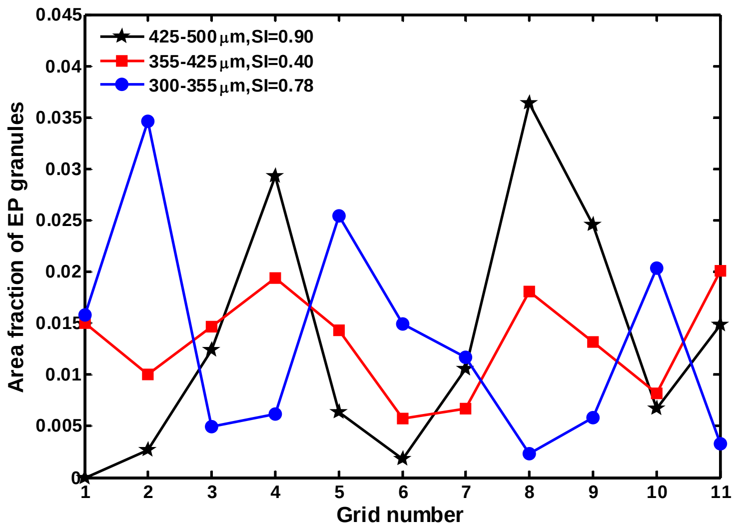


Figure 4.15: 40 *g* binary mixture containing equal weight percentage of TAED/EP granules.

To verify the segregation mechanisms for EP granules in the ternary mixtures (with equal mass of TAED, BP and EP granules), 40 *g* heaps containing BP and TAED (with different sieve cut sizes of 300-355, 355-425, 425-500 *μm*) and EP granules (mode size) are then prepared and the SI of EP particles are measured (Figure 4.16). It can be observed that a fully-mixed condition of EP granules in the ternary mixture is generated by adding them into the binary mixture of BP and TAED with the narrow sieve cut size of 355-425 *μm*, which is in agreement with the finding of binary mixtures as reported in previous section. Despite the fact that the unity size ratio of higher sieve cut sizes of TAED and BP has been reported as a better mixed binary mixture (section 4.2.1.2), lower range of sieve cut size of BP and TAED is recommended to be used for achieving a mixed condition of EP granules in the ternary mixture. The findings suggest that optimising the particle size distribution of components could be a way of reducing the segregation arising from particle size and density variation.



(A)



(B)

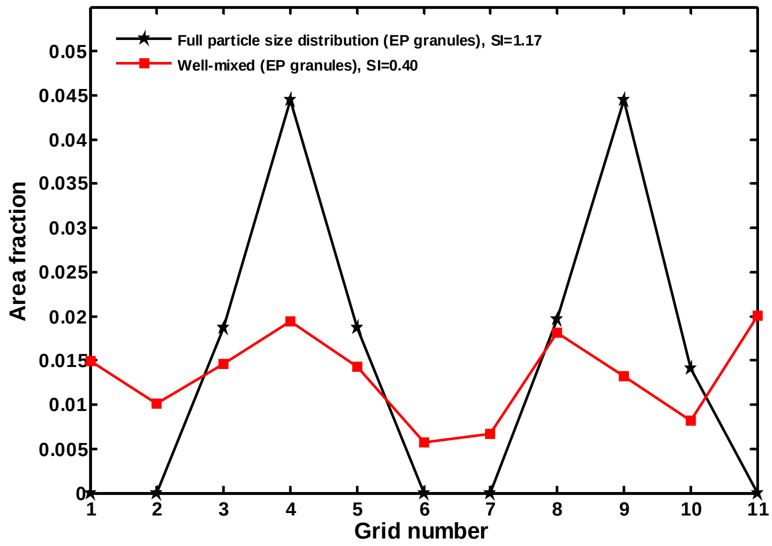
Figure 4.16: (A) Ternary mixture and (B) concentration map/SI of EP granules in heaps containing equal weight percentage of BP/TAED/EP granules.

It has been mentioned that spherical particles behave like free-flowing particles in mixtures of spherical and irregular particles, preferring to migrate to the surface of the heap. On the other hand, irregular particles build up around the centre of the heap (Enstad, 2001; Swaminathan and Kildsig, 2002). Angle of repose of particles could be strongly influenced by their shape properties during heap formation. Table 4.5 shows the angle of repose of different sieve cut sizes of BP and TAED particles. It can be deduced that the angle of repose of EP granules at their mode size, which is obtained equal to 16.01±1.18, is less than those obtained for different sieve cut sizes of BP and TAED particles. Thus in this case, the effect of angle of repose/shape segregation of EP granules could be insignificant for the trends seen in Figure 4.14 to Figure 4.16 compared to segregation arising from other material properties of components, notably size and density.

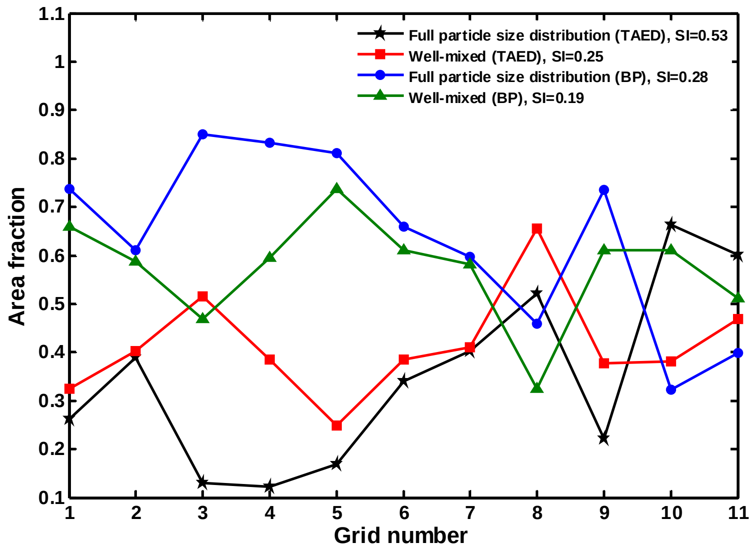
Table 4.5: Angle of repose of TAED and BP particles (20 *g*) at different sieve cut sizes.

		Sieve cut size (*μm*)				
		250-300	**300-355**	**355-425**	**425-500**	**500-600**
Angle of repose°	**BP**	40.01±1.07	39.50±1.78	39.38±1.37	36.06±1.63	34.48±1.68
	TAED	39.7±1.55	37.11±1.27	34.71±1.02	33.43±1.13	32.91±1.91

The SI of BP, TAED and EP granules in the case of ternary mixture heap with full particle size distribution of components (Figure 4.12 and Figure 4.13) is then compared with those of the mixed ternary mixture (Figure 4.16), (results are presented in Figure 4.17). It can be observed in Figure 4.17 that the segregation of component could be reduced by applying the optimum sieve cut sizes of components in the ternary mixture.



(A)

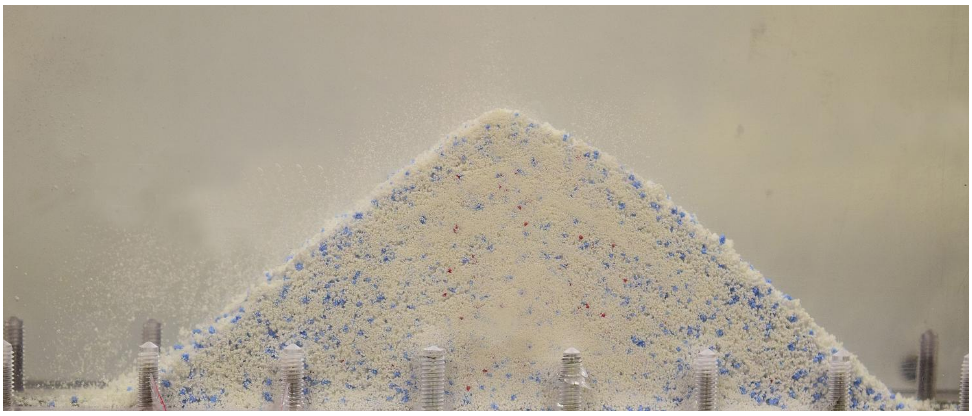


(B)

Figure 4.17: Concentration map and SI information of the ternary mixtures before and after applying the optimum sieve cut sizes of components, (A) EP granules, (B) BP and TAED.

4.2.2.4 Segregation in ternary mixture with exact composition ratio of components

In this section, segregation of components is evaluated when the heap is produced by preparing the ternary mixture containing the exact weight percentage ratio (92.6 BP/ 5.55 TAED/ 1.85 EP granules) which is mainly used in detergent formulation. For this purpose, experiments were carried out using the exact weight percentage ratio in detergent formulation for both full size distributions (Figure 4.18-A) as well as the optimum sieve cut sizes of components for a mixed ternary system (Figure 4.18-B) as explained before in section 4.2.2.3. The SI of components in these ternary mixtures were then measured.



(A)

(B)

Figure 4.18 (A) Ternary mixtures comprising full size distribution BP, TAED and EP granules with 92.6/5.55/1.85 weight percent ratio, (B) mixed ternary mixture with the fully-mixed sizes.

The SI of EP granules and TAED reduced from 1.36 and 0.55 (for the full particle size distribution) to 0.67 and 0.30 (for the optimum sieve cut sizes of components for mixed ternary system, shown earlier), respectively. From comparison of the SI of EP granules obtained for the heap containing the equal mass of components (shown in Figure 4.13) and the exact composition ratio of components (Figure 4.18-A), it can be inferred that the SI of EP granules in the case of the latter case is higher than that of the former one, presumably due to their less weight percentage. Therefore, segregation could become even more intense when the ingredients are used in low content level. Overall, SI of EP granules reveals that this component is prone to extensive segregation. Even vibration could further increase the segregation of EP granules, which is described in the next section. Therefore, it is critical to mitigate the segregation of this component to achieve a mixed mixture of laundry detergent powders. Using narrow sieve cuts to mitigate segregation, as shown earlier, could not be practical in most industrial manufacturing operations. As a small amount of enzymes is used in detergent formulation, manipulating the surfaces of enzyme granules by making them sticky could be an option for the minimisation of segregation of this component which will be explored in the next chapter.

4.3 Segregation of enzyme granules during vibration

As described in chapter 2, segregation of components could become intense during vibration, a condition occurring particularly during transportation in trucks caused by the road conditions, left or right turns and/or difference in road levels (Lu et al., 2008). In this section, the segregation of minor ingredient enzyme granules (the highly segregated material as shown in section 4.2) was investigated by applying an intense vibration to the ternary mixture inside of the heap box using the system shown in Figure 4.1.

Segregation of enzyme granules in ternary mixture containing full particle size distribution of BP, TAED and uncoated EP granules (92.6/5.55/1.85 wt % ratio) is studied. An intense vibration (frequency= 50 *Hz*, amplitude=15 *mm*) was applied to the ternary mixture using the system shown in Figure 4.1. At different times of vibration (15, 30, 60, 300, 600 and 900 *s*), the heap of ternary mixture was pictured to measure the segregation of EP granules. Figure 4.19 shows the heaps of ternary mixture after vibration at different times. After vibration, the minor ingredient EP granules moved upward from the center towards the apex of the heap (due to probably Brazil nut effects) and gradually accumulated in the corners of the heap. The Brazil nut effects, also defined as up-thrusting segregation mechanism, takes place when the co-operative action of particles makes the larger/dense particles to move upward in the bed of powders. Different factors could influence the Brazil nut effects of particles during vibration, such as particle size ratio and percolation (Liao, 2016), vibration frequency and amplitude (Ellenberger, 2006), internal friction and elasticity (Liao et al., 2014; Brito et al., 2008) and the particle density (Bose and Rhodes, 2007). Therefore, both material characteristics and vibration conditions are contributing to the Brazil nut effect of EP granules during vibration. Figure 4.20 shows the concentration map of EP granules obtained for different grids. As illustrated in Figure 4.20, the concentration of EP granules significantly increases in the corner grids (number 1 and 9) after vibration time, enhancing the SI of this component and it nearly reaches to equilibrium after a time around 300 *s*. This could be due to the free mobility and high restitution coefficient of rounded EP granules. This will be shown in the next chapter, where the restitution properties of EP granules, before and after particle coverage by fine BP particles, are compared and therefore particle coating is proposed as a technique to hinder their segregation.

