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An assessment of substrate–binder interactions in model granule systems

Part III Linear elastic fracture mechanics

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Linear elastic fracture mechanics was used to investigate the mechanical properties of four model dry granule systems with porosities of between 35% and 55%. The deformation and fracture behaviour of the agglomerates varied according to their porosity, the identity and quantity of the binder component, and the nature of any substrate–binder interfacial interactions. All the agglomerates deformed elastically but failed by plastic deformation of the binder component, in agreement with previously reported theoretical predictions.

1. Introduction

It is widely recognised that dry granule strength is important in determining the processability and final performance of many consumer products (e.g. washing powder, fertilizers, pharmaceuticals). The mechanical properties of such agglomerated materials will be strongly influenced by the size, shape and porosity of the granules and the presence of any flaws or stresses. These variables are notoriously difficult to control and as a consequence many of the testing techniques described in the literature only provide very empirical results. In an attempt to overcome the problems associated with these traditional granule testing methods, Adams and co-workers have recently described a three-point beam bending test for dry agglomerate systems [1–3]. This approach has enabled both the deformation and fracture behaviour of dry agglomerate systems to be investigated in detail. Recent results from this laboratory [4] have shown that the structural and morphological properties of dry granules can be influenced by substrate–binder interfacial interactions. These interactions occur as a result of the different surface energetic properties of the substrate and binder components [5]. The aim of the present study was to develop agglomerate testing methods that could be used to study the effect of substrate–binder interactions on the mechanical properties of some model dry granule systems.

1.1. Background

The influence of substrate–binder interactions on the mechanical properties of dry granule systems has previously been considered by a number of authors. Onada [6] predicted that the strength of model dry granules would depend upon the degree of binder spreading over the substrate particles. From theoretical considerations it was proposed that "pendular type" bonds would be at least twice as strong as "coated type" bonds. Within each bonding system the volume fraction of the binder, the binder tensile strength and the agglomerate porosity were identified as critical parameters. Cutt [7] measured the friability of granules formed from a model substrate, glass ballotini, and two polymer binders of differing surface energies, polyvinylpyrrolidone (PVP) and hydroxypropylmethylcellulose (HPMC). With hydrophilic ballotini, the granules formed using PVP were stronger and less friable than those formed using HPMC, but when the surface character of the glass was changed (to hydrophobic) the granules formed with the PVP were weaker and more friable than before. Unfortunately, no attempt was made to compare granules of an equivalent porosity or binder volume content. Opakunle and Spring [8] and Jaiyeoba and Spring [9] investigated the effect of changing the substrate "wettability" on the tensile strength of typical pharmaceutical dry granules. In both cases it was reported that a reduced substrate "wettability" resulted in a reduced dry granule strength. More recently, in a study using microcrystalline cellulose as the substrate, Zajic and Buckton [10] investigated the properties of the dry granules formed with aqueous solutions of PVP and HPMC. The results showed that granules formed with PVP were considerably more friable than those made with HPMC, contrary to the trend observed by Cutt [7]. It was proposed that the difference in friabilities was due to the different spreading tendencies of the two polymer binders over the microcrystalline cellulose. However, no attempt was

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made to normalize the effects of granule porosity, binder content by volume or binder tensile strength and therefore the validity of the conclusions reached by these authors is questionable. Rowe [11] has also attempted to investigate the effect of substrate–binder interactions on the mechanical properties of pharmaceutical dry granules by retrospectively analysing the results of Krycer *et al.* [12]. For a series of paracetamol formulations, the interactions between the substrate and a range of polymer binders were predicted and related to the granule friability, tablet strength and a tablet capping index. It was noted that as binder spreading improved so the mechanical properties of the granules and tablets also improved. In this case the varying cohesive properties of the binders were taken into account and the conclusions were supported by scanning electron micrographs of the dry granules.

From the results of the studies described above and those obtained recently in this laboratory [4, 5] it appears that substrate–binder interactions will be important in determining the mechanical properties of dry granular systems. However, no study has yet managed to probe these interactions in a carefully controlled way. The aim of this work was to apply the precise testing methods of Adams and co-workers to a well-defined series of model granule systems so that such a controlled analysis might be made.

1.2. Theory

When a load is applied to a solid body, internal stresses are induced which result in the material becoming strained. For perfectly elastic materials the stress to strain ratio is constant and is known as the Young's modulus, E, of that material. The Young's modulus of a dry granular material is one of many properties that contribute to its overall mechanical "strength". For most agglomerate systems, the final mechanical properties will also depend on the fracture behaviour of the material. Agglomerates are usually considered to fracture in a brittle manner and this type of behaviour can be characterized using the principles of fracture mechanics. Fracture mechanics theory describes the resistance of a material to cracking by considering the energy balance at the crack tip. The strain at the crack tip acts as a driving force to create new surfaces and thus causes cracking. The elastic stress field at the crack tip is characterized by the stress intensity factor, K, and crack propagation occurs when this reaches a critical value, the critical stress intensity factor, K_{IC}. An alternative fracture mechanics parameter, G_{IC}, the critical strain energy release rate can also be considered. Both K_{IC} and G_{IC} are equivalent measures of the "strength" of a material.

