



High shear granulation of binary mixtures: Effect of powder composition on granule properties: Effect of powder composition on granule properties

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1	HIGH SHEAR GRANULATION OF BINARY MIXTURES: EFFECT OF
2	POWDER COMPOSITION ON GRANULE PROPERTIES.
3	
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2 ABSTRACT

3 The granular product being designed in this work required the use of two different 4 powders namely limestone and teawaste; these materials have different bulk and particle 5 densities. The overall aim of the project was to obtain a granular product in the size range 2 6 4mm. The two powders were granulated in different proportions to using 7 carboxymethylcellose (CMC) as the binder. The effect of amount of binder added, relative 8 composition of the powder, and type of teawaste on the product yield was studied. The results 9 show that the optimum product yield was a function of both relative powder composition and 10 the amount of binder used; increasing the composition of teawaste in the powder increased 11 the amount of binder required for successful granulation. An increase in the mass fraction of 12 teawaste in the powder mix must be accompanied by an increase in the amount of binder to 13 maintain the desired product yield.

14 KEYWORDS

15 Binary-mixture, high shear granulation, attrition; contact angle; wetting; granule strength

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17

1 1. Introduction

High shear wet granulation process (HSWG) is a size enlargement process that involves conversion of primary powder particles into larger entities with improved characteristics. Some of the advantages of HSWG include increased bulk densities, improved flow properties, reduced powder segregation and better handling properties. HSWG has been applied in several industries for example detergent, food, pharmaceutical and agricultural, to enhance the powder processibility [1-5].

Granulation of a mixture of powders is very common especially in the pharmaceutical
industries where several powder components are required to perform different functionalities.
Some of the common mixtures used in the pharmaceutical industries are lactose/ micro
crystalline cellulose (MCC) [6-8]; lactose / mannitol [9] and starch/lactose [10-14]. In most
granulation applications the raw materials are of comparable bulk densities.

13 Granulation of binary mixtures of powders has always proven to be a challenge especially 14 if the powders have differing physical properties. Some of the challenges encountered include 15 segregation of the powder particles during the mixing, preferential nucleation of the 16 component. This often leads to a granular product with inhomogeneous composition. The 17 interaction between the powder particles and the binder particle is crucial. In-fact wettability 18 of the powder components has a significant influence on the success or failure of the 19 granulation process as it impacts the nucleation process. Contact angle measurements are 20 used to indicate the degree of wetting of solid surface by liquid droplets. The high values of 21 contact angle show low wettability whilst, small values of contact angle show high 22 wettability. For instance, if one of the components of the powder is hydrophobic this could 23 result in preferential granulation of the hydrophilic component [15]. It has also been shown

that as the hydrophobicity of formulation increases the average size of the granules decreases
and the granule structure depend on the formulation wettability [16].

Percolation theory has been used to describe wet agglomeration of binary mixtures in high shear mixer in by other researchers [17]. According to their theory it was concluded that if the components exhibit similar growth properties the growth properties would be additive. However, if the components show different growth properties the mixing ratio of the components would control the growth properties of the mixture or intermediate growth properties would be exhibited.

9 In the current research project, granulation of two different powder materials was 10 necessary to produce a product for application as an improved soil conditions. Each of the 11 components; limestone and teawaste perform different roles. Limestone modifies the pH of 12 acidic soils while teawaste improves the soil texture introduces organic matter in the soil. In 13 the current study the challenge faced was that the two powders have huge difference in the 14 density which often leads to segregation of the components; limestone (~2700 kg/m³) is 15 denser than teawaste (~800kg/m³).

16 The aim of this research was to investigate the effect of the relative compositions of the 17 teawaste and limestone on product yield, attrition strength and granule mass mean size. 18 Optimum binder requirements of the different formulations were also investigated. The effect 19 of washing teawaste on binder requirement and other granules properties was also studied.