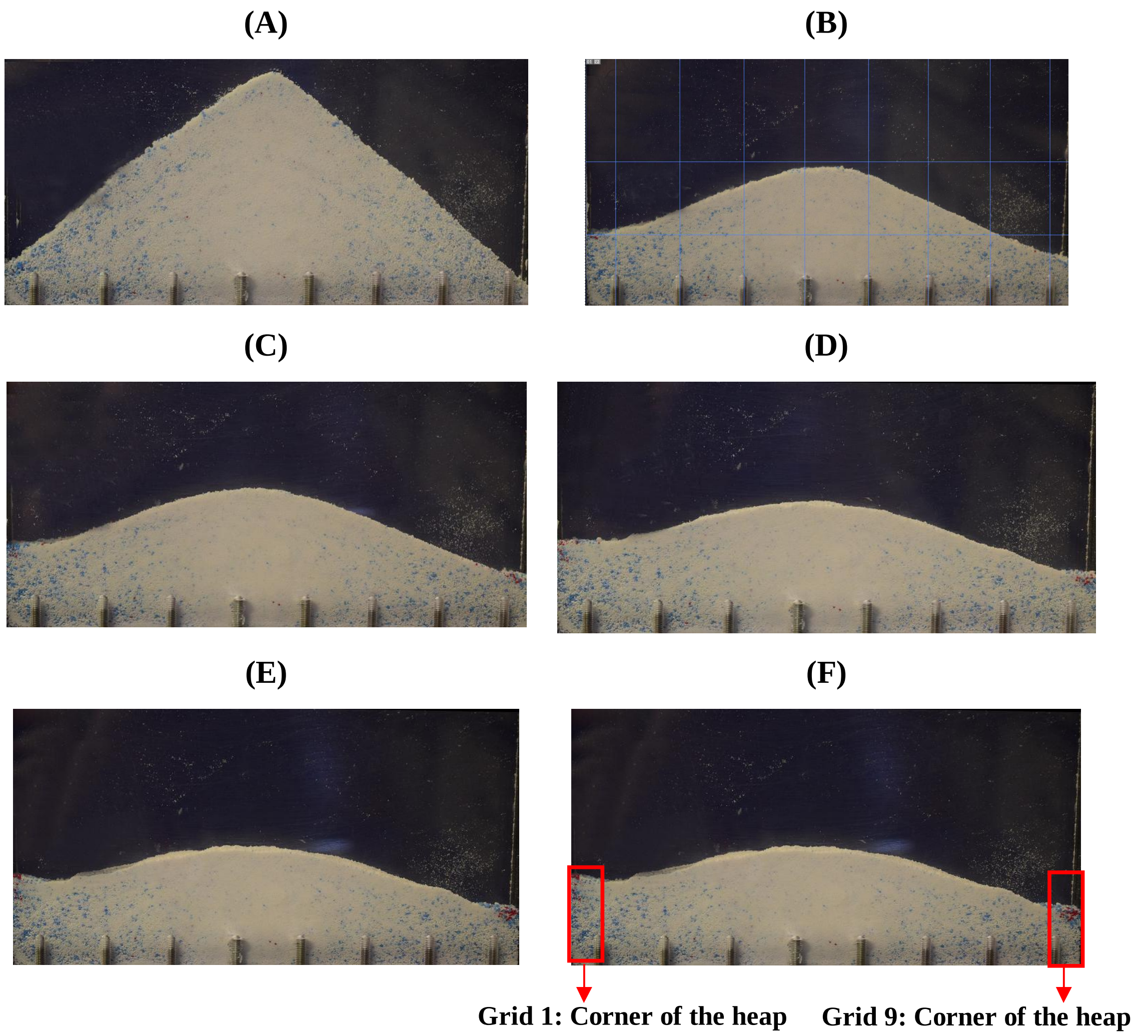


Figure 4.19: Ternary mixture containing BP, TAED and EP granules (92.6/5.55/1.85 wt % ratio) (A) before and after vibration at (B) 15, (C) 60, (D) 300, (E) 600 and (F) 900 *s* (frequency= 50 *Hz*, amplitude=15 *mm*).

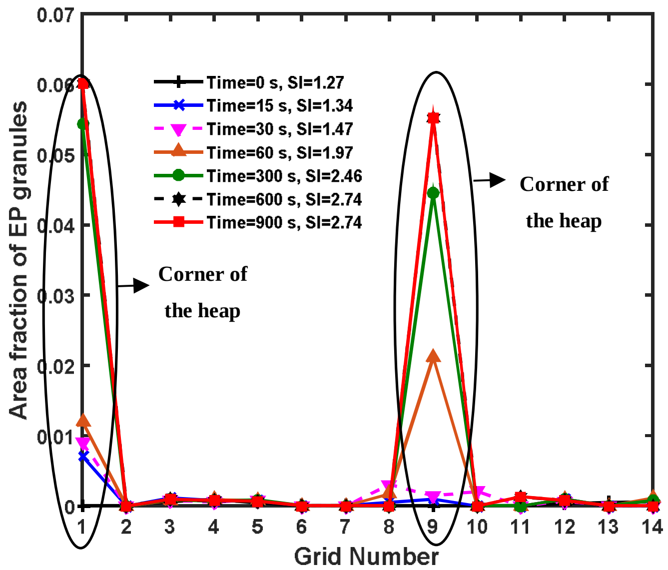


Figure 4.20: Concentration map/SI of EP granules after vibration times of 15, 30, 60, 300, 600 and 900 *s*.

4.4 Concluding remarks

Segregation of the main constituents of laundry detergent powders has been investigated by looking at the effect of particle properties, particularly size, shape and density, on the segregation of components. Tetraacetylethylenediamine (TAED) particles, spray-dried synthetic detergent powder referred to as Blown Powder (BP) and Enzyme Placebo Granules (EP granules) were considered as a model formulation.

The results show that EP granules, the component used as low content level ingredient in the ternary mixture, highly segregate towards the centre of the piles due to their higher density and round shape rather than BP and TAED particles. Therefore, segregation minimisation of EP granules must be further addressed. Many researches in the literature demonstrated the importance of varying material properties, notably size and density, on the segregation of granular materials (Liao et al., 2015; Liu et al., 2013; Cho et al., 2012; Shenoy et al., 2015; Remy et al., 2010). However, competing behaviour of the trajectory of small and large/dense particles during heap formation of real powder formulation has not been fully investigated. For a ternary mixture studied here, sieve cut size of BP and TAED particles in the range of 355-425 μm has been found as optimum criteria for fully-mixed EP granules (with the mode particle size distribution). At the mentioned sieve size ranges, a balance between size segregation and density segregation could be achieved, which further resulted in segregation reduction of components. The SI of EP granules could be reduced from 1.36 to 0.67 by applying the mentioned sizes rather than using their full particle size distribution. The results showed that the segregation of EP granules was more intense than other ingredients (BP and TAED) and hence their segregation reduction is crucial. As manipulating the size ranges of components could not be achievable in many industrial manufacturing operations, therefore other applicable approaches for the segregation reduction of the low-dose enzyme granules must be studied which is the scope of chapter 5.

Chapter 5
Investigation of segregation reduction of enzyme granules by particle modification

5.1Introduction

It is shown in chapter 4 that enzyme granules are prone to highly segregate in the mixture of laundry detergent powders, both during filling and vibration. The segregation of the low content level ingredient enzyme granules was reported to take place mainly because of density variation between the components. Higher density of EP granules than BP and TAED particles makes them accumulate into the centre of the piles of the ternary powder mixtures. In this chapter, particular attention is given to the segregation minimization of minor ingredient, both during filling and vibration. Desired properties for segregation minimisation of low content level ingredient enzyme granules will be investigated, by discussing the underlying segregation mechanisms. Two approaches are used for the segregation minimisation of low-dose enzyme granules: 1) applying a sticky material to the surfaces of EP granules before mixing them into the mixture of BP and TAED, 2) structural modification of EP granules before mixing them into the mixture of BP and TAED.

The chapter is divided into two main sections:

1. Investigation of desired properties for segregation minimisation of low content level ingredient enzyme granules, where a thin layer of liquid coating is applied to the surfaces of particles before mixing.

2. The process of the structural modification of EP granules by granulation technique is then investigated. The modified EP granules are then mixed to the mixture of BP and TAED to see its effect on the segregation mitigation of EP granules.

5.2 Effect of surface coating on the segregation of particles

In this section, the effect of particle coating by a thin liquid layer on the segregation minimisation of EP granules is evaluated. Polyethylene glycol (PEG, Pluriol E 600) is used as coating agent, due to its compatibility with the laundry detergent formulation. In addition, the primarily laboratory testing showed its potential over other compatible coating agents (such as lower molecular weight PEGs, Sokalan cp5 and neutralized Linear alkylbenzene sulphonic acid, LAS paste) for the segregation reduction of EP granules. A blade Kenwood kitchen mixer (Figure 5.1-A) was used for this purpose while the liquid was added dropwise into the powder bed by means of a syringe. Flowability of the materials were investigated using Schulze shear cell instrument and FT4 device (Figure 5.1-B). In this section, segregation reduction of minor ingredient enzyme granules is addressed and then an optimum level of coating material for adequate particle surface coverage is presented based the flowability analysis.

(A)

FT4 device

Schulze shear cell

(B)

Figure 5.1: (A) Schematic of the mixing device for coating of EP granules and (B) Schulze shear cell instrument and FT4 device for the flowability analysis.

5.2.1 Segregation reduction of low content level ingredient by coating

Different amounts of PEG (0.5 to 3.5 wt % with the increment of 1 wt %) were spread over EP granules surfaces to evaluate its effect on their segregation. The coated EP granules were added to the mixture of BP and TAED particles (with full particle size distribution) and mixed to make a ternary mixture (92.6/5.55/1.85 wt % ratio of BP, TAED and EP granules, respectively). The SI of EP granules was then measured after generating the heap of ternary mixtures using image processing and Equation 2.7. Three experiments were performed to check the experimental reproducibility and the average data for the segregation of EP granules were then reported. It has been shown that the segregation of EP granules decreases as coating level is increased (Figure 5.2), with the coefficient of variation of 0.06, 0.09, 0.06, 0.06 and 0.08 for 0, 0.5, 1.5, 2.5 and 3.5 wt% coating levels, respectively. The ternary mixtures before and after 3.5 wt% coating are shown in Figure 5.3. A relatively good distribution of EP granules (red particles) throughout the ternary mixture could be observed after applying the coating material.

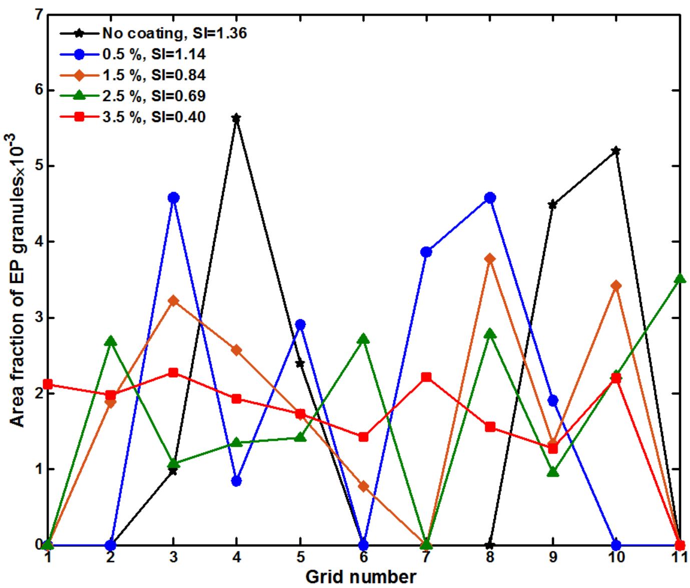
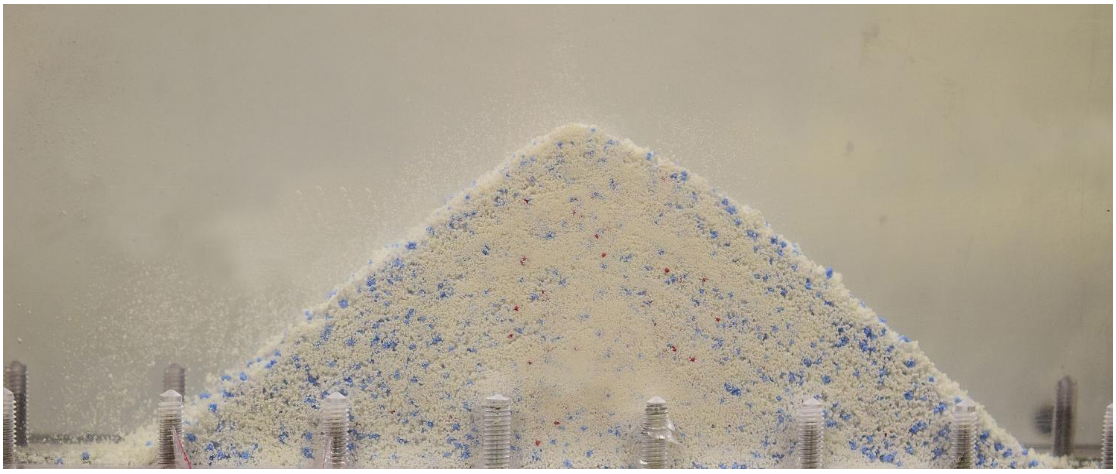
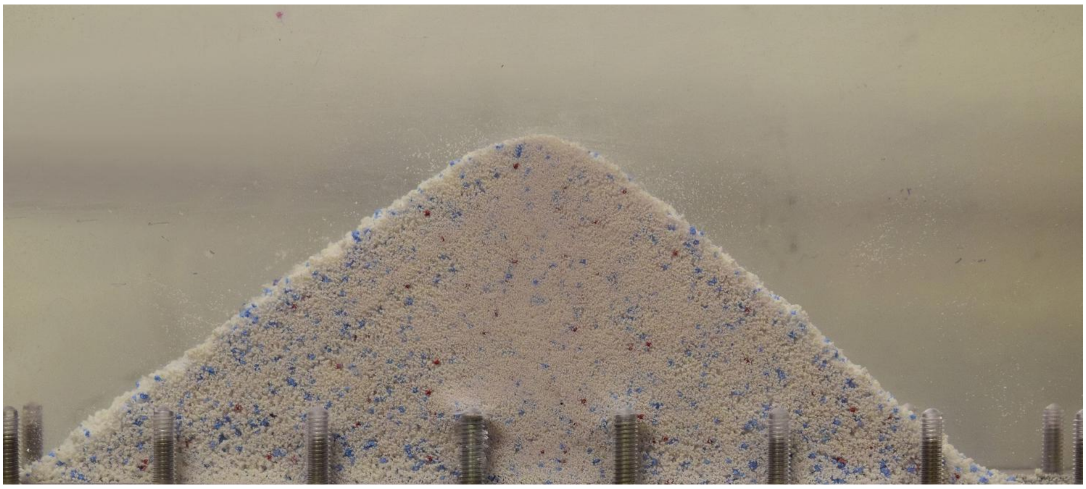


Figure 5.2: Concentration map and SI of EP granules versus coating percentage of PEG.



