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Research Article

Evaluating the Fracture Toughness of Sucrose Crystals Using Microindentation Techniques

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The brittleness of pharmaceutical crystals influences their ability to form compacts of acceptable quality. While many macroscopic methods are available to elucidate the fracture behavior of materials, the porosity, inhomogeneity, and anisotropy of pharmaceutical compacts render it difficult to interpret the results of these tests. Microindentation techniques may be used to evaluate both the flow and the fracture characteristics of small crystals, so that it is not necessary to test compacts. The flow and fracture behavior of sucrose, the model substance used in this study, were anisotropic. The fracture surface energy, derived from the average fracture toughness value, is of the same order of magnitude as the surface free energy, indicating that sucrose fractures in a brittle manner.

KEY WORDS: sucrose; microindentation; fracture toughness; brittleness; hardness.

INTRODUCTION

Many crystalline materials will fracture if they are stressed above a critical level. The value of this stress depends upon the properties of the material, the configuration of the test system, and the environmental variables. The science of fracture mechanics was developed to elucidate the fundamental material properties that control fracture behavior and to discover their relationship with the external variables (1). The ultimate goal of fracture mechanics is a better prediction and control of fracture.

Organic crystals often exhibit brittle behavior during compaction. Fragmentation facilitates consolidation, but compacts comprised of brittle materials may cap or laminate easily and may exhibit unacceptable friability during subsequent processing. Therefore, there is considerable economic incentive to elucidate the fracture behavior of organic crystals of pharmaceutical interest.

The fracture behavior of engineering materials is investigated routinely. Several specimen geometries have been used extensively; the notched three-point and four-point bend specimens, double-cantilever beam specimens, and edge-cracked tension specimen are commonly used (2).

None of these tests is easily applied to pharmaceutical compacts, which are usually thin and cylindrical. The diametral compression test is used most frequently to assess the fracture characteristics of these specimens.

Continuum mechanics may be applied to the analysis of these test configurations to determine the intensity and distribution of stresses and displacements. The parameter which relates the applied forces to the displacements in these analyses is the stress-intensity factor, which depends only upon the applied stress and the geometry of the test system. In truly brittle materials, the stress intensity factor at failure (K_c) is related to the surface free energy of the material if cracking occurs under equilibrium conditions. In most materials, K_c is also a function of the nonequilibrium kinetics, deviations of the crack surface from planarity, plasticity, and other dissipative terms (1). Nevertheless, if the conditions under which the test operates are specified and carefully controlled, K_c may be considered to be a predictive material property. A fracture mechanics analysis of any test configuration requires prior knowledge of the length and shape of the crack which initiates failure. The porosity and inhomogeneity of compacts make it difficult both to locate this crack and to ascertain its critical characteristics.

Therefore, several empirical and semiempirical approaches have been developed to assess the brittleness of pharmaceutical materials. Among these are the analysis of the shape of the Heckel plot (3), variations of the diametral compression test which consider the work required to fracture a compact (4), and the brittle fracture index, which compares the tensile strength of compacts with and without a small, central, cylindrical hole (5). Unfortunately, the complicated microstructure of tablets, and the presence of residual stresses which arise during the decompression phase of the compaction cycle make it difficult to interpret these tests in terms of fundamental material properties.

It would be simpler to analyze the results of tests performed on fully dense polycrystalline specimens or from test pieces cut from single crystals. However, large, relatively flawless, organic crystals are difficult to obtain, and the preparation of suitably oriented test specimens is often difficult or impossible. They are inherently brittle, are suscep-

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tible to thermal shock, and degrade easily under conditions which are usually employed to produce large single crystals or fully dense polycrystalline specimens of other materials.

Microindentation tests are used widely to assess the flow characteristics of brittle materials and have been used recently to evaluate the fracture behavior of small crystals (1,6–9). In this context, the toughness is defined as the critical stress intensity factor for tensile fracture under plane strain conditions. This definition is compatible with that cited in ASTM (10) and in the microindentation literature. It must be contrasted with an alternate definition of toughness, i.e., the work of fracture, used frequently in the pharmaceutical and dynamic fracture literature.