1 2. Experimental Methods

2 2.1 Materials Characterisation

3 2.1.1 XRD and particle size analysis of the powders

4 Limestone powder supplied by Kilwaughter Chemicals Ltd, UK, was used as one of the 5 raw materials. X-ray diffraction (XRD) analysis of the powder limestone that it was mainly 6 composed of calcite and quartz minerals [4]. Value tea purchased from Tesco was used as the 7 second powder component in the granulation experiments. It was used in two forms, first as 8 received referred to as fresh tea (FT) and secondly it was washed in fresh hot water and dried 9 to simulate used tea (UT). The particle size distributions of limestone and used-tea measured 10 by Malvern Mastersizer are shown in Fig. 1. The mass median diameters (d_{50}) of limestone, 11 FT and UT powders were $31.5 \pm 4.5 \ \mu\text{m}$; $311 \pm 10 \ \mu\text{m}$ and $413 \pm 31 \ \mu\text{m}$ respectively. The 12 other attributes of the particle size distributions are summarised in Table 1.

13 **[Fig. 1]**

14 [Table 1]

Carboxymethylcellulose (CMC) salt supplied by Calbiochem, UK was used to make binder in this research project. A homogenous mix was obtained adding the CMC powder to the vortex formed by stirring the deionized water with an impeller rotating at high speed (490 rpm) over a period of 30 minutes. The CMC concentration in the solution was 5g/L. The binder solution was stored in sealed jars until use. The viscosity of the binder solution was measured with Brookfield Viscometer RVDV-II Pro (Brookfield Engineering Laboratories, USA) was found to be ~6600 mPas. The comparison between the specific pore volume and surface area of teaswaste and
 limestone particles obtained from literature [18-20] is summarised in

Table 2. The table shows the surface area and specific pore volume of teawaste (UT) is
 higher than that of limestone.

3 [Table 2]

4

2.1.2 Fourier Transform Infrared (FTIR) spectroscopy

FT-IR was principally employed as a qualitative technique for the assessment of the chemical structure of fresh tea (FT) and the used tea (UT). The IR spectra of the samples were recorded on a PerkinElmer Spectrum 100 spectrophotometer to characterize the change in the functional groups of the material surface before and after washing with hot water (using a KBr disk technique in the range of 400 - 4000 cm⁻¹). The results for the analysis are shown in Fig. 2. The results do not show any significant difference between the two samples as the main peaks are still present in both samples.

12 **[Fig.2]**

13

2.1.3 Contact angle measurements

14 The interaction between the binder droplets and the powder was analysed using the contact angle measurement. The goniometer method is the most common, simple and practical 15 16 method to measure the contact angle. The contact angles on the prepared surfaces were 17 monitored using a FTA1000B goniometer instrument (First Ten Angstroms Inc., USA). For 18 each sample, five different readings were recorded and the contact angle values were 19 averages of the five measurements made on different points of the sample surface. 20 Measurements were obtained on loose beds and on compacted beds (tablets). 50 g binary 21 mixtures of teawaste and limestone with teawaste mass fractions of 0, 0.25, 0.5, 0.75 and 1.0 22 were obtained by mixing teawaste and limestone in the granulator for 5 minutes. For loose 23 bed tests, small homogenous 0.5g samples were taken from the binary mix and particles were 24 spread on to a glass plate to form a thin layer. The contact angle was then measured by

1 introducing the binder droplet (volume of ~15 µl). For the second set of measurements, 2 samples of the 0.5g were collected from the binary powder mix and then compressed into 3 tablets by applying a load of 8kN using a manual hydraulic press (Atlas 15T Manual 4 Hydraulic Press, Specac Inc. USA). Fig. 3 shows the particle distribution on the surfaces of 5 the tablets with different compositions. It can be seen in these images that the number of 6 teawaste particles on the surface increases as the mass teawaste mass fraction is increased as 7 expected. The images also show that the teawaste particles are angular and fibre. Binder 8 droplet was then introduced on the tablet surface to measure the contact angle. Typical images recorded during the measurements are shown in Fig. 4. 9

10 **[Fig. 3]**

11 **[Fig. 4]**

12 **2.2 Production of the granules and drying**

The granulation experiments were carried out in a small bench scale high shear granulator; Kenwood (KM070, Kenwood, UK). The granulator has a stainless steel mixing bowl with a total capacity of 6.7 L and is also equipped with two blade impeller which also undergoes "planetary mixing" motion around the mixer during granulation. The rotational speed of the impeller can be varied between 100 and 213 rpm.

