

Review article

# Nucleation, growth and breakage phenomena in agitated wet granulation processes: a review

Simon M. Iveson<sup>a,\*</sup>, James D. Litster<sup>b</sup>, Karen Hapgood<sup>b</sup>, Bryan J. Ennis<sup>c</sup>

<sup>a</sup> Centre for Multiphase Processes, Department of Chemical Engineering, University of Newcastle, Callaghan NSW 2308, Australia

<sup>b</sup> Department of Chemical Engineering, University of Queensland, St. Lucia QLD 4072, Australia

<sup>c</sup> E & G Associates, 3603 Hoods Hill Rd, Nashville, TN 37215, USA

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## Abstract

Wet agglomeration processes have traditionally been considered an empirical art, with great difficulties in predicting and explaining observed behaviour. Industry has faced a range of problems including large recycle ratios, poor product quality control, surging and even the total failure of scale up from laboratory to full scale production. However, in recent years there has been a rapid advancement in our understanding of the fundamental processes that control granulation behaviour and product properties. This review critically evaluates the current understanding of the three key areas of wet granulation processes: wetting and nucleation, consolidation and growth, and breakage and attrition. Particular emphasis is placed on the fact that there now exist theoretical models which predict or explain the majority of experimentally observed behaviour. Provided that the correct material properties and operating parameters are known, it is now possible to make useful predictions about how a material will granulate. The challenge that now faces us is to transfer these theoretical developments into industrial practice. Standard, reliable methods need to be developed to measure the formulation properties that control granulation behaviour, such as contact angle and dynamic yield strength. There also needs to be a better understanding of the flow patterns, mixing behaviour and impact velocities in different types of granulation equipment. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Granulation, also known as agglomeration, pelletisation or balling, is the process of agglomerating particles together into larger, semi-permanent aggregates (granules) in which the original particles can still be distinguished [1]. In wet granulation processes, this is performed by spraying a liquid binder onto the particles as they are agitated in a tumbling drum, fluidised bed, high shear mixer or similar device. The liquid binds the particles together by a combi-

nation of capillary and viscous forces until more permanent bonds are formed by subsequent drying or sintering.<sup>1</sup>

Granulation is an example of *particle design*. The desired attributes of the product granules are controlled by a combination of formulation design (choosing the feed powder and liquid properties) and process design (choosing the type of granulator and the operating parameters). Some of the desired properties of granulated products

<sup>1</sup> Some granulation processes are arranged so that the predominant mechanism of particle growth is by coating successive layers of a melt, solution or slurry onto the surfaces of seed particles where it solidifies or crystallises to form an “onion skin” effect (common in spouted and fluidised beds). This review does not consider this form of granulation but is confined to the agglomeration of pre-existing particles by addition of a liquid binder. This review is also restricted to processes where granules are formed by agitation and so does not include extrusion or tableting processes.

\* Corresponding author. Tel.: +61-2-4921-5684; fax: +61-2-4960-1445.

E-mail address: cgsmi@cc.newcastle.edu.au (S.M. Iveson).

include: reduced dustiness which minimises losses, inhalation and explosion risks; improved flow and handling which facilitates controlled metering; increased bulk density; reduced pressure loss for fluid flow through a packed bed, which is useful in blast furnaces and leach heaps; controlled dissolution rates; and the co-mixing of particles which would otherwise segregate during handling. Granulated products often maintain a high proportion of the surface area of the original particles, which is useful in applications involving catalysts or requiring rapid dissolution.

Granulation finds application in a wide range of industries including mineral processing, agricultural products, detergents, pharmaceuticals, foodstuffs and specialty chemicals. In the chemical industry alone it has been estimated that 60% of products are manufactured as particulates and a further 20% use powders as ingredients. The annual value of these products is estimated at US\$1 trillion in the US alone [2]. Granulation is a key step in many of these industries. Improper granulation causes problems in down-stream processes such as caking, segregation and poor tableting performance.

Granulation has been a subject of research for almost 50 years. Some of the earliest pioneering work was performed by Newitt and Conway-Jones [3] and Capes and Danckwerts [4] using sand in drum granulators. Since then, a large volume of work has been published studying materials ranging from minerals to pharmaceuticals, granulated in equipment ranging from fluidised beds to high shear mixers. Over the years, a number of books and comprehensive review papers have been written to summarise the state of knowledge in this discipline (e.g. Refs. [5–13]) and it has been a lively topic of discussion at international conferences (e.g. Refs. [14]).

However, in spite of its widespread use, economic importance and almost 50 years of research, granulation has in practice remained more of an art than a science. Existing continuous industrial plants frequently operate with recycle ratios as high as 5:1 and suffer from cyclic behaviour, surging, erratic product quality and unplanned shutdowns [15]. There is no formal methodology for the design or operation of granulation circuits [16]. Engineers do not predict the granulation behaviour of new formulations from their fundamental properties. Neither has it been known how to vary a formulation in order to obtain a desired change in product properties. Expensive and extensive laboratory and pilot scale testing of all new materials is still undertaken [12]. This is a particular problem in industries where there are many and frequently changing formulations with widely varying properties (e.g. food, pharmaceuticals and agricultural chemicals). Regulations often require these new formulations to be registered before there is sufficient material available for laboratory and pilot scale granulation tests. Even when pilot scale testing does occur, there is still a significant failure rate during scale up to industrial production.

However, we are now close to being able to change this poor state of affairs. In the last decade, there have been significant advancements in our understanding of granulation. We now have a qualitative understanding of the effects of different variables on granulation behaviour, and our knowledge is advancing rapidly enough such that we should soon be able to make quantitative predictions based on a sound scientific understanding of the underlying phenomena. In particular, following the pioneering work of Ennis et al. [17,18], binder viscosity has been recognised as an important parameter in controlling granulation behaviour. There has also been a growing awareness of the importance of powder wetting and liquid distribution in controlling granule nucleation and subsequent growth behaviour (e.g. Refs. [19–23]). These recent advances in understanding, together with the fact that there have been no major reviews of this topic in the last 5 years, make it appropriate as we begin a new century to review the extent of our current knowledge and highlight the areas requiring further research.

This paper is based upon the view that there are fundamentally only three sets of rate processes which are important in determining wet granulation behaviour. These are: wetting and nucleation; consolidation and growth; and breakage and attrition [1,20,24,25]. Once these processes are sufficiently understood, then it will be possible to theoretically predict the effect of formulation properties, equipment type and operating conditions on granulation behaviour, provided that these can be adequately characterised.

We first give a brief background of the transition to this new view from the more traditional ways of describing granulation. Then the three main sections of this paper discuss in turn the wetting and nucleation, consolidation and growth, and attrition and breakage processes. The current state of understanding in each of these areas is critically reviewed. Deficiencies in understanding are highlighted with suggestions made for future research. The conclusions summarise the findings and major recommendations. This review does not cover equipment design and selection issues or population balance modelling of granulation systems. The interested reader should consult the reviews referred to above for further information on these topics.

## 2. The changing description of granulation processes

Granulation behaviour has traditionally been described in terms of a number of different mechanisms, some of which are shown in Fig. 1a (e.g. Ref. [26]). However, such a picture of many competing mechanisms is daunting. Quantitative prediction of granule attributes is difficult. In addition, the demarcation between these mechanisms arbitrarily depends on the cut off size between granule and non-granular material, which depends on the measurer's interests and ability to count small particles. These mecha-

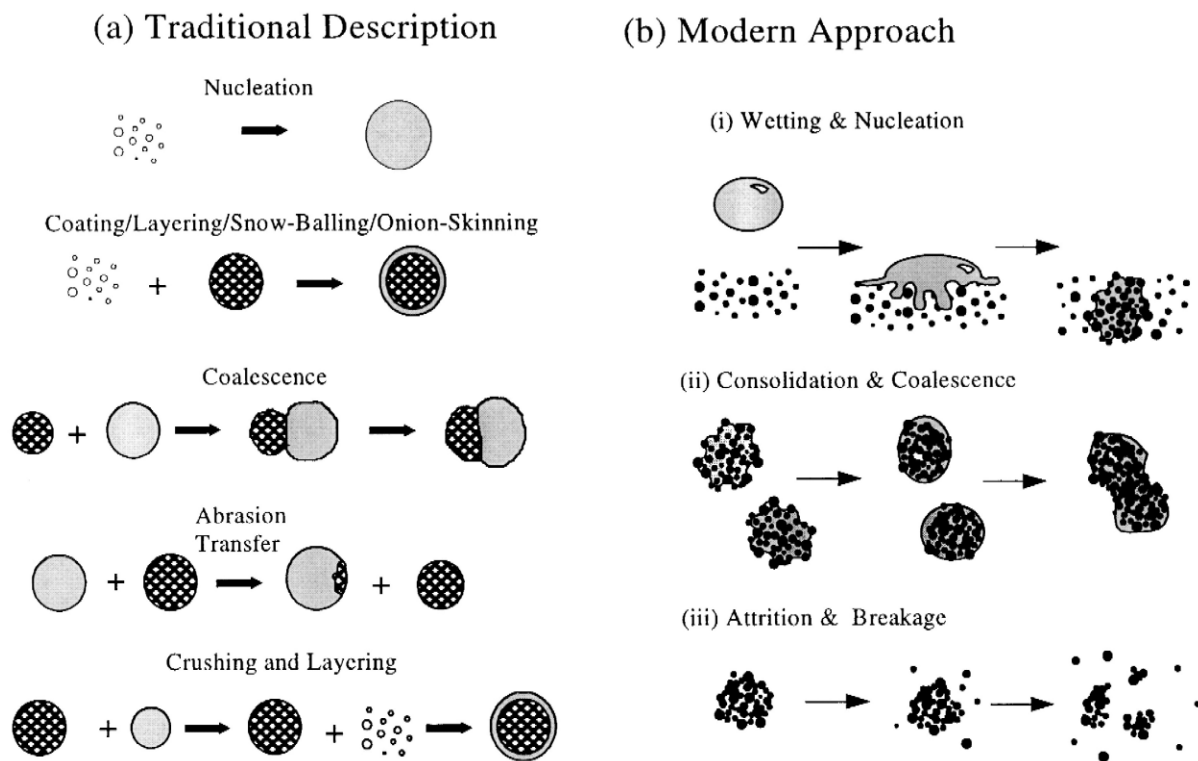


Fig. 1. Schematic of granulation processes (a) Traditional view (after Sastry and Fuerstenau [26]); (b) Modern approach [1].

nisms could all be considered as cases of coalescence and/or breakage. It is simply the size of the coalescing particles and the availability of surface liquid which varies from case to case.

Hence, it is becoming more common to view granulation as a combination of only three sets of rate processes (Fig. 1b) (e.g. Refs. [1,20,24,25]):

1. *Wetting and nucleation*, where the liquid binder is brought into contact with a dry powder bed, and is distributed through the bed to give a distribution of nuclei granules;
2. *Consolidation and growth*, where collisions between two granules, granules and feed powder, or a granule and the equipment lead to granule compaction and growth; and
3. *Attrition and breakage*, where wet or dried granules break due to impact, wear or compaction in the granulator or during subsequent product handling.

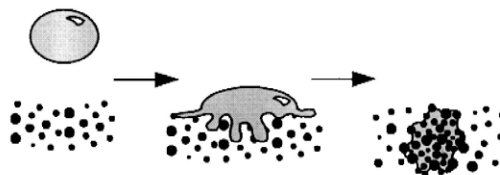
It is this latter approach which is adopted in this review. Section 3 discusses wetting and nucleation, Section 4 discusses consolidation and growth and Section 5 discusses breakage and attrition.

### 3. Wetting and nucleation

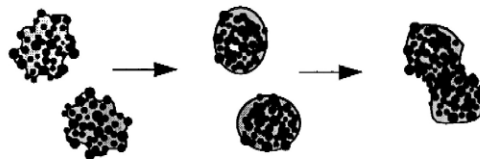
Wetting and nucleation is the process of bringing liquid binder into contact with dry powder and attempting to distribute this liquid evenly throughout the powder. It is

### (b) Modern Approach

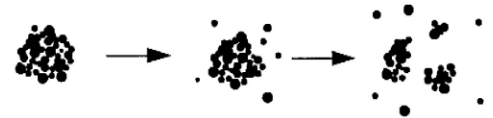
#### (i) Wetting & Nucleation



#### (ii) Consolidation & Coalescence



#### (iii) Attrition & Breakage



regarded as an important stage in granulation processes (e.g. Ref. [1,20]) but is rarely identified and separated from other effects such as coalescence and attrition. Many studies have focused on granule growth but have given no details of the binder addition method or the extent of binder distribution. Consequently, our knowledge of the processes controlling nucleation is limited.

In this section on wet granulation nucleation and binder dispersion processes, we will focus on the *nucleation zone* (also called the *wetting zone* [27]). We define this as the area where the liquid binder and powder surface first come into contact and form the initial nuclei. The size distribution of these initial nuclei depends critically on the processes happening in the nucleation zone, although other processes in the rest of the granulator, such as mechanical mixing, may subsequently alter this distribution.

Two processes are important in the nucleation zone. Firstly, there is *nuclei formation*, which is a function of wetting thermodynamics and kinetics. Secondly, there is *binder dispersion*, or effective mixing of the powder and binder, which is a function of process variables. Choosing a poor combination of powder and binder (for example, a high contact angle) or using an inefficient binder dispersion method (for example, high liquid flow-rate, poor spray characteristics) both produce a product that is difficult to control and reproduce.

#### 3.1. Nucleation thermodynamics

Nucleation is the first step in granulation where the binder begins to wet the powder and form initial agglomer-

ates. Whether or not wetting is energetically favourable is driven by thermodynamics. Studies of wetting thermodynamics have focused on two aspects: the contact angle between the solid and the binder, and the spreading coefficients of the liquid phase over the solid phase and vice versa.

The solid–liquid contact angle of the system directly affects the characteristics of the granulated product. For instance, Aulton and Banks [28] mixed increasing proportions of a hydrophobic powder (salicylic acid with a contact angle of  $\theta = 103^\circ$ ) with a hydrophilic powder (lactose with contact angle  $\theta = 30^\circ$ ) in a fluidised bed granulator. As the contact angle of the powder mixture increased (i.e. wettability of the powder mixture decreased), the mean granule size decreased. Jaiyeoba and Spring [29] performed similar experiments using a ternary mix of powders. However, the size distribution of the third component also changed and may be at least partly responsible for the observed changes in granule size and properties. Gluba et al. [30] granulated several different powders with varying contact angle in a drum granulator. They defined the “sucking ability” of a powder as the volume of water sucked in by a powder sample of given size, which is related to the contact angle. They applied the theory of moments and compensated for the slightly different initial particle size distributions. Mean granule size increased while the variance and asymmetry decreased as the sucking ability (or wettability) of the powder improved.

Wetting and nucleation can also be described using surface free energies. The spreading coefficient  $\lambda$  is a measure of the tendency of a liquid and solid combination to spread over each other and is related to the works of adhesion and cohesion:

$$\text{Work of cohesion for a solid: } W_{CS} = 2\gamma_{SV} \quad (3-1)$$

$$\text{Work of cohesion for a liquid: } W_{CL} = 2\gamma_{LV} \quad (3-2)$$

$$\text{Work of adhesion for an interface: } W_A = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} \quad (3-3a)$$

$$W_A = \gamma_{LV}(\cos\theta + 1) \quad (3-3b)$$

where  $\gamma$  is the surface free energy,  $\theta$  is the solid–liquid contact angle and the subscripts “L”, “S” and “V” denote liquid, solid and vapour phase respectively. The work of cohesion is the work required to separate a unit cross-sectional area of a material from itself. The work of adhesion is the work required to separate a unit area of an interface. Eq. (3-3b) is derived by substitution of the Young–Dupre equation,  $\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos\theta$ . However, this is only valid for  $\theta > 0^\circ$ .

The spreading coefficient  $\lambda$  is the difference between the works of adhesion and cohesion. Spreading coefficients indicate whether spreading is thermodynamically favourable. There are three possibilities in spreading between a solid and a liquid: the liquid may spread over the

solid ( $\lambda_{LS}$ ) and create a surface film; or the solid may spread or adhere to the liquid ( $\lambda_{SL}$ ) but no film formation occurs. The third possibility is that both the liquid and solid have high works of cohesion, and the solid–liquid interfacial area will be minimised. Spreading coefficients for each phase can be calculated using the following relationships [31]:

$$\lambda_{LS} = W_A - W_{CL} \quad (3-4a)$$

$$\lambda_{SL} = W_A - W_{CS} \quad (3-5)$$

Spreading will occur spontaneously when the spreading coefficient is positive. The works of adhesion and cohesion can be calculated from measurements of the fractional polarity and surface free energy of the system [32,33]. Rowe [32] hypothesised that two modes of nuclei formation exist depending on the value of the spreading coefficients. When  $\lambda_{LS}$  is positive, the binder will spread and form a film over the powder surface and liquid bridges will form between most contacting particles, creating a strong, dense granule. When  $\lambda_{SL}$  is positive, bonds will form only where the liquid and powder initially touch because the liquid will not spread or form a film. Granules formed in this case have fewer bonds and consequently would be weaker and more porous.

Separate studies by Krycer and Pope [34] and Zajic and Buckton [33] confirm that differences in granule properties can be correlated with the spreading coefficient. Krycer and Pope [34] did not calculate the spreading coefficient directly from measurements of the fractional polarity. Instead they used Eqs. (3-2) and (3-3b) to give the “work of spreading”:

$$\lambda_{LS}^* = \lambda_{LV}(\cos\theta - 1) \quad (3-4b)$$

This is equivalent to  $\lambda_{LS}$  for contact angles greater than zero, but has a maximum value of zero and so cannot predict the positive spreading coefficients which occur when  $\theta = 0$ . The best spreading occurs when the work of spreading is closest to zero. Paracetamol granulated with 4 wt.% HPMC had the least friable granules and a work of spreading closest to zero. Electronmicrographs of the HPMC granules showed binder films on the particle surfaces and many liquid bridges at the particle contacts. In contrast, the granules bound with 4 wt.% sucrose solution had a more negative coefficient of spreading, were the most friable, and electronmicrographs revealed no film formation and few interparticle bonds. Granulation in each case was successful, but the nuclei morphologies and final properties varied considerably [34].

### 3.2. Nuclei formation kinetics

In practice, the liquid may not have enough time to reach its equilibrium state, due to interference from the mixing process occurring simultaneously in the granulator. The nuclei size distribution is a function of both wetting

kinetics and thermodynamics. As the wetting process proceeds, the fluid penetrates into the pores of the powder surface, forms a nucleus and migrates outwards as the nucleus grows. The need to study nucleation kinetics has only recently been identified [19,25] and some work has begun in this area. The ‘destructive nucleation growth mechanism’ in high shear granulation developed by Vonk et al. [35] proposes multiple steps in nucleation including breakage and is discussed further in Section 5.1.1.

The relative sizes of the droplet to primary powder particles will influence the nucleation mechanism. Schaefer and Mathiesen [36] proposed two different nucleation mechanisms, depending on the relative size of the droplets to the particles (see Fig. 2). If the drop is large compared to the particles, nucleation will occur by *immersion* of the smaller particles into the larger drop. This produces nuclei with saturated pores. Nucleation with relatively small drops will occur by *distribution* of the drops on the surface of the particles, which will then start to coalesce. This will produce nuclei which may have air trapped inside. Although these mechanisms were proposed for melt agglomeration, they have been extended to cover wet granulation by Scott et al. [21].