(A)



(B)

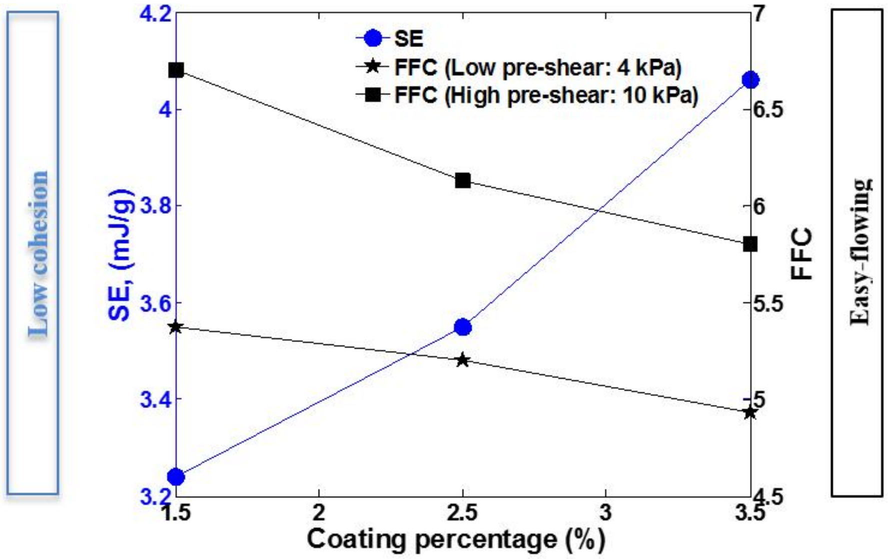
Figure 5.3: Ternary heap (92.6/5.55/1.85 weight percent ratio of full size distribution BP, TAED and EP granules (A) before and after (B) 3.5 % coating by PEG.

The results of this investigation were also compared with those obtained by simulation using the Discrete Element Methodology (DEM). In the research of Alizadeh et al. (2018), segregation of granules mixture containing BP, TAED and EP granules was simulated during heap formation of a ternary powder mixture. It is found that 2.5 wt% coating level could decrease the SI of EP granules by 40% and therefore a reasonable match between the results of the experiments and simulations was observed. The corresponding adhesion value was expressed as equivalent interfacial energy and was determined by calibration using the amount of the angle of repose of the desired coated material.

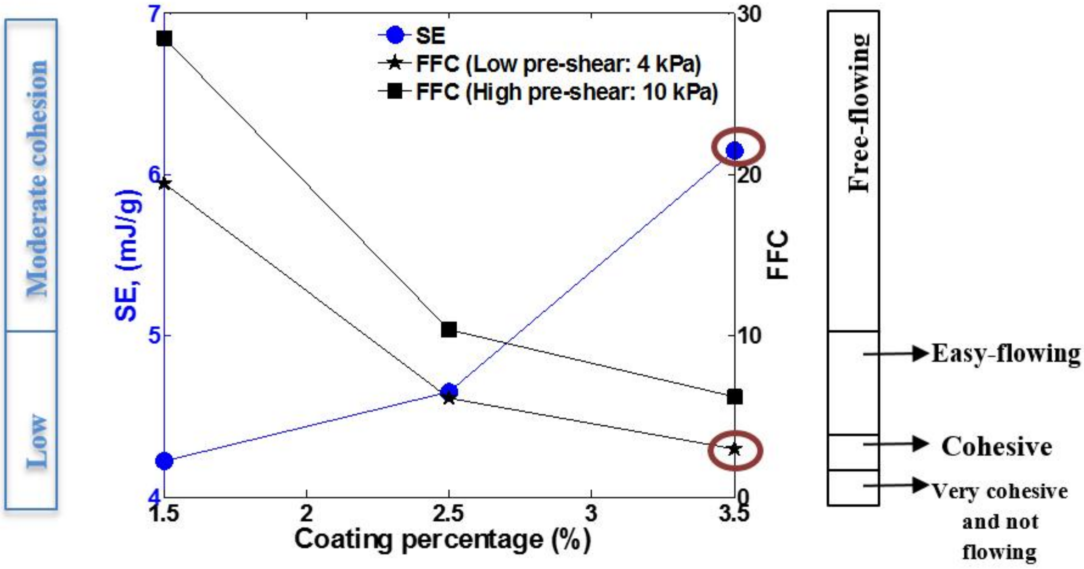
Overall, segregation of EP granules was shown to be decreased after the particle surface coating by PEG. However, it should be noted that increasing the coating level could adversely influence the flowability of the powders and therefore the optimum coating level for an acceptable flowability of the particles is also required to be explored which is addressed in section 5.2.2.

5.2.2 Determination of the optimum coating level

The flowability of both coated EP granules and the bulk of mixture have been analysed using the Schulze shear cell instrument and FT4 device (Figure 5.4). In the Schulze shear cell, the yield locus of the bulk of powders is determined and expressed in term of the Flow Function (FFC), the ratio of consolidation stress to the unconfined yield strength. In FT4 device, due to gentle upward motion of blade, a low stress environment could be generated in powder bed and hence cohesion becomes a very significant factor. The Specific Energy (SE) of the bed of powders, defined as the energy required to withdraw a rotating impeller out of a powder bed, could then be estimated. Using both instruments, it is possible to evaluate the flow behavior of coated materials according to the regimes shown in Table 5.1.



(A)



(B)

Figure 5.4: Flowability of the (A) ternary mixture, and (B) EP granules alone after coating.

Table 5.1: General flow regimes in Schulze shear cell and FT4 instrument (Schulze, 2008; Freeman, 2007).

Schulze shear cell, FFC		**FT4, SE *(mJ/g)***	
FFC<1	Not flowing	SE<5	Low cohesion
1<FFC<2	Very cohesive	5<SE<10	Moderate cohesion
2<FFC<4	Cohesive	SE>10	High cohesive material
4<FFC<10	Easy flowing		
FFC>10	Free flowing		

It can be observed from Figure 5.4-A that the mixture's flow property does not change significantly with the coating levels of 1.5 to 3.5 wt % (remains in easy-flowing regime and low cohesion regions, respectively for Schulze shear cell and FT4). However, the behaviour of coated EP granules on their own shifts notably to the moderate cohesion in FT4 and cohesive regime in Schulze shear cell, particularly at lower pre-shear, with 3.5 wt % coating level (Figure 5.4-B). However, the flow behavior of both mixture and EP granules stay in easy-flowing and low cohesion (obtained respectively using Schulze shear cell and FT4 data analysis) for the 2.5% coating level. Overall, Figure 5.2 shows that increasing the coating level (from 0.5 to 3.5%) could decrease the segregation of EP granules. However, the results of Figure 5.4 demonstrate that increasing the coating level to 3.5 % could adversely impact the flowability of the EP granules themselves. Therefore, increasing the coating level more than 2.5% is not recommended for this powder formulation since it could compromise the flowability of enzyme granules. Therefore, 2.5 wt % coating level could be adequate to reduce the segregation of EP granules without compromising the flowability of both mixture and EP granules themselves. Segregation reduction of EP granules after applying optimum coating level (2.5 wt%) is also evaluated by NIR technique (similar to the approach presented in the section 3.5). Using the proposed technique, more quantities of the material could be analyzed after heap formation. For this purpose, the ternary mixture (containing BP, TAED and coated EP granules) is poured through a funnel into the grid box shown in Figure 3.24. The extracted powder mixtures were then scanned by the MicroNIR and the results were compared with those of the uncoated case, as shown in Figure 5.5. As illustrated in Figure 5.5, the SI is reduced from 0.70 to 0.25 after applying the optimum coating level. The magnified segregation extent of EP granules measured using surface (Figure 5.2) versus depth analysis (Figure 5.5) could be due to packing style of particles towards the wall, surface properties and wall effects (Alizadeh et al., 2017; Alizadeh et al., 2017).

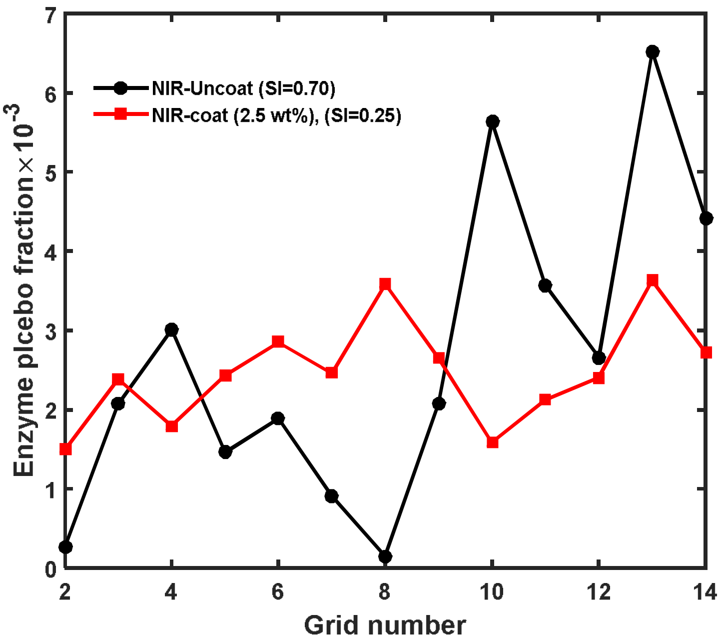
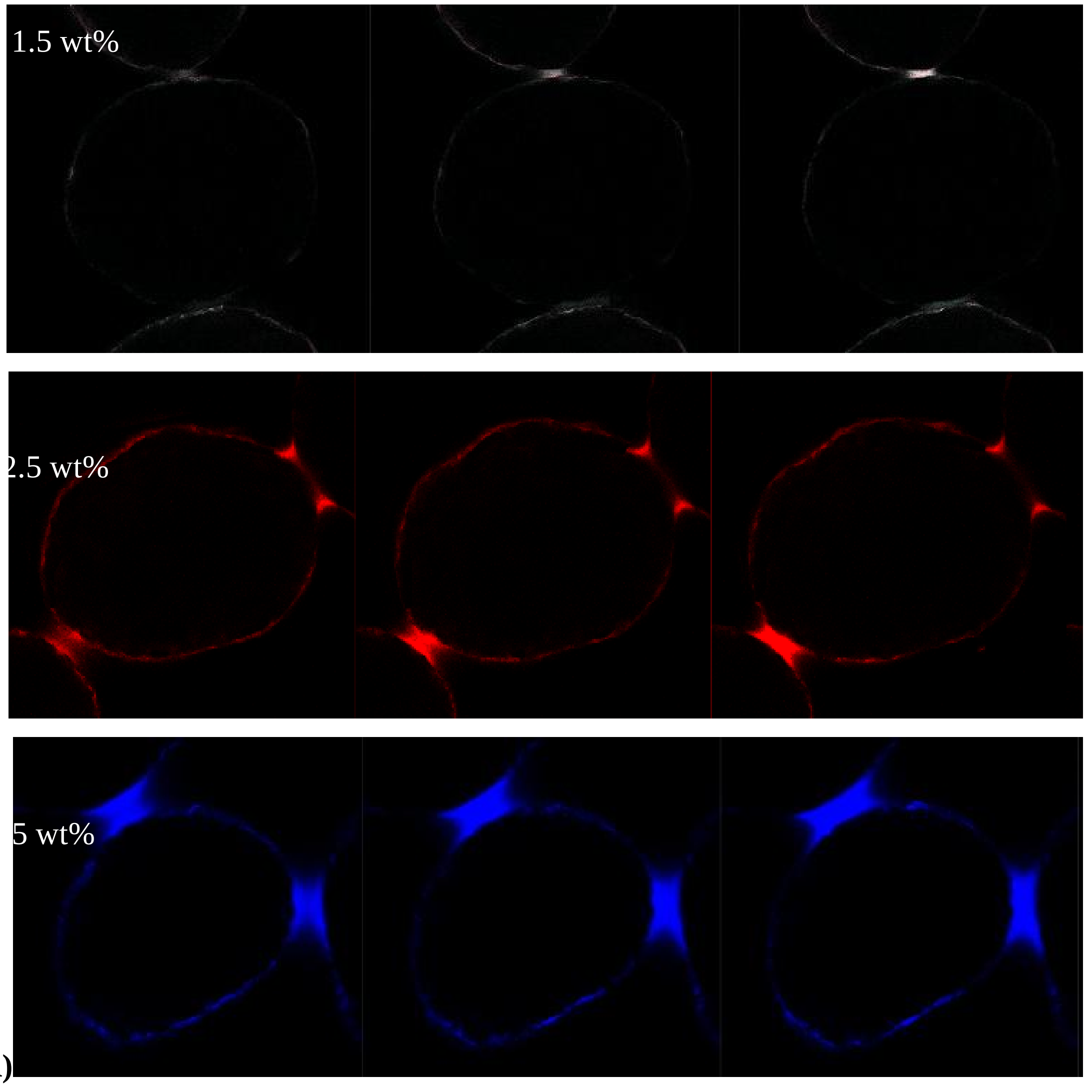


Figure 5.5: Scanning the extracted powder mixture, before and after EP granules coating, using NIR technique.