The use of fracture mechanics to characterize polymeric materials has been described by Williams and co-workers [13, 14]. It has been shown that the critical stress intensity factor, K_{IC}, and the critical strain energy release rate, G_{IC}, can be used to describe crack initiation and propagation in polymers provided that the zone of plastic deformation at the crack tip is small compared to the dimensions of both the specimen and the crack. It has also been shown that it is possible to compensate for limited crack-tip yielding by replacing the measured crack length with an "effective" crack length which takes into account the extent of any plastic deformation. Adams and co-workers [1–3] have adopted a very similar approach for describing the fracture behaviour of dry agglomerate systems. In these systems, the effective crack depth is thought to include a "process zone" ahead of the crack tip where microcracking and ductile yielding occur. The measured values of K_{IC} from dry agglomerate systems have been related to the size of this process zone and also to the attrition behaviour of real agglomerates during processing [2, 3, 15].

2. Experimental procedure

2.1. Materials

Glass ballotini (Englass Ltd, Leicester, UK) were chosen as a model substrate material. Glass has a hydrophilic nature which can be readily altered using a silanizing agent to produce a hydrophobic surface. Both hydrophilic and hydrophobic model substrates were utilized in this study to enable the affect of changing substrate surface character to be assessed. The substrates consisted of non-porous, smooth surfaced, spherical particles with a mean diameter of 12 μm (range 1–30 μm). There were no significant differences in the morphology, size distribution or true density of the two types of ballotini [4, 5].

The model substrates were wet massed with aqueous solutions of two commonly used polymeric binding agents; polyvinylpyrrolidone (PVP) (Kollidon K90, BASF, Cheadle, UK) and hydroxypropylmethylcellulose (HPMC) (Pharmacoat 606, Shin-Etsu Chemical Co., Tokyo, Japan). The concentration of the binder solutions was varied to produce dry agglomerate specimens with either 1.99% or 3.90% volume fraction of dry binder.

The surface free energies and polarities of the substrates and binders have been previously measured and their most likely interactions predicted [5]. These data are summarized in Tables I and II.

2.2. Methods

Agglomerate beam specimens were prepared using a method based on those described previously [1, 2]. The model substrates were wet massed with known quantities of the polymer binder solutions in a mixer

TABLE I Surface free energy and polarity of the model substrates and the polymer binder solutions

Material	Surface free energy, γ (mN m^{-1})	Fractional polarity, x^p
Hydrophilic glass	71.7	0.67
Hydrophobic glass	24.6	0.12
PVP	66.3	0.44
HPMC	46.5	0.69

TABLE II Summary of the substrate–binder interactions predicted in [5] (+ , favoured; − , unfavoured)

Material		PVP	HPMC
Hydrophilic glass	Substrate–binder adhesion	+	+
	Binder film formation	+	+
	Binder spreading	−	+
	Substrate spreading	−	−
Hydrophobic glass	Substrate–binder adhesion	−	−
	Binder film formation	−	−
	Binder spreading	−	−
	Substrate spreading	+	−

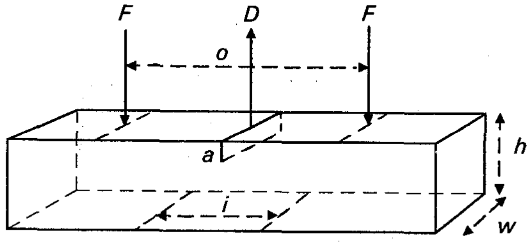

Figure 1 The arrangement of the four-point beam bending test rig. *F*, force; *D*, displacement of beam; *h*, height of beam; *w*, beam width; *i*, distance between inner supports; *o*, distance between outer supports; *a*, notch depth.

torque rheometer and "typical" wet granules produced [5]. An aluminium alloy mould was lightly dusted with PTFE powder (as a release agent) and filled with a known mass of the wet granular material. This material was gently consolidated from above with a Perspex platen to expel any entrapped air before the mould was disassembled and the beam released. This procedure produced beams with final dimensions of approximately 100 mm × 10 mm × 10 mm. The majority of beams were left intact but some had a small (1.5–3.0 mm deep) notch introduced across the centre of their upper surface with a razor blade. Both the notched and the unnotched beams were dried at 50 °C for 24 h and stored at 20 ± 1 °C and 40 ± 5% RH for at least 1 week prior to testing. The equilibrated agglomerate beams were weighed and measured so that their porosities could be calculated. Where appropriate, the depth of the notch was also measured using a travelling microscope (Griffin and George Ltd, London, UK).

