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The characterization of the mechanical properties of microcrystalline cellulose: a fracture mechanics approach

ALI B. MASHADI AND J. M. NEWTON*

The School of Pharmacy, University of London, 29–39 Brunswick Square, London WC1N 1AX, UK

The mechanical properties of compressed beam specimens of microcrystalline cellulose (Avicel pH 101) have been assessed in terms of the tensile strength (σ_t), Young's modulus (E) and the following fracture mechanics parameters: the critical stress intensity factor (K_{IC}), the critical strain energy release rate (G_{IC}) and the fracture toughness (R). Increase in the compaction pressure used to form the beams resulted in compacts with higher values of tensile strength, Young's modulus, K_{IC}, G_{IC} and R, indicating that the compacts became less brittle as their porosity decreased. Extrapolation of the values of σ_t, E, K_{IC}, G_{IC} and R to provide values at zero porosity indicated that the material had values of 30 Nm m^{-2}, 0·0103 GPa, 1·21 MN $m^{-3/2}$, 1·98 × 10^2 Nm^{-1} and 2·19 × 10^3 Nm^{-1}, respectively. These provide a range of values whereby a fuller characterization of the mechanical properties of pharmaceutical materials can be made.

The mechanical properties of materials can be characterized by a variety of methods, the choice of test often being closely related to the use of the material. Pharmaceutically, because powders are subjected to compression in punch and die systems to form tablets, those systems are often used to assess the mechanical behaviour of powders, e.g. for their resistance to change in volume (Roberts & Rowe 1985, 1986). The method of Fell & Newton (1970) can be used to characterize the formed compact by its tensile strength and its tensile strength variability (Stanley & Newton 1977). Rees & Rue (1978) used cylindrical specimens to determine the 'work of failure' of some direct compression excipients. Another means of characterization of pharmaceutical materials is the four-point beam bending tests as reported by Church & Kennerley (1984) who found a decrease in porosity of Avicel beams resulted in an increase in the mean tensile fracture stress and the mean Young's modulus. The Spriggs' equation (1961) can be used to produce a straight line relation between porosity and Young's modulus.

$$E_\varepsilon = E_o \, Exp \, (-b\varepsilon) \qquad (1)$$

where E_o is Young's modulus at zero porosity, E_ε is Young's modulus at porosity ε, and b is a constant (Kerridge & Newton 1986). Young's modulus describes the stiffness of a material and in general materials can be classified by this modulus into a range of typical values (Kelly & Mills 1986).

* Correspondence.

Fracture toughness

The measurement of the fracture toughness of materials is often used as part of a general study of their fracture characteristics (Evans 1974). This approach is based on the concept that for a crack to grow under static loading, two conditions are necessary. 1. The stress must be high enough to initiate fracture. 2. The energy released by crack growth must be at least as much as that required to form the new fracture surfaces. The stress field near the crack tip will be proportional to the general stress in the material and the square root of crack length which has the dimensions (stress) × $(length)^{\frac{1}{2}}$ and is called the stress intensity factor (K). This is related to the rate of strain-energy release (G) with crack growth, by the elastic modulus of the material.

$$K^2 = E \, G \text{ (for plane stress)} \qquad (2)$$

where E is Young's modulus.

The crack will grow when the stress in the specimen has been raised sufficiently for K and G to reach their critical values, K_{IC} and G_{IC}, i.e. the critical stress intensity factor and the critical strain energy release rate. Either of these parameters can be used as a measure of the resistance of the material to cracking (Jayatilaka 1979). The critical stress intensity factor, K_{IC}, has become well-established for the assessment of the fracture behaviour in materials. The three-point or four-point bend test is usually used to determine this parameter. The value of K_{IC} can be calculated from the dimensions of the beam, the maximum load and the notch depth when

this load is reached. There are several formulae, obtained by different stress-analysis techniques but all are effectively equivalent; the one obtained by Brown & Srawley (1969) is:

$$K_{IC} = 3\ P_{IC} a^{0.5}(L_1 - L_2)\ \gamma/2\ bh^2 \qquad (3)$$

where P_{IC} = load at fracture, a = notch length, L_1 and L_2 = outer and inner loading spans, b = beam width, h = beam thickness, and

$$\gamma = 1.99 - 2.47\ (a/h) + 12.97\ (a/h)^2 - 23.17\ (a/h)^3 + 24.80\ (a/h)^4 \qquad (4)$$

(in pure bending) and will be used herein.