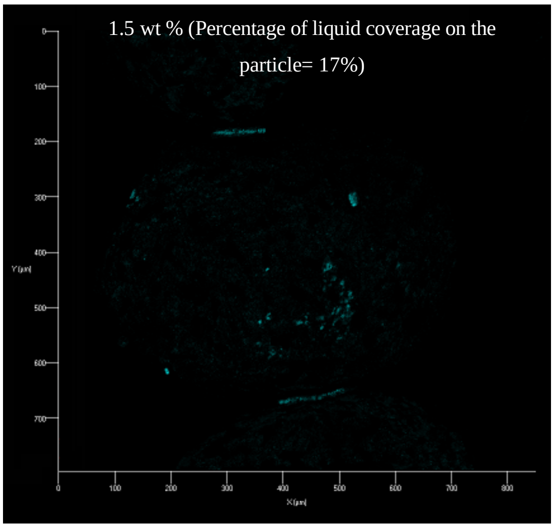
Further characterization of EP granules after 2.5 wt% coating level by PEG is done and the results are reported in section 5.2.3.

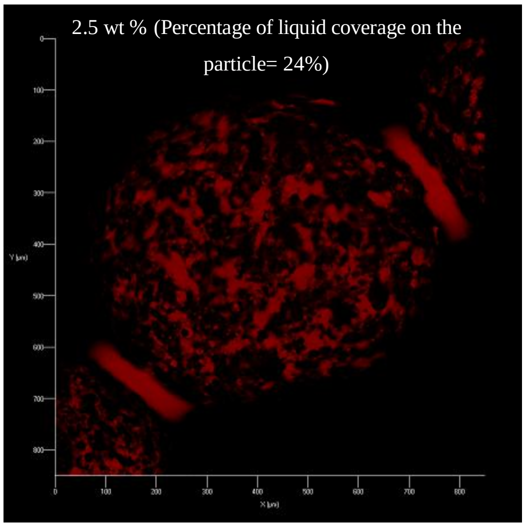
5.2.3 Characterization of the optimum coating level

Using confocal imaging, it is possible to obtain the 3D structure and the cross-sectional view of tiny liquid layer (Depypere et al., 2009). In this study, 1.5 to 3.5 wt % coating levels of PEG on the EP granules have been analysed using a Zeiss LSM880 Confocal Laser Scanning Microscope. For this purpose, a small amount of fluorescent pigment was added to PEG which enabled differentiation between EP granule and the coating liquid. The liquid coating is shown by green, red and blue colour for 1.5, 2.5 and 3.5 wt % coating levels of PEG, respectively. Representative cross-sectional views of the liquid coating and the top view of the 3D liquid coverage (area equal to the half size of particle volume) of one single enzyme granule are shown in (Figure 5.6). Figure 5.6 also shows the bridging between different particles. It can be observed that the liquid layer coverage and the liquid bridge volume are increased by increasing the coating percentage (Figure 5.6-A). It is shown in Figure 5.6-B that the percentage of surface liquid coverage is increased from 17 to 24 and 28% (obtained by the image processing) by increasing the coating level from 1.5 to 2.5 and 3.5 wt%, respectively. The percentage of liquid coverage for the optimum coating percentage (2.5%) is estimated as 24%. The method of obtaining the percentage of surface liquid coverage is summarized as follow: 1) the average pixel number of the coated liquid on the surface of particle is first measured using the selection tool of the image processing software, 2) the total average pixel of the entire particle has been separately measured using the image processing software and 3) finally the average pixel of the coated liquid on the surface of the particle was divided by the total average pixel of particle to estimate the liquid coverage percentage. It can be seen in both cross-sectional view and the top 3D view of 1.5 wt % liquid coating level that majority of the granule surface is not covered by the liquid, confirming that an inadequate coating level can be achieved when 1.5 wt % PEG is used.



(A)





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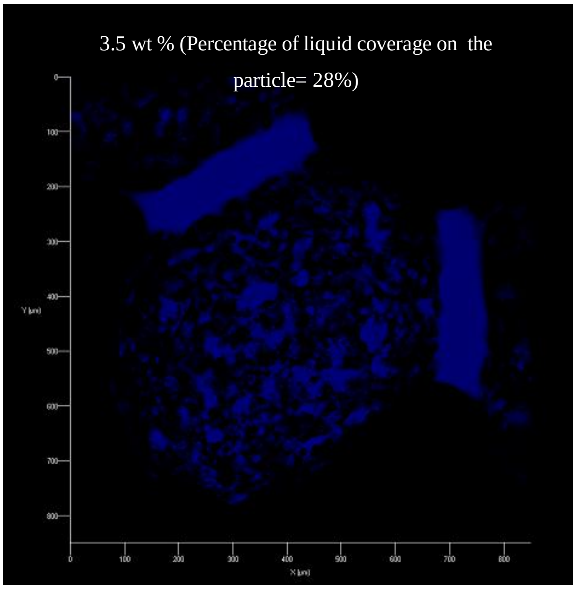
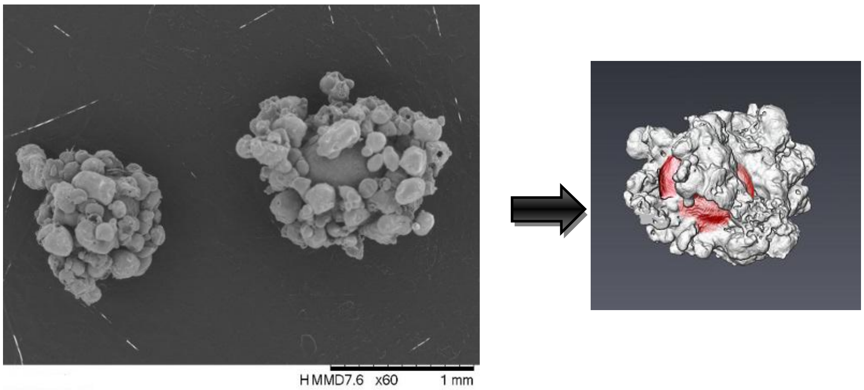
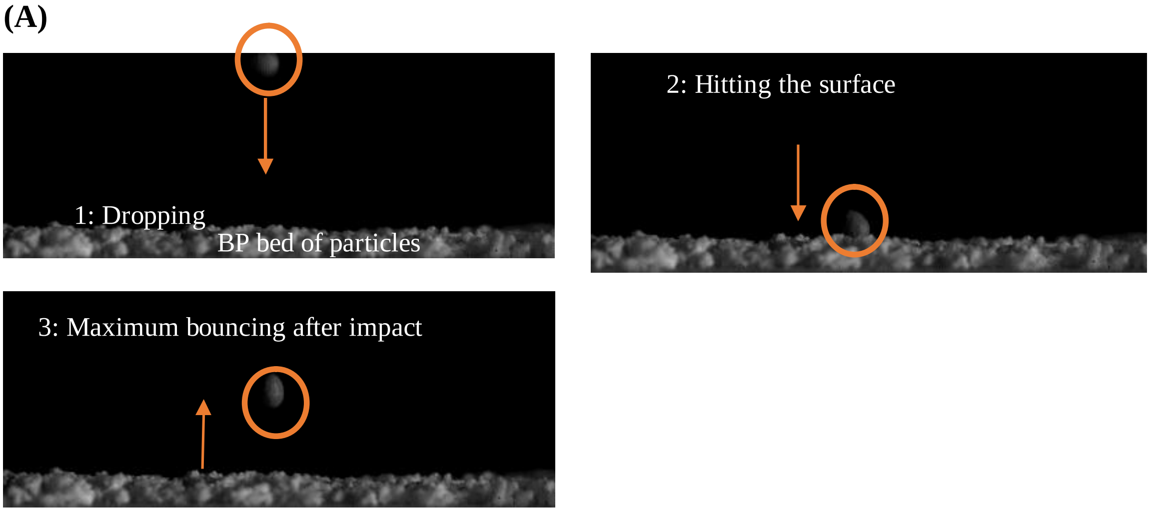


Figure 5.6: (A) Cross-sectional view image of coating, (B) top view picture of 3D coating coverage by PEG obtained by confocal laser scanning microscope.

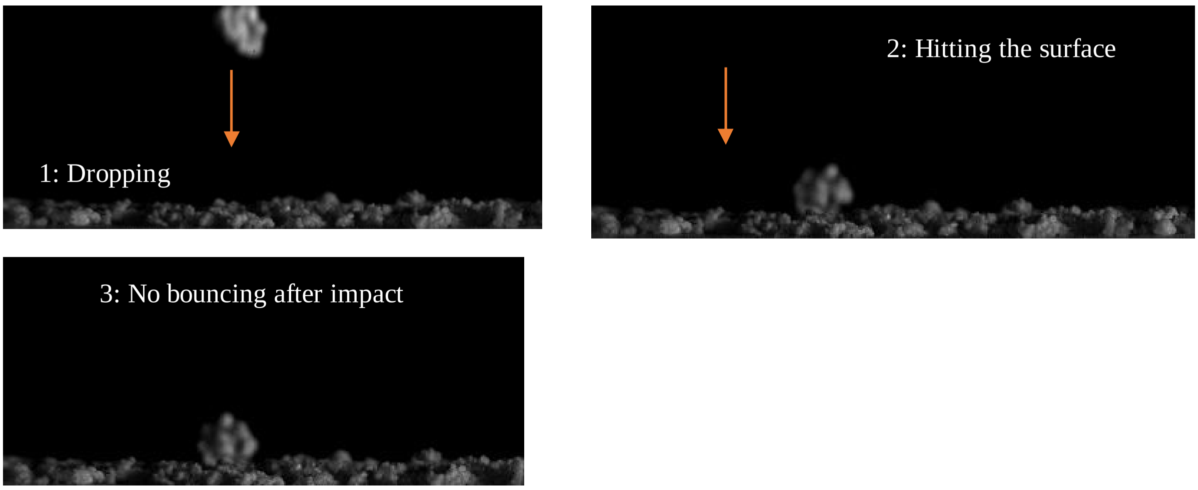
The SEM image of 2.5 wt % coated EP granules after mixing with TAED and BP is shown in Figure 5.7-A. Attachment of fine BP particles onto the surfaces of the coated EP granules could modify their shape and produce rougher surfaces. This could reduce their free movement in the mixture by the process of interlocking leading to a reduction of the segregation of EP granules as compared to the case of free-flowing round granules. In fact, the process of interlocking of some rough EP granules could mitigate segregation, retarding their movement to the center of the pile. Attachment of BP granules on the surfaces of EP granules could even change the restitution of the EP granules on impact (Figure 5.7-B). For this purpose, the impact of a single EP granule (before and after BP coverage) to the surface covered by BP particles, was filmed by a high-speed camera at 4000 fps. No bouncing of the EP granule (when it was covered by BP particles) could be observed after the impact, probably due to the interlocking between the rough EP granules and the bed of BP particles), whilst the round EP granules bounced off the surface.



(A)



EP granules



(B) **Coated EP granules after mixing with BP particles**

Figure 5.7: (A) SEM photo and X-ray tomogram of coated EP granules with PEG after mixing with TAED and BP and (B) impact properties of EP granules before and after coating/mixing with BP particles.

The segregation mechanisms of EP granules, before and after coating, were further evaluated by particle trajectory in the research of Alizadeh et al. (2018) using DEM simulation. In the mentioned research, it was demonstrated that the original rounded shape EP granules could penetrate more deeply into the bed of the ternary mixture, escaping from the shearing top layer of avalanching materials. In contrast, less penetration into the heap of powders and more spread over the heap surface was observed for the case of coated EP granules due to particle surface modification.