The four-point bending of a rectangular specimen has been cited as a preferred method for determining the mechanical properties of solids and composites [16–18]. The method used in this study was based on those described previously [17–19]. A CT40 Mechanical tester (Engineering Systems, Nottingham, UK) was used with the loading arrangement shown in Fig. 1. Loads were applied at a rate of 1 mm min^{-1} and the force, F, and central deflection, D, monitored by means of a load cell and a linear voltage displacement transducer (LVDT) connected to a BBC Model B microcomputer (Acorn Computers Ltd, UK). The tensile stress, σ, was calculated from the applied force and the strain, ε, was calculated from the vertical displacement at the mid-point of the beam [20] (Equations 1 and 2). The Young's modulus, E, was then determined from the slope of the line of best fit through this data (Equation 3) and the K_{IC} and G_{IC} estimated using Equations 4, 5 and 6 [21].

$$\text{Tensile stress, } \sigma = \frac{3F(o-i)}{2h^2w} \quad (1)$$

where F is the force, o is the distance between outer supports, i is the distance between inner supports, h is the height of the beam, and w is the beam width.

$$\text{Strain, } \varepsilon = \frac{Dh}{2[(i^2/8) + (i(o-i)/4] + [(o-i)^2/12)]} \quad (2)$$

$$\text{Young's modulus, } E = \text{stress/strain} \quad (3)$$

$$\text{Critical stress intensity factor, } K_{\mathrm{IC}} = \sigma_{\mathrm{IC}} a^{1/2} v \quad (4)$$

where a is the notch depth and v is the compliance.

$$\text{Compliance, } v = 1.99 - 2.47(a/h) + 12.97\,(a/h)^2 - 23.17\,(a/h)^3 + 24.80\,(a/h)^4 \quad (5)$$

$$\text{Strain energy release rate, } G_{\mathrm{IC}} = (K_{\mathrm{IC}})^2/E \quad (6)$$

3. Results and discussion

3.1. Elasticity of the model dry agglomerates

A representative stress–strain profile for the unnotched agglomerate beams is shown in Fig. 2. Schubert [22] previously noted that dry agglomerates exhibit almost linear stress–strain plots and concluded that they can be classified as brittle materials. For the agglomerate specimens considered in this study there was clearly some degree of plastic deformation occurring as the stress–strain plots were not perfectly linear. This is not surprising, because they all contained at least 1.99% polymer binder by volume. Adams *et al.* [2] reported that agglomerate beams formed from sand and PVP showed an unacceptably high degree of plasticity when tested under ambient conditions, and to alleviate this problem these authors desiccated and chilled their beams prior to testing. Such a procedure undoubtedly minimizes the plasticity of the agglomerates but also reduces the practical relevance of the results. The plasticity of the agglomerate beams formed in this work was similar to that of many other materials that have been characterized using fracture mechanics (e.g. compacted dry powders) and therefore it was not considered necessary to desiccate or chill the beams before testing.

The porosity of each agglomerate beam was calculated from its mass and exterior dimensions, taking into account the proportions of substrate and binder present. The porosities varied between 35% and 55% according to the degree of consolidation induced during the manufacturing process. This range of porosities is slightly lower than that reported previously [1, 2]. The minimum porosity achieved was similar to that found in a randomly packed bed of spherical particles [23].

The Young's modulus values determined for the agglomerate beams were typical of those usually obtained for soft elastic materials [21]. They were also between those reported in the literature for glass

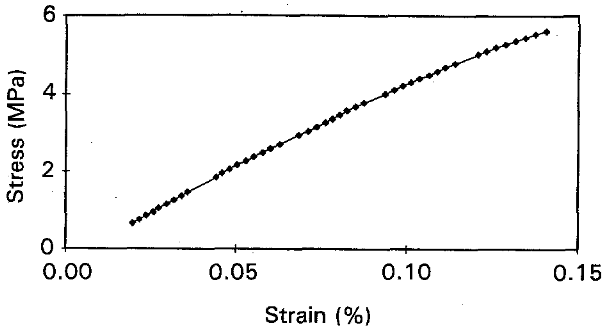

Figure 2 Typical stress–strain plot for an unnotched agglomerate beam (hydrophilic glass, 3.90% PVP, 39% porosity).