18 A parameter λ is defined in the following equation (Eq. 1) was used to indicate the 19 powder composition:

$$20 \qquad \lambda = \frac{m_{k\alpha}}{m_{k\alpha}} \tag{1}$$

21 where m_{tea} is the mass of tea and m_{tot} is the total mass of powder (limestone + teawaste), 22 respectively. 1 This binary mix was pre-mixed for about half a minute at an impeller speed of 103 rpm. 2 At the end of the pre-mixing stage the granulator was stopped to allow addition of the 3 granulating fluid. After addition of the required amount binder the wet mass was mixed for 4 half a minute and the granulator was interrupted at the end of this period to allow removal of 5 caking material from the walls of the vessel. Granulation was then continued for a further 30 6 seconds to give total granulation time of a minute.

In preliminary studies experiments to compare the performance of the three different powders; fresh tea, used tea and limestone were carried out. This involved granulating the three different powders using same granulation and formulation conditions; the CMC binder with a concentration of 5g/L was used. The same procedure described above was used.

Different masses of binder were added to the binary mixture to give different liquid to
solid ratio according to Table 1. Unless stated otherwise, the total batch size of was 50 g.

The factors that were investigated are liquid/solid ratio, powder composition and teawaste
type (particle size). The list of experiment carried out is shown in Table 3.

15 [Table 3]

After granulation, each batch of granules was transferred into flat aluminium trays with dimensions 236 x 297 x 59 mm, ensuring that the granules were evenly spread on the tray surface. The granule trays were then transferred into an oven (Binder FD249, Binder GmbH, Germany) and dried for 12 hours pre-set at temperature of 60 °C. Subsequent to drying the granules were allowed to cool to room temperature and then stored in sealed bags until needed.

1 **2.3 Product characterisation**

2 2.3.1 Size Analysis

Retsch sieves (Retsch GmbH, Germany) were used for the size analysis and the aperture
sizes are of the sieves ranged from 350 to 4000 µm. The stack of sieves with the granules was
placed on an orbital sample shaker, Stuart Orbital Shaker, supplied by Cole-Parmer UK. The
speed of the shaker was set to 180 rpm and the sieving duration to 5 min.

The goal of the granulation was to make granules in the size range 2 to 4 mm which is the
typical size range of commercial fertiliser granules. The percentage of granules in this size
range was referred to as the product yield (n) is calculated by following equation;

$$10 \qquad \eta = \left(\frac{m_r}{m_B}\right) \times 100\% \tag{2}$$

11 where m_r is the mass of granules in required size range and m_B is the mass of total 12 granules produced in a batch.

13 The mass mean granule size was determined from the sieve analysis data using the14 following equation;

15
$$\overline{d}_m = \frac{\sum_{i=1}^n m_i \overline{x}}{\sum_{i=1}^n m_i}$$
(3)

16 where m_i is mass of granules in the interval x_i to x_{i+1} with an arithmetic average size of \overline{x} .

17 **2.3.2 Attrition Test**

18 The granule attrition strength was determined using the method previously described in 19 [4]. In this procedure a samples of the granules (5 grams) is subjected to attrition forces by 20 shaking them mechanically on a sieve shaker and recording the mass loss as a function of time. Granules in the size range 2 to 4 mm were used in this test. The attrition loss which is
defined as the percentage mass of the granules due to attrition was calculated using;

3
$$A_r(t) = \frac{m(t)}{m_0} \times 100\%$$
 (4)

4 where m(t) is the mass of the granules retained on the sieve at the end of the test and m_0 5 is the initial mass of the sample.