5.2.4 Effect of vibration on coated enzyme granules

Mobility of EP granules after coating by PEG has been tested by exposing the ternary mixture, containing coated EP granules, to the vibration. For this purpose, another series of vibration tests were carried out for the ternary mixture containing full particle size distribution of BP, TAED and coated EP granules (92.6/5.55/1.85 wt % ratio) at the optimum coating level (2.5 wt% PEG) described earlier. The same frequency and amplitude (frequency= 50 *Hz*, amplitude=15 *mm*), used in the section 4.3 (chapter4), was applied to the ternary mixture. The resulting heaps of ternary mixture, containing the coated EP granules, as well as the concentration map of EP granules after vibration at different times are shown in Figure 5.8 and Figure 5.9, respectively. As illustrated in Figure 5.8 and 5.9, the coated minor ingredient EP granules moved towards the corners of the heap by time, increasing the SI of EP granules like the case of uncoated granules. However, it can be deduced from Figure 5.8 and 5.9 that the SI of coated EP granules in the ternary mixture is less than that of uncoated one at different times of vibration. By comparison of the SI of coated and uncoated after the equilibrated time (900 s), (Figure 5.10), it can be deduced that the coated EP granules are less segregated in the corners of the heap after 900 s vibration as compared to the case of uncoated ones. This might be due to the reduced mobility of the rough EP granules (SEM photo is shown in Figure 5.7-A) and changed restitution properties of this component (Figure 5.7-B) after coating by BP and the interlocking effect.

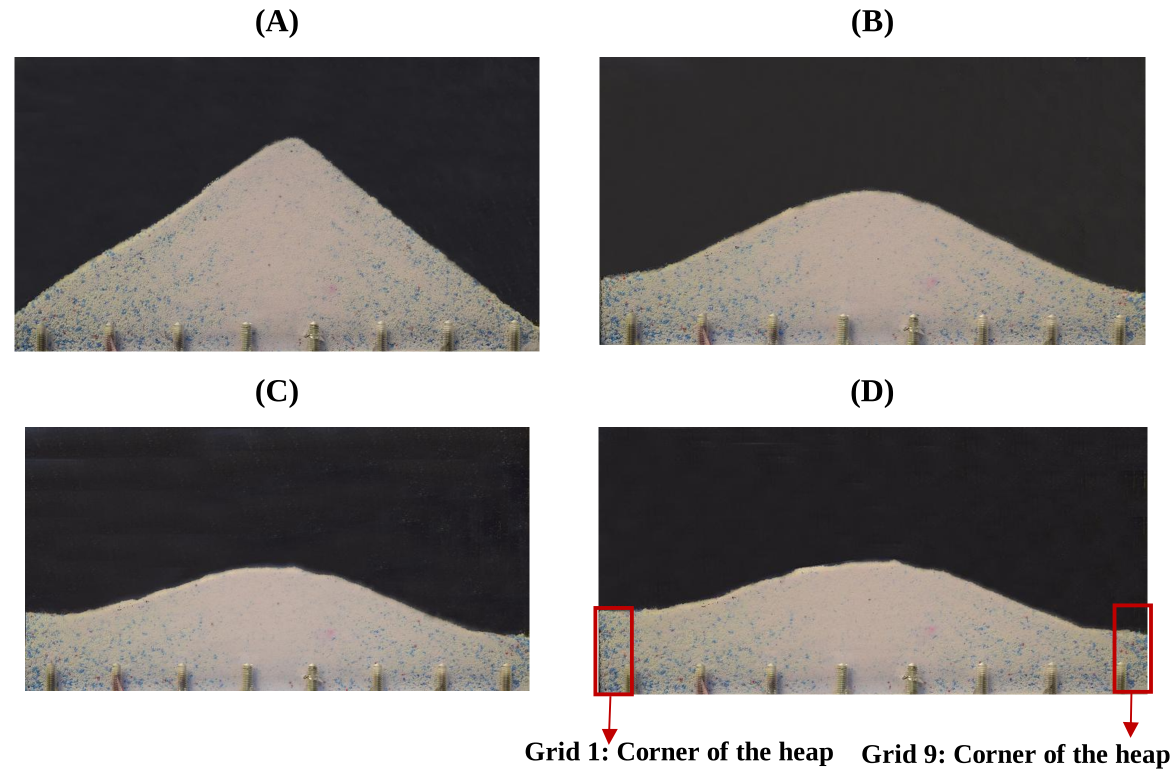


Figure 5.8: Ternary mixture containing BP, TAED and coated EP granules (92.6/5.55/1.85 wt % ratio) (A) before and after vibration at (B) 15, (C) 300 and (D) 900 *s* (frequency= 50 *Hz*, amplitude=15 *mm*).

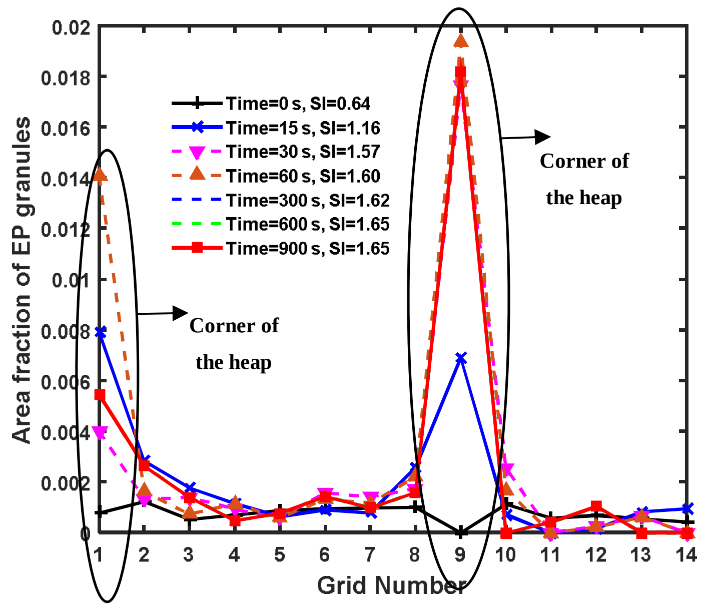


Figure 5.9: Concentration map/SI of coated EP granules (2.5 wt %) after vibration times of 15, 30, 60, 300, 600 and 900 *s*.

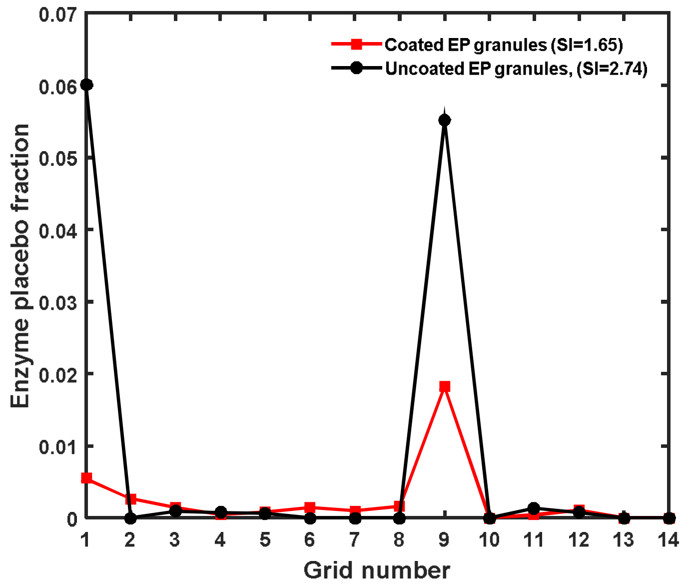


Figure 5.10: Concentration map/SI of coated (2.5 wt %) and uncoated EP granules in the ternary mixture after vibration time of 900 *s*.

According to the above-mentioned results, segregation of the minor ingredient enzyme granules could be reduced during filling and vibration by applying a thin layer of coating material to the particles. It is found that the surfaces of EP granules could be covered by fine BP particles after the coating and mixing with TAED and BP, which further could reduce the segregation. The aim of the next section is therefore to investigate the effect of particle structural modification on density-driven segregation of minor ingredients of EP granules in laundry detergent powder mixtures. Granulation technique has been applied to produce the modified granules with large particles of enzyme at their core, surrounded by fine particles of Blown powder (BP) by means of aqueous Polyethylene glycol (PEG) of higher molecular weight as binder.

5.3 Effect of structural modefication on the segregation of particle

5.3.1 Procedure of particle structural modification

Seeded granulation technique has been examined in this work to modify the rounded shape of EP granules and investigate its effect on density-driven segregation of particles. Rahmanian et al. (2011) proposed the seeded granulation technique for producing the granules with large particles at their core surrounded by fine particles. A similar concept is used here to change the structure of EP granules by layering of fine BP particles onto larger nuclei/seed EP granules.

Granulation of powders has been performed in a small scale high shear wet granulator (MiPro, ProCepT, Zelzate, Belgium) equipped with a 250 *mL* bowl (Figure 5.11). According to Rahmanian et al. (2011) seeded granulation effectiveness could be improved when particles of varied particle sizes are used during the granulation process. In this study, the mode size of particle size distribution of EP granules (600-710 μm, based on British standard sieve analysis) and BP (212-250 μm, based on British standard sieve analysis) were used to modify the EP granules by seeded granulation. The mixture (~100 *g*) of BP and EP granules was first added to the granulator bowl and then 5 % binder was sprayed on the powder mixture using a syringe. Aqueous solution of PEG has been widely applied as binder for the wet granulation purpose (Talu el al., 2001; Rodriguez et al., 2002; Saleh et al., 2005; Rahmanian et al., 2011) and therefore aqueous solution of PEG 4000 was used in this study. The solid-to-solid ratio (S/S) of EP granules to BP was found according to the approximate surface area coverage of EP granules by the BP particles which is estimated as 0.80.

For the granulation process, three representative impeller speeds were used: 300 *rpm* (low-speed), 500 *rpm* (medium-speed) and 700 *rpm* (high-speed). Extracted samples of different granulation time intervals (30, 60 and 90*s*) were then dried overnight in an oven followed by delumping through sieving. Particle size distribution and the shape of approximately 20 *g* dried granules were then analysed using standard sieve analysis and optical microscopy, respectively.

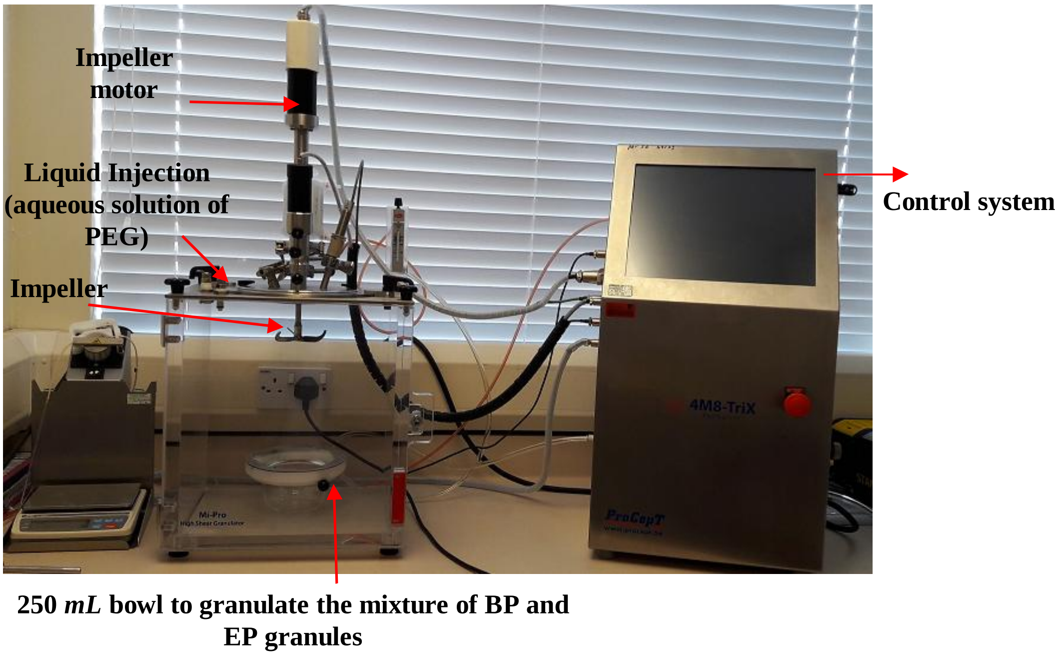
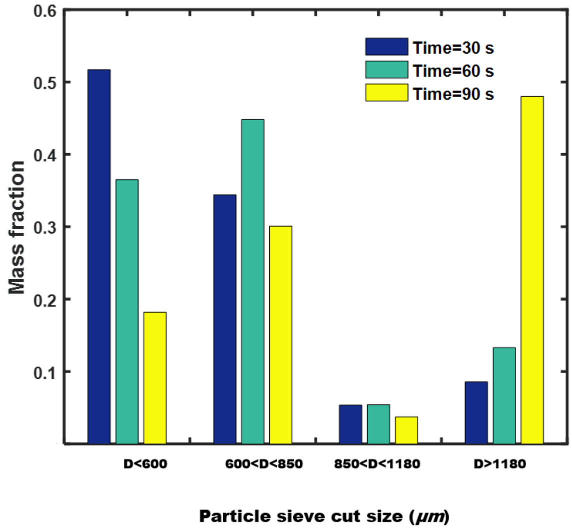


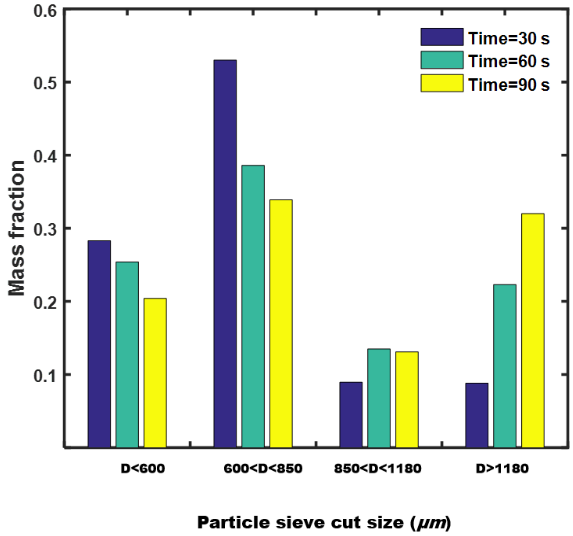
Figure 5.11: High shear wet granulator system.