Nuclei formation kinetics will depend on similar parameters regardless of the drop and particle size ratio. In the immersion case, once a wetting liquid binder contacts the powder, it penetrates into the capillary pores to form a highly saturated initial agglomerate. There are no models for the imbibition of drops into powders (Fig. 3a), but a theory does exist for penetration of a single drop into a porous surface [37]. This approach applies the Washburn equation where flow is driven by the capillary pressure and resisted by viscous dissipation. Two cases of drop penetration were considered, constant drop drainage area and receding drop drainage area. The theoretical penetration time,  $\tau$ , for the constant drawing area (CDA) case is given by [37]:

$$\tau_{\text{CDA}} = \frac{2V_o^2}{\pi^2 \varepsilon^2 r_d^4 R_{\text{pore}}} \frac{\mu}{\gamma_{\text{LV}} \cos \theta} \quad (3-6)$$

where  $V_o$  is the total drop volume,  $r_d$  is the radius of the drop footprint on the powder surface,  $\varepsilon$  is the surface porosity (which may differ from the bed porosity),  $\gamma_{\text{LV}}$  is

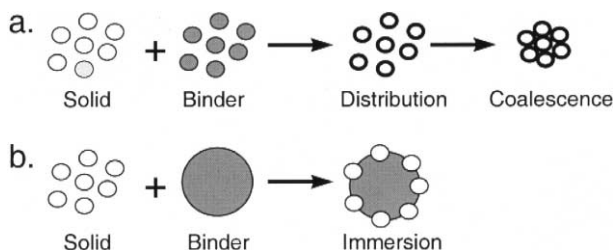


Fig. 2. The nucleation formation mechanism may depend of the relative sizes of the droplet to primary particle size. (a) Distribution mechanism. (b) Immersion mechanism (adapted from Ref. [36]).

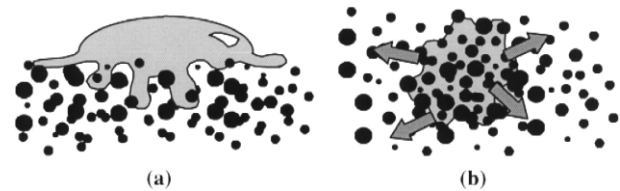


Fig. 3. Single drop nucleation. (a) Initial nuclei formation due to imbibition of the drop into the powder. (b) Liquid migration within the powder bed causing nuclei growth.

the liquid surface tension,  $\mu$  is the liquid viscosity,  $\theta$  is the solid–liquid contact angle and  $R_{\text{pore}}$  is the effective pore radius based on cylindrical pores. Preliminary validation of this model on glass powder is promising [38].

Thus, the penetration time depends on both wetting thermodynamics (represented by the adhesion tension  $\gamma_{\text{LV}} \cos \theta$ ) and the wetting kinetics (strongly affected by the liquid viscosity and effective pore size of the powder bed). The retarding effect of viscosity on nucleation kinetics has been identified only recently [39] although general studies of viscous effects in granulation report that viscous binders are more difficult to distribute and may cause a change in nucleation mechanism [18,40–42].

Once the liquid has penetrated the bed surface, the rate of migration within the bed and the final nucleus size will depend on similar parameters (see Fig. 3b). Schaafsma et al. [43] have modelled in detail the layering growth of the initial nuclei due to saturation differences as a function of time. This mechanism is similar to that proposed by Butensky and Hyman [24]. Flow is induced by the capillary pressure difference between the fully saturated pores inside the nuclei and the unsaturated pores at the outer surface. The predicted nuclei size correlated well with nuclei grown from a single drop on a small dish of powder.

This approach assumes that the initial drop penetration stage (Fig. 3a) is almost instantaneous with liquid migration below the bed surface (Fig. 3b) being the rate limiting step. This assumption is valid for non-viscous, wetting liquids such as water on lactose formulations or paper (e.g. Ref. [44]). However, the initial drop penetration time varies considerably depending on the powder and binder used, and is particularly slow for viscous binders [38]. A combined drop penetration and nuclei growth model would provide a more complete picture of drop penetration kinetics and nuclei morphology.

There may be some conditions under which the forces in the granulator are sufficient to destroy the nuclei. The deformation and destruction of nuclei due to shear forces have been studied using a modified couette shear device [25,45] and this work is discussed further in Section 5.1.2.

### 3.3. Binder dispersion

The degree of binder dispersion indicates the quality of the mixing between the powder and the binder fluid, and is

strongly affected by the binder delivery method. In the non-inertial regime proposed by Ennis et al. [18] (see Section 4.3.1.1) the rate of nuclei growth is totally dependent on the presence and distribution of binder. Good binder dispersion infers uniform wetting and controlled nucleation. Mort and Tardos [20] hypothesised that the degree of dispersion of the binder is reflected in the product size distribution. If all particles contain an equal amount of binder, their physical properties should be the same and produce a narrow size distribution. If the binder is unevenly distributed, some nuclei will be more saturated than others and their growth will be preferential. This has been confirmed by other workers [46,47] in experimental studies where the proportion of “lumps”, defined as granules larger than 2 mm, was used as a measure of binder dispersion. All studies were performed in mixer granulators, and several different methods of adding the binder solutions were used. Atomisation together with a high impeller speed produced the best binder distribution. The “concentration” of lumps was highest during the initial liquid addition phase (i.e. the lumps were formed during nucleation, not during the growth phase).

Irrespective of the method of binder delivery, an initially bimodal nuclei size distribution is inevitable, as instantaneous uniform liquid distribution is physically impossible [24,48]. Knight et al. [19] demonstrated in a high shear mixer that the bimodal granule distribution can persist for some time and that the largest granules were the most saturated (see Fig. 4).

### 3.3.1. Binder delivery

There are three main ways to add the binder solution in wet granulation: pouring, spraying and melting. The solu-

tion delivery method alters the final granule properties. There are three operating variables in wet binder delivery: drop size distribution, binder flow-rate and the size of the spray zone.

Systematic investigation of how the nuclei and granule size distributions change in response to changes in the solution delivery method have been limited, but progress is being made [19,21]. Knight et al. [19] added PEG1500 to calcium carbonate powder in a high shear mixer in three ways: pouring, spraying and melting. Other conditions, including mixing and temperature, were kept constant. The method of binder addition affected both the initial nuclei size distribution and the subsequent granule growth behaviour. Similar experiments using the same materials and equipment by Scott et al. [21] showed that granules formed by pouring began with a bimodal size distribution which then became uni-modal as granulation proceeded. The granules formed were also larger, less porous, and had faster growth kinetics. The constituent feed particle size distribution in each granule size fraction was analysed by dissolving the binder. Many of the “small granules” consisted of large ungranulated primary feed particles, while the large granules were predominantly agglomerates of small primary feed particles.

When the binder is poured into the granulator, the initial liquid distribution is poor [46] and the fraction of coarse granules increases [19] compared to an atomised binder. Adding the binder by pouring creates local patches of high moisture content and preferential growth. Similarly, Schaefer and Mathiesen [36] found in melt granulation that increasing the binder particle size increased the initial nuclei size and the subsequent granule growth rate. Binder distribution became worse as binder viscosity in-

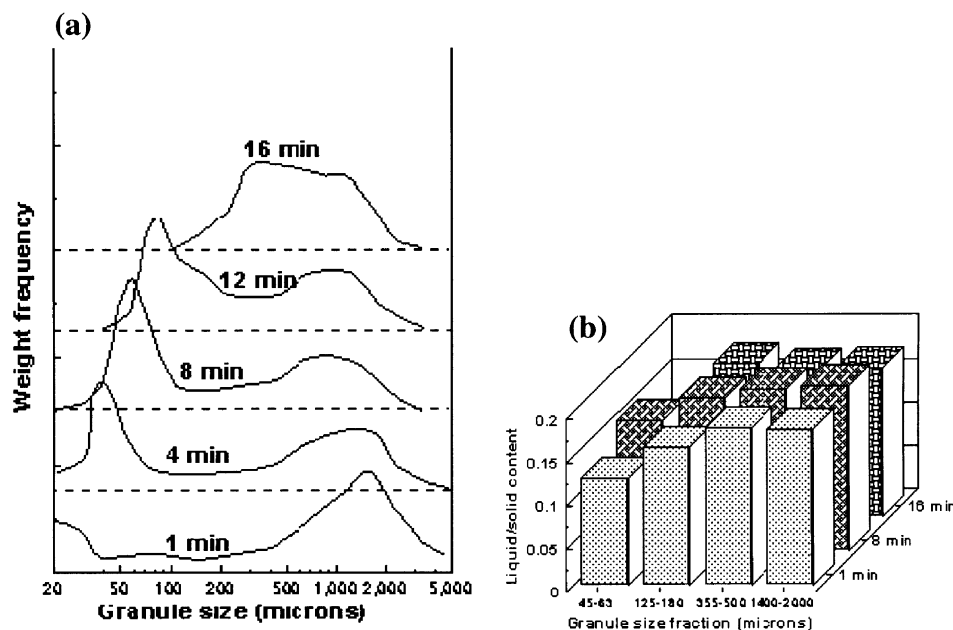


Fig. 4. (a) Persistence of bimodal granule size distribution as a result of mal-distributed binder. (b) Binder content as a function of granulation time and granule size fraction. (Source: Ref. [19]).

creased, leading to wide, and even bimodal, granule size distributions. Wauters et al. [49] compared the drum granulation growth of material, which was pre-wetted by kneading in a plastic bag, with material wetted by spraying on binder in situ. Pre-wetting distributed the binder evenly and produced a narrow agglomerate size distribution. Spraying the same amount of binder into the drum created a wide agglomerate distribution and caused segregation within the drum, due to an uneven binder flux across the drum. However, their results are difficult to interpret, with both pre-mixed and high spray flow rates giving rapid growth, but with a medium binder spray rate giving no growth.

A controlled spray droplet size distribution leads to a more controlled granule size distribution [24,50], as the size and distribution of the droplets determine the nuclei size distribution. Several authors [51–55] have found a strong correlation between the drop size and nuclei size distributions in fluid bed granulators. Waldie [55] found that one drop tended to form one granule according to the relation:

$$d_g \propto d_d^n \quad (3-7)$$

where  $d_g$  is the granule diameter,  $d_d$  is the drop diameter and  $n$  is a correlation coefficient. For lactose and 5% PVP solution,  $n = 0.80$  and for ballotini  $n = 0.85$ . This relation held over a large range of drop sizes (from 35 to 3000  $\mu\text{m}$ ). Schaafsma et al. [43] performed similar experiments with water and lactose and calculated a correlation coefficient of  $n = 0.89$ .

However, there are other cases where drop size has a negligible effect on nuclei size. For example, in high shear mixers, the granule product size appears almost independent of the atomised binder droplet size [46], as the intensive shear forces crush the initial flocs and agglomerates formed during the nucleation stage. A minor influence on the product granule size was detected when the agitation intensity was very low. The only case where the binder addition method strongly influences the size distribution of granules formed in high shear mixers is during melt granulation, where the binder viscosity is extremely high [36]. These results suggest that more than one mechanism of liquid distribution exists—liquid may be absorbed into the powder through capillary flow, or it may form over-wet lumps which are then redistributed by mechanical mixing.

One of the most widely studied variables affecting binder distribution is the solution flow-rate. Rankell et al. [56] granulated aluminium hydroxide powder and sucrose in a fluidised bed and varied the water spray rate from 10 to 25 l/h. The initial rate of agglomeration (nucleation) increased as the binder spray rate increased. Similar results are reported by other workers in fluid beds [57,58] and for pulsed spraying [27]. There is general agreement that an increase in flow-rate causes an increase in mean granule

size, although the magnitude of the effect is difficult to determine as changes in spray-rate are usually accompanied by changes in the drop size distribution. Depending on the type of spray nozzle used, the drop size may increase or decrease as the flow-rate is increased. Few authors provide details of the drop size of the spray as a function of flow-rate.

The nozzle position and the spray angle are commonly used to alter the size of the spray zone (or nucleation zone). The location and shape of the nucleation zone (e.g. circular, annular, flat spray) can also alter the binder dispersion and nucleation [59]. Large spray angles and high nozzles both increase the area of the bed exposed to the binder spray. This reduces the likelihood of binder droplets coalescing, and hence reduces the size and spread of the nuclei produced. Several workers state that as the nozzle height increased, the average granule size decreased [56,58]. Others report a narrowing of the distribution with increased nozzle height but no change in mean granule size [60]. These variations demonstrate the strong dependence on particular equipment set-ups [59] and that no equipment-independent parameter or controlling group currently exists for reliably describing the nucleation zone conditions.

### 3.3.2. Powder mixing

Efficient powder mixing is essential to binder dispersion in all granulators. High powder flux through the spray zone allows more uniform distribution of the powder and the binder fluid by carrying local patches of high binder content out of the nucleation zone and providing a constant supply of fresh powder into the nucleation zone. However, mixing is a difficult variable to manipulate.

Powder flux studies are rarely separated from other processes occurring simultaneously in the granulator. Rankell et al. [56] varied the feed rate of sucrose powder to a continuous fluid bed from 18 to 38 kg/h and found the mean granule size decreased due to ‘powder dilution’ effects. An increased powder flux through the nucleation zone reduces the granule size, as there is less time and less binder volume available for agglomeration per unit powder. The product size was constant at a given powder feed rate, indicating that a new steady state condition was reached for each powder flux.

In a fluidised bed granulator, Schaafsma et al. [27] found that surface mixing in a fluid bed was the limiting factor to avoid overwetting and collapse of the bed. Work by Tsutsumi et al. [61] recommends fast fluidised bed granulators for achieving a narrow size distribution. The turbulent gas flow promotes good powder and binder mixing, and the dilute particle density minimises granule coalescence, creating a nucleation and breakage only granulator. The final granule properties are controlled by the binder properties (spreading coefficients, contact angle) and the spray drop size distribution.

Increasing the impeller speed in a mixer granulator aids binder dispersion by increasing both the shear forces in the granulator and the powder flux through the spray zone. Although many workers [46,47,62–64] have studied the effect of impeller speed on binder dispersion and final granule size, these dual effects have not been clearly distinguished. Improved binder dispersion due to an increased powder flux through the nucleation zone has been obscured by the focus on shear forces. Powder flux through the nucleation zone is expected to have an important influence, especially when the nuclei formation kinetics are relatively slow.

### 3.3.3. Quantifying liquid distribution

In the past, the nucleation zone conditions have not been described adequately to allow replication by other workers with different equipment, or even the same type of equipment at a different scale. An attempt to standardise the description of nucleation zone conditions across equipment scales has been made by Tardos et al. [25] and Watano et al. [65]. They suggest measuring binder delivery in terms of the binder flow-rate compared to the size of the spray zone and the powder flux through the spray zone. An increased powder flux through the nucleation zone reduces the granule size as there is less likelihood of drop coalescence and less binder volume available for agglomeration per unit powder [56]. Watano et al. [65] measured the granule size distribution as a function of gas velocity, spray zone size and equipment scale in an agitated fluidised bed granulator. In this case, increasing the gas velocity will increase the powder turnover and flux through the spray zone. All experiments used an identical spray nozzle, but the relative size of the spray zone compared to

the bed dimensions decreased as the granulator was scaled up. The best binder dispersion and consequently the narrowest distribution was produced with a high gas flow-rate at the smallest scale i.e. the highest powder flux and the largest spray zone (see Fig. 5). A similar approach was taken by Schaafsma et al. [27] who looked at the rate of surface renewal in a fluidised bed compared to the spraying rate.

Litster et al. [22] have quantified spray conditions as a function of the major operating variables. In the spray zone, the drops produced by the nozzle at a given volumetric flow-rate  $\dot{V}$  with an average droplet size  $d_d$  cover a certain projected area of powder per unit time. This area of droplets is distributed over some spray area  $A$  on the powder bed surface. The dimensionless spray flux is defined as:

$$\Psi_a = \frac{3\dot{V}}{2\dot{A}d_d} \quad (3-8)$$

where the powder surface is traversing the spray zone with a flux  $\dot{A}$ . The dimensionless spray flux is a measure of binder coverage on the powder surface.

A high spray flux value indicates that the binder solution is being added too quickly compared to the powder flux rate. Droplets will overlap each other on the powder surface, causing drop coalescence and a wider nuclei size distribution. A low spray flux value indicates that the ratio of powder flux to solution flow-rate is sufficiently high that each drop lands separately and the nuclei are swept out of the spray zone before being re-wet by another drop. Low  $\Psi_a$  values result in a well-dispersed binder where one droplet tends to form one granule Fig. 6.

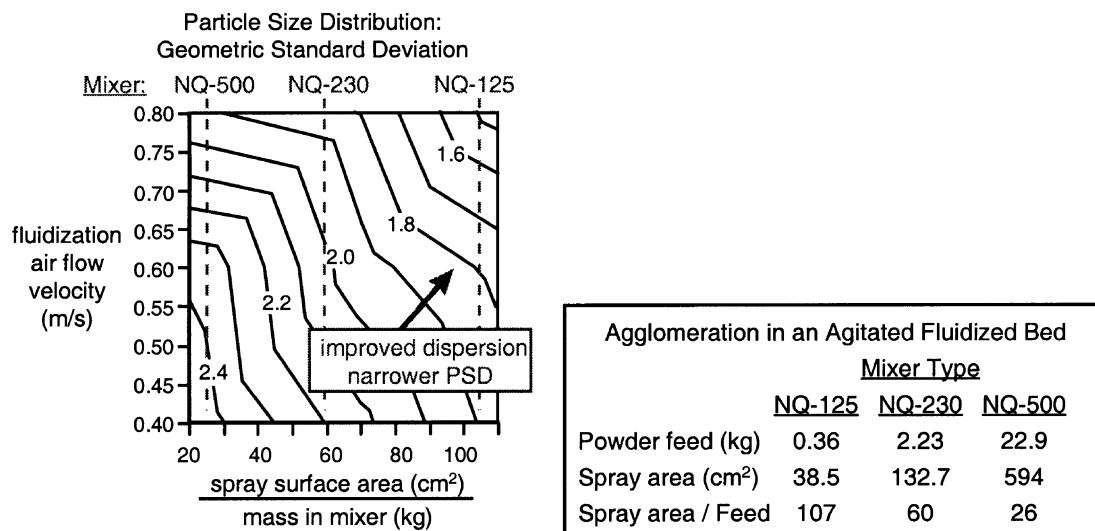


Fig. 5. Geometric standard deviation of granule size in an agitated fluid-bed granulator as a function of gas fluidisation velocity and binder dispersion (measured using spray surface area to mass in mixer). Figure from Mort and Tardos [20]. Original data from Watano et al. [65] and analysed by Tardos et al. [25].



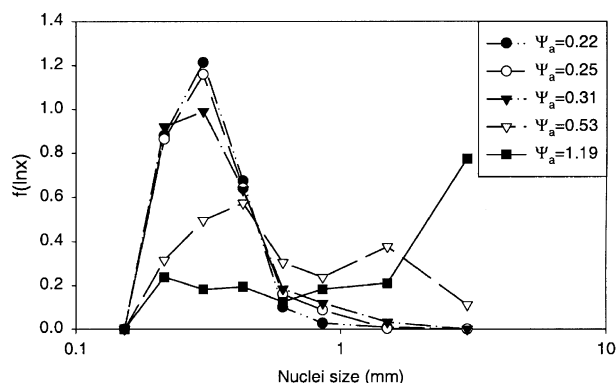


Fig. 6. Effect of dimensionless spray flux on nuclei size distributions for lactose with water at 310 kPa. As  $\Psi_a$  decreases the nuclei size distribution becomes smaller and narrower (Data from Litster et al. [22]).

Ex-granulator experiments with red dye and image analysis demonstrated that changes in dimensionless spray flux correlate with a measurable difference in powder surface coverage. Size analysis shows that spray flux controls the size and shape of the nuclei size distribution. At low  $\Psi_a$ , the system operates in the drop controlled regime, where one drop forms one nucleus and the nuclei size distribution is narrow. At higher  $\Psi_a$ , drop overlap increases and eventually the powder surface “cakes” creating a much broader size distribution. For controlled nucleation with the narrowest possible size distribution, it is recommended that the dimensionless spray flux be less than 0.1 to be in the drop controlled regime [22].

### 3.4. Nucleation regime map

Nucleation is a combination of single drop behaviour (e.g. the penetration time controlled by contact angle and other material properties) and multiple drop interactions (e.g. the spray flux controlled by the spray zone characteristics and other operating variables). Depending on the particular formulation properties and operating conditions, different mechanisms may dominate. Litster et al. [22,66] postulated that three nucleation regimes exist: *drop controlled*, *mechanical dispersion controlled* and *intermediate* regime.

In the drop controlled regime, the controlling property is the droplet size. The binder droplets penetrate into the powder bed pores almost immediately, and the nuclei distribution reflects the drop size distribution. In this region, one drop tends to form one granule provided that two key conditions are met:

1. The powder flux through the spray zone must be fast enough that drops which hit the powder surface do not overlap (low  $\Psi_a$ ).
2. The drop must wet into the bed completely before bed mixing brings it into contact with another partially absorbed drop on the bed surface (fast drop penetration time).