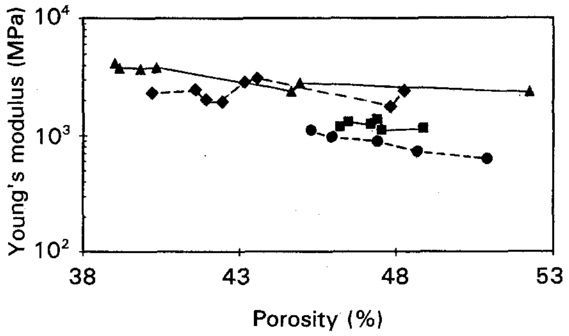

Figure 4 Young's modulus of agglomerate beams formed from hydrophilic glass. (◆) 1.99% vol/vol PVP, (▲) 3.90% vol/vol PVP, (●) 1.99% vol/vol HPMC, (■) 3.90% vol/vol HPMC.

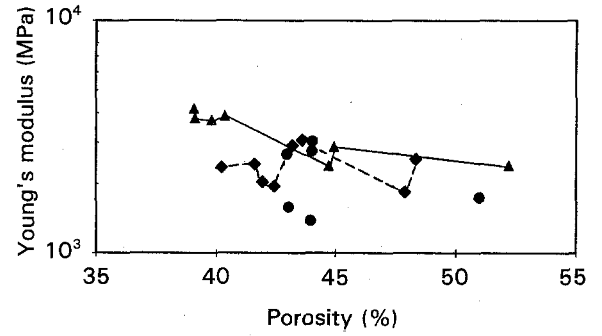

Figure 3 Young's modulus of agglomerate beams. (◆) 1.90% vol/vol PVP and hydrophilic glass (this study), (▲) 3.90% vol/vol PVP and hydrophilic glass (this study), (●) ≈1.82 and 3.61% vol/vol PVP and sand [2].

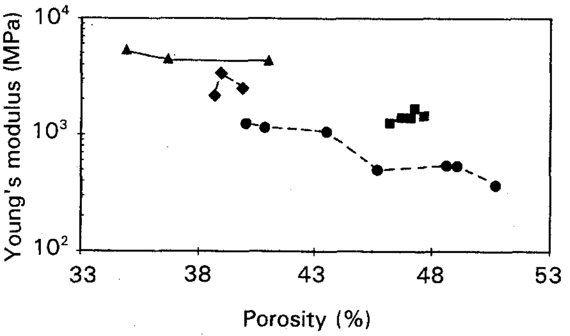

Figure 5 Young's modulus of agglomerate beams formed from hydrophobic glass. (◆) 1.99% vol/vol PVP, (▲) 3.90% vol/vol PVP, (●) 1.99% vol/vol HPMC, (■) 3.90% vol/vol HPMC.

ballotini ($\approx 6.4 \times 10^4$ MPa) [24] and for dry unbound glass agglomerates (≈ 2.0 MPa) [25]. Fig. 3 compares the Young's moduli of the agglomerate beams formed from PVP and hydrophilic glass in this study with those formed from PVP and sand by Adams *et al.* [2]. Considering that these beams were manufactured and tested under different conditions, the results show very good agreement.

For each of the substrate–binder combinations, the Young's modulus was found to vary significantly with the porosity of the agglomerates. It has been observed previously that both the Young's modulus and the K_{IC} of agglomerate beams vary with porosity [1, 2]. This is probably due to a changing number of cohesive and adhesive contacts within the porous agglomerates. Similar observations have been made for beams made of compressed dry powders [17–19] and several theoretical and empirical relationships have been proposed [26–28]. The most widely used of these relationships is due to Spriggs [26] ,

$$E = E^0 e^{-yz} \quad (7)$$

where E is the Young's modulus at porosity z, E^0 the Young's modulus at zero porosity, e the natural logarithm constant, y a constant, and z the porosity. Spriggs [26] suggested that the value of the constant y in this equation indicates the proportion of open to closed pores within the compacted material. A similar relationship may also hold true for agglomerated systems. When the results of this study were plotted according to Spriggs' equation, a good fit was obtained (Figs 3–5). Typically a 20% reduction in the porosity of the beam resulted in a 10- to 20-fold increase in the Young's modulus. For all of the substrate–binder combinations, the gradient of the "line of best fit" through the data (y in Spriggs' equation) was very similar, suggesting that each substrate–binder combination considered produced dry agglomerates with similar types of pores.