Microindentation tests are not used universally for two reasons: (i) analytic solutions of the indentation stress field are not available and only approximate solutions have been derived even for the simplest contact behavior [i.e. elastic contact (11)]; and (ii) the deformation field is not homogeneous and anisotropy and fracture complicate the problem immensely.

As a result, the microindentation fracture mechanics approach to the assessment of K_c is strictly semiempirical: the dimensions of a microindentation hardness impression and the associated cracks may be used to develop an indentation fracture relationship which must be calibrated with the known fracture parameters of a wide range of materials. The microindentation approach employed in this study is quasistatic in character. The fracture resistance of semibrittle solids can change with increasing strain rates since the energy dissipated by dislocation motion at the tips of rapidly propagating cracks may be decreased. The impact situation has been considered in the ceramics literature, albeit to a lesser extent (12).

Engineering materials, tested on a microscopic scale, are used in macroscopic structures. It is important that the results of microindentation tests adequately predict the behavior of these materials under an arbitrary stress field. For these materials, a full characterization of the stress and strain fields during microindentation is ultimately desirable. Fortunately, the processing of pharmaceutical solids usually entails contact forces. Therefore, the hardness and indentation fracture resistance alone provide valuable information, and fully analytic solutions are not essential.

In the present study, the microindentation fracture behavior of single crystals of sucrose is assessed using microindentation fracture mechanics.

MATERIALS AND METHODS

Small crystals of sucrose (0.25–0.75 mm in diameter, Fisher Scientific, Lot 99258/2085) were tested as received. The impurities in these crystals are listed in Table I. Larger crystals (1–4 mm in diameter) were prepared by slowly evaporating a saturated aqueous solution of sucrose prepared from the crystals described above at 23°C for a period of 3–6 months. The crystals were collected and washed for 1 min with pure methanol to remove traces of crystallization solution. The purity of the crystals was verified using melting-point determinations (melting range for all crystals, 185–193 ± 2°C). The washing procedure was considered to be complete when the surfaces of the crystals were optically smooth and minute etch pits began to appear.

Table I. List of Impurities in the Sucrose Crystals Used in the Study

Impurity	Percentage (w/w)
Insoluble matter	0.003
Loss on drying	0.05
Sulfated ash	0.005
Chloride	0.0005
Nitrogen compounds	0.002
Sulfate	0.002
Cu	0.0001
Fe	0.0001
Pb	0.0001
Reducing sugars ($C_6H_{12}O_6$)	0.01

The crystals were stored for at least 2 weeks at 30 ± 5% RH in an environmentally controlled room prior to testing. The water content of the crystals is stable at the level shown in Table I over a large range of relative humidities (approximately 20–60%). The as-received crystals were often multiply twinned, but single crystals were selected for testing. These possessed a platy habit, in which the (100) and (001) faces predominated.

The crystals grown from solution were prismatic (Fig. 1), the predominant faces being (001) > (100) > (110) > (011) > (101) ⩾ (111). This habit corresponds to that described in the literature (13).

Some surfaces {(100), (010), (001)} were prepared by abrading the crystals with decreasing grades of emery paper and then polishing with Linde B polishing powder (0.05 μ, Micro Metallurgical Ltd., Richmond Hill, Ont.) using methanol as the lubricant. This permitted the characterization of the indentation behavior of (010) surfaces, which were not originally present in the crystals. (100) surfaces were also prepared by cleaving the crystals, since sucrose exhibits perfect cleavage on this plane (14). Microindentation testing was performed using a Leitz-Wetzlar Miniload hardness tester (Ser. No. 4762). The temperature at which the tests were performed was usually 23°C.

A crystal was mounted in plasticene so that the surface to be indented was normal to the indentation direction. This was achieved by maximizing the intensity of light reflected from the surface when the crystal was viewed under the microscope attachment. The 40× objective was then used to select an indentation site.

