

An experimental study of the variability in the properties and quality of wet granules

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Abstract

For wet high-shear granulation, there can be a considerable variability in product quality in terms of the size, binder content, porosity, and appearance. Using the same equipment and feed material, it has been shown that such variability can be reduced by optimising the operating protocol. The associated narrowing of the range of mechanical properties for granules formed using an optimised procedure is exemplified by measurements of a number of parameters such as the coefficient of restitution.

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1. Introduction

Granulation has been widely used in the chemical, agricultural, pharmaceutical, foodstuff and mineral industries to convert fine powder into larger entities known as granules. In high-shear granulation, this is achieved by agitating fine powder and liquid binder in a mechanical mixer. The size distribution, porosity, strength, binder distribution and morphology are some of the important properties that represent granule quality. For example, oversized granules and fines commonly have to be separated in order to meet a target product performance specification. The separation process and subsequent recycling involve a significant on-cost and may impair the final product properties.

There is a considerable volume of literature concerned with the properties of granules, especially size distribution [1–7]. However, much of the reported work has focused upon investigating granulation mechanisms under specific operating conditions, rather than attempting to improve the product quality in terms of granule variability. Thus, it is well understood that there is a significant scatter of the binder content in granules of different sizes from the same batch [4–6,8]. Generally, it has been found that there is a

greater liquid/solid ratio in the larger granules compared with the smaller granules throughout a process.

The evolution in the granule porosity during granulation has also been widely investigated. From earlier studies [1,2] to those carried out more recently [3,4,6,7], it has been reported that the porosity initially decreases rapidly and then asymptotically tends to a stable equilibrium value during a granulation process. However, these studies were concerned primarily with the measurement of porosity as a means for understanding granule consolidation, rather than the extent of porosity variation and how to control this variation.

There are relatively few studies concerning granule appearance, more specifically shape and surface condition [5,7]. Knight et al. [5] observed that the sphericity of granules reduced with increasing impeller speed. They attributed this observation to the high extent of deformation and breakage due to impact of the granules with the impeller. Johansen and Schaefer [7] investigated the effect of binder viscosity and primary particle size on granule shape and found that a low viscosity and a smaller particle size seemed to facilitate an improvement in the granule sphericity. The explanation given was that a small particle size enhances granule strength to an extent that it is sufficient to resist deformation from impeller impact, and a low viscosity provides granules with sufficient deformability to become more rounded. Consequently, intermediate mechanical properties should ensure optimal sphericity, as

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extremes in primary particle size or viscosity will result in either non-malleable or highly deformable granules, respectively. Again, these investigations were limited to the influence of the feed material properties on granule appearance under constant operating protocols rather than examining the possibility of optimising these conditions.

In summary, the quality of a granular product is related to the properties of the feed materials, the equipment design and the operating conditions. Optimising the operating conditions is invariably the most cost-effective approach for reducing the variability in the properties. In the current paper, the properties of granules prepared under different operating conditions are compared for a particular granulator and particle/binder system. The emphasis is upon demonstrating the potential of the approach rather than attempting to provide generic optimisation principles for mixer granulators. The work is valuable for model as well as commercial systems. For example, the control of granule geometry is crucially important in the study of the mechanical behaviour of granules, in terms of deformation, coefficient of restitution [9] and dynamic strength. High sphericity greatly facilitates data analysis and is required to minimise granule rotation and oblique restitution following impact.