Within each of the different substrate–binder combinations, the Young's modulus of the beams was observed to increase with increasing binder volume fraction (Figs 4 and 5). A similar concentration effect has been reported for agglomerate beams formed from sand and PVP [2] and is probably due to an increasing number or area of substrate–binder contacts within the agglomerates. With the hydrophilic substrate, the Young's modulus at any given porosity was always higher for beams made with PVP rather than HPMC (Fig. 4). The same trend was also observed for the beams made from the hydrophobic substrate (Fig. 5). This rank order of elasticity is identical to that reported for the free binder films [29] and is the same as that indicated by the works of cohesion of the binders [5]. It appears that the cohesive properties of the binders dominate the deformation behaviour of the agglomerates even when the binder is present at relatively low concentrations. Thus it is not possible to compare directly the effects of substrate–binder interactions occurring in dry granules produced using different polymer binders.

Figs 6 and 7 show the experimental data rearranged to illustrate the effect of changing the substrate surface energetic properties. At the lower concentration of

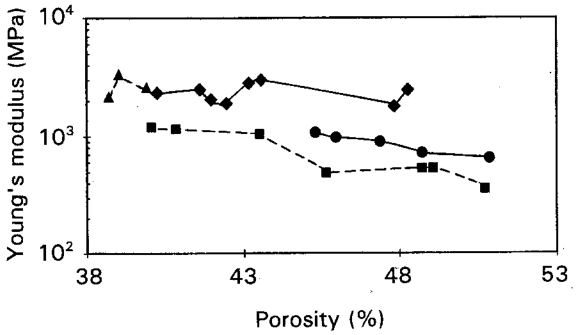

Figure 6 Young's modulus of agglomerate beams formed at 1.99% vol/vol binder content. (◆) PVP and hydrophilic glass, (▲) PVP and hydrophobic glass, (●) HPMC and hydrophilic glass, (■) HPMC and hydrophobic glass.

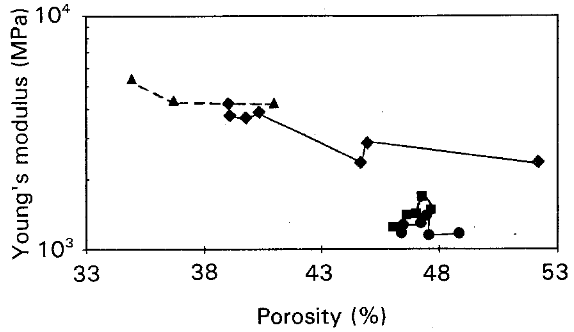

Figure 7 Young's modulus of agglomerate beams formed at 3.90% vol/vol binder content. (◆) PVP and hydrophilic glass, (▲) PVP and hydrophobic glass, (●) HPMC and hydrophilic glass, (■) HPMC and hydrophobic glass.

HPMC there was a small but consistent difference in the moduli of the agglomerates formed with the two different model substrates. At any given porosity a more rigid granule was formed with the hydrophilic substrate than with the hydrophobic substrate. As all the properties of the model substrates except their surface energetics are identical, this difference can be attributed to the different substrate–binder interactions occurring within each of the model substrate–HPMC systems (Table II) [4, 5]. With the hydrophilic substrate all of the possible substrate–binder interactions are favoured, whereas with the hydrophobic substrate none of them are favoured. Thus it appears that dry granules formed from a strongly interacting substrate-binder system offer a greater resistance to deformation than those formed from a poorly interacting system.

At the lower concentration of PVP there was no significant difference in the elasticity of the beams formed from the two different model substrates (Fig. 6). This was surprising because the interactions predicted and observed for these substrate–binder combinations were quite different (Table II) [4, 5]. It is conceivable that such a result might occur if the effects of substrate–binder interactions in one system are matched mechanically by the effects of different interactions in the other. In this case, with the hydrophilic substrate, adhesion and film formation were good but spreading was poor, and with the hydrophobic substrate, adhesion and film formation were poor but spreading was good. As each of these different interactions will contribute to the overall elasticity of the agglomerates it is possible for granules to be formed which experience different substrate–binder interactions but still exhibit similar elastic moduli. Clearly the net mechanical effect of the substrate–binder energetic interactions cannot be predicted from theoretical or structural considerations alone, thus emphasizing the need for the further development of controlled agglomerate testing techniques.

At the higher concentration of the two polymer binders the moduli of the agglomerate beams did not vary significantly with substrate identity; instead the deformation behaviour was dominated by the identity of the binder (Fig. 7). For this to occur the agglomerate deformation most likely takes place primarily within the binder phase. It is proposed that at this concentration the binder is able to envelope completely the substrate particles, even in those systems where adhesive interactions are relatively poor. In this situation the substrate–binder system will behave like a filled binder matrix rather than a classical agglomerate system, and the deformation behaviour of the composite will be determined primarily by the cohesive properties of the binder (Fig. 8). An analogous effect has been described for filled polymer films [30] and in this instance a critical pigment volume concentration (CPVC) is reached as the pigment concentration is increased beyond the point at which the polymer can just form a continuous film. Notably the attainment of the CPVC is accompanied by marked changes in the mechanical properties of the film. Rumpf [31] has also described two different types of dry agglomerate structure, one in which binder bridges were localized at the points of contact between the particles and one in which the space between the particles was partially or entirely filled with binder. It was calculated that in the first agglomerate type substrate–binder adhesion, substrate and binder cohesion and agglomerate porosity would all affect the ultimate tensile strength of the dry granules. The results of this study suggest that the agglomerate types proposed by Rumpf [31] probably exist in practice and confirm that the theoretically important factors can have a significant influence on the measured mechanical properties of dry agglomerates.