The indenter was cleaned with acetone and allowed to

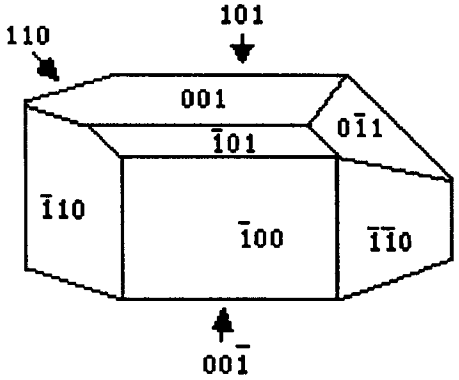

Fig. 1. Habit of large, prismatic crystals of sucrose.

dry. By the release of a trigger, it was then lowered slowly onto the surface of the crystal, over a period of 15 sec and full load was maintained for 10 sec. The indenter was subsequently raised almost instantaneously. Vibrations, which could give rise to false low hardness values (15), were avoided throughout the testing procedure. The criteria established by O'Neill (16) regarding the operation of the Vickers Hardness Test were adopted.

A 147-mN load, the minimum possible with this instrument, was employed for the majority of the indentation tests. At this load, at least one diagonal of the indentation was usually clearly defined. Excessive chipping, which usually obscured the edges of the indentations, occurred at higher loads. A 136° pyramidal, diamond indenter (Vickers) was employed. The indentations and cracks which resulted were measured using the scale in the eyepiece of a Leitz microscope which was calibrated daily.

The magnitude of flow and fracture anisotropy were determined from Vickers indentations made on (100), (001), (010), and (110) faces, with diagonals of the indentations oriented so that they were either parallel to or rotated 45° from the edges of the crystal.

RESULTS AND DISCUSSION

The dislocation density, determined by counting the number of etch pits in a given area, was fairly uniform and approximately equal to 10^6 cm^{-2} in the smaller sucrose crystals. In the larger crystals two regions with distinctly different dislocation densities, 10^6 and 10^7 cm^{-2}, respectively, were observed. Only those regions of lower dislocation density were tested.

A typical indentation is illustrated in Fig. 2. The quantities required in the fracture mechanics analysis of cracks associated with the indentation test are the hardness, Young's modulus, and the crack length. The Vickers Hardness Number (VHN; 136° pyramid) was calculated from the mean diagonal length (Fig. 3) according to Eq. (1) for indentations oriented both normal to and 45° from the edges of the (001), (100), and (110) faces which were originally present on the crystal.

$$\text{VHN} = \text{load/area of contact} = 1.854 \cdot P/d^2 \text{ (MPa)} \quad (1)$$

P = load (N)
d = mean indentation diagonal (mm)

The VHN of (100) cleavage faces, and (010) surfaces prepared as described earlier, were also determined. VHN did not change significantly with orientation on a given face, did not vary significantly from face to face (Table II), and was independent of the size of the crystals. However, the defect structure, which can influence the flow and fracture behavior of crystalline materials, is often dependent upon crystal size. Direct extrapolation of the results of this study to predict the behavior of fine powders is not *a priori* justified.

Organic materials are ordinarily expected to be relatively soft, however, the magnitude of the hardness of sucrose crystals (~650 MPa) is similar to that of iron (17). The molecules of sucrose are intramolecularly and intermolecularly hydrogen-bonded in the crystal. These bonds are directional and permit a more open, lattice-like crystal structure. Hydrogen bonds possess a strength of approximately the same magnitude (25–42 kJ mol^{-1}) as that of dispersion forces [<25 kJ mol^{-1} (18)] which predominate in the bonding of many hydrocarbons (19). However, the directionality of the hydrogen bonds in sucrose may result in a yield of relatively high value. This is the case with ice which possesses a high flow stress, with the yield being controlled by thermal activation (20). The temperature-dependent flow properties of sucrose and ice were found to be similar when compared on temperature scales which were normalized to their respective melting temperatures (21).


Fig. 2. Typical indentation on a (100) face of a sucrose crystal.

Fracture invariably occurred, and the chipping at the edges of the indentations increased with increasing indentation load. It is possible that the increased elastic compliance associated with the cracks could accommodate reversible penetration of the indenter, thereby altering the apparent hardness value. However, if a crystal, the surface of which had been prepared by grinding and polishing as described above, was indented within minutes of the final polishing, fracture either was suppressed entirely or was decreased significantly. The size of the indentation was the same, regardless of the presence or absence of cracking. Brookes