6 The attrition resistance constant, κ, was determined by fitting the A_r versus time plots to
7 equation;

$$8 \qquad A_r(t) = 100 \exp(-\frac{t}{\kappa}) \tag{5}$$

9 In Eq. (5), the attrition resistance coefficient, κ , can be interpreted as the time it takes to 10 loss 63.3% by mass due to attrition. A higher attrition resistance coefficient indicates better 11 resistance of the material to attrition. The difference in the resistance of the granules from the 12 different batches to attrition is evaluated using this coefficient.

13 **2.3.3 Granule Strength measurements**

The strength of granules in the size range 1 to 2 mm was determined from compression of a bed of granules in a confined cylindrical die using a method previously described in [12, 21]. The beds of granules were compressed to a maximum compression force of 500 N using a compression test speed of 10 mm/min. The force-displacement data obtained during the compression of bed or granules were analysed using a method described previously [11, 12, 21-23] to obtain the single granule strength. Eq (6) was fitted to the plot of lnP versus natural strain to obtain the granule strength parameter.

21
$$\ln P = \ln\left(\frac{r}{\alpha}\right) + \alpha\varepsilon + \ln\left(1 - e^{-\alpha\varepsilon}\right)$$
(6)

1 In Eq (6) α is a pressure coefficient, τ the Adams parameter, P is the applied pressure 2 and ε is the natural strain.

3 **3. Results & discussion**

4 **3.1 Effect of powder composition on wettability**

5 Contact angle measurements can be used as an indication of the degree of wetting between a liquid and solid surface; high values of contact angle (>90°) indicate low wettability whilst 6 7 low contact angles (<90°) indicate high wettability [24]. Contact angle measurements of the 8 CMC droplet with surfaces of different compositions are presented in Fig. 5. It is clear from 9 these results that the contact angle increased as the composition of the teawaste in the binary 10 mixture was increased. For measurements taken on a loose powder bed, the values of contact 11 angle for pure samples of teawaste and limestone were 131.82° and 110.87° respectively; 12 showing that limestone exhibit better wettability to the CMC droplet compared to teawaste. 13 Binary mixtures of teawaste and limestone had intermediate values of contact angles. Contact 14 angles measurements were also repeated on smoother surfaces (compacted powder bed, 15 tablets) and similar trends were obtained i.e. increasing the composition. The contact angle of 16 the CMC droplet was lower on the pure limestone tablet surface (83.35°) compared to the 17 teawaste tablet surface (116.85°).

18 **[Fig. 5]**

19 Contact angles measurements on compacted surfaces were lower than those on loose 20 powder beds in all cases. The difference in these measured values of contact angle from loose 21 powder bed and compacted powder bed can be attributed to difference in the surface 22 roughness. The compacted surface have smoother surface compared to the loose surface 23 which is in agreement with earlier reports from literature [25].

1 Comparison of the surface roughness of compacted powder bed and loose powder bed was 2 done by capturing the images of the surfaces and analysing the images with ImageJ software. 3 The highest of the peaks in the images are proportional to the height of the surface asperities. 4 The results presented in Fig. 6 show that the compacted surface has a relatively smoother 5 surface compared to the loose powder bed.

6 [Fig 6]

7 **3.2 Influence of powder type on size and granule size distribution**

8 Preliminary granulation experiments of the three different powders using the same binder 9 and granulation conditions showed that for the same amount of binder and similar granulation 10 condition, the limestone powder was the easiest to granulate followed by fresh tea and then 11 used tea. The results shown in Fig. 7 show that the mean size of the granules obtained 12 increased in the order; UT < FT < Limestone. The means size of the granules also produces 13 when limestone was the powder was twice that of fresh tea and thrice that of used tea. The 14 observed trends are to be expected considering the difference in the particle sizes and pore 15 sizes of the particles reported in Table 2. The pore volume of used teawaste is higher than 16 that of limestone by several orders of magnitude. It would be logical to expect the pore 17 volume of the used teawaste to be higher than that of fresh tea since washing of the teawaste 18 is expected to open the pores.