3.2. Fracture behaviour of the model dry agglomerates

The fracture behaviour of the notched agglomerate beam specimens was measured at a single polymer binder concentration, 3.90% vol/vol and notches were formed in the beams prior to drying to reduce any prestressing to a minimum. Adams *et al.* [2] showed that for agglomerate beams made from sand and PVP, the critical stress intensity factor, K_{IC}, increased as a function of the notch depth to beam height ratio, $a:h$. For $a:h$ ratios greater than 0.15 the experimentally determined K_{IC} was proposed to be a good estimate of the true K_{IC}. Mullier *et al.* [1] also noted that for $a:h$ ratios greater than 0.40 the value of the compliance, v, used to calculate K_{IC} (Equations 4 and 5) became unacceptably high. In this study, notches of between

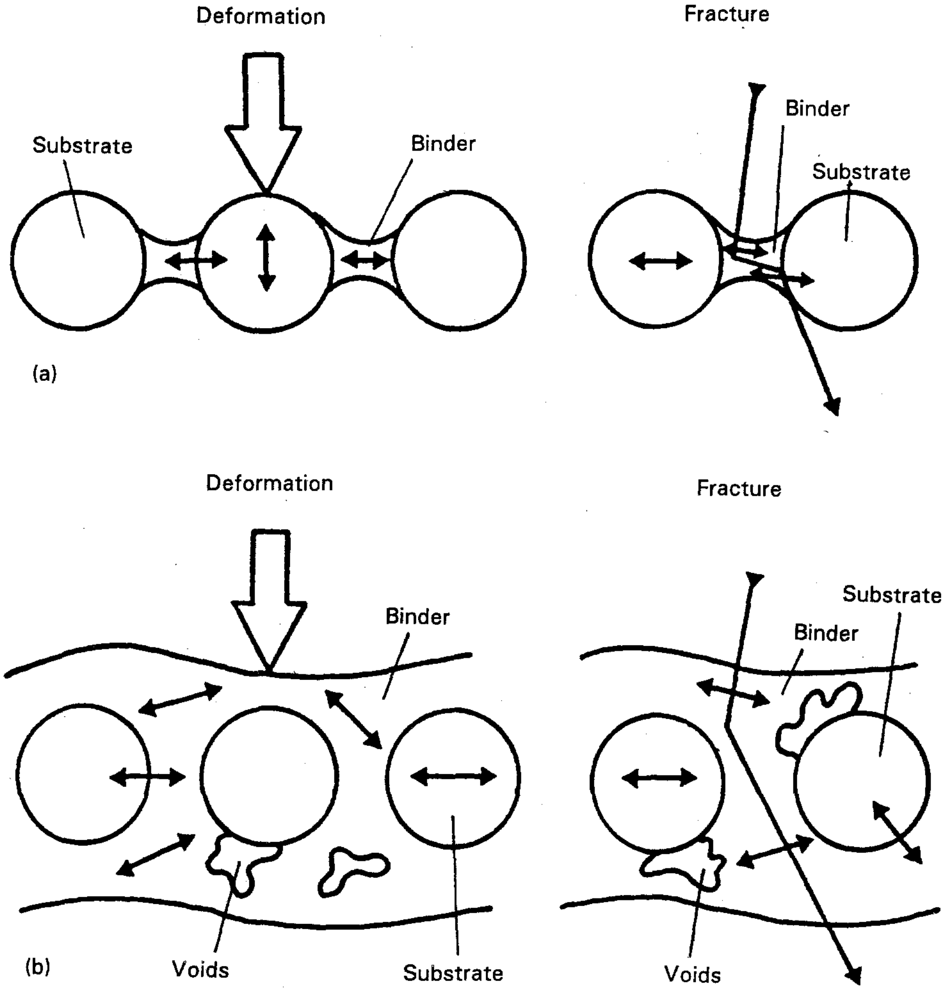

Figure 8 The variation of deformation and fracture behaviour with changing agglomerate structure. (a) Low binder concentration, classical agglomerate structure; deformation and fracture behaviour dependent on a balance of adhesive and cohesive forces. (b) High binder concentration, filled binder structure; deformation and fracture behaviour dominated by binder cohesive forces. ◀——▶, forces.