2. Experimental

2.1. Materials and equipment

2.1.1. Materials

Four different grades of calcium carbonate powder with a range of mean particle sizes were used as the dry powder feed material. They were produced from white marble by comminution and classification (Omya, France). The grades are termed Durcal 5, Durcal 15, Durcal 40 and Durcal 65, and the particle size distributions were measured using a laser light scattering instrument (Sympatec). Characteristic values of the particle sizes of the solid powder are presented in Table 1. The true density of the solid particles is approximately 2750 kg/m^3 . The span is calculated as the difference between the diameters at the 90th and 10th percentiles relative to the median diameter, $D(v; 0.5)$. The true solid density is taken from the literature [7]. Polyethylene glycol (PEG 400) was used as the liquid binder. It behaves as a Newtonian fluid and has a viscosity of 134 mPa s and the density, ρ_b , is 1127 kgm^{-3} at 25°C . The

Table 1
Characteristic value of size distributions of the calcium carbonate powders

Calcium carbonate grade	Characteristics of volume-based size distribution, μm			Span
	D10	D50	D90	
Durcal 5	2.8	6	23	3.36
Durcal 15	5.9	15	52.7	3.25
Durcal 40	7.8	23	86	3.4
Durcal 65	10.2	35	103.3	2.66

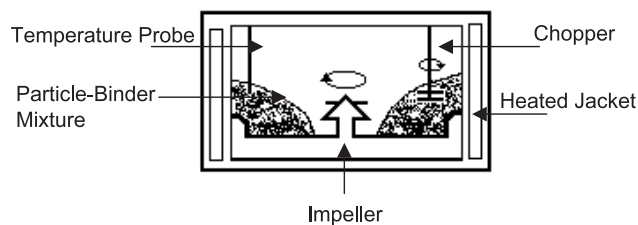


Fig. 1. A schematic diagram of the Zanchetta Roto Junior high-shear mixer.

viscosity was measured using a Contraves Rheomat 115 viscometer.

2.1.2. Equipment

Granulation was performed in a Zanchetta Roto Junior granulator and also a food processor with a modified impeller designed to have a similar geometry to the Roto Junior granulator. Granules produced for assessment of the size distribution, binder content and porosity were manufactured in the Roto Junior granulator, which has a nominal capacity of 10 l (see Fig. 1). There are two agitators in this mixer: one is a three-bladed impeller that is vertically mounted on a central axis on the base of the bowl, and the other is a lid-mounted chopper that is offset from the centre of the granulator. The chopper is smaller than the impeller (45 and 265 mm diameter, respectively). The impeller speed can be adjusted in the range of 100 – 800 rpm , and the chopper up to a speed of 1400 rpm . All experimental results presented in this paper were obtained from granules manufactured in the Roto Junior granulator, except for the study of appearance. The selection of the smaller scale mixer (food processor) for the appearance studies was based on time and material efficiency considerations. The food processor has a nominal capacity of 2 l , allowing larger numbers of experiments to be conducted using fewer materials and less time. It was found that there was a reasonable similarity in the pattern of the variability in the properties of granules made with the two granulators, allowing a qualitative comparison between the results.

2.2. Granulation

Granulation was conducted using a *normal* or *non-optimised* operating protocol and also three *optimised* protocols. The non-optimised protocol was based upon constant operating conditions: impeller speed of 300 rpm and chopper speed of 1400 rpm . The optimised protocols utilised modified operating conditions and techniques that cannot be described in detail here for proprietary reasons. All the results presented are for the optimised protocol that produced the highest granule quality of the three examined, except in the case of the binder content measurements for which data from the three different optimised protocols (termed optimised 1, optimised 2 and optimised 3) are described.

The following procedure was carried out in a typical experiment:

- (i) *Dry powder addition*: 3 kg of dry powder was used in the Roto Junior granulator and 250 g in the modified food processor. In all cases except for the appearance studies Durcal 40 was used.
- (ii) *Binder addition*: a quantity of the binder (PEG 400), depending on the pre-defined solid–binder ratio, was poured on to the powder bed directly before the impeller was started in all cases. The binder ratio, S , as defined by the mass ratio of binder to solid particles, was maintained at 0.15, except for the cases specified.
- (iii) *Granulation initiation*: after completing the powder and binder addition, the granulation commenced immediately as the impeller was started. The impeller running time was equal to the granulation time, and was set to 35 min, except for the cases specified.
- (iv) *Sampling*: for the purpose of assessing the final product in terms of, for example, the size distribution and the scatter in the binder content, sample granules were collected by scooping out a small quantity (30–50 g) from random positions in the stationary bed after mixing for 35 min. For the cases involving granules of the same size but prepared with different granulation times, the samples were collected using a sieving procedure. This was achieved by terminating the granulation at a recorded time and then sieving the whole batch of material to the required size. Removing granules with a specific size will change the size distribution of those remaining and thus only one sample was taken from each batch.