Powder mixing characteristics relative to capillary pressure and binder viscosity should dominate in the mechanical dispersion regime. Viscous or poorly wetting binders are slow to flow through the powder pores and form nuclei. Drop coalescence on the powder surface (also known as “pooling”) may occur and create a very broad nuclei size distribution. In this regime, nucleation and binder dispersion occur by mechanical mixing and agitation, and the solution delivery method (drop size, nozzle height etc.) has a minimal effect on the nuclei properties.

In the intermediate regime, both drop penetration dynamics and shear force dispersion are significant. Clumps of unevenly distributed binder will form if the binder addition rate exceeds the binder dispersion rate. Wetting kinetics compared to binder flux and exposure time should control the nucleation. This regime would be most difficult to control.

Based on this idea, Hapgood et al. [23] proposed a preliminary version of the nucleation regime map, shown in Fig. 7. This regime map incorporates some parts of the “transformation maps” proposed by Mort and Tardos [20]. Testing is in the early stages and the exact positions of the regime limit lines are currently unknown. On the vertical axis is drop penetration time ( $t_p$ ), indicating single drop behaviour and material properties. The penetration time is made dimensionless by the particle circulation time ( $t_c$ ). The horizontal axis is the dimensionless spray flux, which takes into account multiple drop behaviour. The map centres around the drop-controlled regime, where one drop makes one nuclei, provided the drop penetrates fast enough and the drops are well separated from each other. If validated, this nucleation regime map will allow the effect of changing formulation properties or operating conditions to be predicted beforehand.

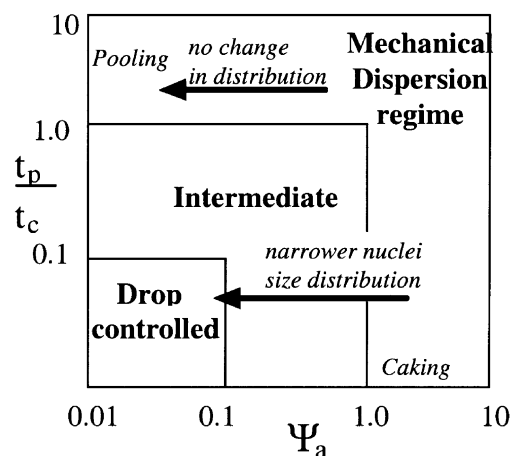


Fig. 7. Nucleation Regime Map proposed by Hapgood et al. [23]. In the drop-controlled regime, one drop tends to form one granule as the spray droplets penetrate quickly into the powder and are well dispersed. In the mechanical dispersion regime, one or both of these conditions are not met, and binder dispersion occurs instead by mechanical mixing and shear forces.

### 3.5. Particle segregation during wetting and nucleation

Segregation of multi-component mixtures during granulation is a common problem and of particular concern to the pharmaceutical industry, where most of the research in this area has been concentrated. Most pharmaceutical drugs are hydrophobic, used in low dosages (5 wt.% drug or less) and require a small surface area to control dissolution and absorption. Drugs therefore tend to have a small particle size, less than 30  $\mu\text{m}$ . However, the excipient powders are generally much larger in size to avoid problems with fluidisation and handling of very fine powders [57]. The dual problems of size difference and drug hydrophobicity make segregation difficult to avoid.

The mechanisms of segregation are not fully understood, and many causes have been suggested including solubility differences, binder fluid migration, binder fluid flow-rate, and abrasion. Migration of the binder fluid to the outer layers of the granule during drying is one of the most common explanations for segregation. The drug components are transported with the flowing fluid and redeposited at the surface as the fluid evaporates [67,68]. Abrasion may then remove the enriched outer granule layers creating drug-enriched fines.

An alternative explanation is that the binder preferentially wets the more hydrophilic particles, hence promoting their growth at the expense of the hydrophobic ones. Crooks and Schade [57] granulated 5% phenylbutazone with lactose while varying the flow-rate of a 10% PVP binder solution. The larger, more saturated granules grew by layering the ungranulated feed powder (rich in drug) onto the wet surface. At low spray rate (5 ml/min) the drug was concentrated in the coarse and fine fractions (see Fig. 8). Homogeneity improved with increasing binder flow-rate suggesting that preferential wetting does control segregation, although even at high flow rates there was still a higher fraction of drug in the fines fraction.

Experimental studies of drug content uniformity often present conflicting evidence. For instance, Whitaker and

Spring [67] granulated lactose powder with either sulphanimide sodium (high solubility) or sulphacetamide (low solubility) at three drug concentrations (0.02%, 1% and 2%). The granulation results were the same for both drugs: the fines were drug enriched when 0.02% drug was used, and conversely, the fines were drug depleted at 1% and 2% drug content. Hence, the solubility of the drug had no effect on the drug migration in this case, but the cause of the concentration effects is unknown.

Miyamoto et al. [69] report the opposite effect of solubility. They used factorially designed experiments to study the effect of the volume of binder solution (water) and the concentration of HPC on several variables including drug content uniformity. They used two formulations with differing drug solubilities: ascorbic acid (high solubility) and ethenazamide (low solubility). They observed that high solubility and high HPC concentration improved drug distribution, contrary to Whitaker and Spring [67]. They proceeded to optimise the formulation without further systematic investigation.

High concentrations of HPC as a binder will increase the liquid viscosity and reduce its ability to migrate to the surface. This is the most likely cause of Miyamoto's results. Warren and Price [68] have investigated this using lactose and calcium phosphate based formulations with various povidone and hydroxypropyl methylcellulose binder solutions (viscosities ranged from 1 to 1000 cps). Drug migration decreased as the binder viscosity increased and was almost entirely eliminated above 90 cps. They suggest that low viscosity binders can be drawn to the surface by the entry suction pressure as drying proceeds, bringing the soluble drug to the granule surface where abrasion subsequently creates drug enriched fines. However, viscous binders retard the rate of fluid flow, and evaporation occurs faster than fluid migration. The fluid vaporises inside the granule, leaving the drug safely inside the interior.

In order to advance our understanding of component segregation behaviour during granule nucleation and

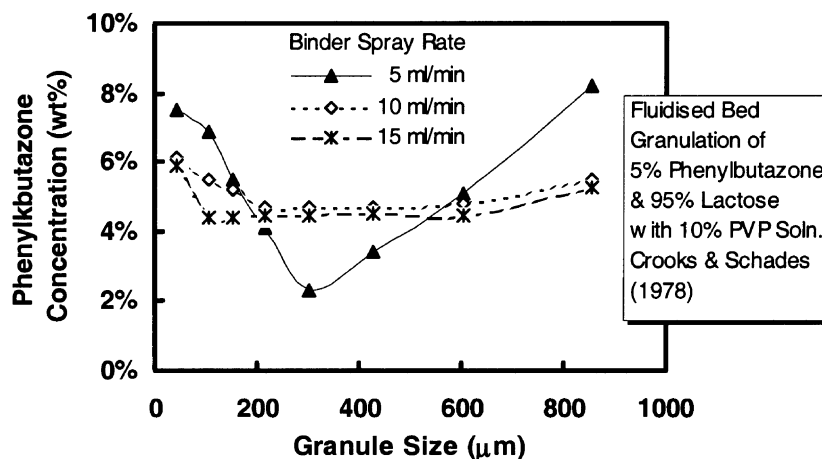


Fig. 8. Segregation of drug component into fines fraction during fluid bed granulation (Data: Crooks and Schades [57]).

growth, much more carefully designed and detailed experiments are required. Most of the work in this area either manipulates too many variables at once (e.g. volume of binder solution and amount of HPC binder simultaneously) or fails to report other experimental parameters. Many papers aim to report the behaviour of a particular powder and drug system, without explaining the causes of this behaviour (e.g. Miyamoto's factorial experimental design). We need to move beyond this 'black box' approach, as we have done in nucleation over the last decade, and concentrate on discovering how to control segregation using a fundamental understanding of the mechanisms involved. This is a growth area for research.

### 3.6. Conclusion

Recent advances in granulation are demonstrating the importance of controlled nucleation. A better understanding of the variables and their interactions has been reached, and a number of new controlling groups have been identified. For instance, the importance of nucleation kinetics has now been recognised. The fact that the thermodynamics of wetting can be influenced or overridden by other processes occurring in the granulator is beginning to emerge.

The improved understanding of nucleation that we have gained over the last decade is reflected by a general change of attitude towards nucleation in the granulation community. Research papers over the last 10 years are beginning to report in some detail the nucleation mechanism used, even when the primary focus of the paper is growth or breakage. However, there is still room to improve in reporting experimental nucleation conditions. Vital parameters such as drop size distribution, spray areas, nozzle heights, and time of liquid addition are still often missing from published papers.

Quantifying binder dispersion conditions to remove equipment dependence and allow better repeatability of experiments is a recent direction in the research. Several groups in the world are working simultaneously in this area and progress is expected to be rapid. The powder flux through the spray zone or powder surface renewal rate is a recent and promising idea. Suggested operating spray flux values, nucleation regime maps and the ability to make *quantitative* statements about controlling nucleation conditions are on the way as we enter what promises to be an exciting period in nucleation research.

## 4. Granule growth behaviour

Granule growth occurs whenever material in the granulator collides and sticks together. For two large granules this process is traditionally referred to as *coalescence*, whereas the sticking of fine material onto the surface of large pre-existing granules is often termed *layering*. However, the distinction between these two processes is arbitrary

depending on the cut-off size used to demarcate fine from granular material. These growth processes may begin as soon as liquid is added to an agitated powder mass (i.e. simultaneous with the wetting and nucleation stage) and may continue on well after liquid addition has been completed. In some systems, however, insufficient liquid is added to promote further growth, and the granule size is determined purely by the nucleation conditions.

Whether or not a collision between two granules results in permanent coalescence depends on a wide range of factors including the *mechanical properties* of the granules and the *availability of liquid binder* at or near the granule surfaces. During agitation, granules gradually consolidate which increases their liquid pore saturation and alters their mechanical properties. Hence, consolidation often has a pronounced effect on granule growth behaviour and must be considered in conjunction with it. Therefore, the mechanical properties and consolidation behaviour of wet granules are discussed first, before moving onto a detailed review of granule growth behaviour.

### 4.1. Mechanical properties of liquid-bound granules

Granules can exist in a number of different states of liquid saturation. These were first described by Newitt and Conway-Jones [3] and are shown in Fig. 9. In the *pendular* state particles are held together by liquid bridges at their contact points (pendular bonds). The *capillary* state occurs when a granule is saturated—all the voids are filled with liquid and the surface liquid is drawn back into the pores under capillary action. The *funicular* state is a transition between the pendular and capillary state where the voids are not fully saturated with liquid. The *droplet* state occurs when the particles are held within or at the surface of a liquid drop. It is also possible to have a *pseudo-droplet* state where unfilled voids remain trapped inside the droplet. This is more likely to occur in poorly wetting systems [31]. During granulation, it is possible for the saturation state of the granules to shift from the pendular state through to the droplet state, either due to the continuous addition of liquid binder and/or due to consolidation reducing the granule porosity.

Liquid-bound granule strength is dominated by two categories of forces: liquid bridge and inter-particle friction. The liquid bridges can generate both static surface tension forces and dynamic forces due to the liquid viscosity. These forces are now discussed.

#### 4.1.1. Static strength

The static strength of a pendular liquid bridge consists of two components. There is a capillary suction pressure caused by the curvature of the liquid interface and a force due to the interfacial surface tension acting around the perimeter of the bridge cross-section. There can also be a buoyancy force due to the partial submersion of the spheres, but Princen [70] showed that this was negligible for spheres less than 1 mm in diameter.

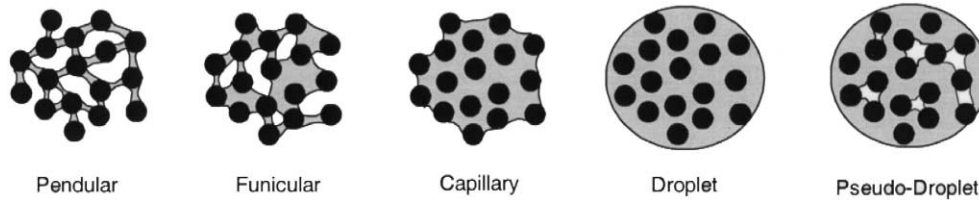


Fig. 9. The different states of saturation of liquid-bound granules (After Newitt and Conway-Jones [3] and York and Rowe [31]).

The capillary suction pressure,  $\Delta P_{\text{cap}}$ , generated by the curvature of the liquid bridge is given by the Laplace–Young equation:

$$\Delta P_{\text{cap}} = \frac{2\gamma_{\text{LV}}}{r} = \gamma_{\text{LV}} \left( \frac{1}{r_1} - \frac{1}{r_2} \right) = \gamma_{\text{LV}} \left( \frac{\ddot{y}}{[1 + \dot{y}^2]^{3/2}} - \frac{1}{[y(1 + \dot{y}^2)]^{1/2}} \right) \quad (4-1)$$

where  $\gamma_{\text{LV}}$  is the liquid surface tension and  $r$  is the curvature of the bridge surface.  $r$  can be calculated from the two principal radii of curvature of the surface,  $r_1$  and  $r_2$ , as shown in Fig. 10. These can be evaluated at any point along the bridge profile,  $y(x)$ , using the derivatives in the third equality of Eq. (4-1).

Eq. (4-1) cannot generally be solved analytically. Hence, it is common to approximate the liquid bridge profile as a toroid. However, a toroid does not have a constant mean surface curvature. This has led to debate as to whether the surface tension and capillary pressure terms should be evaluated at the mid-point of the bridge (the so-called “gorge” method) or at the contact line with one of the spheres (the “boundary” method):

$$F_{\text{gorge}} = \pi \Delta P r_2^2 + 2\pi r_2 \gamma \quad (4-2a)$$

$$F_{\text{boundary}} = \pi \Delta P a^2 \sin^2 \phi + 2\pi a \sin(\phi) \sin(\theta + \phi) \quad (4-2b)$$

Hotta et al. [71] present numerical and experimental results which support the boundary method, whereas Lian et al.

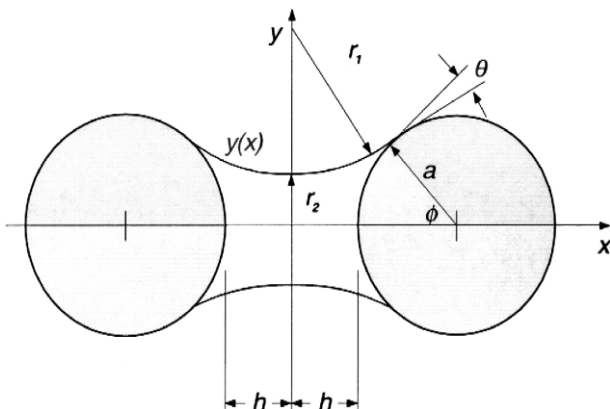


Fig. 10. Schematic of a pendular bridge between two equi-sized spheres.

[72] found that the gorge method gave the best estimate of the total force.

Rather than rely on an analytical solution to a profile approximation that is known to be flawed, Willet et al. [73] numerically solved the full Laplace–Young equation and then fitted empirical expressions to the results. For  $V/a^3 < 0.001$  (where  $V$  is the bridge volume) they found that:

$$\frac{F}{2\pi a \gamma_{\text{LV}}} = \frac{\cos \theta}{1.0 + 2.1 \left( \frac{h^2 a}{V} \right)^{1/2} + 10.0 \left( \frac{h^2 a}{V} \right)} \quad (4-3)$$

Note that the bridge force turns out to be directly proportional to the liquid adhesion tension ( $\gamma_{\text{LV}} \cos \theta$ ) of the system. More complex expressions are also available for larger bridge volumes and the case where the two spheres are not of equal size [73].

The normal force generated by liquid bridges at inter-particle contacts activates inter-particle *friction forces*. Other forces such as electrostatic and Van der Waal forces are insignificant in wet systems with particles larger than 10  $\mu\text{m}$  in size [74].

There is a large body of experimental work on the static strength of liquid-bound granules. These measures have either been direct tensile tests (e.g. Refs. [74,75]) or uniaxial compression tests where the granule or compact is assumed to fail due to tensile stress (e.g. Refs. [3,76]). Schubert [77] describes the different methods available to measure the strength of moist agglomerates. There are two main parameters of interest that are usually reported: peak yield stress and the maximum strain before brittle failure.

Peak yield stress always increases with decreasing size of the constituent particles [3,74,78–80]. This is because there is a larger volume density of interparticle contacts when smaller particles are used and the smaller average pore size also increases capillary and viscous forces. Similarly, granule strength is also higher if the constituent particles have a wide size-distribution [78,79] or if the granule is compacted to a lower porosity [3,76]. Large, mono-disperse particles produce weak, easily deformed granules.

Granule strength decreases as binder surface tension is lowered [3,76]. This is because the capillary suction pressure and surface tension forces are both proportional to liquid surface tension. Likewise, it is also expected that granule strength will decrease as the contact angle in-

creases (more hydrophobic), although there are no experimental studies to prove this, largely due to the difficulty of varying contact angle while keeping all other parameters constant.

Rumpf [74] developed a widely quoted model for predicting the tensile static strength of a liquid-bound granule. He assumed that granules were a matrix of equi-sized spheres that failed by sudden rupture of the liquid bridges between every particle across the whole fracture plane. For a granule in the funicular and capillary states, the tensile strength  $\sigma_t$  is given by:

$$\sigma_t = SC \frac{1 - \varepsilon}{\varepsilon} \frac{\gamma_{LV} \cos \theta}{d_p} \quad (4-4)$$

where  $S$  is the liquid pore saturation,  $C$  is a material constant (for uniform spheres  $C = 6$ ),  $\varepsilon$  is the granule porosity,  $d_p$  the surface-average particle diameter,  $\gamma_{LV}$  the liquid surface tension and  $\theta$  is the liquid–solid contact angle. Many variations of Rumpf's approach have been presented in the literature to include effects such as the finite separation distance between particles [81] and the effects of particle size distribution [82].

Eq. (4-4) predicts that granule strength is proportional to liquid surface tension and saturation, increases with decreasing porosity and is inversely proportional to particle size. All these trends have been observed experimentally for granules made from relatively large, mono-sized particles (e.g. Ref. [83]). However, quantitatively the theory is usually incorrect. For large, monosize particles, the theory over-predicts granule strength. Wynnyckyj [84] believes that this is because it fails to account for the presence of extensive pore networks in granules. Failure occurs by crack growth along these pore structures, not by sudden failure across the whole plane. The strength in these cases is better measured using three-point bend tests and has been found to be proportional to porosity to the fourth power [85].

Eq. (4-4) also under-predicts the strength of granules made from fine, widely sized particles and incorrectly predicts the effect of binder content. For coarse particles, increasing binder content generally increases granule strength up to the saturation state [3,74,75,78]. However, in fine particle systems, there is a maximum strength at around 20% to 30% liquid saturation, and after that the strength decreases rapidly as liquid saturation increases (e.g. Refs. [86–89]; see Fig. 11).

These opposing trends are a result of the opposite effects of liquid content on inter-particle friction and liquid bridge capillary forces [76]. Capillary forces increase with increasing liquid content up to the capillary state (Eq. (4-4)). However, liquid binder can also lubricate inter-particle contacts, thus reducing frictional forces. Hence, the effect of liquid content depends on which force is dominant. For coarse particle systems, interparticle frictional forces are insignificant and so the lubrication effect is

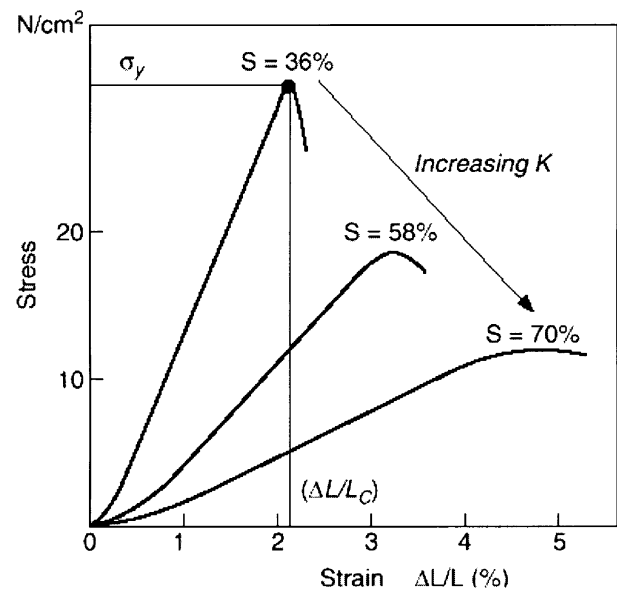


Fig. 11. Stress vs. strain curves for uniaxial compression of liquid bound powder showing the effect of increasing liquid content in altering behaviour from brittle to plastic (Source: Holm et al. [89]).

negligible. However, for finer, more broadly sized samples, the frictional forces dominates and so adding liquid decreases granule strength.