Once K_{IC} is known, G_{IC} can be calculated from equation (2).

Fracture toughness (R) or the energy necessary for crack propagation can be obtained by applying the equation used by Roberts et al (1978).

$$R = \frac{P_{IC}\delta/2}{bh - ab} \qquad (5)$$

where δ is displacement and the other terms are as defined. This allows the material to be placed on a scale of normalized toughness values reported by Kelly & Mills (1986).

Thus there are additional parameters available to assess the mechanical properties of pharmaceutical compacts.

MATERIALS AND METHODS

Preparation of the powder

Avicel pH-101 (FMC) was used as received. Rectangular beams 100 × 10 × h mm (where h is the beam thickness) were produced by filling a rectangular die with 7·61 ± 0·01 g of Avicel and compressing with a hydraulic press (Tangyes). Ten beams were prepared at each of varying maximum upper punch pressures and were stored in a closed container for one week before testing. Beam thickness after ejection was measured, using a dial gauge micrometer, at either end and the centre and a mean of the values was taken as the average thickness.

Load displacement measurements on compacted beams

Pre-notching of the specimens was with a glass cutter, which gave a 0·5 mm deep notch. The specimens were loaded in an Instron Testing Machine (Instron Ltd Model TT-CM) in four-point bending (Fig. 1) using a fracture rig (Rabie 1981) connected to a tensile load cell. The inner span of the fracture rig experienced pure bending and was 20·18 mm and the outer span was 61·16 mm. Loads were applied at cross-head rates of 0·025 mm min^{-1}. The displacement of the beam was measured by a linear variable differential transducer (LVDT) (Model DG 2·5, Sangamo, UK). The load cell and displacement transducer outputs were connected to a X-Y plotter (Gould). Young's modulus values were determined with un-notched specimens (Church & Kennerley 1984).

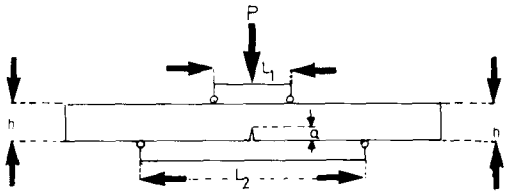

FIG. 1. Fracture rig for four-point bending of rectangular beam.

RESULTS AND DISCUSSION

After the material had been compressed, the Heckel (1961a, b) equation was used to estimate the mean yield pressure, from the results of monitoring thickness changes as a function of pressure. The value of the mean yield pressure obtained was 110 MNm^{-2}, which is comparable to 109 MN m^{-2} obtained by McKenna & McCafferty (1982). Those workers also concluded that the mechanism of deformation of Avicel was by plastic deformation and also independent of particle size.

It has been suggested that Avicel can be visualized as a special form of cellulose fibril in which the crystals are compacted close enough for hydrogen bonding to occur (Reier & Shangraw 1966).

Young's modulus (E)

Young's modulus for Avicel beams was determined in four-point bending of rectangular beam specimens. This method was used because a greater portion of the beam is under maximum stress

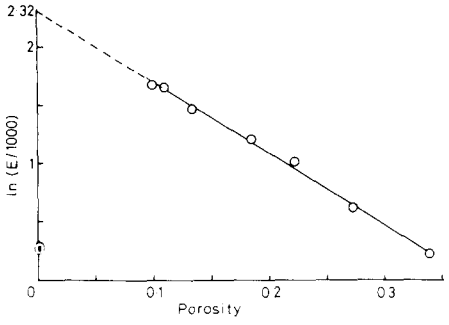

FIG. 2. Young's modulus as a function of beam porosity.