2.3. Granule properties and the measurement

2.3.1. Granule size and distribution

The granule size distributions were measured using a Retsch Camsizer, which is based on optical image analysis of the projected area. A narrow distribution without bimodality based on this measure is often associated with a product of high quality.

2.3.2. Extent of binder scatter

The compositional quality of the granules was assessed through examination of the extent of the scatter in the binder composition. For individual granules in a specific size class (4.35–4.75 mm), it is presented in terms of the standard deviation, which is based on measurements of 20 individual granules. The binder content of a single granule was determined from the loss in weight after heating for 2 h at 600 °C. This method assumes that the binder may be removed completely at the elevated temperature without causing a reduction in the mass of calcium carbonate [4]. To determine the binder content of an individual granule, it is required to measure the mass of individual wet granules and mass of the granule residue, i.e., solid particles, after

burning out the binder. The mass of individual granules was measured using an analytical balance: a GR-202, supplied by A&D, Japan, which has an accuracy of ± 0.1 mg. In order to minimise the error in mass of the dry ash caused by the adsorption of water from air, the residue of the granule (ash) was placed in a desiccator and weighed as quickly as possible.

2.3.3. Granule porosity

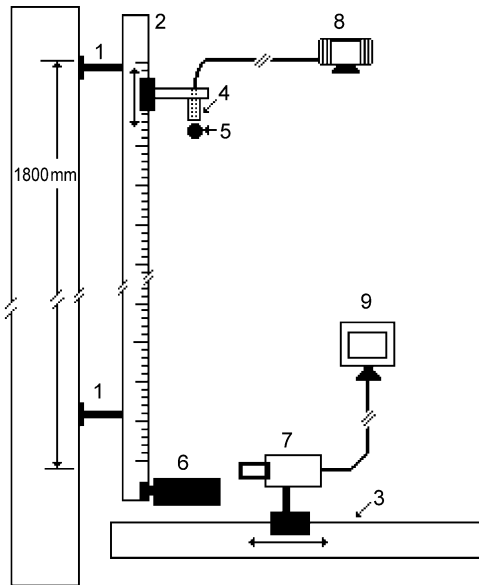
Granule quality was also assessed by the extent of scatter in the porosity. The average porosity (pore volume fraction) of a group of granules, ϕ_p , was determined from the measured apparent density of a collection of granules, ρ_a , and the true density of the granules, ρ_t , using the following equation:

$$\phi_p = 1 - \frac{\rho_a}{\rho_t} \quad (1)$$

The true density of the granules was determined from the measured binder mass fraction, ϕ_1 , the solid mass fraction, ϕ_s , the density of the liquid binder, ρ_l , and the solid particle density, ρ_s , using the following equation:

$$\rho_t = \frac{\rho_l \rho_s}{\rho_l \phi_s + \rho_s \phi_1} \quad (2)$$

The apparent granular density was measured by using the liquid displacement technique, which is similar to the method described by Iveson et al. [3]. The liquid used in this work was ‘Evolve’ CH15, a formulation of highly refined non-aromatic hydrocarbons (Chlor-Chemicals, UK). The surface tension, viscosity and density of the liquid are 17.6 mN/m, 1.05 mPa s and 0.747 g/ml at room temperature, respectively. Twenty granules were weighed and immersed in a burette filled with the liquid, which had a capacity of 20 ± 0.03 ml. The upper and lower limits on the capacity are important as they provide an estimate of the precision of the granule volume of approximately 0.5%. The apparent density of the granules was calculated from the volume of liquid displaced. The technique assumes that the liquid does not penetrate into the granule pores. This assumption was confirmed by a simple experiment involving the addition of a small amount of red colorant to the liquid. The granules were then removed and cut in half and it was observed that the liquid did not penetrate any of the granules. There was also no interaction between the Evolve CH15 and the PEG 400. The measurement procedure initially involved adding 20 granules to the burette that contained 20 ml of the liquid. The immersion of the granules caused an increase in the level of the liquid (~ 1 ml). The displaced volume of liquid was collected in a container that was weighed to a precision of ± 0.1 mg. The volume of the collected liquid was calculated from the mass of the liquid and its density. The extent of the scatter in the porosity for individual granules in a specific



1-Anti-vibration mounts, 2-Vertical optical bench, 3- Horizontal optical bench, 4-Nozzle, 5- Granule, 6-Target, 7-High-speed camera, 8-Vacuum pump, 9-PC.

Fig. 2. Schematic diagram of the free fall equipment.

size class (4.0–4.35 mm) is presented in terms of the standard deviation, which is based on measurements of 10 groups each containing 20 individual granules. This technique is not suitable for the measurement of a single granule. However, the standard deviation in individual granules can be determined from the group standard deviation under certain conditions. This can be achieved by assuming that the granule system is well mixed and that the number of individual granules in each group is sufficiently large to have the same standard deviation. Thus, the standard deviation on an individual basis, σ_i , can be determined using the following relationship:

$$\sigma_i = \sqrt{m} \cdot \sigma_n \quad (3)$$

where σ_n is the standard deviation on a group basis, n is number of individual granules in each group and m is the number of groups measured.

2.3.4. Granule shape

The roundness of a product granule, Ω , was calculated using the following equation by measuring the largest and smallest diameter, D_{\max} and D_{\min} , respectively. [10]:

$$\Omega = 1 - 2 \times \frac{D_{\max} - D_{\min}}{D_{\max} + D_{\min}} \quad (4)$$

A total of 20 individual granules were measured and a mean roundness was calculated.

2.3.5. Measurement of the restitution coefficient

The coefficient of restitution was measured in the current work as the ratio of the final rebound to initial impact speeds of a granule impacting onto a massive rigid target. This

parameter can be used to compare the mechanical properties of granules produced under different conditions (optimised and non-optimised). It was measured by releasing individual granules from a specific height and allowing them to impact normally onto an effectively semi-infinite glass target (see Fig. 2). Care was taken to record only impact events that occurred without rotation during impact and rebound, and only when granules rebounded normal to the target. The impact and rebound velocities were recorded by using a high-speed (8000 frame/s) CCD camera (Redlake, USA), which allows the velocity measurements to be made with an accuracy of approximately 5%. At each height, more than 20 individual granules were tested and only data from impacts in which there was no visible rotation and with normal rebound are presented.

3. Results and discussion

3.1. Size distribution

In high-shear granulation, the size distribution of the final product depends on the properties of the feed materials and the operating conditions of the particular granulator as discussed previously. Generally, it has been found that rather wide and bimodal distributions are produced by this process [4–7]. It has been proposed that consolidation is likely to be the dominant mechanism during granulation after the liquid binder has been completely distributed in the powder system [4,5]. This suggests that the pattern of the granule size distribution in the initial stage is probably maintained throughout the process. Fig. 3 shows a comparison of the size distributions for granules produced under the normal and optimised (optimised 3) operating protocols after mixing for 35 min. The span of the distributions for the non-optimised and optimised operating protocols are