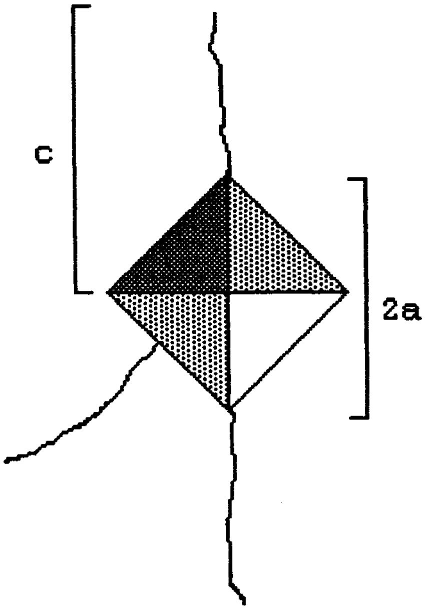

Fig. 3. Illustration of the quantities required to calculate the indentation fracture toughness.

Table III. Lengths of Radial Cracks Produced During Indentation of Sucrose Crystals[a]

Fracture Plane	Indentation Plane	$c \pm 95\%$ CI (μm)	n (Number of Measurements)
(010)	(001)	33 ± 6	7
(010)	(100)	32 ± 5	8
(100)	(001)	32 ± 3	13
(100)	(110)	40 ± 3	10
(110)	(001)	36 ± 2	12
(110)	(001)	34 ± 5	7
(110)	(001)	34 ± 2	13
(001)	(100)	31 ± 1	15
(001)	(110)	31 ± 1	15
(011)	(100)	33 ± 4	7
(011)	(100)	36 ± 4	7
(011)	(100)	36 ± 3	8
(101)	(110)	36 ± 1	15
(101)	(110)	36 ± 1	13
(101)	(010)	36 ± 1	13

[a] Cracking usually occurred on or near low-index crystallographic planes.

(22) asserts that fracture is unimportant in hardness measurements, and numerous investigators of indentation fracture toughness (23) assume that hardness values determined from indentations associated with cracks give a true measure of the material's hardness. This assumption was adopted in the present study.

Fracture Behavior

The lengths and orientations of the radial cracks which surrounded the indentation were recorded for each face tested and are tabulated in Table III. While the length of most cracks did not change during extended periods of observation, occasionally a crack would appear or extend suddenly as the indentation was being observed. The variability of the data in Table III may arise if the cracks were approaching an equilibrium length at an immeasurably slow rate.

Lateral cracks, which appear as a light halo around the indentation in Fig. 2, also occurred on (100) planes. The length of these cracks was extremely variable and depended upon the interval of time between indentation and measurement. Cracks often grew slowly, "popped in" suddenly several minutes after indentation, or disappeared with time. Apparently well-developed lateral cracks appeared to be approximately 50 μm in length.

Cracking was not observed, if surfaces which were prepared by grinding and polishing (100, 001, 010), were tested immediately (within 2 min). As the interval between surface preparation and testing was increased, cracks began to appear, and their final lengths also increased (Table IV) to a value which, within experimental error, was identical to that found with the unabraded surfaces (Table III).

This behavior suggests that the finishing procedure caused residual compressive surface stresses which suppress fracture (24). It is apparent from Table IV that recovery occurred rapidly, however, the testing temperature is a large fraction of the melting temperature (23°C = $0.65 \star T_m$), and diffusion processes are expected to be important in this regime. These observations increase confidence in the fracture data tabulated above, since at least 1 day elapsed between such surface preparation and testing.

Fracture appeared to be anisotropic. When the indenter was aligned so that its diagonals were parallel to the trace of the lowest index planes on the face being tested {(100), (001),

Table II. Vickers Hardness Numbers of Various Faces of Sucrose Crystals

Face	c^a	n^b	d^c	VHN^d	95% CI
001	5	31	20.7	636	±45
100	7	35	20.5	649	±44
110	5	17	20.6	642	±54
010	2	10	20.5	649	±64

[a] Number of crystals tested.
[b] Total number of indentations.
[c] Mean indentation diagonal (μm).
[d] Vickers hardness (MPa).

Table IV. Effect of Annealing at Room Temperature After Polishing on Fracture Behavior[a]

Time after Polishing (Min)	Crack Length (μm, from Edge of Indentation)
2.0	0 ± 1
4.0	16 ± 4
6.0	27 ± 4
10.0	21 ± 6
20.0	34 ± 4
60.0	33 ± 3

[a] The 95% confidence interval is shown (n = 6).

