Brittle–Ductile Transitions in Sucrose and the Influence of Lateral Stresses During Compaction

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Abstract

Sucrose, in a range of particle sizes, has been compacted to investigate both the effect of brittle–ductile transition and the effect of lateral stresses on the deformation stress as measured using Heckel plots.

All particles with a diameter greater than $30 \mu m$ exhibited cracking in line with both theoretical predictions and literature data from hammer and ball milling. In addition, crack lengths in compressed particles examined microscopically were very similar to those predicted from the deformation stress, confirming the applicability of the model.

Pharmaceutical materials range from those that are brittle and consolidate by fracture or fragmentation (e.g. the inorganic carbonates and phosphates) to those that are ductile and consolidate by plastic deformation or flow (e.g. microcrystalline cellulose). Many materials consolidate by both fragmentation and plastic flow, the dominant mechanism depending on their particle size. The particle size at which the behaviour changes is termed the brittle–ductile transition (Kendall 1978a).

This behaviour manifests itself in compaction through a change in the Heckel plot (Heckel 1961a, b). Below the brittle–ductile transition, the reciprocal of the gradient of the central linear portion of the graph (now defined as the deformation stress, σ_d (Roberts et al 1989)) is independent of particle size and numerically equal to the yield stress, σ_y, of the material. Above the brittle–ductile transition σ_d decreases with increasing particle size. In grinding the brittle–ductile transition is the point at which it is impossible to comminute particles of the material by compression induced by hammer or ball milling (Kendall 1978a).

In both compaction and comminution, the critical size at the brittle–ductile transition, d_{crit}, is given by the expression (Kendall 1978a):

$$d_{crit} = [AK_{IC}/\sigma_y]^2 \qquad (1)$$

where K_{IC} is the critical stress intensity factor of the material and A is a constant equivalent

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to $(32/3)^{0.5}$ or $3 \cdot 27$ for rectangular-shaped particles.

While it is relatively easy to predict the critical particle size and there is reasonable agreement between theoretical predictions and experimental measurements for a variety of materials (Roberts & Rowe 1987; Roberts et al 1989; Rowe & Roberts 1996), the experimental deformation stresses at large particle sizes are always greater than theoretical predictions. In recent work on the compaction of sodium chloride (Roberts et al 1997) it was suggested that this effect was due to lateral stresses resulting from the interaction between particles of sodium chloride in the powder bed and die-wall radial forces affecting crack growth within the particles. Consequently the authors applied the approach proposed by Kendall (1978b) to explain the constraining effect of lateral stresses on crack growth in perspex blocks and suggested that the deformation stress is given by the following equation:

$$\sigma_d = (32/2)^{\frac{1}{2}} \cdot K_{IC}/d^{\frac{1}{2}} (1 - 4\Psi a/d)^{-1} \qquad (2)$$

where d is the particle diameter, a is the crack length and Ψ is the ratio of the radial stress to the axial applied stress. The radial stress will be a function of Poisson's ratio, porosity, contact area and interparticulate and die-wall friction. It is interesting to note that where $a = 0$ (i.e., at the brittle–ductile transition), equation 3 can be derived, which can be simplified to equation 1 using $\sigma_y = \sigma_d$.

$$\sigma_d = (32/3)^{\frac{1}{2}} \cdot K_{IC}/d^{\frac{1}{2}} \qquad (3)$$

Rearranging equation 2 gives equation 4:

$$a/d = (1/4\Psi) - (32/3)^{1/2} \cdot K_{IC}/4\Psi\sigma_d d^{1/2} \quad (4)$$

Calculation of the crack length, a, for a range of particle diameters can be determined using this equation and can be compared with fractographic evidence to provide further proof as to the applicability of these concepts. The purpose of this study is to investigate the applicability of these concepts to sucrose.

Materials and Methods

Sucrose, in a range of particle sizes, was obtained from Tate & Lyle (Liverpool, UK). Median particle sizes were measured using image analysis (Quantimet 520, Cambridge Instruments, Cambridge).