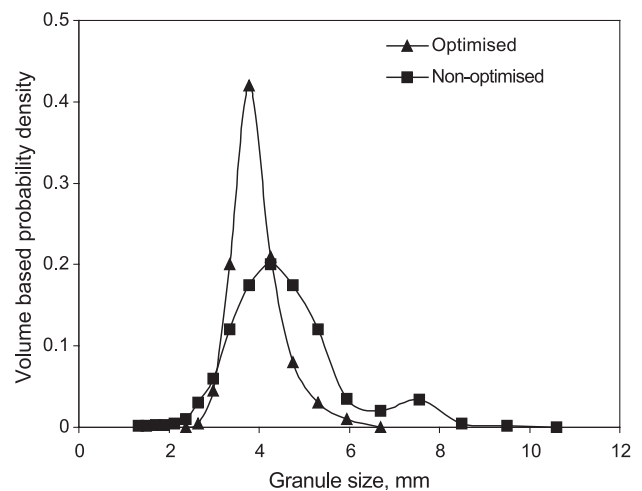


Fig. 3. Comparison of the size distribution of granules produced using the optimised and the non-optimised operating conditions. Durcal 40 is the powder material, PEG 400 is the binder and the binder ratio is 0.15.

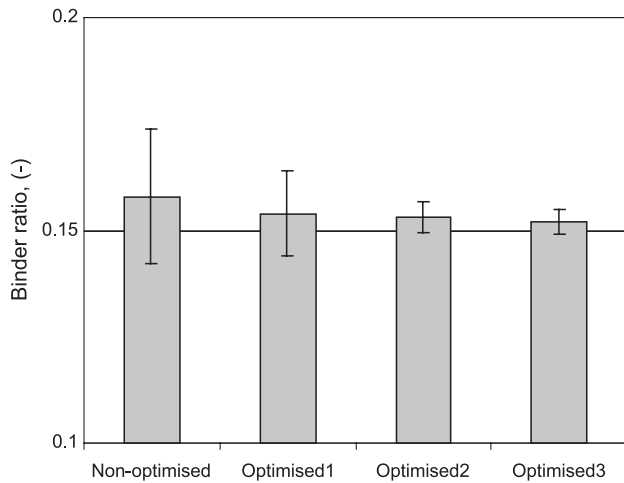


Fig. 4. Comparison of the standard deviation in the binder content for individual granules (size 4.35–4.75 mm) produced by the different operating conditions. Durcal 40 is the powder material, PEG 400 is the binder and the binder ratio is 0.15.

0.63 and 0.39, respectively. These results show that the size distribution of the final product can be narrowed significantly by optimising the operating conditions, at least for the current system.

3.2. Binder distribution

As mentioned previously, it has been reported that there invariably is a significant variation in the binder composition for granules of different sizes depending on the method of binder addition and the intensity of the mechanical agitation [4–6,8]. Furthermore, the current work shows that there is considerable scatter in the binder composition on an individual granule basis within the same size class. Fig. 4 shows a comparison of the binder content (binder ratio) and standard deviations in the binder contents for granules from the same size class (4.35–4.75 mm) produced using the different granulation protocols. It demonstrates that the extent of the binder variability on an individual granule basis can be reduced significantly using optimised granulation protocols. In this case, results from several alternative optimised protocols are presented, showing that (a) an improved protocol may not always represent a global optimum as might reasonably be expected and (b) optimisation is not necessarily path dependent since similar performance may be achieved using different protocols. In summary, the results clearly exemplify the potential value of examining a range of operating conditions in industrial sectors where a small variation in the binder content of the final product is required.

3.3. Porosity

It has been mentioned earlier that the granule porosity reduces quickly to a stable value during the initial stages

of granulation. Moreover, it has been found that the consolidation rate is strongly related to the binder content in the granules for a given set of operating conditions; the consolidation rate increases with increasing binder content [3]. Accordingly, it is reasonable to assume that the variation in the porosity is related directly to that of the binder content. For the optimised and non-optimised protocols, Fig. 5 shows a comparison of the extent of the variation in the porosity for individual granules as calculated using Eq. (3). It can be seen that the scatter decreases with increasing granulation time for both protocols. However, the extent of the variation produced by the optimised protocol is significantly less than that for the non-optimised procedure.