5.3.2 Modification of the EP granules by granulation

As reported in the literature, wetting and nucleation, coalescence and growth, consolidation and breakage are the important mechanisms of granule formation (Shanmugam, 2015; Hansuld and Briens, 2014; Mahdi et al., 2018). In this study, wetting, nucleation and growth mechanisms must be controlled in such a way that the seeded EP granules, covered by a fine BP layer, are produced. In another word, surface coverage (coating) of EP granules by fine BP layer must be controlled in such a way that only the surface roughness of EP granules is changed without further granule growth. According to the initial sizes of EP granules and BP particles, the ideal size of the seeded granules (maximum one layer surface coverage) would be in the size range between 850<D<1180 μm, referred in this work as primary seeded granules. Particle size range between 600 to 850 μm mainly represents the unseeded EP granules, while particle size less than 600 μm and more than 1180 μm mainly contains the fine BP particles and lumps (due to the granule growth), respectively. As operating condition of the granulator could influence the effective seeded granulation, the effects of the impeller speed and time of granulation were investigated. Figure 5.12 shows the granule size distribution as a function of different operating conditions.



(A)



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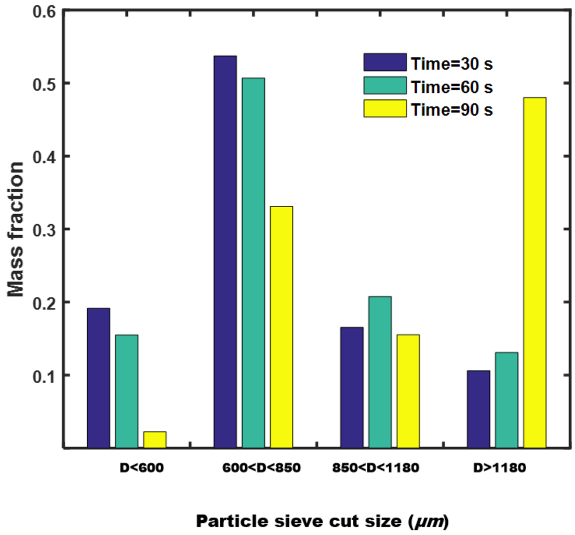


(C)

Figure 5.12: Granule particle size distribution as a function of granulation time and impeller speed, (a) 300, (b) 500 and (c) 700 *RPM*.

As shown in Figure 5.12, the amount of primary seeded granules (850<D<1180 μm) increased as the impeller speed was increased from 300 to 700 *RPM*. In fact, the kinetic energy must have been high enough at larger impeller speeds which produced more seeded granules (Rahmanian et al., 2011). In addition, the amount of primary seeded granules for all impeller speeds reduced when the granulation time was increased from 60 to 90 *s*, indicating the significant growth of primary seeded granules (850<D<1180 μm) at time 90 *s*. Therefore, granulation time of 60 *s* is used for modifying the EP granules, where wetting and nucleation (i.e., adherence of on layer of fines in this study) mainly happened. To find the efficient impeller speed for modifying the EP granules, around 200 particles of primary seeded granules (850<D<1180 μm) at 60 *s* were analysed using optical microscopy. It has been observed that the primary seeded granules mainly contain three types of granules: granulates of BP, EP granules and EP granules covered by BP (referred as seeded EP granules), Figure 5.13. The effective impeller speed has then been chosen based on its efficiency in the production of only seeded EP granules. The resulting Pie charts have been illustrated in Figure 5.14.

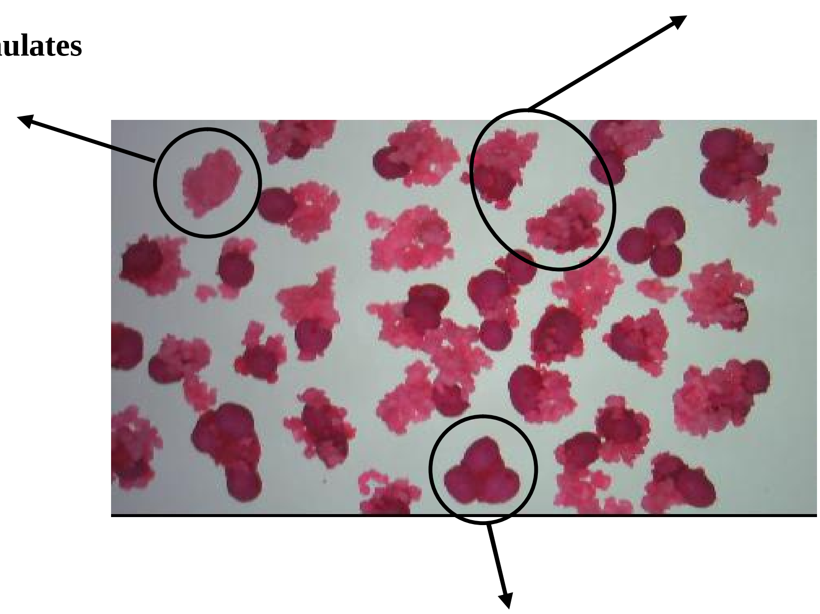


Figure 5.13: Different types of granulates observed for the extracted primary seeded granules (850<D<1180 μm).

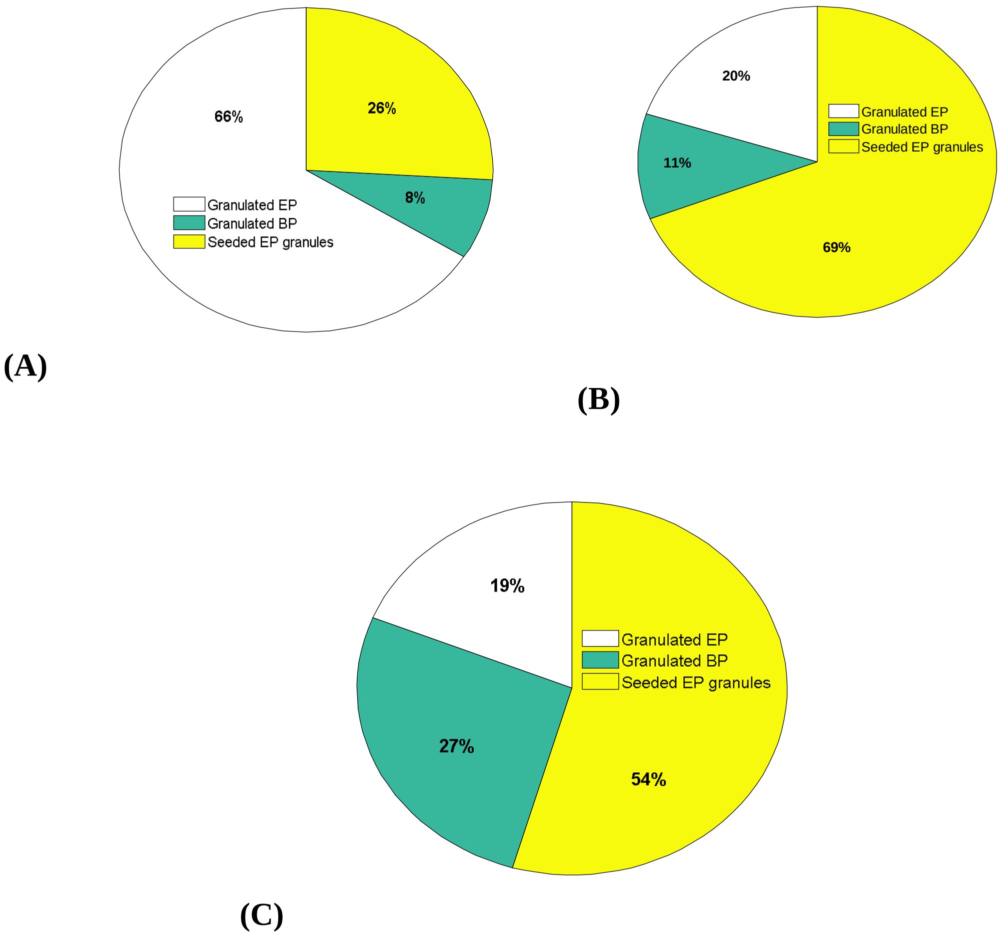
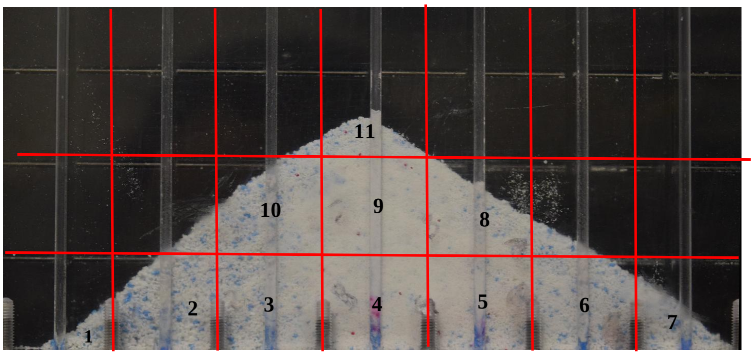


Figure 5.14: The obtained Pie chart for the scanned granulates obtained from granulator at different impeller speeds of (A) 300, (B) 500 and (C) 700 *RPM*.

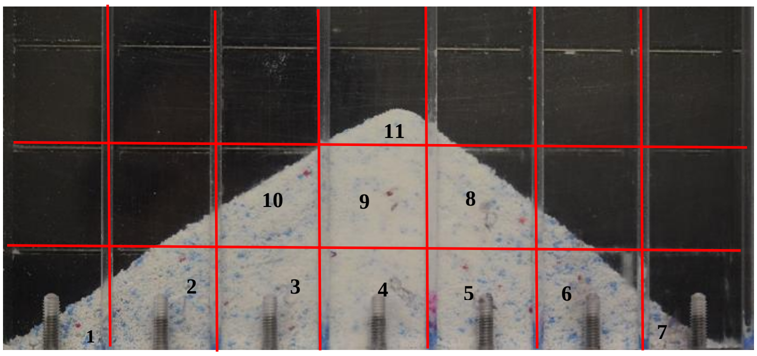
In the study of Rahmanian et al. (2011), less seeded granulates is reported to be obtained at lower impeller speeds. On the other hand, seeded granulation is enhanced at higher impeller speeds which is attributed to the higher kinetic energy exerted to the system. However, very high impeller speeds could also increase the agglomeration breakage (Knight et al., 2000). In the current study, the granulator produced the most seeded EP granules (~70 %) at impeller speed of 500 *RPM* (Figure 5.14). On the other hand, decreasing the impeller speed to 300 *RPM*, resulted in the generation of mostly EP granulates (~66 %). It is probably due to the impeller's less energy to shear and spread the liquid on the particles, causing the formation of less seeded EP granules and more EP granulates. It should be noted that at impeller speed of 700 *RPM*, the amount of seeded EP granules was decreased which must be due to the formation of more BP granulates. Overall, primary seeded granules obtained from the granulator at time of 60 *s* and impeller speed of 500 *RPM* were used further for the homogeneity analysis of the EP granules.