The critical strain before failure generally increases with increasing binder content (Fig. 11; [75,89]). For saturated, sub-micron particle size, alumina compacts, Franks and Lange [80,90] observed that the failure behaviour could be altered by adjusting the packing density or the attractive forces between the particles. High packing densities and strong attractive forces resulted in brittle behaviour, whereas low attractive forces produced assemblies which flowed plastically.

Hence, there has been a large amount of work done measuring the mechanical properties of liquid-bound particulate assemblies. However, the majority of this work has been performed at relatively slow and invariant strain rates. In granulation applications, it is the amount of *impact* deformation that is critical in determining growth behaviour [7,79,91–93]. Impact velocities as high as 1 m/s would be typical in many types of equipment. Hence, dynamic forces may become significant, particularly when viscous binders are involved. Relatively little work has been done to measure granule strength at high strain rates, although it has recently become a topic of interest.

#### 4.1.2. Dynamic strength

The strength of a dynamic pendular liquid bridge between two spherical surfaces  $F_v$  can be approximated using lubrication theory [94]:

$$F_v = \frac{3\pi\mu r_p^2}{2h} \frac{dh}{dt} \quad (4-5)$$

where  $r_p$  is the particle radius and  $2h$  is the gap distance between the spheres. Mazzone et al. [95] and Ennis et al. [17] experimentally verified Eq. (4-5) and were the first to highlight the fact that for viscous binders dynamic bridge strength could exceed the static bridge strength by several orders of magnitude under industrially relevant conditions.

In contrast, Harnby et al. [96,97] measured the strength of pendular water bridges and found that the maximum bond strength *decreased* as the rate of separation increased. They speculated that at high separation velocities, the liquid adjacent to the particles does not move appreciably and hence as the liquid bridge lengthens, the neck narrows rapidly. For water bridges, where capillary forces dominate over viscous ones, the decrease in capillary strength of this narrow bridge neck is more significant than any increase in viscous strength due to the higher separation velocity. Hence, it is the relative importance of viscous and surface tension forces which determines the effect of strain-rate on bridge strength.

Adams et al. [98,99] have performed discrete element modelling (DEM) simulations of dynamic granule impacts. They simulated the collision of agglomerates of several thousand 60- $\mu\text{m}$ -diameter, elastic spherical particles at velocities ranging from 0.5 to 5 m/s. Granules were in the pendular state with liquid of 0.025 N/m surface tension and viscosity ranging from 1 to 100 mPa s. The simulations included the effects of normal and shear viscous forces, friction, capillary forces, liquid bridge rupture and elastic particle deformation. Over this range of conditions, they found that coalescence always occurred. Granule strength was controlled by viscous and interparticle frictional energy dissipation, with surface energies (capillary forces) playing only a small role. The relative magnitude of viscous and frictional effects varied with the collision velocity. The viscous forces dominated at low collision velocities where little inter-particle movement occurred, while both viscous and frictional effects were significant at higher collision velocities. These simulations emphasise the important role of viscosity and the fact that the relative importance of different mechanisms varies with strain rate.

Iveson and Litster [100] calculated the granule dynamic yield strength of cylindrical pellets of wet granular material by measuring the amount of deformation experienced during impacts at 1.4 to 2.4 m/s. They found that increasing binder viscosity, decreasing surface tension and decreasing particle size all increased the pellet strength (Fig. 12). For the viscous binder (glycerol), yield stress increased steadily with binder content in the range studied, whereas for the water-based binders there was some suggestion of a maximum in strength at some critical binder content. Again, these results suggest that viscous, capillary and frictional forces can all make major contributions to dynamic granule strength.

Franks and Lange [101] performed uniaxial, unconstrained compression tests on saturated, sub-micron alumina particle compacts. In some cases, increasing the

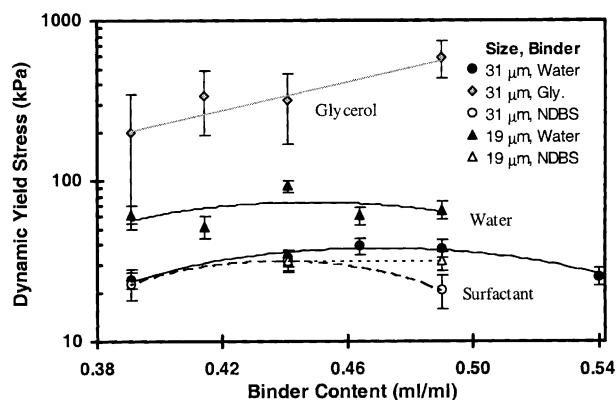


Fig. 12. Effect of binder content on dynamic yield strength for two different sized ballotini with water, glycerol and NDBS surfactant solutions (Source: Iveson and Litster [100]).

strain-rate from 0.5 to 20 mm/min increased the compact yield stress by an order of magnitude from 0.01 to 0.1 MPa.

Beathe et al. [102] measured the strength of wet powder compacts at speeds up to 0.15 m/s. For 35  $\mu\text{m}$  surface-mean sized glass ballotini with a range of different binders, they found that the dimensionless pellet peak flow stress ( $St_r^* = \sigma_{\text{peak}} d_p / \gamma_{LV}$ ) depended on the ratio of viscous to capillary forces, characterised described by the capillary number,  $Ca = \mu \dot{\epsilon} d_p / \gamma_{LV}$ , where  $\mu$  is liquid viscosity,  $\dot{\epsilon}$  is the strain rate and  $d_p$  is the surface-mean particle size. This relationship is shown in Fig. 13.

Another dynamic effect that may be significant during wet agglomeration is *liquefaction*. This occurs when a saturated particle assembly is vibrated at a frequency which prevents the pressure in the liquid phase from dissipating. The liquid phase supports the load and the stress on the particle matrix drops to zero, allowing the particles to become mobile. The mass then loses its yield stress and behaves as a liquid. Deysarkar and Turner [103] found that the yield stress and effective viscosity of an iron-ore paste could be reduced by more than 90% simply by applying low frequency (10 to 30 Hz) vibrations of amplitudes of 0.2 to 0.5 mm. This frequency appears to be within the range that might occur in many typical granulators. However, only one author [84] has mentioned liquefaction's possible influence on granulation phenomena. It has yet to be considered in any of the published models or simulations of granule deformation behaviour.

These results highlight the fact that the yield behaviour of granules in the dynamic environment inside a granulator is likely to differ significantly from that measured in low strain-rate tests.

#### 4.1.3. Granule strength summary

Granule strength is controlled by three forces—capillary, viscous and frictional. These forces are inter-related in a complex way and their relative importance can vary greatly with strain rate and formulation properties.

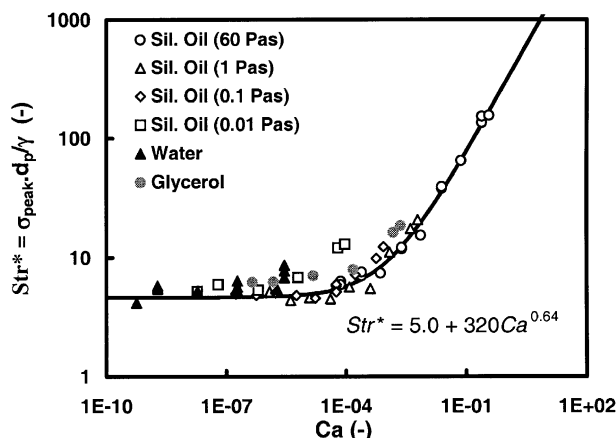


Fig. 13. Dimensionless pellet peak flow stress vs. capillary number (Source: Beathe et al. [102]).

Hence, it is important that the mechanical properties of granules be measured at strain-rates appropriate to the granulation conditions being studied.

Hence, the traditional models of wet granule strength which assume static conditions and do not include all three of the forces involved are fatally flawed. The often quoted model of Rumpf, Eq. (4-4), and most of its extensions all ignore crack growth and consider only capillary forces. These models may be suitable for coarse particles held together by non-viscous binders, but are invalid for granules composed of fine particles, bound with viscous binders or stressed at high strain-rates.

Developing models which are capable of predicting the complex interactions of capillary, viscous and frictional forces that occur during granule impacts will be a challenging task, but one that is very important to the advancement of this field. The DEM type simulations appear to be making some headway in this area, although it remains to be seen whether they can predict the complex effects of binder content, liquefaction and other variables such as particle morphology.

#### 4.2. Granule consolidation

As granules collide with other granules and equipment surfaces they gradually consolidate. This reduces their size and porosity, squeezes out entrapped air and may even squeeze liquid binder to their surface. Porosity controls granule strength. Granules with high porosity are weak and friable. These granules will break and generate dust during handling which is undesirable in most cases. However, for many products it is also desirable that the granules be porous in order to facilitate fast dispersion and dissolution. Hence, granule porosity is an important product property to control and optimise.

Granule porosity is also important in controlling granule growth mechanisms. In many systems, granules experience a long period of little growth, variously referred to as the

“nuclei”, “no growth”, “induction” or “compaction” phase [6,42,104,105]. If consolidation eventually squeezes liquid binder to the surface, then rapid coalescence growth may follow. Consolidation also has a complex effect on the mechanical properties of granules. Granule yield stress generally increases as granule porosity decreases [74]. This decreases the amount of deformation when two granules collide which decreases the likelihood of coalescence. However, consolidation also increases the pore saturation, which in turn increases granule plasticity [89] and the availability of liquid at the granule surface. Both of these effects will aid coalescence. If granules become fully saturated, then the frequent impacts they experience may cause them to liquefy which would further aid coalescence [84]. Hence, the net effect of consolidation on granule growth is uncertain and will probably depend strongly on the formulation and binder properties.

Several workers have measured granule porosity changes during batch granulation experiments. Porosity initially decreases quickly and then levels off to a stable equilibrium value (e.g. Refs. [3,46,106–108]; Fig. 14). This behaviour has been empirically described by an exponential decay model [108]:

$$\frac{\varepsilon - \varepsilon_{\min}}{\varepsilon_0 - \varepsilon_{\min}} = \exp(-kN) \quad (4-6)$$

where  $\varepsilon$  is the average granule porosity after  $N$  drum revolutions,  $\varepsilon_0$  is the initial average porosity of the feed,  $\varepsilon_{\min}$  is the minimum porosity reached by the tumbling granules and  $k$  is the consolidation rate constant.

##### 4.2.1. Binder content

Binder content has a complex effect on the rate and extent of consolidation. Increasing the amount of low viscosity binders (e.g. water) has generally been found to increase both the initial rate and the final extent of granule

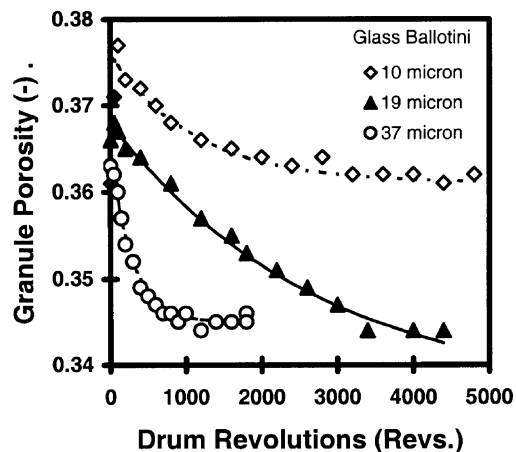


Fig. 14. Granule porosity vs. number of drum revolutions for three grades of glass ballotini granulated with 0.417 ml/ml of glycerol. Lines show the best fit of Eq. (4-6) [108].

consolidation [106,108–110]. The additional moisture appears to increase particle mobility (by acting as a lubricant) which allows them to re-arrange into more compact configurations [74,76]. Schæfer et al. [111] also found that increasing the amount of a viscous binder (PEG6000  $\approx$  1100 mPa s) increased the amount of consolidation in a high shear mixer. In contrast, Iveson et al. [108] found that increasing the amount of a high viscosity binder (glycerol) decreased the rate and extent of consolidation of glass ballotini in a tumbling drum. This was believed to be because, in this case, liquid viscous forces dominated over inter-particle friction forces, and so the increase in viscous forces when more binder was added was more significant than any decrease in inter-particle friction.

#### 4.2.2. Binder viscosity

Likewise, increasing the viscosity of a binder also increases the viscous forces between particles and so generally decreases the rate of consolidation [18,41,92,108]. However, there appears to be a critical value of binder viscosity below which binder viscosity does not affect the consolidation rate. This occurred at approximately 10 mPa s in a laboratory drum granulator and 1000 mPa s in a high shear mixer granulator [39]. Below this critical value, it is probable that inter-particle friction forces are the dominant mechanism resisting consolidation. In this region, the more viscous binders may act as better lubricants by keeping particle surfaces apart and hence increasing binder viscosity may actually increase the consolidation rate [112].

#### 4.2.3. Binder surface tension

The effect of binder surface tension on consolidation has received relatively little attention. Ritala et al. [112] found that varying binder surface tension from 48 to 68 mN/m did not appear to significantly affect consolidation in a high shear mixer. Iveson and Litster [113] found that decreasing binder surface tension from 72 to 31 mN/m in a tumbling drum, increased the *rate* of consolidation, but decreased the *extent* of consolidation. Decreasing surface tension will decrease the capillary pressure holding particles together, which decreases inter-particle friction. This will allow particles to re-arrange more easily [110]. However, lowering surface tension also weakens granules, allowing them to dilate or shear apart more easily.

#### 4.2.4. Particle size

Decreasing average particle size decreases the rate of granule consolidation [111,113]. Smaller particles increase the volume density of inter-particle contacts and also decrease the average pore size through which fluid must be squeezed during consolidation. Both these factors retard consolidation. Decreasing particle size also tends to increase the minimum porosity reached due to the greater strength of the assembly [109,113]. However, the particle morphology and size distribution will also strongly influence the minimum porosity reached.

#### 4.2.5. Equipment speed and type

The effect of equipment speed on consolidation is variable. Increasing pan rotation speed [110] or mixer impeller speed [112,114] have both been found by some workers to increase the rate of granule consolidation. Likewise, use of a chopper resulted in considerably lower porosity granules in a Lödige high shear mixer [115]. However, Eliassen et al. [116] found that for low viscosity binders in a high shear mixer, increasing impeller speed increased the amount of breakage and shear which delayed densification, resulting in less-spherical granules with a higher porosity.

When comparing different granulation devices, an increase in process intensity generally increases the amount of consolidation. Sherrington [117] compared coarse sand mixtures ( $> 70 \mu\text{m}$ ) in a drum and paddle mixer and Ganderton and Hunter [109] compared  $4 \mu\text{m}$  calcium phosphate powder in a pan and  $z$ -blade mixer. In both these cases, the mixers produced denser granules. However, for  $20 \mu\text{m}$  lactose powder, Ganderton and Hunter [109] found that the mixer produced granules with a *higher* porosity than the pan. Again, this was speculated to be because for these weaker granules (due to the coarser particles), the shear forces in the mixer were sufficient to cause dilation of the granules.

The effect of equipment size on granule consolidation will depend on the strength of the formulation and whether the average impact forces that granules experience increase or decrease. This will depend on the heuristic used to scale up the equipment speed [118]. Schæfer et al. [114] found that less consolidation occurred during scale-up of high shear mixers, since there was a lower relative swept volume.

Whether these effects of equipment type and speed are due simply to changes in the frequency of collisions or to changes in the energy of collisions (or both) is not always clear. These two causes can only be distinguished if experiments are run until a stable minimum porosity is clearly reached (which is rarely done). If the minimum porosity varies, then this indicates that impact energy is having an influence. If the minimum porosity is identical in both cases, then it must only be the frequency of impacts which is changing the consolidation rate.

#### 4.2.6. Correlation of consolidation with granule strength

All the factors which decrease granule consolidation rate are the same ones which also increase granule strength. Iveson and Litster [113] found a correlation of the form:

$$k \propto e^{-Y/B} \quad (4-7)$$

when they compared the dynamic strength  $Y$  and consolidation rate constant  $k$  of granules made from glass ballotini with water and glycerol binders. If this relationship can be verified and extended to other systems, then it may provide a basis for developing methods to a priori predict granule consolidation behaviour simply by measuring granule dynamic strength.



This correlation also indicates that the same three forces influence granule dynamic strength and consolidation—capillary and viscous forces in the liquid binder and inter-particle friction forces [113]. These forces are quite different in nature. Capillary forces are conservative—they always act to pull particles together. Viscous and friction forces are dissipative, resisting both consolidation and dilation of the particle assembly. Viscous forces are highly strain-rate dependent, whereas the other two are probably less so. These forces are also inter-related in a complex way. Capillary forces generate the normal forces between particles which activates inter-particle friction. Increasing liquid content may simultaneously increase viscous and capillary forces, but decrease inter-particle friction due to the lubrication effect.

Therefore, unless the dominant force(s) is known in any given situation, it is impossible, *even qualitatively*, to predict the effect of a given change on granule consolidation behaviour. This complexity probably explains the shortage of theoretical models of the consolidation process. There are only two available in the literature, neither of which included all three forces [18,110].

#### 4.2.7. Consolidation models

Ouchiyama and Tanaka [110] assumed granules were held together by the capillary pressure of the binder. This pressure generates a normal force activating friction at inter-particle contacts. They considered how the coordination number of particles in the granule increased when forces were applied. They ignored the effects of binder viscosity and did not consider particle detachment that might occur due to dilation of the assembly. The granule consolidation rate was given by:

$$\frac{d\varepsilon}{d\tau} \cong - \left\{ 1 - \frac{(1 - \varepsilon)^3}{\varepsilon K_\varepsilon} \right\}^n \quad (4-8)$$

where  $\varepsilon$  is the granule porosity at time  $t$ ,  $K_\varepsilon$  is the dimensionless granule compaction rate which is proportional to the energy of impact and particle size and inversely proportional to the interparticle friction and binder adhesion tension,  $n$  is a parameter describing distribution of granule impact energies and  $\tau$  is the dimensionless compaction time which is proportional to the frequency of impacts. Setting  $d\varepsilon/d\tau = 0$ , the minimum porosity the system reaches,  $\varepsilon_{\min}$ , after an infinite time is [92]:

$$\frac{\varepsilon_{\min}}{(1 - \varepsilon_{\min})^3} = \frac{1}{K_\varepsilon} \quad (4-9)$$

Eq. (4-8) predicts that the consolidation rate is proportional to particle size and the energy of granule collisions and inversely proportional to liquid surface tension. Both of these trends have been observed experimentally. However, Eq. (4-9) predicts that the dimensionless compaction rate and minimum porosity are linked—if the compaction rate

increases then the minimum porosity will decrease (i.e. increase the amount of consolidation). This prediction contradicts the experimental results of Iveson and Litster [113] who found that  $k$  and  $\varepsilon_{\min}$  were independent parameters.

Ennis et al. [18] considered the effect of binder viscosity on granule consolidation. They predicted that the amount of consolidation per collision would increase according to:

$$\frac{\Delta x}{h} = 1 - \exp(-St_v) \quad (4-10)$$

where  $\Delta x$  is the reduction in inter-particle gap distance  $h$  and  $St_v$  is the viscous Stokes number ( $8\rho u_0 a/9\mu$  where  $\rho$  is particle density,  $u_0$  is collision velocity,  $a$  is particle radius and  $\mu$  is binder viscosity). Hence, increasing binder viscosity and decreasing particle size should decrease the rate of consolidation and increasing the impact energy should increase the rate of consolidation. These trends have been observed experimentally.