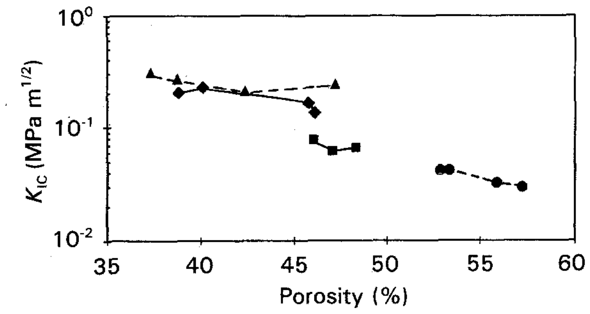

Figure 9 Critical stress intensity factor, K_{IC}, of agglomerate beams formed with 3.90% vol/vol binder. (◆) PVP and hydrophilic glass, (▲) PVP and hydrophobic glass, (●) HPMC and hydrophilic glass, (■) HPMC and hydrophobic glass.

1.5 and 3.0 mm were formed in 10 mm high beams resulting in a:h ratios of between 0.15 and 0.30. This should provide a good estimate of the limiting K_{IC} value whilst restricting the compliance to a reasonable level.

It is generally assumed that the failure of dry agglomerates occurs either by cohesive failure of the binder or by adhesive failure of the substrate–binder interface. This failure may be tensile or by shearing at a failure plain within the granule. It has been proposed that shearing is most likely to be affected by the spreading tendency of the substrate and binder phases, whereas, tensile failure will be more strongly influenced by the cohesive properties of the binder [11]. In this study, the agglomerate beams were subjected to purely tensile stresses and thus their failure behaviour was expected to be dominated by the cohesive properties of the binders.

The K_{IC} values for the model substrate agglomerate beams varied with porosity in an identical manner to the Young's modulus values (Fig. 9). This pattern of K_{IC} variation is identical to that found for beams made from compacted dry powders [19, 32]. The gradient of the line of best fit was similar for all the data sets indicating that the effect of porosity on fracture behaviour of the agglomerates was similar in each of the different substrate–binder systems. Comparison of the results obtained in this study with those reported previously [1, 2] showed very close agreement (Fig. 10). This is despite the wide range of substrate sizes and shapes, the slightly different binder concentrations and molecular weight grades, the variable storage conditions and the different test geometries and specimen sizes used in each of these studies. Further investigations into the importance of all these variables are clearly required.

The K_{IC} values for the beams made from a single model substrate showed that the PVP agglomerates

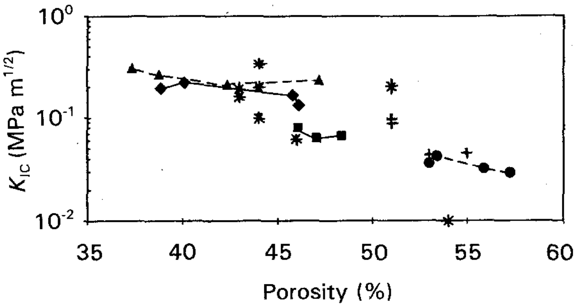

Figure 10 Critical stress intensity factor, K_{IC}, of agglomerate beams form this study and the literature. For key, see Fig. 9 (*) PVP and sand [1, 2], (+) PVP and hydrophilic glass.

were always more resistant to fracture than the equivalent HPMC agglomerates. A similar trend has been noted for free films prepared from these two polymer binders [29] and this suggests that the tensile failure of the dry agglomerates is dominated by the cohesive properties of the polymer binding agent as predicted earlier. A comparison of the agglomerate beams made from a single binder and the two different model substrates showed no meaningful variation K_{IC} with changing substrate surface properties (Fig. 9). This is consistent with the appearance of the fracture surfaces in dry agglomerates formed from these systems [4] and the predictions made previously. It was also proposed earlier that the concentration of binder within an agglomerate is likely to be critical in determining its elastic properties and the same principle may also apply to its fracture behaviour. The concentration of binder used to prepare the notched beams was 3.90% vol/vol and previously this had been thought to be high enough to ensure that a continuous matrix of binder enveloped all the substrate particles. Under these circumstances the stress required to cause failure of the beam may well be determined primarily by the cohesive strength of the binder with substrate–binder interactions having only a secondary effect (Fig. 8). The level of polymer binder used in this part of the study was greater than that used in some commercial applications and thus the properties of the agglomerates studied may not be typical of those encountered in practice. Clearly for the effect(s) of substrate–binder interactions on the failure of agglomerates to be determined unequivocally, a series of similar experiments need to be performed over a wide range of binder concentrations.