3.4. Appearance

The growth mechanism is probably the major factor that initially controls the shape of granules. Those formed by a layering mechanism are likely to be spherical [5,7], while those formed by a coalescence mechanism are likely to be initially ‘dumbbell’ or more likely ‘pear-shaped’. When granules are sufficiently deformable, they are easily rounded to a spherical shape. Thus, the final geometry of a granule is determined by two factors: the growth mechanism and the deformability of the granules. Increased granule deformability can be achieved by increasing the phase volume of the binder [2,3,11]. Additionally, an extension of the mixing time at an adequate impeller speed can also compensate for defects caused by a low binder content. The influence of granulation mechanisms on the final granule shape is difficult to predict. However, the current work has shown that the shape can be improved by modifying the operating conditions as discussed below.

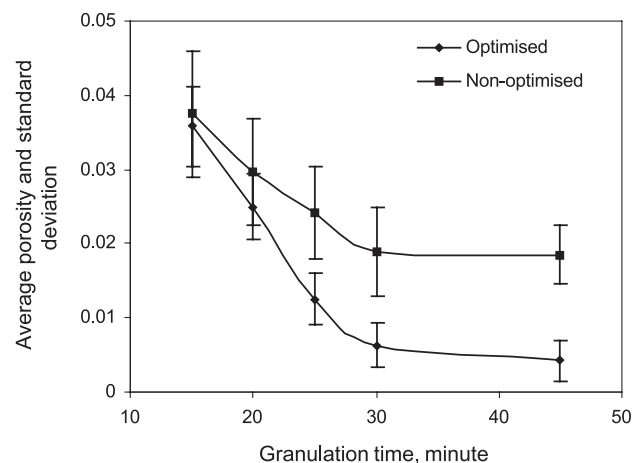


Fig. 5. Comparison of the standard deviation in the porosity for granules (size 4.35–4.75 mm) produced by the optimised and the non-optimised operating conditions. Durcal 40 is the powder material, PEG 400 is the binder and the binder ratio is 0.15.

Fig. 6 shows the appearance of representative granules produced under different operating conditions and for a range of primary particle sizes and binder contents. The improvement in the sphericity arising from optimising the operating conditions is evident from Fig. 6a. It was found that the average roundness, Ω , of 20 granules was approximately 0.97 for granules from the optimised protocol (Fig. 6a(i)), while it was 0.89 for granules from the non-optimised protocol (Fig. 6a(ii)). The evolution in the granule appearance from a dry, powdery rough surface to a wet and smooth surface with increasing granulation time is exemplified in Fig. 6b. This arises from the compaction of the granules during the granulation process, which causes the binder to be transported to their surfaces.

Consequently, the granulation time is an essential factor to be considered when a specific granule surface finish is required.

Fig. 6c and d shows the influence on the appearance of granules that were produced from different primary particles and binder ratios. There is clearly some variation in the appearance as a result of varying the primary particle size in the range 6–35 μm and the binder ratio in the range 0.115–0.19. The surfaces of the granules appear to be smoother as the primary particle size is reduced (Fig. 6c). It is probable that granules with smaller primary particles are less readily damaged in the high-shear environment due to their greater dynamic strength compared with those formed from larger primary particle sizes. As