#### 4.2.8. Consolidation summary

In summary then, although there is some understanding of the effects of different process variables on the rate and extent of granule consolidation, there are currently no quantitative models for predicting the rate or extent of consolidation of a particular formulation under a given set of operating conditions. Any such model will need to include the inter-related effects of capillary, viscous and frictional forces. This means that it is currently impossible to predict a priori what level of consolidation and liquid saturation a given formulation will reach. This is an important goal to achieve in order to be able to predict a formulation's growth behaviour.

### 4.3. Granule growth

As mentioned previously, the large number of different growth mechanisms traditionally described in the literature can all be considered as combinations of coalescence and/or breakage phenomena. In this section, we discuss granule growth behaviour. This is a rate process, which may reach a maximum size and/or a dynamic equilibrium with breakage processes (see Section 5). First, the theoretical models for predicting granule coalescence are described. Then the range of growth behaviours observed in the literature are summarised, together with a discussion of the effects of different variables.

#### 4.3.1. Modelling granule growth

There are a large number of theoretical models available in the literature for predicting whether or not two colliding particles will coalesce (Table 1). These models involve a wide range of different assumptions about the mechanical properties of the particles and the system

Table 1  
Summary of coalescence models available in the literature

Authors	Type <sup>a</sup>	Comments
Ouchiyama and Tanaka [91]	Class II	Distinct compression and separation zones in drum granulator; Plastic deformation; Adhesive force; Force balance.
Ennis et al. [18]	Class I	Head on collisions; Viscous fluid layer; Coefficient of restitution; Energy balance.
Moseley and O'Brien [119]	Class I	Collisions at an angle; Elastic deformation; Adhesion energy; Energy Balance.
Simons et al. [120,121]	Class II	Capillary bridge rupture energy.
Adams et al. [98,99]	Class I	DEM simulations of agglomerate collisions including friction, viscous and capillary forces, pendular bridge rupture and particle elastic deformation.
Seville et al. [122]	Class II	Balance between particle contact time and visco-plastic sinter neck growth time.
Thornton and Ning [123]	Class I	Head on collisions; Elastic–plastic deformation; Adhesion energy; Energy balance.
Liu et al. [124]	Class I	Head on collisions; Elastic–plastic deformation; Viscous fluid layer; Energy balance.

<sup>a</sup>According to classification of Iveson [125].

characteristics. Some were developed specifically for wet granulation processes, whereas others were developed for predicting the onset of sintering or defluidisation in fluidised beds or the capture efficiency of air filters.

Two fundamentally different approaches have been taken to modelling coalescence [125]. Class I models assume that the granules are free to move and that elastic properties are important. Initial coalescence only occurs if the kinetic energy of collision is entirely dissipated—otherwise the granules will bounce apart. Various combinations of energy dissipation mechanisms are considered by different workers, including elastic losses, plastic deformation, viscous and capillary forces in the liquid binder and adhesion energies of the contact surfaces (see Table 1). It is implicitly assumed that if the initial impact results in coalescence, then none of the subsequent impacts will be able to break the two granules apart again.

Class II models assume that elastic effects are negligible during the initial collision, usually because the granules are plastic in nature and/or physically constrained by surrounding granules. Hence, all colliding granules are in contact for a finite time, during which a bond develops between them. However, permanent coalescence only occurs if this bond is strong enough to resist being broken apart by subsequent collisions or shear forces. The strength of the bond is assumed to depend on factors such as the initial amount of plastic deformation and the length of time the two particles were in contact.

In reality, many systems will involve a combination of both these factors [125]. The initial collision must be “successful”, but the bond formed must also be strong enough to survive subsequent collisions. This is particularly likely to be an issue in equipment where there are regions of widely varying process intensity, such as in a high shear mixer with different chopper and ploughshare speeds. Iveson [125] proposes a theoretical framework for combining Class I and Class II models together, but our ability to do so is restricted by our limited understanding of the flow patterns, contact times, distribution of impact forces and bond strengthening processes within granulators. In addition, most of the models consider only head-on,

co-linear collisions. Few consider angular or non co-linear collisions or shear effects.

Granule growth behaviour depends, among other things, on the deformability of the colliding granules and the availability of liquid at or near the granule surfaces to bind the two granules together. Two classes of collisions can be identified—those where little or no permanent granule deformation takes place and those where significant permanent plastic deformation occurs. Selected models for these two cases are now described in more detail.

*4.3.1.1. Coalescence of non-deformable granules.* In systems where the impact forces are very small and/or the granules are extremely rigid, relatively little permanent deformation occurs during granule collisions. Typical examples would be in a fluidised bed where agitative forces are relatively gentle, during the initial nucleation stages of granulation where individual solid particles are first colliding, or during the later stages of granulation when granules become rigid due to consolidation and/or evaporation of the binder.

In these situations, granule coalescence will only occur if there is a liquid layer present at the surface of the particles or granules to bind them together. Ennis et al. [18] modelled this situation by considering the impact of two solid, non-deformable spheres, each of which is surrounded by a thin viscous binder layer (Fig. 15). Success-

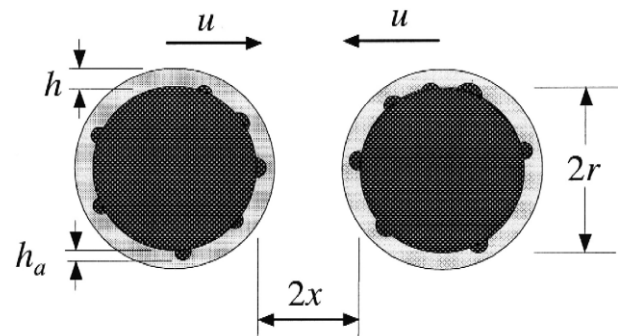


Fig. 15. Schematic of model used by Ennis et al. [18].

ful coalescence was assumed to occur if the kinetic energy of impact was entirely dissipated by viscous dissipation in the fluid and elastic losses in the solid phase. Capillary forces were neglected on the basis that for viscous binders under dynamic conditions, viscous forces dominated over capillary forces [95]. During rebound, the liquid bridge was assumed to rupture at the same distance at which the two liquid films first touched (i.e.  $2h$ ).

The model predicts that collisions will result in coalescence when the viscous Stokes number ( $St_v$ ) is less than some critical viscous Stokes number ( $St_v^*$ ) where:

$$St_v = \frac{8\rho ru}{9\mu} \quad (4-11)$$

and

$$St_v^* = \left(1 + \frac{1}{e}\right) \ln\left(\frac{h}{h_a}\right) \quad (4-12)$$

$r$  is the harmonic mean granule radius of the two spheres ( $1/r = 1/r_1 + 1/r_2$ ),  $\rho$  is the granule density,  $u$  is half the relative velocity of impact,  $\mu$  is the liquid viscosity,  $e$  is the coefficient of restitution,  $h$  is the thickness of the liquid surface layer and  $h_a$  is the characteristic height of surface asperities (Fig. 15).

$St_v$  is the ratio of kinetic energy to viscous dissipation. During batch granulation,  $St_v$  increases as granules grow in size. This leads to three stages of granulation. The *non-inertial* regime occurs when  $St_v \ll St_v^*$ . All collisions are successful regardless of the size of the colliding granules. As the granules grow larger, the *inertial* regime occurs when  $St_v \approx St_v^*$ . The likelihood of coalescence now depends on the size of the colliding granules. The harmonic mean size is biased towards the smaller of the two colliding granules. Therefore, collisions between two small or one small and one large granule are more likely to succeed than collisions between two large granules. Eventually, the system enters the *coating* regime when  $St_v \gg St_v^*$ . Here all collisions between granules are unsuccessful. These three regimes of growth have been observed experimentally in many granulators [18].

Strictly speaking, this model is only valid for predicting the maximum size of granules which can coalesce. It says nothing about the *rate* of granule growth—this will be a function of the frequency of collisions between granules. However, in any granulator, there is no one single granule collision velocity. Rather there is a range of collision velocities and hence a range of  $St_v$ . Hence, as the average  $St_v$  increases, there is not a sudden transition from growth to no growth. Rather the proportion of collisions which satisfy the criteria of  $St_v < St_v^*$  will decrease and hence the observed growth rate will also decrease.

Agglomerate growth is promoted by a low  $St_v$  and a high value of  $St_v^*$ . For instance, increasing binder content will increase the binder layer thickness,  $h$ , which will increase  $St_v^*$  and hence increase the granulation rate—a commonly observed behaviour in many systems. Likewise,

since increasing binder viscosity and decreasing impact velocity both reduce  $St_v$  (Eq. (4-11)), it might appear that these two changes will always increase the growth rate. However, these two variables also indirectly influence  $St_v^*$ . Increasing binder viscosity decreases the rate of granule consolidation. This will reduce the thickness of the liquid layer squeezed to the granule surface, which inhibits coalescence by decreasing  $St_v^*$ . Increasing binder viscosity may also alter the granule coefficient of restitution, another variable in  $St_v^*$ . Hence, there may be an optimum binder viscosity for promoting granule growth [120]. A high-viscosity binder might initially inhibit growth by preventing liquid being squeezed to a granule's surface, but once the liquid is there, the higher binder viscosity will aid granule growth. Similarly, increasing the impact speed will increase the rate of consolidation, which increases the liquid layer thickness, aiding coalescence. Therefore, the effects of variables such as collision speed and binder content on granule growth rate will depend on their net effect on the ratio of  $St_v:St_v^*$  [41]. This may be time-dependent and will not always be easy to determine beforehand.

The model of Ennis et al. [18] is significant because it was the first model to consider dynamic affects such as viscous dissipation. However, the model is limited by its many assumptions. It is only valid for non-deformable, surface wet granules where the viscous forces are much larger than capillary forces.

**4.3.1.2. Coalescence of deformable granules.** In other systems, significant amounts of deformation do occur during granule collisions. As well as aiding coalescence by dissipating collision energy through plastic deformation, this deformation also creates an area of contact which helps to hold the granules together. A number of workers have developed models for predicting the conditions under which deformable granules will coalesce.

Ouchiyama and Tanaka [91] considered surface-dry, deformable granules in a drum granulator. They assumed that in the constant-angular-velocity region of the drum, an axial compressive force acts on each pair of granules. This deforms the granules and creates a contact zone between them with a cohesive strength proportional to the area of contact. In the tumbling region of the drum, each granule dumbbell is then exposed to pairs of forces perpendicular to a tangent common to the contacting granules which tend to separate the granules (Fig. 16). The compressive forces were assumed to be independent of granule size whereas the tangential separating forces were assumed to be proportional to the volumes of the granules in contact.

Using these assumptions they predicted the probability ( $P$ ) of two granules of size  $D_1$  and  $D_2$  coalescing in terms of a characteristic limiting size,  $D^*$ . This relationship for  $D^*$  was simplified [126] to:

$$D^* = A_1(K^{3/2}\sigma_{st})^a \quad (4-13)$$

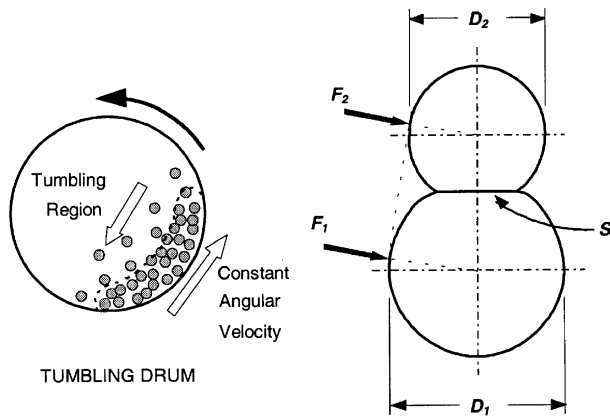


Fig. 16. Ouchiyama and Tanaka's model of coalescence between two granules of size  $D_1$  and  $D_2$  which form an area of contact,  $S$ , in the constant-angular-velocity region and then are exposed to a pair of forces,  $F_1$  and  $F_2$ , in the tumbling region of the drum [91].

where  $A_1$  and  $a$  are constants independent of granule size for a given system,  $K$  is a measure of the granule deformability and  $\sigma_{st}$  is the tensile strength of the bond area formed between the granules.

Kristensen et al. [79] further simplified Eq. (4-13) by assuming that the inter-granule bond strength was equal to the tensile strength of the granules. For small deformations of plastic spherical granules, they obtained:

$$(D^*)^{2/a} = A_3 \frac{l_{cr}^3}{\sigma_{cr}} \quad (4-14)$$

where  $A_3$  is a constant,  $l_{cr}$  is the critical strain ( $=l_c/D$ ) at failure with critical stress,  $\sigma_{cr}$ .

This equation predicts that granules will coalesce more easily when they have a low critical stress and large critical strain. During granulation, consolidation increases granule strength which reduces their tendency to coalesce. However, consolidation also forces excess liquid to the granule surface. At a certain stage of the process, this growing liquid saturation and free surface liquid increases surface deformability sufficiently to overcome the effect of increasing granule strength. Kristensen et al. [79] used this equation to draw a regime map of granulation in terms of the critical stress and strain of the binder-particle mixture. Growth rate would increase as a formulation shifted from being high critical stress and low critical strain to low stress and high strain.

This model is restricted to deformable granules with no surface liquid layer. The biggest obstacle to applying this model is the uncertainty of the bond strength term,  $\sigma_{st}$ . This will be a complex function of the particle and liquid properties and the amount of re-arrangement which occurs during impact. It is certainly not equal to the bulk tensile strength of the granules (as assumed by Kristensen et al. [79]) since a newly formed granule dumbbell can be easily broken across this surface. Some preliminary experimental measurements of how bond strength develops between two

granule surfaces have begun [127] but much more research is required in this area.

An alternative model for coalescence of deformable granules is that of Liu et al. [124] who extended the Ennis model to include the effect of plastic deformation of the granules. Granules were assumed to have a strain-rate independent elastic modulus ( $E$ ) and plastic yield stress ( $Y_0$ ). They considered two cases: surface wet granules (Fig. 17) and also surface dry granules where liquid is squeezed to the granule surfaces by the impact.

Coalescence is assumed to occur when the kinetic energy of impact is all dissipated through viscous dissipation in the liquid layer and plastic deformation of the granule

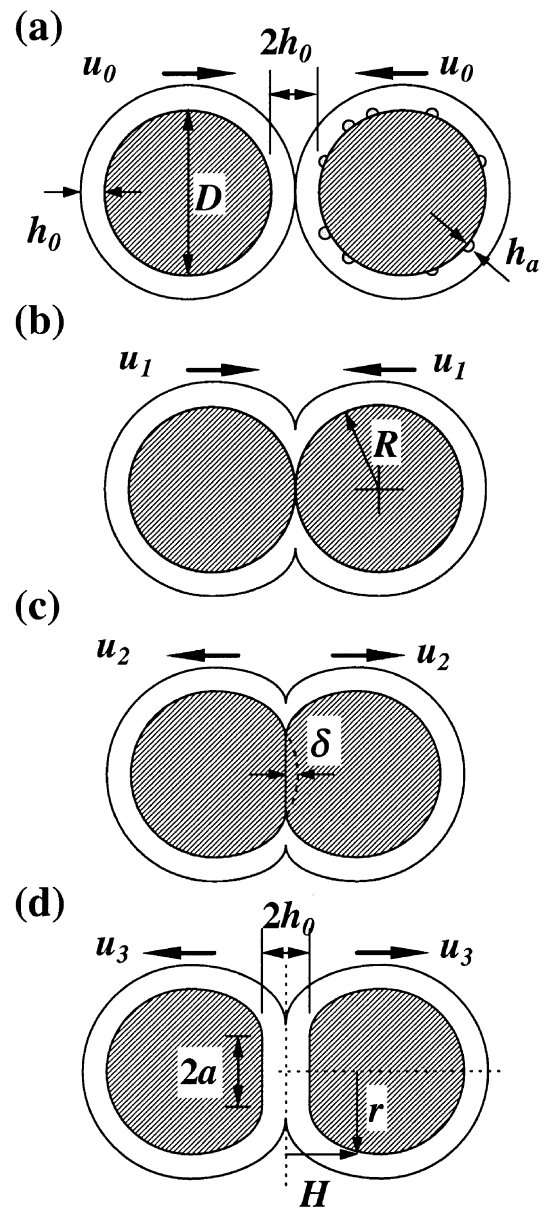


Fig. 17. Schematic diagram of the model used to predict coalescence of surface wet, deformable granules. (a) Approach stage. (b) Deformation stage. (c) Initial separation stage. (d) Final separation stage [124].

bulk. The model gives the conditions for two types of coalescence, termed type I and type II. Type I coalescence occurs when granules coalesce by viscous dissipation in the surface liquid layer before their surfaces touch. Type II coalescence occurs when granules are slowed to a halt during rebound, after their surface have made contact. The critical condition for Type II coalescence is given by the following result:

$$\begin{aligned} & \left( \frac{Y_d}{E^*} \right)^{1/2} (St_{\text{def}})^{-9/8} \\ & < \frac{0.172}{St_v} \left( \frac{\tilde{D}}{h_0} \right)^2 \left[ 1 - \frac{1}{St_v} \ln \left( \frac{h_0}{h_a} \right) \right]^{5/4} \\ & \quad \times \left[ \left( \frac{h_0^2}{h_a^2} - 1 \right) + \frac{2h_0}{\delta''} \left( \frac{h_0}{h_a} - 1 \right) + \frac{2h_0^2}{(\delta'')^2} \ln \left( \frac{h_0}{h_a} \right) \right] \\ & \quad \times \left[ 1 - 7.36 \left( \frac{Y_d}{E^*} \right) (St_{\text{def}})^{-1/4} \right. \\ & \quad \left. \times \left( 1 - \frac{1}{St_v} \ln \left( \frac{h_0}{h_a} \right) \right)^{-1/2} \right]^2 \end{aligned} \quad (4-15)$$

where  $St_v$  is the viscous Stokes number, Eq. (4-11) and  $St_{\text{def}}$  is the Stokes deformation number:

$$St_{\text{def}} = \frac{\tilde{m}u_0^2}{2\tilde{D}^3 Y_d} \quad (4-16)$$

$\tilde{D}$  and  $\tilde{m}$  are the harmonic mean granule diameter and mass, respectively and  $\delta''$  is the extent of permanent plastic deformation given by:

$$\begin{aligned} \delta'' &= \left( \frac{8}{3\pi} \right)^{1/2} (St_{\text{def}})^{1/2} \tilde{D} \left[ 1 - \frac{1}{St_v} \ln \left( \frac{h_0}{h_a} \right) \right] \\ & \quad \times \left[ 1 - 7.36 \left( \frac{Y_d}{E^*} \right) (St_{\text{def}})^{-1/4} \right. \\ & \quad \left. \times \left( 1 - \frac{1}{St_v} \ln \left( \frac{h_0}{h_a} \right) \right)^{-1/2} \right] \end{aligned} \quad (4-17)$$

$St_{\text{def}}$  is the ratio of impact kinetic energy to plastic deformation in the granule matrix i.e. this number indicates the amount of plastic deformation expected if there were no liquid layer at the surface. An equivalent Stokes deformation number was derived by Irfan-Khan and Tardos [45] for predicting the maximum size of granules which can survive in a shear field (see Section 5).

The predictions of this model are shown in Fig. 18. For surface-wet granules, the model predicts that at low  $St_{\text{def}}$ , the likelihood of coalescence depends only on the critical

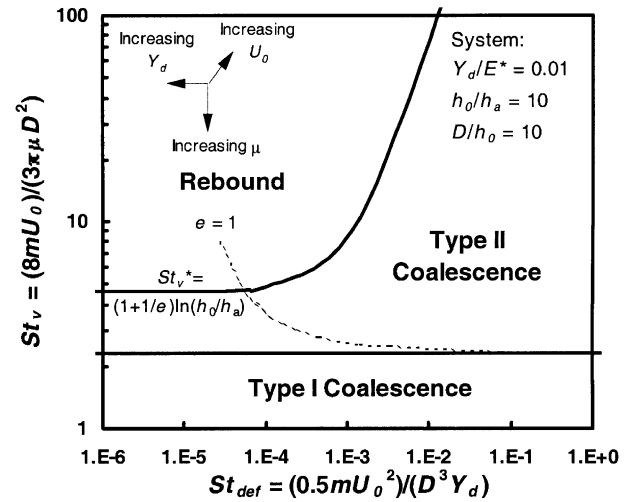


Fig. 18.  $St_v$  vs.  $St_{\text{def}}$  showing regions of rebound and coalescence for surface wet deformable granules (Source: Liu et al. [124]).