19 **[Fig. 7]**

20 **3.3 Effect of Liquid/solid Ratio**

Liquid to solid ratio is one of the most important variables in granulation; hence several reports in literature have investigated the influence of this variable on the granulation process [12, 13, 26]. In this work it is expressed as ratio of mass of binder to mass of powder being

granulated. For the same powder mass the higher the liquid to solid ratio the higher the amount of binder added. The results presented in this section were obtained for tests in which powder was a mixture of limestone and fresh tea, (w/w) ratio of the teawaste to limestone was kept constant at 0.75. The role of binder in granulation is to form bridges or bond between the powder primary particles. Greater availability of binder should promote granule growth due to increased probability of bond formation. Typical cumulative size distribution plots of batches of granules formed using different liquid to solid ratios is shown in Fig. 8(a).

8 [Fig. 8]

9 Increasing the liquid to solid ratio results in the cumulative size distribution curve shifting 10 to the right (see Fig. 8 (a)). Fig. 8(b) shows the plot of granule mass mean size as a function 11 of binder concentration. It is interesting to note that the presence of tea in the powder 12 formulation (75%) alters the amount of binder required for successful granulation. Higher 13 than usual liquid to solid ratios were used to ensure significant change in the size distribution 14 of the particles. Increasing the liquid to solid ratio for 0.95 to 1.15 resulted in an increase in 15 granule mean size from about 2.5 to about 3.35mm.

16 The effect of amount of the binder used during granulation on the product yield is shown 17 in Fig. 9. Whereas, increasing the amount of binder causes a monotonic increase in the 18 average size of the batch, slightly different trend was observed in terms of product yield. 19 Increasing the liquid to solid ratio from 0.95 to 1.0 causes an increase in the product yield 20 though a further increase beyond this value caused a reduction in the product yield. This can 21 be explained by rapid increase in the overgrowth of the granules which result in formation of 22 coarse granules i.e. granules with size greater than product. A similar observation had been 23 made in our previous work [4].

24 **[Fig. 9]**

1 Attrition is a size reduction mechanism whereby a granule loses mass by loss of particles 2 at the surface of the particles due to friction when the granules rub against each other or other 3 surfaces. The attrition resistance coefficient gives an indication of the how strong are the 4 granules can resist attrition. The results presented in Fig. 9 show the effect of the binder 5 concentration on the attrition strength of the granules. For this formulation increasing the 6 liquid to solid ratio from 0.95 to 1.05 does not significantly change the attrition resistance of 7 the granules. However a further increase of the liquid to solid ratio to 1.1 and above results in 8 huge increase in the attrition resistance of the granules.

9 A higher attrition coefficient indicates the granules have strong resistance to attrition as it 10 would take a longer time to reduce loss particles from the peripherals of the granules due 11 attrition. When fresh tea (FT) is used in the formulation at a mass fraction of 0.75, increasing 12 in the liquid to solid ratio results in increase in the attrition resistance. This is in agreement 13 with earlier results reported in literature [4, 27, 28].