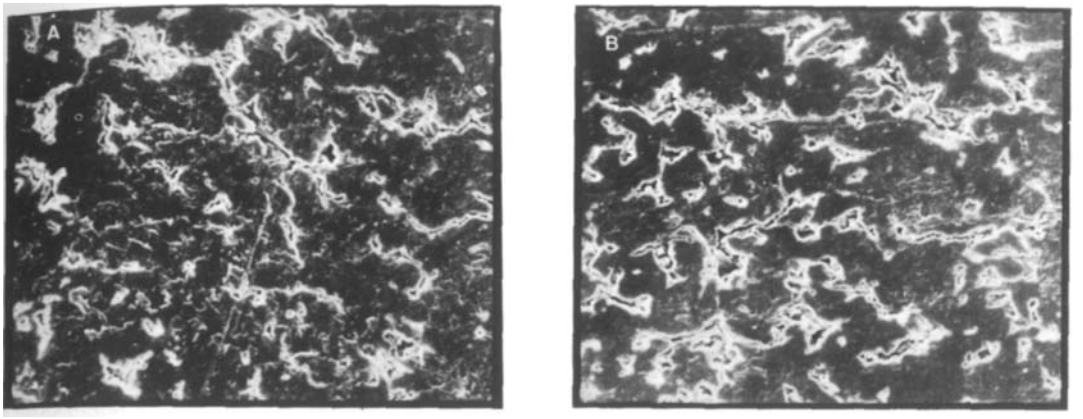

FIG. 3. Electron micrographs of the surface of Avicel PH-101 beam specimen prepared at (A) high compaction pressure and (B) low compaction pressure.

(Duckworth 1951; Berenbaum & Brodie 1959; Newnham 1975). The results in Fig. 2 illustrate that as the porosity of Avicel beams decreases there is an increase in Young's modulus value with an E_o of 0·0103 GPa. It has been suggested that the slope of this graph (value of b) is associated with the proportion of open and closed pores present, the open pores exhibiting a stronger influence on Young's modulus (Spriggs 1961). The theoretical value of b is a measure of the rate of change in the modulus with porosity. The value of b obtained for Avicel is 6·23 which implies that there is a strong influence of porosity on the modulus and, if the Spriggs theory regarding the significance of the slope is true, then it may be concluded that there are more open than closed pores in the compact (see S.E.M. pictures, Fig. 3).

Avicel exhibits a low Young's modulus value which corresponds to that of polymeric materials such as PVC and would be classified as ductile as opposed to brittle.

Tensile fracture stress (σ_t)

The fracture stress as a function of the beam porosity is shown in Fig. 4. The results are presented as described by Duckworth (1953) namely

$$\sigma_t = \sigma_o \exp(-a\varepsilon)$$

where σ_t is the fracture stress, σ_o is the fracture stress at zero porosity, a is the material constant. The value for the fracture stress at zero porosity is 30 N mm^{-2}.

Critical stress intensity factor (K_{IC})

Some pharmaceutical compacts can behave like brittle materials, with little or no plastic deformation before fracture. Brittleness is the result of no significant dislocation motion being possible in the material to allow an overall plasticity. Fracture in such materials could result either from inherent flaws

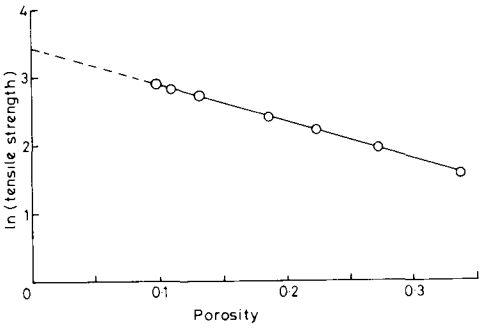

FIG. 4. Fracture stress as a function of beam porosity.

or from flaws produced as a result of limited plasticity (Jayatilaka 1979). The critical stress intensity factor (K_{IC}) describes the state of stress at the edges of a crack at the onset of fracture. For Avicel beams, K_{IC} was measured at different porosities. The results in Fig. 5 illustrate that the value of K_{IC} decreases steadily as compacts become more porous, i.e. less resistance is offered to crack propagation. The relation between K_{IC} and porosity is linear and extrapolation to zero porosity yields a value of 1·21 MNm$^{-3/2}$ which corresponds to the values for very brittle materials such as ceramics.