Stokes number,  $St_{\text{vis}}$ , as per the original model of Ennis et al. [18]. In this region the collisions are all fully elastic. However, as  $St_{\text{def}}$  increases, the coalescence region extends over a wider range of  $St_{\text{vis}}$ . This is because permanent granule deformation occurs which aids coalescence in two ways: (i) it dissipates some of the impact energy, and (ii) it creates a flat surface between the two granules which creates a greater viscous dissipation force during rebound. Unlike the model of Ennis et al. [18], this model predicts that when plastic deformation is significant, increasing impact velocity may actually improve the likelihood of coalescence by shifting a system from the rebound region back into the coalescence region.

Fig. 19 shows the predictions of Liu et al. [124] for the case where the granules are initially surface dry. A liquid layer of either constant thickness  $h_0$  or variable thickness  $\delta''$  is assumed to be squeezed into the contact zone by the impact deformation. In the low  $St_{\text{def}}$  region, no permanent plastic deformation occurs. Hence, no liquid binder is squeezed to the surface to prevent granule rebound. Above a critical value of  $St_{\text{def}}$ , the probability of coalescence becomes a function of  $St_{\text{vis}}$  and  $St_{\text{def}}$  in a similar way to the surface-wet case.

Although an improvement on the model of Ennis et al. [18] this model still suffers many of the same limitations. Capillary forces have been neglected. No account has been taken of any additional bond strength term due to particle interlocking between the two granule surfaces. The assumptions in the model are limited to cases where the amount of deformation is small. At higher deformations, there is also the possibility that granules may break during collisions (Section 5).

#### 4.3.2. Granule growth behaviour

The evolution of the granule size distribution during granulation is usually reported by plotting average granule

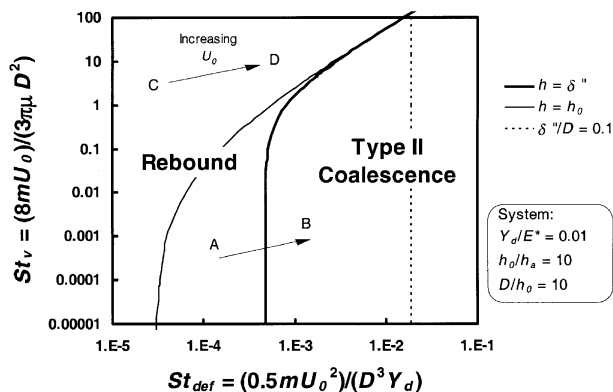


Fig. 19. Coalescence criteria for collision of surface dry granules [124].

size (usually mass-mean or mass-median) vs. time (e.g. Fig. 20). These plots show a number of characteristic regions [42,93,128]:

- **Nucleation** during which nuclei agglomerates are first formed as the liquid binder is added (Section 3).
- **Induction period** (also known as the “nuclei region” or “compaction stage”) during which the nuclei agglomerates are consolidated but do not grow substantially.
- **Coalescence growth** (or the transition region) occurs if granules are sufficiently deformable to coalesce without the presence of surface liquid or else when the agglomerates have consolidated sufficiently to squeeze moisture to the surface.
- Then there may be a final slow **ball growth** region where growth occurs slowly by a combination of crushing and layering, abrasion transfer or coalescence. A maximum granule size may or may not be reached.
- **Breakage and attrition** may follow in systems where the granules dry out and become weakened (Section 5).

There is not always a clear demarcation between these regions. Moist coarse feed may quickly densify and pass rapidly through the nucleation, induction and transition regions. Fine ground powders usually show all of the first four regions quite clearly [6]. These behaviours have been observed in a range of granulation equipment types including fluidised beds, drums and high-shear mixers.

It should be noted, that although widely used, these plots do not fully describe granule growth behaviour. The average size conceals the shape of the size distribution which may be important if the binder has been poorly distributed (see Fig. 4). These plots also do not reveal the underlying growth mechanisms. These subtleties can only be revealed by examining the full granule size distributions and through the use of tracer studies [78,120].

For closely sized materials, the growth rate (rate of increase of average granule size) has been found to be

more or less constant with time [3,4]. However, for more broadly sized materials the growth rate increases as the system moves from the nucleation region through the transition region, before dropping off again [129]. This was speculated to be because for broadly sized particles the increasing appearance of water at the granule surface due to consolidation dominates the decrease in granule deformability.

Kapur and Fuerstenau [128] found that in the ball-growth region, growth occurred by the coalescence and abrasion-transfer mechanisms. They used relatively fine-sized limestone powders. However, Capes and Danckwerts [4] found that in the ball-growth region, granules grew by the crushing and layering mechanism. They used coarse, narrowly sized sands in their work. Linkson et al. [78] explained these different findings by proposing that small, broadly sized particles promoted growth by coalescence (since these granules are too strong to be crushed) and that narrowly sized, coarse particles grew by crushing and layering (since these granules are relatively weak).

**4.3.2.1. Granule growth regimes.** Iveson and Litster [93] proposed that there are two broad categories of granule growth behaviour: *steady growth* systems where granule size increases linearly with time and *induction growth* systems where there is a delay period during which little growth occurs (cf. Figs. 20 and 22). These two classes of behaviour have been observed in both tumbling drum granulators and high shear mixers [42,78].

*Steady growth* occurs in systems with weak, deformable granules (low strength and/or high impact forces). Granules grow by either the crushing and layering mechanism or else they deform, creating a large contact area during impact which promotes coalescence. Steady growth is generally exhibited by relatively coarse, narrowly sized particles with low viscosity binders.

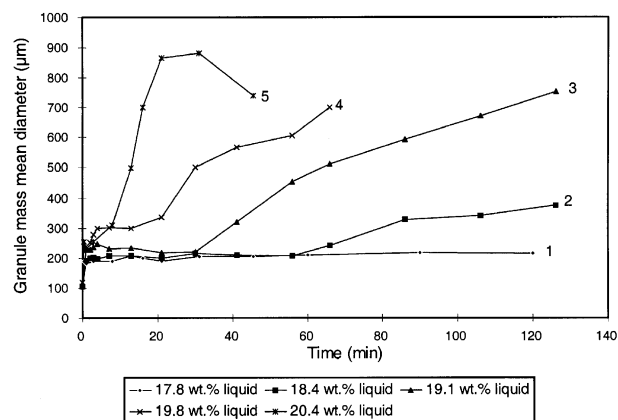


Fig. 20. Effect of liquid content on the growth behaviour of sodium sulphate and cellulose mixtures during batch granulation in a Lödige high shear mixer: (1) Nucleation only; (2–4) Induction time followed by rapid growth; (5) rapid growth followed by breakage (Source: Hoornaert et al. [42]).

*Induction growth* occurs in systems which are relatively strong. The granules do not deform sufficiently during impact to coalesce without the presence of liquid at the surface. Hence, after the initial nuclei form, there is a delay period during which little growth occurs. If the granules consolidate sufficiently to squeeze liquid to the surface, then they will begin to grow quickly until a critical size is reached, above which the torque experienced by dumbbell pairs becomes too large for further coalescence growth. Induction growth is generally seen in systems with fine, widely sized particles and/or viscous binders. Induction growth has not been reported in fluidised beds, probably because the impact forces are too low to cause significant granule consolidation.

Iveson and Litster [93] postulated that the type of granule growth behaviour which a system exhibits is a function of only two basic parameters: the maximum pore liquid saturation and the amount of granule deformation during impact. Granule pore liquid saturation will vary during batch granulation as the granules consolidate and any soluble components gradually dissolve. Therefore, they used the maximum granule pore saturation ( $s_{\max}$ ) as the measure of liquid content:

$$s_{\max} = \frac{w\rho_s(1 - \varepsilon_{\min})}{\rho_l \varepsilon_{\min}} \quad (4-18)$$

where  $w$  is the mass ratio of liquid to solid,  $\rho_s$  is the density of the solid particles,  $\rho_l$  is the liquid density and  $\varepsilon_{\min}$  is the minimum porosity the formulation reaches for that particular set of operating conditions. The liquid saturation term must include any extra liquid volume due to solids dissolution, but should not include liquid which is absorbed into porous particles.

The typical amount of deformation during impact was characterised by a Stokes deformation number:

$$St_{\text{def}} = \frac{\rho_g U_c^2}{2Y_g} \quad (4-19)$$

where  $U_c$  is the representative collision velocity in the granulator and  $\rho_g$  and  $Y_g$  are the granule density and dynamic yield stress, respectively. Both  $Y_g$  and  $\rho_g$  will vary with the formulation properties and granule porosity and should be measured at the characteristic porosity reached by the granules in the granulator,  $\varepsilon_{\min}$  (Eq. (4-6)). The Stokes deformation number is a measure of the ratio of impact kinetic energy to the plastic energy absorbed per unit strain. It takes into account both the process agitation intensity and the granule mechanical properties.

The type of granule growth behaviour as a function of  $s_{\max}$  and  $St_{\text{def}}$  was plotted on a regime map (Fig. 21). Steady and induction growth have already been discussed. *Nucleation only* growth occurs when granule nuclei form, but there is insufficient binder to promote further growth [24,117]. *Crumb behaviour* occurs when the formulation is

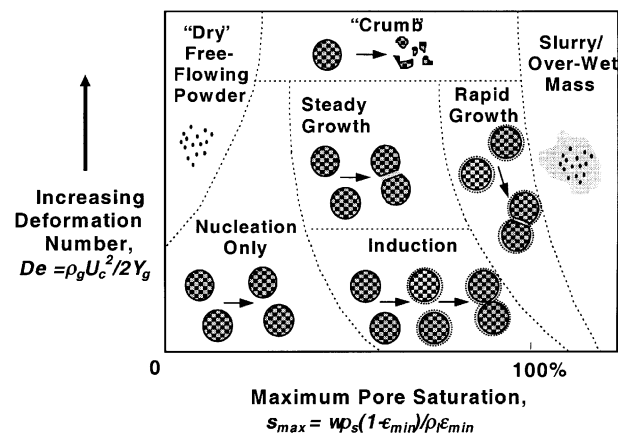


Fig. 21. Granule growth regime map (Adapted from Iveson and Litster [93]).

too weak to form permanent granules, but instead forms a loose crumb material which cushions a few larger granules which are constantly breaking and reforming [4]. *Overwetting* occurs when excess binder has been added and the system forms an oversaturated slush or slurry.

Preliminary verification of this regime map was performed using drum granulation data for the granulation of sands with water and ethanol solutions, and glass ballotini with water and glycerol solutions. It was also used to explain the many observed effects of parameters such as binder content, particle size, and binder viscosity and surface tension which have been observed in the literature (Section 4.3.2.2).

However, although it is successful at qualitatively explaining the observed effects of different parameters, this regime map requires further experimental validation with a range of materials under different granulation conditions in order to quantitatively locate the various regime boundaries. It is also currently limited to being a *descriptive* tool, not a *predictive* one. This is because the two parameters,  $s_{\max}$  and  $St_{\text{def}}$ , require a priori knowledge of the maximum extent of consolidation ( $\varepsilon_{\min}$ ) since this affects granule yield stress and pore saturation. Another significant shortcoming is the very simplistic rheological model used to describe the mechanical properties of the granules. It is assumed that the granules are rigid-plastic materials. Wet granular materials are actually complex viscoelastic-plastic materials with strain-rate and history dependent behaviour. Subsequent work suggests that binder viscosity needs to be included as a third independent parameter on the map and also highlights the great difficulty of comparing different types of equipment because of the uncertainty of the correct characteristic impact velocity [130].

#### 4.3.2.2. Effects of different parameters on granule growth behaviour

*Binder content.* Increasing binder content increases a formulation's maximum pore saturation which shifts it to

the right on the granule growth regime map, from nucleation through one of the two growth types and eventually to a slurry (Fig. 21). In steady growth systems, the granule growth rate increases rapidly with increasing binder content [3,79,111,128,131] (Fig. 22). This is because moist granules tend to be more easily deformable (due to reduced inter-particle forces), have lower coefficients of restitution and have more binder available at their surfaces, all of which aid coalescence growth, Eqs. (4-10), (4-11) and (4-15). Ritala et al. [132] showed that it was the pore saturation which was the critical factor—the growth curves for dicalcium phosphate with a wide range of different binders all collapse onto one curve when plotted against granule pore saturation (Fig. 23).

Increasing the liquid content reduces the amount of consolidation required for granules to become saturated and usually also increases the rate of consolidation (Section 4.2). Hence, in induction type systems, increasing the binder content usually decreases the length of the induction period (e.g. Fig. 20; [42,49]). The increase in binder content will also usually increase the final equilibrium size reached.

**Particle size.** Decreasing particle size increases granule yield strength, which moves a formulation downwards on the growth regime map from crumb, to steady growth to induction growth behaviour (Fig. 21; [93]). Above a critical particle size, wet powder masses become too weak to form granules and instead form a loose crumb material. The critical particle size depends on the binder surface tension [4], viscosity [79] and presumably also on the particle size distribution, morphology and surface roughness.

Below this critical size, granules made from relatively large and/or mono-dispersed particles tend to grow more quickly [4,79]. This is because large, narrowly sized particles produce weak, deformable granules with low coefficients of restitution. This aids coalescence growth, Eq. (4-11) and (4-15). In addition, weak granules also break apart more easily, enabling continued growth by a combined crushing and layering mechanism.

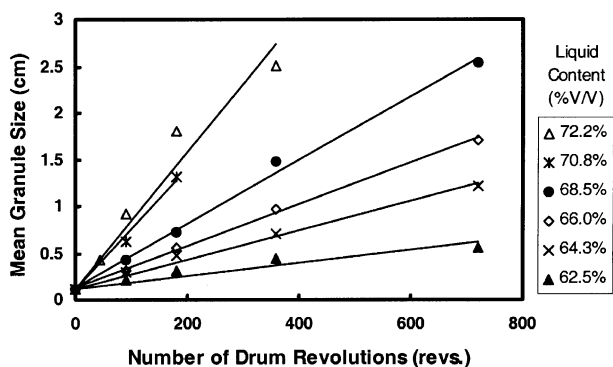


Fig. 22. Granule size vs. number of drum revolutions for the drum granulation of 67  $\mu\text{m}$  silica sand with varying moisture contents (Source: Newitt and Conway Jones [3]).

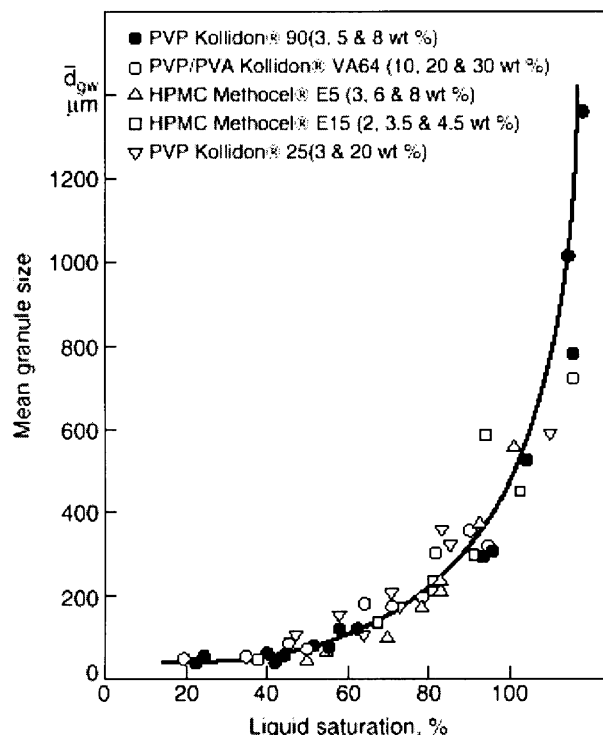


Fig. 23. Mean granule size vs. pore saturation for calcium hydrogen phosphate with a range of different binders in a 25-l high shear mixer (Source: Ritala et al. [132]).

Granules made of fine or wide-size distributions are stronger and less deformable and so tend to grow more slowly and reach a smaller maximum size [133]. As particle size becomes even smaller, granules become so strong that they do not deform sufficiently to coalesce unless there is already binder present at their surface. These formulations have an induction period during which sufficient consolidation must take place to squeeze binder to the surface. Hence, decreasing particle size can shift a system from steady to induction growth [78,93].

**Binder surface tension.** Decreasing binder surface tension lowers a formulation's dynamic yield strength [100] which increases  $St_{\text{def}}$ . This should shift its behaviour upwards from induction, through steady growth, to the crumb region on the growth regime map (Fig. 21). Systems with low-surface tension binders behave similarly to large/mono-sized particles [4]. Lowering binder surface tension reduced the maximum granule size and results in crushing and layering growth with a large amount of "crumb" material present at any time which cushions the surviving larger granules. Capes and Danckwerts [4] found that granules would only develop if the ratio of surface tension to particle size ( $\gamma_{\text{LV}}/d_p$ ) was greater than 0.46 mN/(m  $\mu\text{m}$ ). Otherwise, only a weak "crumb" would form which constantly broke apart (Fig. 24). This ratio is proportional to the granule tensile strength predicted by the theory of Rumpf, Eq. (4-4), which suggests that there is a minimum strength needed for granules to form and survive.



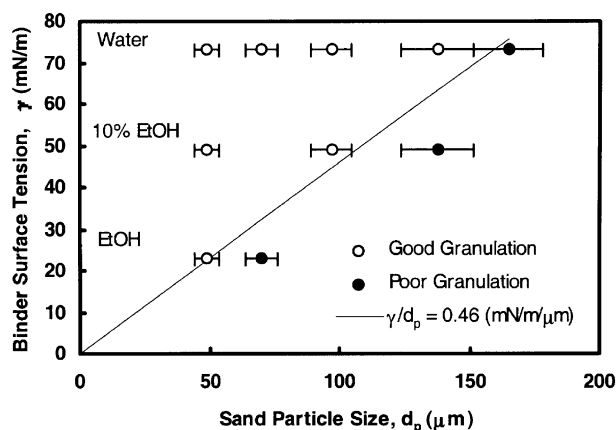


Fig. 24. Binder surface tension vs. particle diameter for drum granulation of sands with water–ethanol solutions showing systems that did and did not granulate satisfactorily (Source: Capes and Danckwerts [4]).

Reducing binder surface tension will make granules weaker and more easily deformable (Section 4.1). According to Eq. (4-15), this should make coalescence easier and hence increase the granule growth rate. However, lowering binder surface tension will reduce the strength of the bond formed between the two colliding granules, which will decrease the likelihood of permanent coalescence, but this is not considered in Eq. (4-15) which only accounts for viscous effects. Therefore, it is unclear what the effect of surface tension will be on the granule growth rate, although it is expected that the maximum equilibrium size of granules will be reduced if surface tension is lowered.

Unfortunately, Capes and Danckwerts [4] did not report whether or not altering the binder surface tension affected the growth rates or maximum size of the systems they studied. Few other workers have systematically studied the effects of varying binder surface tension. Ritala et al. [112] studied five different binder solutions in a 25-l high shear mixer. Kollidon 90, which had a significantly higher surface tension than the other four solutions (67 vs. 46–54 mN/m), did not have any significant difference in growth behaviour, although it did cause a much higher mixer power consumption.

**Binder viscosity.** Binder viscosity influences three of the key rate process involved in granulation: binder dispersion, consolidation and growth. Hence, changes in viscosity can cause varied responses in different systems, since viscosity has different effects on each mechanism.

Increasing binder viscosity generally inhibits binder atomisation and dispersion. Hence, a viscous binder will often form larger initial nuclei [42] and may take longer to disperse uniformly through the powder. This will delay the onset of uniform growth [41]. A more detailed discussion of viscous effects on nucleation behaviour is given in Section 3.

For large particle systems, there is a critical minimum viscosity required to form granules of sufficient strength to survive the process (Fig. 25). Kenningley et al. [92] devel-

oped a simple model to predict the critical ratio of viscosity to particle size by equating the kinetic energy of impact to the energy absorbed by plastic deformation of granules and assuming a maximum strain above which the granules would break. As particle size increases, the critical minimum viscosity required to form granules also increases (Eq. (5-4)). Details of this model are given in Section 5 on breakage and attrition.