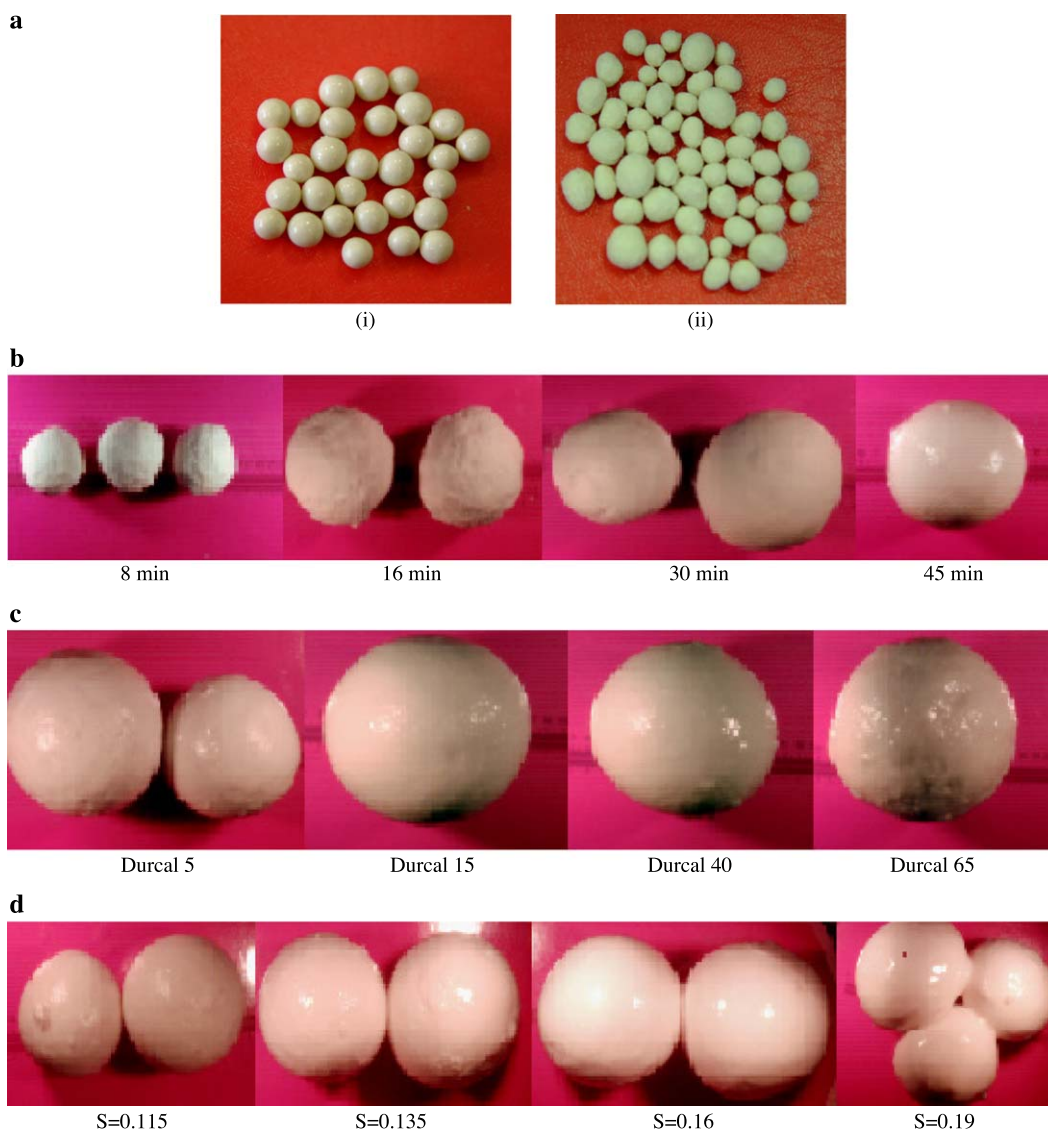


Fig. 6. (a) The typical appearance of group sample granules (mean size about 5.0 mm) made using an optimised (i) and a non-optimised protocol (ii). Durcal 40 is the powder material, PEG 400 is the binder and the binder ratio is 0.15. (b) The influence of granulation time on the appearance of granules (size range 3.0–6.0 mm). Durcal 40 is the powder material, PEG 400 is the binder and the binder ratio is 0.15. (c) The final appearance of the granules (size range 5.0–6.0 mm) made from different primary particle sizes. Durcal 40 is the powder material, PEG 400 is the binder and the binder ratio is 0.15. (d) The final appearance of the granules (size range 5.0–6.0 mm) made from different binder ratios. Durcal 40 is the powder material, PEG 400 is the binder and the binder ratio is 0.15.