Compaction of the various samples was carried out using a compaction simulator with 10-mm circular flat-faced punches lubricated using a slurry of magnesium stearate in ethanol as described previously (Roberts & Rowe 1985). The deformation stress, σ_d, was determined at a punch velocity of 0.033 mm s^{-1} using the Heckel equation (Heckel 1961a, b).

Table 1.   Deformation stress, σ_d, for various particle sizes of sucrose.

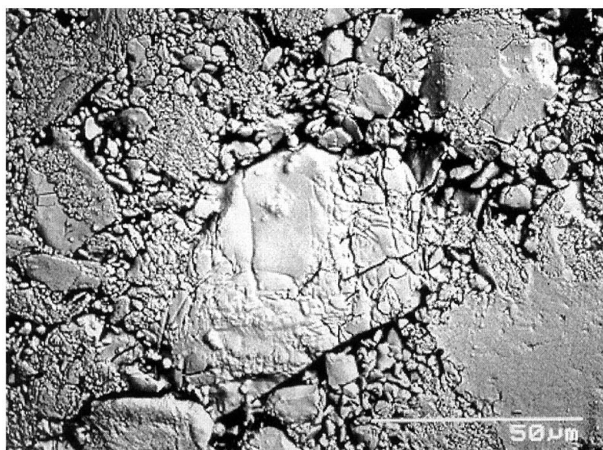| Median particle diameter (μm)	σ_d (MPa)
74	148·1
586	107·0
1399	99·6

Figure 1.   Photomicrograph showing cracks in sucrose crystals below 50 μm in diameter.

Figure 2.   Photomicrograph showing cracks in sucrose crystals below 500 μm in diameter.

$$\ln[1/(1-D)] = (P/\delta_d) + B \quad (5)$$

where D is the relative density measured at compaction pressure P, and B is a constant. Data for the three sizes of sucrose are shown in Table 1. Tablets were also prepared by compacting the smallest- and largest-sized samples at compression pressures of 70 and 150 MPa. These were then sputter coated with gold and examined using scanning electron microscopy (Hitachi S2300) to evaluate the extent of fracture and to measure crack lengths. Figures 1 and 2 are representative photomicrographs from which these data were calculated.

Values for the critical stress intensity factor, K_{IC}, and yield stress, σ_y, of sucrose were taken from the literature: $0.2239 \text{ MPa m}^{1/2}$ for K_{IC}, determined using three point single edge notched beam (SENB) testing (Roberts et al 1993) and 215 MPa for σ_y, calculated using hardness values determined by indentation of single crystals (Duncan-Hewitt & Weatherly 1989).

Results and Discussion

Close examination of the photomicrographs (see Figures 1 and 2 for example) shows that for particles in excess of 30 μm extensive cracking occurred, while for particles below about 20 μm no cracks were observed. This implies that the brittle–ductile transition for sucrose is approximately 20 μm — close to that predicted using equation 1 (12 μm) and shown experimentally using hammer milling (19 μm; Perry & Green 1988) and ball milling (20 μm; Ho & Hersey 1979).

Although cracks can be clearly seen in the photomicrographs it was difficult to obtain sufficient data to confirm the relationship between crack length
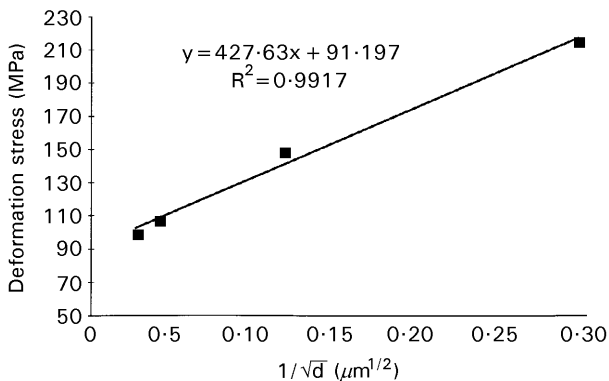
Figure 3. Relationship between the deformation stress and the reciprocal of the square root of median particle diameters for sucrose.
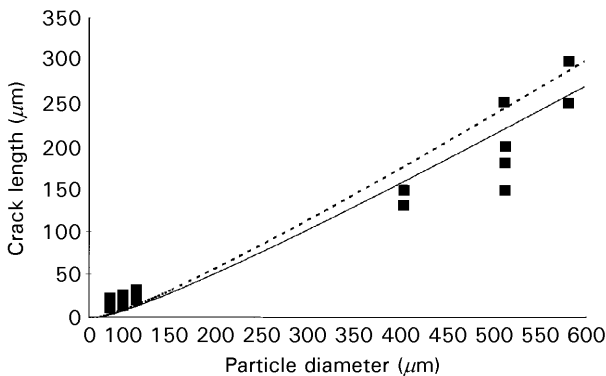