5.3.3 Segregation of the modified EP granules

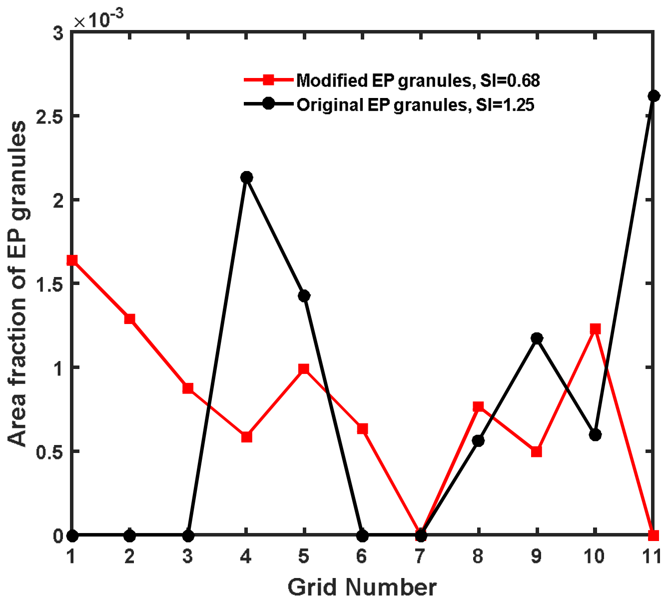
To allow further analysis on the effect of particle structural modification on the homogeneity of EP granules, two ternary mixture heaps (40 *g* each) with exact weight percentage ratio used in detergent formulation (92.6 (BP)/ 5.55 (TAED)/ 1.85 (EP granules) were prepared; one containing the original rounded EP granules (mode size) and the other the modified EP granules (taken from granulator at time= 60 *s*, impeller speed of 500 *RPM* and size range between 850 to 1180 μm). The effect of particle surface modification on the segregation of EP granules is presented in Figure 5.15 using surface image processing. The estimated SI of EP granules is presented beside the concentration maps (Figure 5.15-C), where it can be observed that the SI decreases after particle structural modification.



(A)



(B)



(C)

Figure 5.15: Ternary mixture containing (A) EP granules and (B) modified EP granules, (C) concentration map and SI of EP granules in the ternary mixture before and after particle structural modification by seeded granulation.

The homogeneity of EP granules is also evaluated for some of the extracted powder samples (Grid number: 2, 3, 4, 5, 6, 8, 9, 10 and 11) using Near-Infrared spectroscopy (following to the approach presented in the section 3.5). The optimisation of the spectral information of extracted powder samples has been done according to the Equation 2.9 and 2.10 and the fraction results are presented in Figure 5.16. As illustrated in Figure 5.16, SI decreased from 0.50 to 0.15 after particle surface modification of enzyme granules.

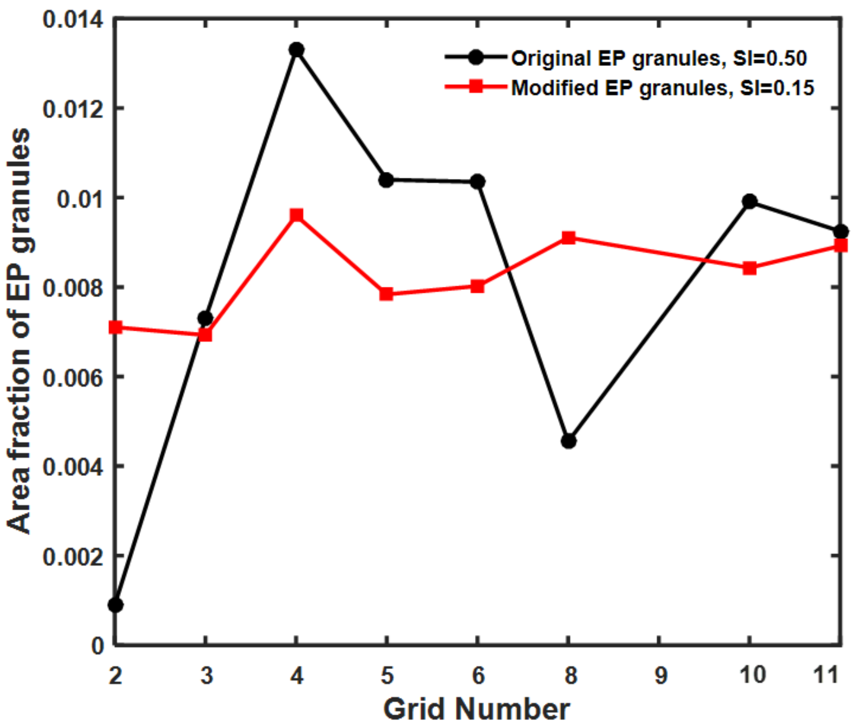


Figure 5.16: Concentration map/SI of the EP granules (obtained by NIR spectral analysis) before and after structural modification.

The better homogeneity of the modified EP granules throughout the bed of powders in the ternary mixture could be because of the modification of particle surface, notably restitution properties and interlocking between the modified EP granules and the BP and TAED particles. Different frames of the impact of the modified EP granules to the surface of BP particles was obtained using the high speed camera and the results are demonstrated in Figure 5.17. As illustrated in Figure 5.17, no bouncing could be observed for the case of the modified EP granules after the impact on the bed BP particle most probably due to the interlocking effect, which is in contrast to the case of the original rounded EP granules (Figure 5.7). Similar hypothesis was reported in the case of applying the coating layer on EP granules (Figure 5.7, section 5.2.3).

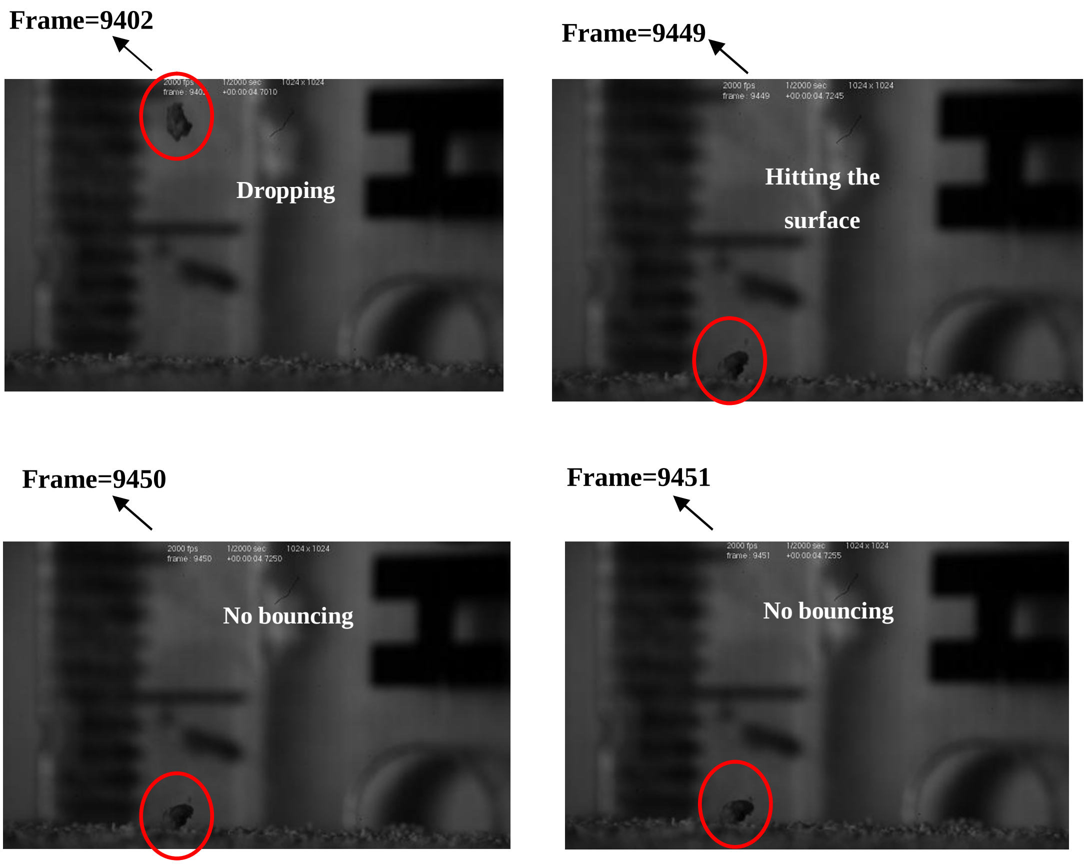
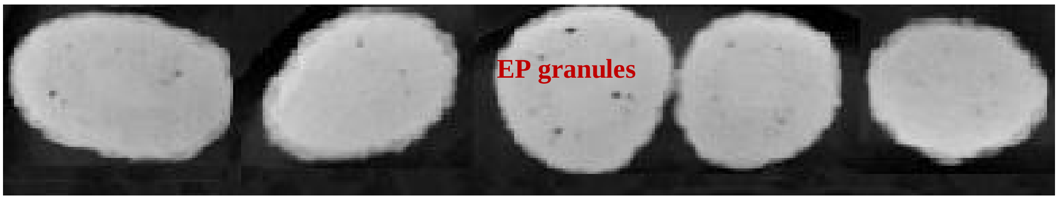
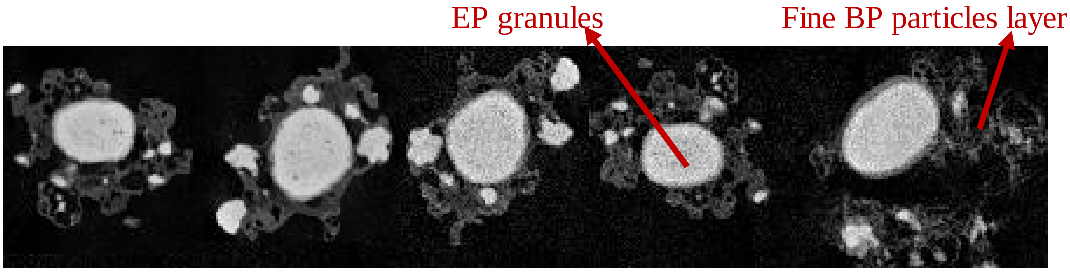


Figure 5.17: Restitution properties of EP granules after particle surface modification by granulation technique (the particle is encircled by a red ring for better visualization).

The cross-sectional views of 5 different EP granules, before and after particle surface modification, obtained by X-ray microtomography are presented in Figure 5.18. Figure 5.18-A shows the original rounded EP granules, while the roughened surfaces of modified EP granules by fine BP layers are presented in Figure 5.18-B. In fact, the surfaces of the modified EP granules became rougher than original rounded EP granules after the granulation process. As mentioned before, the changed particle properties and the process of interlocking could reduce the free movement of dense EP granules in the mixture, mitigating their accumulation into the centre of the piles.



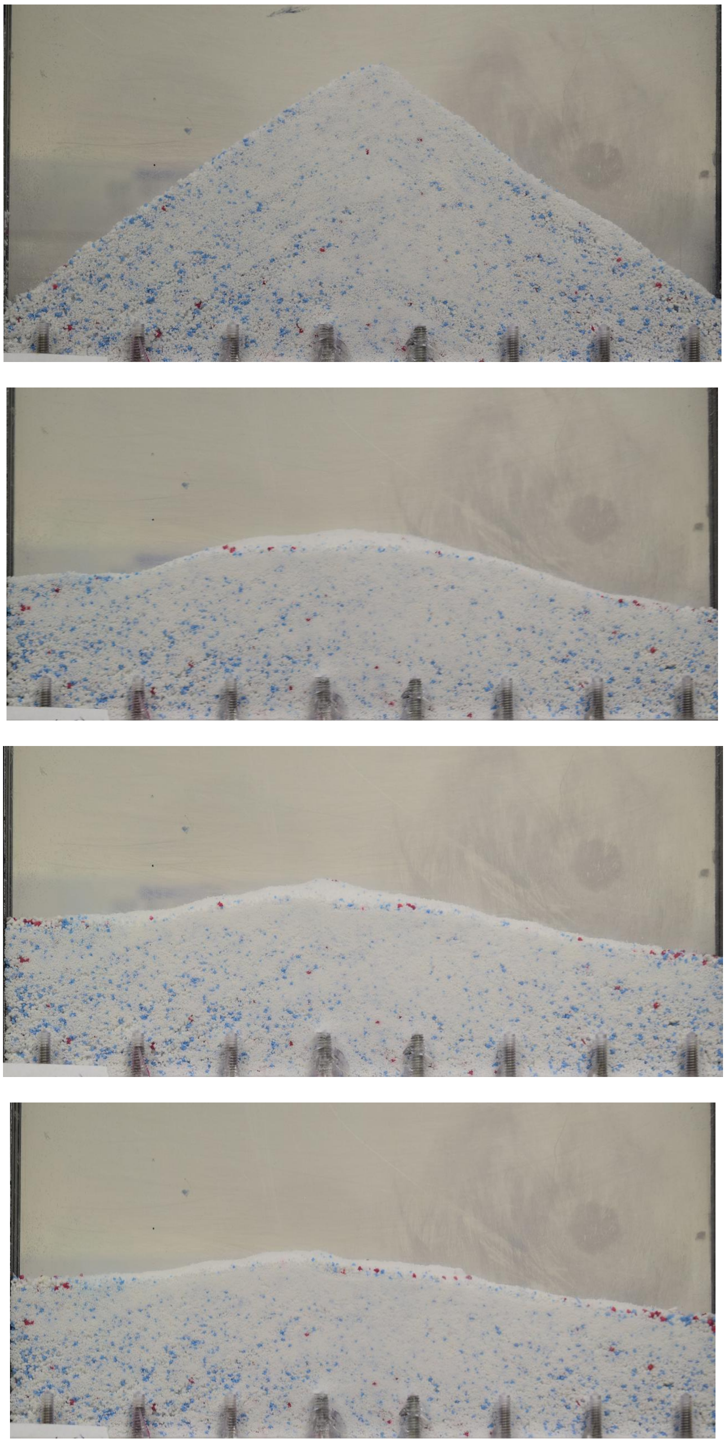
(A) **Rounded EP granules (resolution=2 μm)**



(B) **Modified EP granules (resolution=4 μm)**

Figure 5.18: Cross sectional view of EP granules (A) before and (B) after shape modification.