Increasing binder viscosity reduces granule consolidation rate and increases granule strength (Sections 4.1 and 4.2). This reduces the pore saturation and area of contact formed during collisions, both of which inhibit granule growth, Eqs. (4-11) and (4-15). However, once a viscous binder reaches the surface, it is more effective at dissipating the kinetic energy of collision, and hence promotes coalescence, Eqs. (4-10) and (4-15). Hence, low viscosity binders may promote faster initial growth, but once a viscous binder is squeezed to the surface, it will promote the fastest long-term growth [41]. If binder viscosity is too high, then it may prevent liquid binder ever being squeezed to the surface.

Therefore, in many systems there may be an optimum binder viscosity for promoting granule growth [14,120]. This has been observed in drum granulation experiments with glass ballotini and silicone oils. Simons et al. [120] used 40–92  $\mu\text{m}$  glass ballotini and found the initial equilibrium nuclei size was a maximum at 100 cS. Higher and lower viscosities both gave smaller nuclei. These experiments were stopped after 400 revolutions, so whether or not sufficient binder would ever have been squeezed to the surface to promote rapid growth is unknown. Knight and Seville [39] granulated 90–180  $\mu\text{m}$  glass ballotini. These systems displayed steady growth behaviour, with the fastest initial growth rate occurring at a viscosity of 100 mPa s. Higher and lower viscosities both gave lower growth rates.

Below this optimum viscosity, increasing binder viscosity increases the granule growth rate, Eq. (4-10). Adetayo et al. [134] found such a correlation between growth rate and binder viscosity for various fertiliser formulations with solution viscosities varying between 3.4 and 8.5 cP in a

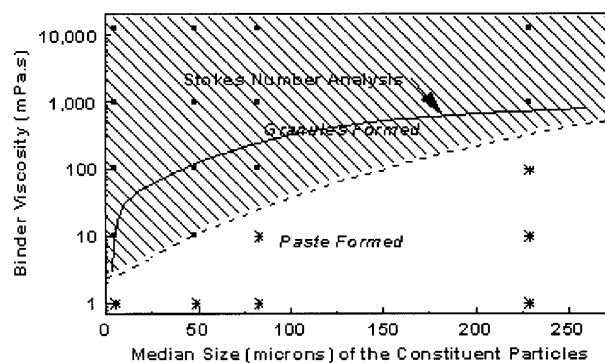


Fig. 25. Binder viscosity vs. median particle size showing regions in which granules did and did not form for agglomeration of glass ballotini with silicone oils in a high shear mixer. Line shows prediction of Eq. (5-4) (Source: Kenningley et al. [92]).

tumbling drum. In fluidised-bed granulation, Ennis et al. [18] found that increasing binder viscosity from 0.036 to 0.17 Pa s increased the final granule size, although the initial rate of granule growth remained the same. In high shear mixer granulation increasing binder viscosity from 0.0034 to 0.009 Pa s has been observed to increase both the rate and extent of granule growth [135]. Ritala et al. [112] observed an increase in growth rate when they increased the concentration of the binder solution for four of the five binders they tested. During melt granulation in high shear mixers, Schæfer and Mathiesen [41] found that for binder viscosities above about 1000 mPa s, “uncontrolled” granule growth occurred unless compensated for by increasing the impeller speed to increase the breakage rate.

However, above the optimum viscosity, the effect of binder viscosity on granule deformability become dominant and granule growth is inhibited, Eq. (4-10). For instance, Hoornaert et al. [136] noted that increasing binder viscosity from 3.9 to 9.3 mPa s increased the initial stable nuclei size and the final size after the induction growth period. However, in later work they found that increasing the binder viscosity further to 16.4 and 22.0 mPa s reduced the final extent of granule growth [42].

These varied observations suggest that the value of the optimum viscosity is highly system dependent. It is likely to depend on the morphology and size of the particles and the type and speed of the granulator.

Iveson and Litster [93] found that binder viscosity also influenced the type of granule growth. During the drum granulation of glass ballotini with water and glycerol solutions, increasing binder viscosity shifted the growth behaviour from steady to induction growth. This occurs because increasing binder viscosity increases granule yield strength, decreasing  $St_{def}$ , which shifts a formulation downwards on the granule growth regime map (Fig. 21).

*Equipment speed and type.* Equipment operating speed has a complex effect on granulation behaviour because it alters both the frequency and energy of collisions between granules. Hence, it can directly affect both the kinetics and extent of granule growth. It can also change the properties of the granules themselves by altering the rate and extent of consolidation, which affects granule pore saturation. At high impeller speeds the temperature of the wet mass is increased, which increases granule deformability by lowering binder viscosity, and also increases the rate of binder evaporation [116]. All these effects are confounded, and hence often confused in the literature when results are discussed.

According to Eq. (4-6), for non-deformable, surface-wet granules, increasing impact speed should decrease the rate and extent of granule growth. This has been observed in fluidised bed granulators. Nienow and Rowe [137] found that increasing the excess gas velocity ( $U - U_{mf}$ ) caused a large decrease in the final equilibrium granule size. Several studies also show an increase in impeller speed reduces the

final granule mean size in high shear mixers or agitated fluidised beds [138–140]. However, care must be taken not to confuse growth and breakage phenomena. Ramaker et al. [140] showed that the decrease in granule size with increasing impeller speed was a reversible process. Experiments with coloured tracers showed that the equilibrium was a dynamic one between coalescence and breakage (see Section 5).

For deformable, surface-dry granules, Eq. (4-10) predicts that increasing impact speed will increase the rate of granule growth due to the increased area of contact formed. This has been observed for increases in drum rotation speed [3] and increasing mixer impeller speed [111,114,131]. However, these results must also be interpreted carefully, since the frequency of collisions has also increased. When Newitt and Conway-Jones [3] compared their drum granulation results on the basis of the number of drum revolutions, the results collapsed onto one curve. Similarly, the high shear mixer results of Schæfer et al. [64] all collapse onto one curve when compared on the basis of the number of impeller revolutions [118]. However, in other cases even when growth rates are compared on the basis of number of impeller revolutions, the higher impeller speed still gave higher growth rates [131]. In later work, Knight et al. [138] showed that there was an upper limit to this effect, beyond which the increasing prominence of breakage acted to reduce the overall growth rate as the impeller speed was further increased.

Hence, provided that breakage does not occur, increasing the equipment speed generally increases the rate of granule consolidation (Section 4.2). Hence, in induction growth systems, increasing equipment speed should reduce the length of the induction period. There is some suggestion of this effect in the high-shear melt granulation results of Schæfer et al. [64], but since impeller speed also affects the temperature, and hence viscosity of the binder, these results are inconclusive. Interestingly, Menon [141] found that the ploughshare speed had no effect on the induction time of a  $Na_2SO_4$  formulation in a horizontal Lödige mixer, which is unexpected.

In high shear mixers, the relative importance of the main impeller and the chopper appear to be strongly dependent on mixer geometry and formulation properties. Knight [131] found that the speed of a chopper with “knife-like” blades had no effect on the granule growth rate in a vertical shaft mixer, although it did reduce the number of large granules. However, Hoornaert et al. [42] found that turning off the “Christmas tree” chopper in a horizontal shaft mixer caused granule growth to stop. This formulation was one which displayed induction growth behaviour and the chopper was thought to be necessary to compact the granules sufficiently to trigger growth.

#### 4.4. Granule growth conclusions

In conclusion, we now have a good understanding of the mechanisms which control granule growth and the

effect of process variables on these mechanisms. There are also a range of coalescence models available for making quantitative predictions about the maximum granule size attainable and the effect of process or formulation changes on granule growth behaviour.

However, none of these models are currently in use industrially to predict or control granulation processes. The reason for this is our lack of knowledge of the various parameters in the models. These models all require a knowledge of the dynamic mechanical properties (e.g. coefficient of restitution, yield stress, elastic modulus, critical strain) of liquid-bound granular assemblies. Hence, there is a need to develop standard experimental techniques for measuring these values *at the strain rates of interest*. This is challenging because of the intermediate range of strain rates involved. Typical granule impact velocities are of the order of 1 m/s. Most commercial load frames will not achieve strain rates this high. However, impact devices such as swinging pendulums and gas guns, are usually designed for much higher strain rates.

Another challenge is to develop models to predict the mechanical properties at different strain rates based on the formulation properties (particle size distribution, liquid surface tension and viscosity, granule porosity, etc.). This modelling task will be difficult because of the three forces involved—capillary and viscous forces in the liquid phase and friction forces at interparticle contacts—which are inter-related in a complex way. Such models will need to account for dynamic effects such as liquefaction which may become important in many granulation processes. DEM simulations have made some progress in this direction, although much further work is required.

A second problem in applying theoretically developed models of coalescence is that we do not have a good understanding of the frequency and velocity of impacts that granules experience in typical granulators. Coalescence models only tell us whether or not a collision of a given energy will result in coalescence. The actual rate of growth will depend on the *frequency* of such collisions. This is a particular problem during scale-up or when comparing two different designs of granulators.

Impact velocity has traditionally been estimated by a single, order of magnitude estimate (such as impeller tip-speed in mixers or  $U - U_{mf}$  in fluidised beds). However, these estimates are crude at best, and fail to capture the fact that a range of impact conditions occur in any device. The controlling parameter may vary with design and operating conditions, such as in high shear mixers where the impeller and chopper speeds have been found to have different effects by different workers.

Hence, now that a theoretical framework is available to sensibly predict and control granule growth behaviour, experimenters need to measure the parameters needed to use these models. It is no longer sufficient to report only the particle size distribution and granule growth curves. Measurements of the mechanical properties of the com-

pacts must be made and the granulator processing conditions characterised. In addition, since consolidation and growth are both rate processes which eventually reach an equilibrium, it is important that experimenters continue experiments until equilibrium is reached. Otherwise, it is difficult to distinguish between kinetic and equilibrium effects.

## 5. Breakage and attrition

In reviewing granule breakage, there are really two separate phenomena to consider:

1. Breakage of *wet* granules in the granulator; and
2. Attrition or fracture of *dried* granules in the granulator, drier or in subsequent handling.

Breakage of wet granules will influence and may control the final granule size distribution, especially in high shear granulators. In some circumstances, breakage can be used to limit the maximum granule size or to help distribute a viscous binder. On the other hand, attrition of dry granules leads to the generation of dusty fines. As the aim of most granulation processes is to remove fines, this is generally a disastrous situation to be avoided.

### 5.1. Breakage of wet granules

#### 5.1.1. Experimental observations

Few investigators have described or studied wet granule breakage in granulation processes. Some preferential growth mechanisms in tumbling granulation may involve attrition or breakage of weak granules (crushing and layering, abrasion transfer) [142]. However, breakage is much more likely in higher intensity mixer and hybrid granulators. The limited work on wet granule breakage focuses on these types of equipment.

Several studies show an increase in agitation intensity (increased impeller speed) reduces the final granule mean size in granulation experiments [138,139,143]. For example, Fig. 26 shows how the median granule size from three scales of agitated fluid bed granulator decreases with increasing agitator tip speed. However, reduction in product size with increased agitation could also be explained by a reduction in the maximum granule size for coalescence (Eq. (4-6)). Therefore, changes to granule size distribution, *on their own*, are insufficient evidence for wet granule breakage as a key mechanism for controlling granule properties.

Nevertheless, wet granule breakage has been identified clearly in high shear mixer experiments by other means. Ramaker et al. [35,140] and Pearson et al. [144] have used coloured tracer granules or liquid to identify breakage of wet granules. Pearson et al. added narrow size fractions of well-formed tracer granules part way through a batch high

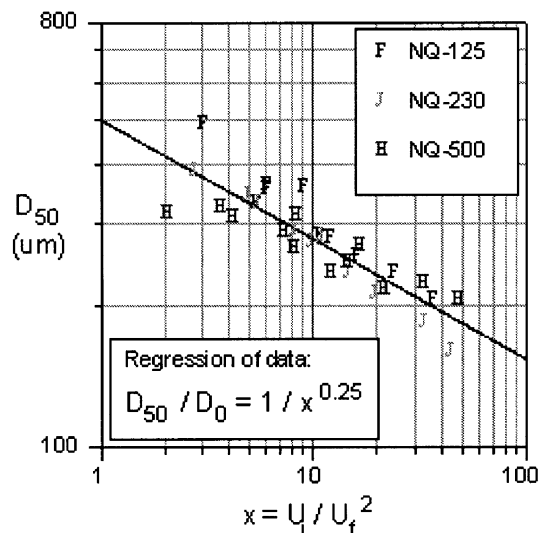


Fig. 26. Effect of impeller speed on median particle size  $D_{50}$  in three agitated fluid bed granulators (Source: Tardos et al. [25]).  $U_1$  is impeller tip speed,  $U_f$  is fluidisation velocity, and  $D_0$  is the  $D_{50}$  intercept at  $x = 1$ . Fluid bed diameter in mm indicated by model number (i.e. NQ-125 is 125 mm diameter).

shear granulation. Some of the tracer granules were broken, leaving coloured tracer fragments in smaller granule size fractions. Large tracer granules ( $> 1$  mm) were more likely to be broken than smaller granules (Fig. 27). Knight et al. [138] showed mean granule size decreased after impeller speed was suddenly increased part way through a batch high shear mixer experiment. This was attributed to granule breakage.

Ramaker et al. added a coloured liquid at the start of the granulation process and observed the dispersion of the dye through a process of “destructive nucleation” where loosely bonded nuclei are broken down into smaller fragments via attrition or fragmentation (Fig. 28). The initial weak nuclei

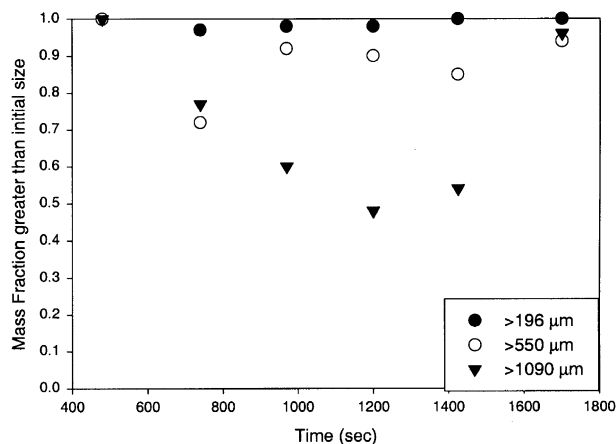


Fig. 27. Breakage of tracer granules in high shear mixers: Effect of tracer granule size on mass fraction of unbroken granules (Source: Pearson et al. [144]).

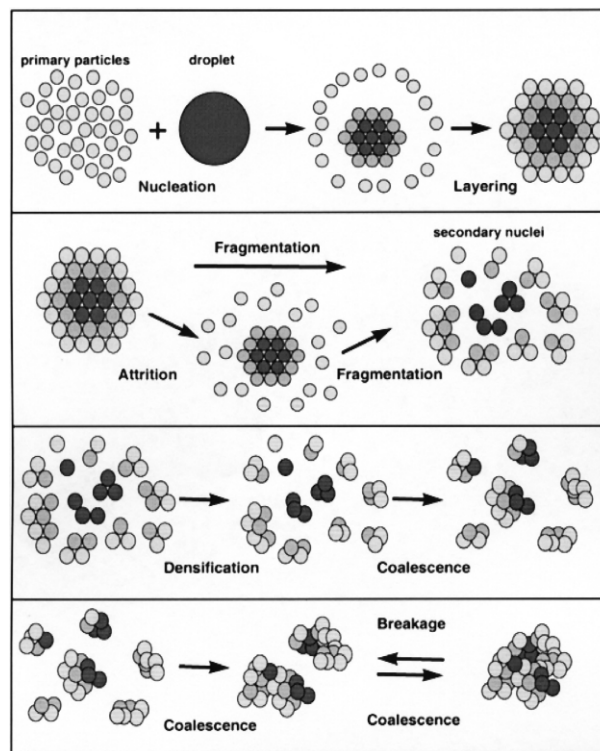


Fig. 28. The destructive nucleation mechanism proposed by Vonk et al. [35].

were quite large in these experiments (5 mm diameter). We can view this process as simply a subset of breakage processes in the granulator. In fact, all binder distribution in the “mechanical dispersion regime” (Fig. 7) is essentially a breakage process and should be treated as such.

In summary, wet granule breakage is potentially an important process affecting binder distribution and granule size in high intensity processes. Therefore it is important to establish the conditions under which breakage will occur.

### 5.1.2. Predicting conditions for breakage

There is very little quantitative theory or modelling available to predict conditions for breakage, or the effect of formulation properties on wet granule breakage. Tardos et al. [25] and Kenningley et al. [92] present the only two serious attempts to predict conditions for breakage of wet agglomerates. Tardos et al. [25] consider granules will deform and break in shear fields if there is sufficient externally applied kinetic energy. This analysis leads to a Stokes deformation number criteria for breakage:

$$St_{\text{def}} > St_{\text{def}}^* \quad (5-1)$$

where

$$St_{\text{def}} = \frac{m_p U_o^2}{2V_p \tau(\dot{\gamma})} \quad (5-2)$$

There are strong analogies to the development of the Stokes deformation number for granule deformation and growth (Section 4.3, Eq. (4-13)). Tardos et al. propose a more general characteristic stress than the dynamic yield stress in Eq. (4-13). They postulate the granule will behave under shear as a Herchel–Buckley fluid i.e.

$$\tau_y(\dot{\gamma}) = \tau_y + k\dot{\gamma}^n \quad (5-3)$$

Two simplifications were considered, neglecting either the apparent viscosity ( $\tau_y(\dot{\gamma}) = \tau_y$ ) or the yield stress ( $\tau_y(\dot{\gamma}) = k\dot{\gamma}^n$ ). In either case, the model predicts granules above a maximum size will break and that this size decreases with increasing shear rate.

Tardos et al. [25,45] measured granule deformation and break up under shear in a novel constant shear fluidised bed granulator. Granules first elongated under shear and then broke at a Stokes deformation number, Eq. (5-2), of approximately 0.2.

There are some limitations to this work. In mixer granulators, granules are more likely to break on impact with the impeller, rather than in shear. We believe the appropriate “critical stress” should be the dynamic yield stress measured under high strain rate conditions, as discussed in Section 4. Even this is an oversimplification. A purely plastic granule will smear rather than break when its yield stress is exceeded. At high impeller speeds such materials will coat the granulator wall or form a Paste. More brittle granules will break at high impact velocity given a maximum stable granule size or a weak crumb. Thus, a lot of information is needed about the granule mechanical properties to predict their breakage behaviour.

Kenningley et al. [92] developed a relationship for breakage (crumb, paste) or survival of granules in high shear mixer granulation by equating the kinetic energy of impact to energy absorbed by plastic deformation of granules. Granule yield strength was assumed to be due to viscous pressure loss for fluid flow between particles by the Kozeny–Carman equation. The amount of strain ( $\varepsilon_m$ ) was given by:

$$\varepsilon_m^2 = \frac{1}{540} \frac{\varepsilon^3}{(1-\varepsilon)^2} \frac{\rho u d_{32}}{\mu} \quad (5-4)$$

where  $d_{32}$  is the Sauter mean size of the granules’ constituent particles. Increasing particle size or decreasing viscosity increase the amount of impact deformation. Above a critical value of  $\varepsilon_m$  (taken as 0.10 by Kenningley et al.), granules will break. Eq. (5-4) showed reasonable agreement with their experimental data (Fig. 23).

The approaches of Tardos and Kenningley both show promise as a basis for predicting wet granule breakage. More data is needed measuring granule breakage for granules with a wide range of (carefully characterised) mechanical properties.

Controlling wet granule breakage gives the opportunity to give a narrow granule size distribution by growing

granules up to a breakage limit [20,25,138,140]. This has been the driving force in the development of some newer granulator designs [139,145]. It is important to note that size distribution control will also depend on the impact velocity *distribution* and turnover of granules through the high impact region (impeller or chopper). Granulators with broad impact velocity distributions and small, uncontrolled turnover through the high impact region are unlikely to ever yield narrow granule size distributions.

## 5.2. Attrition and fracture of dry granules

Most granulation processes involve drying granules either simultaneously (fluidised bed and spouted bed granulators) or immediately after granulation in a separate drier. Attrition or fracture of the granules during granulation, drying or subsequent handling is generally undesirable. Therefore understanding the attrition process and the parameters which affect it is important.