It was suggested in the introduction to this work that the failure of dry agglomerates is likely to be influenced by the presence of stresses induced in the polymer binder during drying. Brown and Yang [33] have shown that for thin polymer films the amount of stress that can be accommodated before crack propagation occurs is a function of the film thickness and it is possible to calculate a film thickness, f, below which cracking is unlikely to occur

$$f = \frac{(K_{IC})^2}{0.36\pi\sigma_{IC}} \qquad (8)$$

where π is a constant. For a typical polymer binder with a K_{IC} of ≈ 0.3 MPa m$^{1/2}$ [34] and a tensile strength of ≈ 50 MPa [29], the polymer film would have to be thicker than 31 μm before it was unable to accommodate all the possible internal stresses and would fail by cracking. This thickness is at least two orders of magnitude greater than that observed in the model dry granules by scanning electron microscopy [4] and that calculated from theory for the highest binder concentration used (≈ 148 nm). Therefore, it is unlikely that the dry agglomerates formed in this study failed by cracking of the polymer binder film unless the distribution of the binder was very uneven and regions of very high binder thickness were formed.

If we consider the relationship between the surface free energies of the granulation components and the G_{IC} of the agglomerates, we can estimate the proportion of the total fracture energy that was dissipated by plastic deformation, γ^*, and this should give some indication of the true mode of failure in the model dry granules. From fracture mechanics theory, the critical strain energy release rate, G_{IC}, can be related to the thermodynamic work of failure

$$G_{IC} = W_a \quad \text{for adhesive failure} \qquad (9)$$

$$G_{IC} = W_c = 2\gamma \quad \text{for cohesive failure} \qquad (10)$$

where W_a is the work of adhesion, W_c is the work of cohesion, and γ is the surface free energy. From a knowledge of the surface energetic properties of our materials and their probable interactions it should thus be possible to predict the most likely mode of failure [35, 36]. Equations 9 and 10 are based on the assumption that the materials are perfectly elastic and for real materials it is necessary to include an additional term to account for the energy dissipated by plastic deformation during fracture

$$G_{IC} = W_a + \gamma^* \quad \text{for adhesive failure} \qquad (11)$$

$$G_{IC} = W_c + \gamma^* \quad \text{for cohesive failure} \qquad (12)$$

where γ^* is a plastic energy term.

Most plastic materials (e.g. polymers) have G_{IC} values in the range 10–1000 Nm^{-1} [37] and works of cohesion between 0.050 and 0.150 Nm^{-1} [5]. Therefore, for this type of material, the plastic energy term will be very large and will effectively dominate the fracture energy requirements of the system. The critical strain energy release rates, G_{IC}, of the agglomerate beams were calculated from the measured Young's modulus and K_{IC} values using Equation 6. The G_{IC} values were in the range 1.67–16.0 Nm^{-1}, typical of many common plastic materials [37]. The G_{IC} varied with the porosity of the beams and the identity of the binder in a similar way to the Young's modulus and K_{IC}; the results were also very similar to those reported for agglomerate beams made from sand or glass ballotini and PVP [1, 2]. Assuming that for a typical agglomerate the G_{IC} is about 10 Nm^{-1} (see above) and the work of cohesion or adhesion is approximately 0.125 Nm^{-1} [5], then the energy dissipated by plastic flow, γ^*, will be about 9.875 Nm^{-1}. This means that approximately 99% of the energy required to cause fracture of the beams is dissipated by plastic deformation and only 1% of that energy is used to create the fracture surfaces. This calculation suggests that although the model dry agglomerates deformed in a semi-brittle manner, their fracture behaviour is more typical of a plastic or ductile material. This is again consistent with the predicted plastic deformation of the binder at or near the interface [11] and is also supported by the appearance of the fracture surfaces in these systems [4].

4. Conclusions

The studies described in this paper confirm that linear elastic fracture mechanics can be used to determine several of the fundamental mechanical properties of dry agglomerate systems. This technique has a sound theoretical basis and allows the properties of agglomerates with a wide range of physical properties (e.g. porosity, binder content) to be studied. The methods developed in this work have enabled both the deformation and fracture behaviour of a series of model dry agglomerates to be considered. In general, the agglomerates deformed in a semi-brittle manner (i. e. elastically) whilst retaining a degree of plasticity, which significantly affected their fracture behaviour. These attributes were determined partly by the cohesive and adhesive strengths of the raw materials and partly by the mode of granule deformation and failure. In turn, these factors were influenced by the relative quantities of the binder and substrate components, the porosity of the agglomerates and the nature of any substrate–binder interfacial interactions. A close correlation was also noted with the available theoretical models and the few practical results previously reported in the literature.

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