In another set of experiments, the mobility of the modified EP granules was tested by exposing the ternary mixture to the vibration. The same frequency and amplitude (frequency= 50 *Hz*, amplitude=15 *mm*), used in the section 4.3 (chapter 4), was applied to the ternary mixture. The resulting heaps of ternary mixture, containing the modified EP granules at different times of vibration, are illustrated in Figure 5.19.



(A) (B) (C) (D)

Figure 5.19: Ternary mixture containing BP, TAED and modified EP granules (A) before and after vibration at (B) 60, (C) 300 and (D) 900 *s* (frequency= 50 *Hz*, amplitude=15 *mm*).

As illustrated in Figure 5.19, the modified EP granules moved towards the corners of the heap by vibration time, similar to the case of uncoated and coated EP granules (described in sections 4.3 and 5.2.4). However, it can be deduced from Figure 5.20 that the number of EP granules that moved towards the heap corners because of vibration (vibration time=900 *s*), is much less than that of the case of uncoated granules, decreasing the SI of EP granules which could be due to the reduced mobility of the modified enzyme granules (Figure 5.18) and changed restitution properties of this component (Figure 5.17) after coating by BP particles layer.

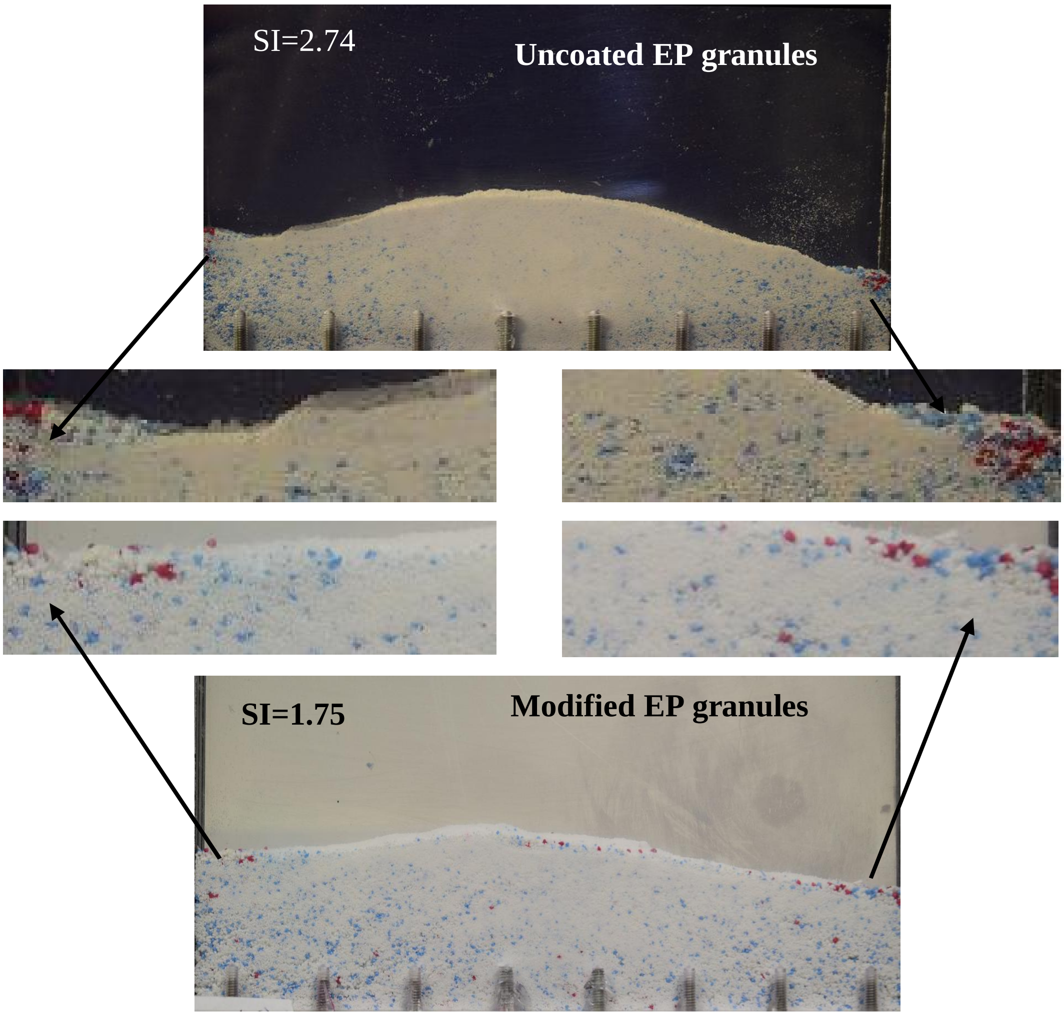


Figure 5.20: Ternary mixture containing BP, TAED and EP granules after 900 *s* vibration (frequency= 50 *Hz*, amplitude=15 *mm*).

Overall, the changed physical properties of the EP granules, notably the surface roughness and the restitution properties, after coverage by BP particles could mitigate their segregation during both filling and vibration.

5.4 Concluding remarks

In this chapter, two approaches were proposed for the segregation minimisation of low-dose enzyme granules: 1) applying a sticky material to the surfaces of EP granules before mixing with BP and TAED, 2) structural modification of EP granules before mixing with BP and TAED.

The results showed that the segregation of EP granules, during both filling and intense vibration, can be reduced by applying a thin layer of a sticky liquid on the enzyme granules in the ternary powder mixture with full particle size distribution of the components. 2.5 (wt%) PEG 600 has been found as an optimum level to reduce the segregation of EP granules without compromising the flowability of the mixture as well as EP granules themselves. The effect of cohesion, as a method of hindering the segregation of granular materials, has been broadly explored in the literature (Liao et al., 2016; Yang, 2006; Liao et al., 2016). However, the results of the current investigation shows that monitoring the flowability of both mixture of powders and coated material must also be considered and therefore the optimum coating level (in such a way that flowability is not compromised) should be addressed for the purpose of granular segregation reduction.

It has been observed that fine particles of BP and TAED components adhere to the coated EP granules and produce rough surfaces which could reduce the mobility of EP granules by enhancing the process of interlocking in the ternary mixture. The SI of EP granules during heap formation was reduced using the proposed optimum coating percentage in the ternary mixture with full particle size distribution of the components. Overall, increasing the roughness of EP granules and the process of interlocking after applying a coating layer to the enzyme particles is reported to be effective on their segregation mitigation. This hypothesis has been further tested by changing the structural properties of particles by other means. In most famous works of the literature, the particle size distribution, density variation, cohesion levels and operational/geometry configuration have been described as contributing factors affecting the segregation of granular materials (Liao et al., 2016; Rodríguez et al., 2015; Jaklič et al., 2015; Hajra and Khakhar, 2011; Meier et al., 2008; Benito et al., 2013; Tai et al., 2010; Liao et al., 2015; Kingston and Heindel, 2014; Xiao et al., 2017; Marmur and Heindel, 2017; Windows-Yule and Parker, 2014; Liao et al., 2016; Yang, 2006). However, the effect of manipulating the surface/structural properties of particles and therefore the effect of particle interlocking on the segregation of granular materials have not been fully addressed.

In this research, the process of granulation was used to change the surface roughness of EP granules, where rounded EP granules and rough BP particles were used as initial seed and the coating layer, respectively. It has been observed that the structure and the restitution properties of the modified EP granules differed from those of the original ones. Changed material properties of the EP granules was found to reduce the segregation of this ingredient both during heap formation and vibration.

Chapter 6
Conclusions

The work undertaken in this research project has resulted in the development of a reliable technique for the uniformity assessment of minor ingredients as well as methodology for the reduction of the segregation of minor ingredients in powder mixtures (during processes of heap formation and vibration). Ternary mixture of laundry detergent formulation comprising spray-dried powder, known as Blown Powder (BP), Tetraacetylethylenediamine (TAED) and Enzyme Placebo Granules (EP granules), has been used as model system. Segregation mechanisms of the powder mixtures were explored by pouring them into a (2D) box to make a heap. The key conclusions which may be drawn from this research are summarised below:

6.1 Segregation measurement techniques

- Numerous uniformity assessment methods of particulate systems have been developed and studied over the last few decades. Different assessment techniques of powder homogeneity have been reviewed in this research. Image analysis is a non-invasive, fast and accurate technique for the determination of powder homogeneity in multicomponent mixtures. A simple methodology has been introduced based on the image segmentation and pixel determination to estimate the fraction of components. However, this technique is suitable for the detection of powders with differentiable colours. Therefore, spectroscopy technique is recommended for material identification, where analysis is independent of the particle colour.
- This research looked at spectroscopy technique based on Near-Infrared, for the determination of the component fractions. Spectroscopic approaches attracted more attention due to their ability to quantify several components (independent of the particle colour), either in at-line, in-line and/or on-line mode. In this research, NIR spectroscopy was used for the evaluation of powder homogeneity due to its relatively low cost as compared to other spectroscopic

instruments. For this purpose, an economic and portable probe (MicroNIR1700® probe, manufactured by JDSU Ltd) was used with wavelength range between 900 – 1700 *nm* and spatial resolution of 6.2 *nm*. The results showed that powder homogeneity analysis of washing powders can be successfully achieved using the proposed NIR system.

- For improving the multivariate regression analysis, different pre-processing methods have been investigated to eliminate the noise arising from the physical phenomena of the spectra, (such as particle size variation). The results obtaining from the regression models are dependent on the pre-processing technique which is influenced by the nature of the pure spectra of the materials. The best pre-processing technique must be selected based on the material specification. For this purpose, scatter correction, spectral derivatives and combined scatter-derivative methods have been explored. It is observed that spectral pre-processing by derivatives can be used to correct both the baseline shift and non-linearities arising from differing physical properties of the components. Furthermore, it is shown that the smoothed second derivative mode (using Norris-Williams technique) gives an accurate determination of the EP granules (low content level ingredient in the studied ternary mixture).

6.2 Segregation mechanisms

- In binary mixture of BP and TAED particles, the segregation increased when their particle size ratio was increased, which was due to angle of repose variations. In addition, the polydispersity index resulting from size/shape variation decreased for the larger sizes of components. Therefore, better size uniformity between particles of larger sieve cut sizes could reduce the segregation in a binary mixture with unity size ratio.

- In the ternary mixture of BP, TAED and EP granules, it is shown that both size and density segregation (due to push-away effect) are the main mechanisms for EP granules. However, the effect of angle of repose/shape segregation of EP granules was found to be insignificant.

- It is further shown that the low-level ingredient EP granules highly segregate towards the centre of the heap due to their higher density as compared to other components. Furthermore, less segregation was observed for BP and TAED particles due to their wider particle size distributions as compared to that of EP granules.

- Segregation of low-level ingredient EP granules was also evaluated when an intense vibration was applied to the ternary mixture containing full particle size distribution of components. It is shown that segregation of enzyme granules could significantly increase by time after vibration, probably due to Brazil nut effects.

6.3 Segregation reduction approaches for the low-content level ingredient

- The effect of particle coating on the segregation reduction of minor ingredient of enzyme granules is evaluated, where a thin layer of Polyethylene glycol (PEG, Pluriol E 600) was applied to the particles. It is shown that segregation of enzyme granules decreased when the coating level increased from 0.5 to 3.5 wt%.

- As increasing the coating level could adversely influence the flowability of the final product, the optimum coating level was obtained according to the flowability results of the bulk of the ternary mixture and enzyme granules themselves. 2.5 wt% coating level was found to be adequate for segregation minimisation of enzyme granules without compromising the flowability of the ternary mixture and enzyme granules themselves. It was observed from SEM pictures that the fine particles of BP could adhere to the coated enzyme granules during mixing, transforming their rounded surfaces to rougher ones. The process of interlocking was reported to be a factor for their segregation reduction. In fact, the process of coating could produce modified enzyme particles with different restitution properties, which further hinders their segregation. This phenomenon could also be effective for segregation reduction of enzyme granules during vibration (due to hindering their free mobility by the process of interlocking).

- The afore-mentioned hypothesis was tested by modifying the surfaces of enzyme granules using granulation technique and investigating their segregation tendency in the ternary mixture. Using the modified enzyme granules in the ternary mixture, the segregation of the low-content level ingredient was reduced which is in a good agreement with the surface coating results. These observations prove that the segregation of minor ingredients could be inhibited by changing their surface properties and therefore their restitution properties and free mobility in the bulk of powder mixtures.

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