14 **3.4 Effect of teawaste to limestone ratio**

15 A series of granulation experiments were carried out using different powder of different 16 compositions of teawaste and limestone powder. The amount of binder required to achieve 17 successful granulation increased with increasing content of teawaste. As expected the mean 18 granule size increased with increasing binder concentration. It is interesting to note in Fig. 19 10(a) the shift to the right of the linear plots as the tea composition is increased. The shift of 20 the curves to the right as the teawaste mass fraction is increase can be explained by more 21 binder requirement of formulation with more teawaste. Increasing the teawaste mass fraction 22 increases the mean particle size of the powder. The specific surface area of the teawaste is 23 higher than that of limestone powder. Also the specific pore volume of the former is higher 24 than that of the later (see Table 2). The higher specific pore volume of the teawaste may be 25 associated with the high binder requirements of the powder; the binder that is added during granulation first fills the pore structure in the powder. Once the pores have been filled or are
saturated additional binder becomes available at the surface of the teawaste particles. It is the
binder that is available at the surface of the particle that contributed to agglomeration process.
It can be postulated that presence of large specific pore volume reduces the amount of binder
available for agglomeration.

6 Increasing the mass fraction of the teawaste in the formulation is expected to result in an 7 increase both the specific surface area of the binary mixture. This explained the increase in 8 the binder requirement as the mass fraction of teawaste is increased. Therefore, the shift of 9 the plots to the right is consistent with literature as more binder is required for granulation of 10 larger primary particles [29-31].

11 It has also been reported in literature [30] that an increase in particle size should be 12 accompanied by an increase in the binder viscosity to ensure granule growth, however, in this 13 work the viscosity of the binder was not changed as the composition of the powder was 14 changed.

15 **[Fig. 10]**

16 The amount of binder used in the granulation was varied to determine the optimum liquid 17 to solid ratio for the different formulations; this is the liquid to solid ratio at which maximum product yield is achieved. The plots of yield versus liquid to solid ratio, for granulation of 18 19 different mass fractions of FT and limestone are presented in Fig. 10(b). It can be noticed 20 from this plot that the three different formulations peak at different values of liquid to solid 21 ratios. The optimum liquid to solid ratio for $\lambda = 0.25$, 0.5 and 0.75 are 0.5, 0.9 and 1.45, 22 respectively. For the same granulation conditions, to maintain the same level of product yield 23 one has to increase the amount of binder used. Increasing the tea mass fraction increased the

proportion of large particles in the mixture. The larger primary particles grow mainly by layering mechanism, where they capture fine particles, but for this to happen the particles have to be covered by a layer of binder and more binder is required to achieve this [32, 33]. Another possible explanation could be the difference in the porosities of the two powders.

5 The attrition resistance coefficients of the granules with different proportions of teawaste 6 (FT) are shown in Fig. 11. At teawaste mass fractions of 0.25 and 0.75, the attrition resistance 7 coefficient increases monotonically with binder content whereas at mass fraction of the 0.5, it 8 increases and then levels off. The results show that as the mass fraction of teawaste in the 9 formulation is increased, more binder will be required to obtain granules with the same 10 attrition resistance.

11 **[Fig. 11]**

12 The results shown presented earlier in Fig. 5 show that the wettability of the binary 13 mixture decreased as the teawaste mass fraction increased. It is probable that changes in the 14 granulation mechanisms occur when the composition of the binary mixture changes which 15 can lead to differences in granule sizes and size distributions.

16 **3.5 Effect of tea type**

17 The influence of washing the tea before granulation was investigated. The results show 18 that the granule size distributions and the mechanical properties of the granules are indeed 19 affected with pre-treatment of the tea. Washing the tea affects the amount of binder required 20 during granulation. Used tea requires more binder to achieve the same level of granulation as 21 the fresh tea. When two formulations having different teawaste to limestone ratios are 22 granulated for the same duration, at the same impeller speed using the same amount of 23 binder, batches with different size distributions were obtained. Fig. 12 shows the difference 24 between the cumulative size distribution of the UT and FT batches for $\lambda = 0.75$ and liquid to

1 solid ratio of 1.15. Results from FTIR analysis shown in Fig. 2 show that the functional 2 groups of the tea are not changed by washing the tea since the dominant peaks for the two 3 samples are similar. The difference in the granule size distributions can therefore not be 4 explained by different chemical interactions. One possible hypothesis to explain the results is 5 that washing the teawaste to produce used-tea altered the particle size distribution of tea, 6 which resulted in different granulation mechanism. Washing the tea might have removed the 7 finer particles from the sample, leaving behind larger particle. The larger particles that are left 8 behind require more binder to bind them together. This is further confirmed by the shift to the 9 right by the results presented in Fig. 12(a).