Figure 5. Relationships between the deformation stress and particle diameter for sucrose. A, brittle–ductile transition; B, predicted for system without lateral stresses; C, D, predicted for system corrected for lateral stresses at values of Ψ of 0·36 (C) and 0·40 (D), together with experimental measurements (■).

Figure 4. Predicted relationships between the crack length and particle diameter for sucrose at $\Psi = 0·36$ (-----) and $\Psi = 0·40$ (——), together with experimental measurements (■).

and particle diameter necessary for the application of equation 2 to predict the deformation stresses, as has been done previously for sodium chloride (Roberts et al 1997).

In order to prove the concept, equation 4 was applied to predict the relationships between crack length and particle diameter. These were then compared with the limited experimental evidence. This was done by first defining the relationship between the experimental deformation stress and the reciprocal of the square root of median particle diameter (Figure 3), and using this to predict the crack length/particle diameter relationships for a variety of Ψ ratios.

Figure 4 shows the predicted relationships together with the experimental results for values of Ψ of 0·36 and 0·40, respectively. These ratios were chosen because they cover the range used previously (Duncan-Hewitt & Weatherly 1990a b; Roberts et al 1997). It can be seen that while for
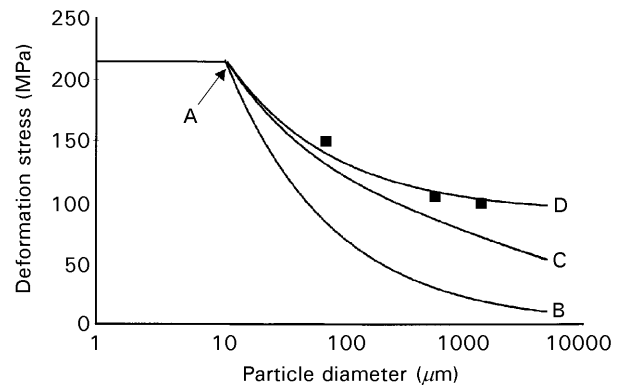
both ratios the prediction is close to the experimental data obtained from the photomicrographs, the better correlation, especially for the larger particle diameters, is when $\Psi = 0·4$. This effect, seen with the higher values of Ψ, is directly comparable with that seen previously for sodium chloride.

The crack length versus particle diameters for the two values of Ψ from Figure 4 were reapplied into equation 2 to show the effect of lateral stresses with the correct a/d on the deformation stress (Figure 5). The results show that, as with sodium chloride, the discrepancy between the experimental deformation stresses determined from Heckel plots at large particle sizes above the brittle–ductile transition is due to lateral stresses resulting from the interaction of other particles within the powder bed and die-wall radial forces affecting crack growth within the particles. Therefore the deformation stress or failure stress for sucrose particles in a constrained die is greater than the unconstrained case (see fracture stress curve in Figure 5). Furthermore, the ratio of the radial stress to the deformation stress, Ψ, for the optimum model for both materials was found to be 0·4, equivalent to a constraint factor as defined by Duncan-Hewitt & Weatherly (1990b) of 2·5.

It is interesting to note the similarities between the approach presented here and that used by Duncan-Hewitt & Weatherly (1990a, b). They used both hardness data and contact area to predict the densification/compaction of various powders according to Heckel plots. In this approach the deformation stresses are modelled. Of course, before the model can be applied universally, the relationship between crack length and particle diameter needs to be determined for a larger number of materials.

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