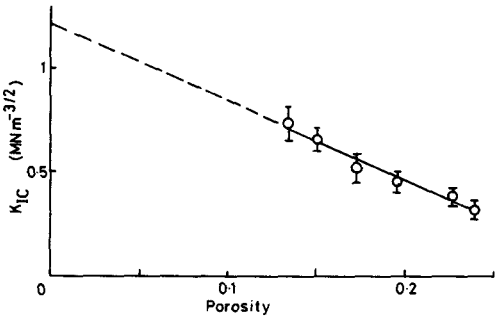

FIG. 5. Critical stress intensity factor (K_{IC}) as a function of beam porosity.

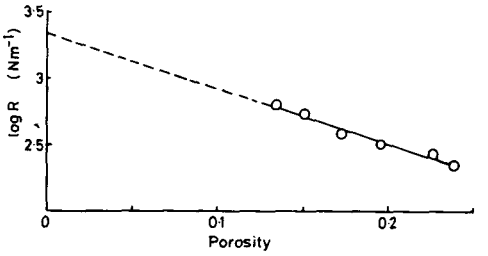

FIG. 7. Fracture toughness (R) as a function of beam porosity.

Critical strain energy release rate (G_{IC})

The derived values for G_{IC} as a function of porosity are shown in Fig. 6. The value of G_{IC} increases with decrease in porosity indicating that the energy required to initiate crack propagation increases as the powder becomes more closely compacted. Again, the relationship between G_{IC} and porosity is linear and extrapolation to zero porosity yields a value of $1{\cdot}98 \times 10^2$ Nm^{-1}, which corresponds to brittle materials, such as ceramics.

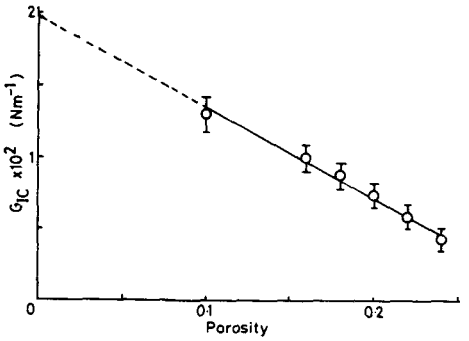

FIG. 6. Critical strain energy release rate (G_{IC}) as a function of beam porosity.

Fracture toughness (R)

The values of the logarithm of the fracture toughness as a function of the porosity of the beam are given in Fig. 7 and allow extrapolation to zero porosity. A value of $2{\cdot}19 \times 10^3$ Nm^{-1} is obtained for R at zero porosity, suggesting that Avicel behaves as a relatively brittle material.

It is clear from the above results that examination of the mechanical properties of pharmaceutical materials by a fracture mechanics approach is possible. The results established for Avicel place the material as polymeric material in terms of rigidity but clearly towards ceramic type of material in terms of crack propagation, as indicated by the critical stress intensity factor, critical strain energy release rate and fracture toughness. It appears likely that Avicel, when compacted as beams, contains predominantly open pores which gradually reduce in size as pressure is applied, thus requiring greater energy to cause catastrophic failure. The relations between compact porosity and the various parameters allow extrapolation to obtain values for these properties at zero porosity. The latter reflect the mechanical properties of the material, whereas values for the specimens or beams combine both the mechanical properties of the material and the formation conditions. The possible evaluation of material properties from this approach may be associated with the test procedure which (as detailed by Stanley 1985) provides evaluation of the material in simple uniaxial tension at the surface of the specimen, as opposed to the more complex stress systems induced by diametral compression (yielding biaxial stress) and the triaxial stresses involved in punch penetration tests.

The evaluation of the response of the materials to compression, tension and shear is fundamental to the understanding of the changes which take place during compaction of pharmaceutical materials. Characterization of fracture mechanics parameters should assist in the understanding of the complex process of tablet formation.

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