10 **[Fig. 12]**

Fig. 12(b) shows the FT is more sensitive to change in liquid to solid ratio; very small changes in the liquid to solid ratio results in significant changes in the granule mean sizes. The other type of teawaste, UT, is less sensitive to changes in the liquid to solid ratio. The differences in the granulation behaviour could be due to difference in the initial particles size distributions of the two types of powder. For the same liquid to solid ratio and other constant variables, FT granules would have a larger granule mean size.

The effect of tea type on the product yield is shown in Fig. 13. Fig. 13 reiterates the point shown in earlier results; more binder will be required to granulate UT compared to FT. For instance, to get a product yield of 78% one would need to use a liquid to solid ratio of about 1.5 when granulating a mixture of used tea and limestone compared to about 1 if fresh tea is used. It can also be noted that the optimum liquid to solid ratio for UT is about 1.5 compared to around 1 for the other type of teawaste.

23 [Fig. 13]

The attrition test results for granules from the two different types of tea are presented in Fig. 14(a) and (b). Fig. 14(a) shows variation of attrition ratio as a function of time. The attrition ratio falls at a slower rate of the FT granules compared to the UT granules. At the end of testing period about 99.7% of FT granules survive attrition compared to 99.2% for the UT granules.

6 **[Fig. 14]**

7 The attrition resistance coefficients of the two types of granules are compared in Fig. 8 14(b); the FT granules have stronger resistance to attrition compared to UT granules. This 9 could be due to differences in the structure of the granules caused by differences in the 10 particle size distributions in each of the individual granules. It must also be noted that 11 different amounts of binder were used in producing the granules.

For a given set of operating conditions the rate of consolidation is dependent on the amount of binder [10, 34]. In the case of high viscosity binder, the rate of consolidation decreases with increasing binder content. In the current work, a high viscosity binder was used, therefore, it is then expected that the rate of consolidation of the granules was lower for the cases where high level of binder were used i.e. granulation used tea and formulation with higher portions of teawaste.

18 **3.6 Effect of formulation variables on granule tensile strength**

The strength of granules produced under different formulation conditions are summarized in Fig. 15. The responses of granule strength to changes in the liquid to solid ratio seem to be influenced by the amount mass ratio of teawaste in the formulation. It can be seen in Fig. 15 (a) that when fresh teawaste is used at lower ratios of teawaste in increasing the liquid to solid ratio results in an initial increase in the granules strength. At higher binder concentrations the UT granules have higher strength compared to the FT granules. The

1 difference between the strength of the FT granules and UT granules widens as the amount of 2 the binder is increased. When mass fraction of the teawaste is increased to 0.5 different trends 3 are observed; increasing the teawaste composition results in a reduction in the granules 4 strength for both UT and FT granules (see Fig. 15 (b)). One would expect the UT granules to have exhibit higher strength compared to FT granules since higher liquid to solid ratio was 5 6 used in their production, but the converse was observed. On increasing the mass teawaste 7 mass fraction further to 0.75 (see Fig. 15(c)) a different trends are observed for UT and FT; 8 for FT increasing the liquid to solid ratios results in an increase in the granule strength; the 9 opposite is observed for the later. Despite the higher levels of liquid to solid ratios used when 10 the teawaste mass fraction is increased in the formulation, there is no noticeable increase in 11 the strength of the granules. The granule strength decreases with increasing teawaste mass 12 fraction (see Fig. 15 (d)), this is in agreement with results from our previous work [35].