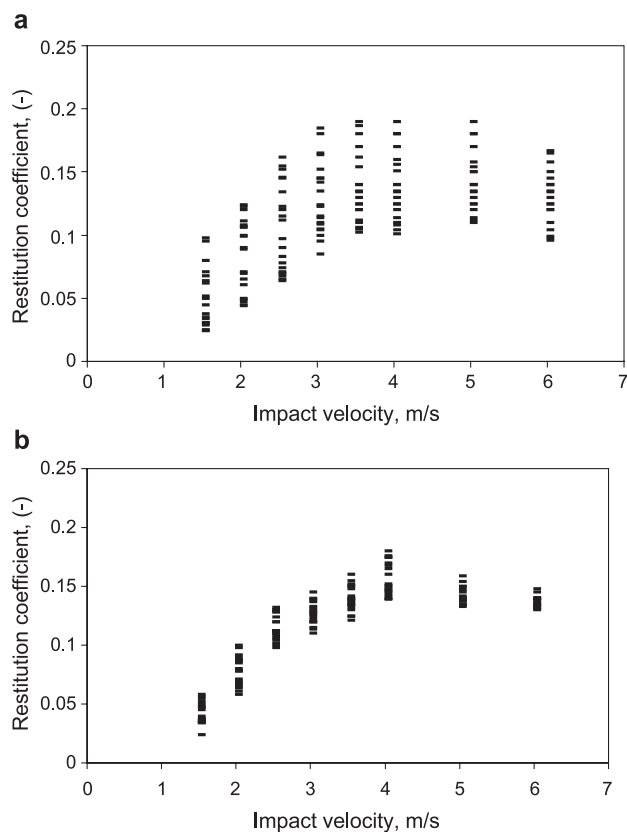


Fig. 7. (a) The coefficient of restitution as a function of the impact velocity for granules produced using the non-optimised operating protocol. (b) The coefficient of restitution as a function of the impact velocity for granules produced using an optimised operating protocol.

would be expected, increasing the binder ratio increases the wetness of the granule surfaces (Fig. 6d). From these images, it can be seen also that the granules with the greatest binder ratio have the smallest sphericity due to their greater deformability. However, the sphericity is also rather less for the granules with the smallest binder ratio due to their restricted deformability as discussed previously. While these effects relate to the feed materials and composition, there is clearly a potential for optimising the operating conditions irrespective of the feed.

3.5. Restitution coefficient

In order to compare the mechanical properties of granules produced using the normal and optimised operating conditions, the coefficient of restitution for granules within the same size class (4.35–4.75 mm) taken from each whole batch was measured. The coefficient of restitution was believed to be one of most sensitive parameters to the granule properties in terms of binder content, porosity, shape, and surface condition [9]. Consequently, the extent of the scatter in this quantity will reflect the uniformity of these properties for the granules. Fig. 7 shows the extent of the scatter in this coefficient as a function of the impact speed for granules made from the

two protocols. There is a considerably larger scatter for the granules produced using the normal compared to the optimised protocol. It is evident that there is a more conclusive relationship between the coefficient and the impact speed for the granules produced using the optimised granulation protocol. However, a residual variation is still observable after reducing the extent of the binder and porosity scatter through the use of an optimised protocol. It is believed that surface quality of the granules (roughness and wetness) plays a significant role in their rebound behaviour [9].

4. Conclusions

It is inevitable that there will be some scatter in the properties of granular products (size distribution, binder content, porosity, shape, and surface finish) due to the complexity of the granulation environment and the growth mechanisms. The current work shows that it is possible to decrease markedly the extent of the variation by modifying the operating conditions. The main factor appears to be achieving tight controls on the composition and porosity since they have an enormous influence on the mechanical properties of granules. It is these properties that dictate the growth mechanisms and subsequent deformations/damage of granules during a granulation process.

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