There is limited fundamental work on the fracture of dry granules but we can draw on more general understanding of the fracture of brittle and semi-brittle materials.

### 5.2.1. Fracture properties of dry granules

From the point of view of breakage, we can consider a dry granule as a non-uniform physical composite rather than an agglomerate of primary particles. The composite possesses certain macroscopic mechanical properties including a yield stress. Instead of porosity, we see an inherent distribution of cracks and flaws. Dry granules fail in brittle or semi-brittle fashion i.e. they fail in tension by the propagation of pre-existing cracks which concentrate stress. Thus, the fracture stress may be much less than the inherent tensile strength of bonds between particles in the granule.

Consider a semi-brittle material failing by crack propagation (Fig. 29). The tensile stress concentrates near the crack tip and is much higher than the applied stress leading to local yielding near the crack tip (the process zone). The crack will propagate from the edge of the process zone. The fracture toughness of the granule  $K_c$  defines the elastic stress field in the granule ahead of the propagating crack and is given by [146,147]:

$$K_c = T\sigma_f \sqrt{\pi(c + \delta_c)} \quad \text{with } \delta_c \sim r_p \quad (5-5)$$

where  $Y$  is a geometrical calibration factor,  $\sigma_f$  is the applied fracture stress,  $c$  is the length of the crack and  $\delta_c$  is the process zone size which in this case is of the same order as the primary particle radii,  $r_p$ . The process zone size is a measure of the yield stress or plasticity of the material in comparison to its brittleness. Yielding within the process zone may take place either plastically or by diffuse microcracking, depending on the brittleness of the material.

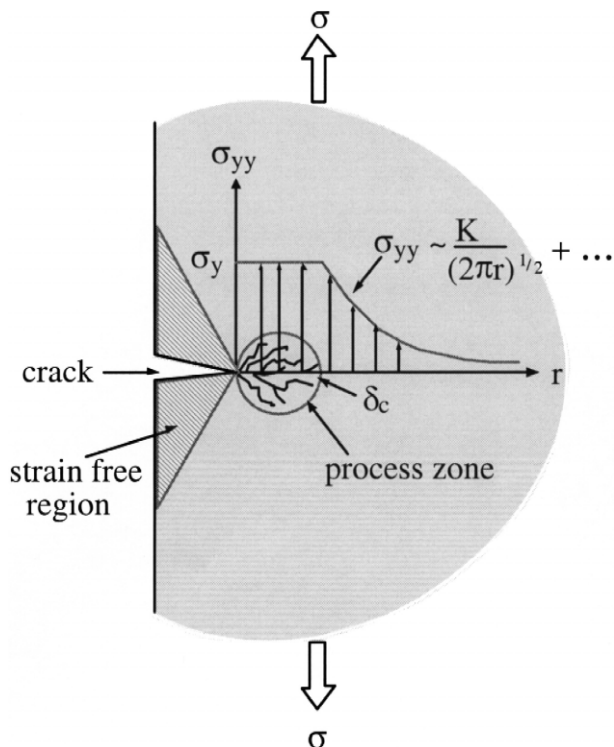


Fig. 29. Fracture of a semi-brittle material by crack propagation.

To measure fracture properties reproducibly, very specific test geometry must be used since it is necessary to know the stress distribution at predefined induced cracks of known length. Three traditional methods are the three-point bend test, indentation fracture testing and Hertzian contact compression between two spheres. These techniques are well established for ceramic compacts and single crystals [148,149].

Fig. 30 shows a schematic of a three-point bend test. Firstly, formulation powder is premixed with liquid binder to the expected level for granulation. A series of bars, each of known crack length, are formed by compacting the moist premix in moulds containing a razor notch. The bars are then dried. The force displacement of the bars is then measured up to fracture in a three-point bend test (Fig. 31).  $K_c$  and  $\delta_c$  are then determined by regressing the measured fracture stress against the known crack length, Eq. (5-5).

The main difficulty with the three-point bend test for agglomerated materials is in the preparation of the bars. Results are sensitive to the way the bars are made and the bar structure will not match exactly the structure of a granule formed in, for example, a mixer granulator. Nevertheless, the technique has been used successfully to study fundamentals of granule fracture, as well as for process troubleshooting [150,151].

Fracture toughness and hardness can also be determined from indentation tests [152,153]. An indent is made in a granule with known maximum force  $F$ . The hardness  $H$  is determined from the area  $A$  of the residual plastic impression and the fracture toughness from the length of the cracks  $c$  propagating from the indent as a function of load:

$$K_c = \beta \sqrt{\frac{E}{H} \frac{F}{c^{3/2}}} \quad \text{and} \quad H = \frac{F}{A} \tag{5-6}$$

where  $E$  is the elastic modulus of the material.

For this technique to be useful for agglomerates, the indentation must be large compared to the size of the feed particles but small compared to the size of the product granule. Careful presentation of the granule to the indenter is also important. This test does have the advantage that measurements can be made on real granules.

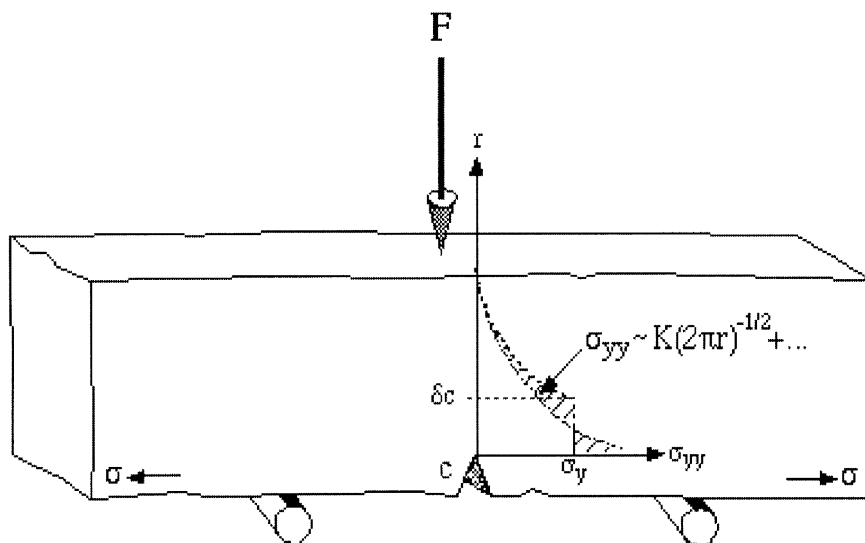


Fig. 30. Schematic of three-point bend test apparatus.

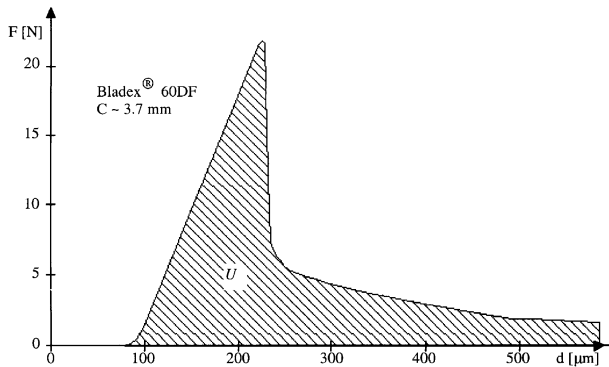


Fig. 31. Three point bend test results: Typical force displacement curve for semi-stable fracture.

The heterogeneous nature of agglomerates means they exhibit more variability in mechanical testing than some other materials and consistent sample preparation is very important. Nevertheless, the key advantage of these tests remains that fundamental properties are measured and the influence of natural flaw distribution on the results is small.

Results from such tests show that typical granule materials have fracture toughnesses in the range 0.01 to 0.06 MPa m<sup>0.5</sup> and process zone lengths of order 0.1 to 1mm (see Table 2).

### 5.2.2. Breakage mechanisms for dry granules

The process zone plays a large role in determining the mechanism of granule breakage. Agglomerates with small process zones in comparison to granule size break by a brittle fracture mechanism into smaller fragments (Fig. 32a). This mechanism is called **fragmentation** or **fracture**.

However, for fracture to occur the granule must be able to concentrate enough elastic energy to propagate gross fracture during collision. This is harder to do as the process zone size increases. For well defined compacts under controlled stress testing conditions, it can be shown both theoretically and experimentally that fracture will

Table 2  
Fracture properties of agglomerate materials [151]

Material	$K_c$ (MPa m <sup>1/2</sup> )	$\delta_c$ (μm)	$E$ (MPa)
Bladex 60 <sup>TM a</sup>	0.070	340	567
Bladex 90 <sup>TM a</sup>	0.014	82.7	191
Glean <sup>TM a</sup>	0.035	787	261
Glean Aged <sup>TM a</sup>	0.045	3510	465
CMC-Na (M) <sup>b</sup>	0.157	641	266
Klucel GF <sup>b</sup>	0.106	703	441
PVP 360 K <sup>b</sup>	0.585	1450	1201
CMC 2% 1 kN <sup>b</sup>	0.097	1360	410
CMC 2% 5 kN <sup>b</sup>	0.087	1260	399
CMC 5% 1 kN <sup>b</sup>	0.068	231	317

<sup>a</sup>DuPont corn herbicides.

<sup>b</sup>50 μm glass beads with polymer binder.

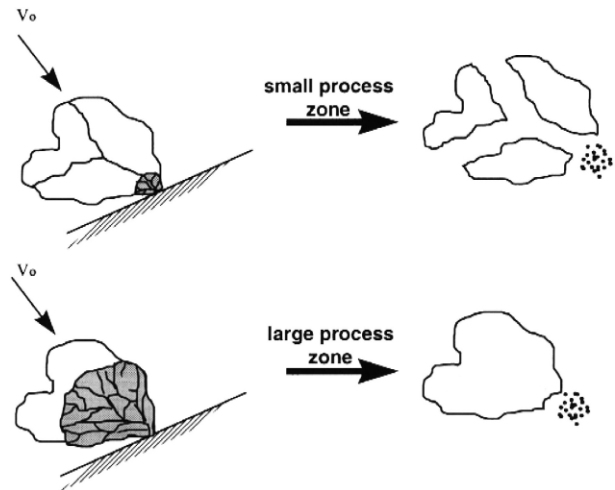


Fig. 32. Schematic of breakage by (a) fracture, and (b) erosion/attrition depending on process zone size.

only occur when the specimen size is significantly larger than the process zone size [154,155]. For many agglomerate materials, the process zone size is of the order of the granule size (see Table 2). These granules will break by **wear**, **erosion** or **attrition** brought about by diffuse microcracking (Fig. 32b) leading to the generation of fine dust rather than a few fragments.

The mode of stress application effects both the attrition rate and the functional dependence on particle properties. There are three classes of stress application: (i) wear and erosion, (ii) impact and (iii) compaction. For abrasive wear of agglomerates, the volumetric wear rate  $V$  is [156]:

$$V \propto \frac{d_i^{0.5}}{A^{0.5} K_c^{0.75} H^{0.5}} P^{1.25} l \quad (5-7)$$

where  $d_i$  is indenter diameter,  $P$  the applied load,  $l$  the wear displacement of the indenter and  $A$  is the apparent area of contact of the indenter with the surface. Note that the wear (erosion) rate is inversely dependent on both the fracture toughness and the hardness.

Experimental studies of the impact breakage of single crystals give a different dependence on material properties [149,157]:

$$V \propto \frac{\rho_p U^2 d_g H}{K_c^2} \quad (5-8)$$

Impact attrition is more sensitive to fracture toughness than abrasive wear. In addition the effect of hardness is *the opposite* to that for wear, since hardness acts to concentrate stress for fracture during impact.

During compaction of single particles or beds of particles, particles break in quasi-static compression. For single particles, the extent of breakage will relate to the fracture toughness of the particles. For beds of particles, the transmission of stress through the bed is complex. The first inflection on the compaction curve for a granular bed in

uniaxial compression, the consolidation starting stress  $P_c$  has been related to the crushing strength of individual particles by several workers e.g. [158–161]. However, compaction curves for granules that show brittle fracture are similar to those for plastic deformation so it is difficult a priori to extract granule mechanical properties from bed compaction tests. Most authors also compare bed compaction results to single granule crush strength, itself not a true property for brittle and semi-brittle fracture.

There is relatively little good quality data relating attrition/erosion rates of granules and agglomerates with which to test these theories. Ennis and Sunshine [151] compared the attrition rate of granules with different properties in a fluidised bed. They found that the attrition rate correlated well with the erosion rates from bars of similar materials and with fundamental granule properties as predicted by Eq. (5-7) (see Fig. 33). This is a good demonstration that quantitative prediction of granule breakage is possible.

There is a need for further studies of this type which measure granule attrition through the three classes of stress application and tie these measurements to fundamental granule properties.

### 5.2.3. Computer simulation of granule breakage

Measurement of average granule (agglomerate) properties is difficult due their heterogeneous nature. In some cases, the agglomerate size is less than 10 times the size of the particles in the agglomerate, making macroscopic granule properties meaningless.

Some researchers have taken a different approach to predicting granule breakage behaviour, using discrete element models (DEM) or similar computer simulations to predict the breakage of agglomerates [162–166]. For example, Subero et al. [165] simulated the breakage of

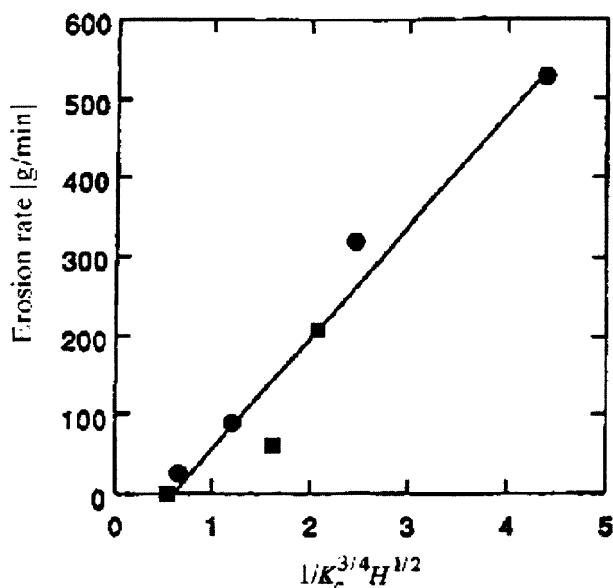


Fig. 33. Erosion rates of granules in a fluidised bed (Source: Ennis and Sunshine [151]).

agglomerates of large spheres with macrovoids and compared results with careful impact experiments.

The value of DEM simulations relies heavily on the accuracy of the models for interparticle adhesion and strength of interparticle bonds. The best potential for the technique is if it can be linked to careful measurement of individual particle and solid binder properties using fine scale equipment e.g. nanoindentation, atomic force microscopy (AFM). This gives exciting possibilities for relating macroscopic granule mechanical behaviour *quantitatively* to microscopic particle–particle and particle–binder interactions.

The combination of computer simulation with careful fine scale measurement remains an open area for research.

### 5.3. Concluding comments on granule breakage

The formulation properties and operating variables that control granule breakage (both wet and dry) are reasonably well known and models are available to predict granule breakage behaviour. This is a promising start. To build on this, further work is needed in several areas:

1. Further development of measurement techniques for macroscopic granule properties (dynamic yield stress, fracture toughness, etc.)
2. Careful measurement of the breakage of *well characterised* granules under conditions similar to those in granulators and granule handling equipment to test existing models.
3. Studies to predict macroscopic granule properties from knowledge of particle–particle and particle–binder interactions using microscopic scale measurement combined with appropriate modelling or computer simulation.

## 6. Review conclusions

In the last decade, substantial progress has been made in understanding and quantifying the mechanisms that control granule attributes. Controlling dimensionless groups for each of the mechanisms are established and in some cases, regime maps are becoming available.

Although still developing, this research is ready to be applied in industry for the design and scale up of granulation processes and products. The first step in design and scale up is to understand which mechanisms are controlling the process. This can now be done through

1. Good characterisation of the formulation (yield stress, contact angle, etc.);
2. Good characterisation of the process (spray characteristics, impeller speed, etc.); and
3. Calculation of the key dimensionless parameters (Dimensionless spray flux, viscous Stokes number, Stokes deformation number, etc.).



Having established the key mechanisms that control the product attributes, sound scale up rules, operating practices and control strategies can be developed.

If granulation is treated as particle design, then formulation parameters and/or the process equipment can be chosen a priori to force one mechanism to be controlling. The logical extension of this thinking is the design of new granulators which physically separate the granulation processes and base design on the new fundamental understanding.

The developments of the past decade should also focus future research in this area. Studies should no longer simply present laboratory granulation results and describe effect of parameters qualitatively. Instead, the following areas given below should be targeted.

- Further development of robust techniques to characterise formulations particularly drop penetration and wetting, mechanical properties of wet granules and pellets at a wide range of strain rates, and mechanical properties of dry granules and agglomerates.

- Experimental studies to understand and quantify flow behaviour of wet mass and granules in mixers and granulators.

- Experimental granulation studies specifically designed to quantitatively validate or extend recently developed theoretical models.

- Studies aimed at predicting macroscopic powder/granule properties from microscopic particle–particle and particle–fluid interactions. Here both sophisticated experimental techniques (e.g. AFM, nanoindentation, micro-rheometer), and computer simulations (e.g. DEM) will be valuable.

In the past, many papers in the area (including from our research group) began with statements such as “granulation is more an art than a science”. Such statements are now out of date. There is a significant and growing quantitative understanding of granulation processes available in the research literature.

### Nomenclature

$A$	contact area in Eqs. (5-6) and (5-7)
$\dot{A}$	powder flux through wetted spray area, Eq. (3-8)
$a$	sphere radius
$C$	a material constant in Eq. (4-4)
$c$	notch length in three point bend test
$D$	granule diameter
$d_d$	binder drop diameter
$d_g$	granule diameter
$d_i$	indenter diameter, Eq. (5-7)
$d_p$	surface-average particle diameter
$E$	elastic modulus of granule
$F$	force used in indentation test, Eq. (5-6)
$F_{vis}$	viscous force between two spheres
$H$	hardness
$h$	thickness of liquid film on granule surface

$h_a$	height of granule surface asperities
$K_c$	fracture toughness of granules, Eq. (5-4)
$K_\varepsilon$	dimensionless granule compaction rate, Eq. (4-8)
$k$	the consolidation rate constant in Eq. (4-6)
$N$	number of drum revolutions
$n$	power exponent in Eq. (3-7)
$\Delta P_{cap}$	capillary pressure difference across liquid–vapour interface
$R_{pore}$	effective pore radius, Eq. (3-6)
$r_d$	drop radius, Eq. (3-6)
$S$	granule pore liquid saturation
$s_{max}$	maximum granule pore saturation
$St_v$	viscous Stokes number = $8\rho ua/9\mu$ defined in Eq. (4-11)
$St_{def}$	Stokes deformation number = $\rho u^2/2Y$ defined in Eq. (4-15)
$s_{max}$	maximum granule pore liquid saturation
$t$	time
$U$	collision velocity
$u$	collision velocity
$V$	volumetric wear rate during an attrition test
$\dot{V}$	volumetric flow rate of liquid binder
$V_0$	drop volume, Eq. (3-6)
$W$	work of adhesion or cohesion
$w$	mass ratio of liquid to solid in granule
$Y$	granule dynamic yield stress
$y(x)$	profile of pendular bridge

### Greek

$\gamma$	surface tension or energy
$\delta_c$	incremental crack length
$\delta''$	extent of permanent granule deformation, Eq. (4-17)
$\varepsilon$	granule porosity
$\varepsilon_0$	initial porosity of granule nuclei
$\varepsilon_{min}$	final minimum porosity reached by tumbling granules
$\varepsilon_m$	granule strain.
$\lambda$	spreading coefficient, Eqs. (3-4a), (3-5b) and (3-5)
$\theta$	liquid–solid contact angle.
$\Psi_a$	dimensionless spray flux, Eq. (3-8)
$\mu$	liquid viscosity
$\rho$	density
$\sigma_t$	granule tensile strength.
$\tau$	dimensionless compaction time, Eq. (4-8).
$\tau_{CDA}$	drop penetration time for constant drawing area case, Eq. (3-6).

### Subscripts

A	adhesion
C	cohesion
L	liquid
S	solid
V	vapour

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