13 **[Fig. 15]**

14 4. Conclusions

15 The granule size distributions, granules strength, product yield are all affected by the relative 16 composition of teawaste; type of teawaste used and amount of the binder added during 17 granulation. Changing teawaste mass fraction changes the wettability of the binary mixture. 18 The amount of teawaste added to the formulation affects the amount of binder required for 19 effective granulation which in turn affects the final properties of the granules produced. 20 Washing the teawaste and drying the tea before granulation also have an influence of the 21 amount of binder required for granulation. Used tea requires more binder for effective 22 granulation compared to fresh tea. The strength of granules with high portion of teawaste (whether used or fresh) was shown to be lower than that of formulations with lower portion 23 24 of teawaste.

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Powder Type		Parameter		
	d ₁₀ [μm]	d ₅₀ [μm]	d ₉₀ [μm]	Span
Limestone	4.7 ± 0.1	32 ± 5	114 ± 5	3.49 ± 0.13
UT	197 ± 4	413 ± 31	1065 ± 22	2.00 ± 0.36
FT	143 ± 3	311 ± 10	681 ± 31	1.73 ± 0.03

2 Table 1: comparison of particle size distribution parameters of UT, FT and limestone powders.

Table 2: Comparison of BET surface area and specific pore volume of Teawaste (UT) and limestone.

Material	Specific Pore Volume	BET Surface Area	Reference (s)	
	x 10 ⁻⁴ [cm ³ /g]	[m ² /g]		
Teawaste (UT)	45.1	30.04	[18]	
Limestone	3.33 - 3.76	0.35 – 1.04	[19-20]	

2	Table 3: Summary	of experimenta	l variables used in the	different g	granulation exp	periments
-	rable 5. Summary	of experimenta	i variabies asea in the	uniterent	si anulation ca	Jermen

 Tea Type
 Ranges of Values of liquid/ solid ratios

 $\lambda = 0.25$ $\lambda = 0.50$ $\lambda = 0.75$

 Fresh Tea (FT)
 0.3 - 0.5 0.7 - 0.85 0.95 - 1.15

 Use Tea (UT)
 0.35 - 0.55 0.8 - 1.0 1.10 - 1.5





Fig. 1: Particle Size distributions of the different powders used in the granulation experiments.



Wave number (1/cm)

Fig. 2: comparison of FTIR spectrum of UF and FT. The characteristic peaks; 1- 3400 cm⁻¹; 2 - 2928 cm⁻¹; 3 - 2854
cm⁻¹; 4- 1737 cm⁻¹; 5-1640 cm⁻¹; 6 - 1297 cm⁻¹; 7 - 1060 cm⁻¹



2 Fig. 3: Comparison of the surfaces of tablets produced from powders with different compositions.



2

Fig. 4: Typical images showing contact angle measurements on surfaces with the different powder compositions (a) to

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Teawaste Mass Fraction (-)

2 Fig. 5: Effect of powder composition on contact angle.









Fig. 6: comparison of roughness of surfaces on which contact angles were measured (a) tablet surfaces (a) layer of
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(b)



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5 Fig. 8 Typical cumulative size distribution curves for batches of granules composed of teawaste (fresh tea) and 6 limestone (0.75 % TW (w/w), (b) Plot of mass mean granules size as a function of liquid to solid ratio.



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3 Fig. 11: Effect of teawaste mass fraction on the attrition strength of the granules.



5 Fig. 12: (a) Effect of tea type on the granule size distribution. (b) Effect of tea type on granule mass size.



2 Fig. 13: Effect of tea type on product yield for teawaste mass fraction of 0.75.



(a)







4 Fig. 15: Variation of granules strength with liquid to solid ratio for formulations of different teawaste ratios (a) $\lambda =$ 5 0.25 (b) $\lambda = 0.5$ and (c) $\lambda = 0.75$. (d) Effect of teawaste fraction on granule strength. Open symbols - Used Tea (UT) 6 and closed symbols- Fresh Tea (FT).