(010)}, cracking invariably occurred from the edges as well as the corners of the indenter. The cracks which emanated from the edges of the indentations appeared to be directed along the family of [110] traces at the edges of the indentation, but sometimes deviated slightly from this orientation 1–2 μm from the origin of the crack. The tips of the cracks along these directions deviated markedly toward alignment with (100) planes, approximately 15 μm from the edges of the indentation. Cracks which were initially directed along the (100) cleavage plane were of the same length or shorter than cracks in other directions. This indicates that the apparent toughness of sucrose crystals is greater in this direction, which is paradoxical since the natural cleavage plane of sucrose is (100).

K_c values were calculated from the lengths of radial cracks emanating from the microindentations (Fig. 3) using both Eq. (2), which assumes (22) a penny-like crack configuration, and Eq. (3), which assumes (9) cracks possessing a configuration similar to that described by Palmqvist (25).

$$K_C = k^a \, (E/H)^{0.5} \cdot (P/c^{1.5}) \tag{2}$$

$$K_C = kp \, (a/l)^{0.5} \cdot (E/H)^{0.67} \cdot P/c^{1.5} \tag{3}$$

K_C = critical stress intensity factor (MPa $m^{1/2}$)
H = hardness (MPa)
E = elastic modulus (MPa)
P = load (MN)
c = crack length (m)
a = half-diagonal of the indentation (m)
l = $c - a$
k^a = constant (0.016 ± 0.004)
kp = constant (0.015; coefficient of variation 0.026)

Equation (2) has been calibrated using many single-crystal and polycrystalline substances giving $k^a = 0.016 \pm 0.004$ and has been subsequently employed by others (26,27). The fit is excellent for polycrystalline materials but not as good for single crystals. However, the fit is improved if the calculations are corrected for the angular orientation of the cracks in single crystals (28).

Equation (3) is based on the assumption of a crack geometry which appears to more closely approximate the crack configuration in sucrose; however, it has not been tested as extensively as Eq. (2). The values for K_C derived from both analyses are listed in Table V. These values were calculated using a mean elastic modulus of 27,000 MPa calculated from Bridgman's compressibility data (29,30) assuming a Poisson's ratio of 0.25 and the mean Vickers hardness for each face.

The values of K_C determined by both approaches are similar and parallel the crack lengths in Table III. This result follows from the use of mean hardness and elastic modulus values. Laugier's approach appears to emphasize the apparent fracture anisotropy.

Fracture toughness appears to be the greatest across the (001) plane and the least across (100) planes for cracks propagating in the [010] direction but not in the [001] direction. This apparent directional anisotropy of fracture toughness could arise from kinetic factors during fracture, from the anisotropy of the elastic moduli of sucrose, or from plasticity associated with crack initiation. If the (001) face of a crystal of sucrose is loaded by a sharp indenter, cleavage along [010] is predicted. In fact, cracks propagate along [110] more readily than cracks in other directions. These cracks first propagate in a controlled manner with increasing load, then begin to deviate to the expected [010] direction as the rate of advance of the crack tip increases {(100) cleavage plane} prior to complete fracture of the crystal. Cracks along [110] could arise from pileup of dislocations in the (110)[001] slip system which are blocked by slip in the (100)[001] system.

Table V. Fracture Toughness Values for Sucrose Crystals[a]

Fracture Plane	Indentation Plane	K_c (MPa $m^{0.5}$ ± 95% CI) Anstis Formula	Laugier Formula
(010)	(001)	0.086 ± 0.024	0.095 ± 0.022
(010)	(100)	0.087 ± 0.022	0.098 ± 0.021
(100)	(001)	0.085 ± 0.012	0.100 ± 0.013
(100)	(110)	0.062 ± 0.007	0.064 ± 0.007
(110)	(001)	0.073 ± 0.005	0.081 ± 0.005
(110)	(001)	0.081 ± 0.020	0.090 ± 0.018
(110)	(001)	0.078 ± 0.005	0.090 ± 0.006
(001)	(100)	0.089 ± 0.003	0.109 ± 0.004
(001)	(110)	0.089 ± 0.003	0.111 ± 0.004
(011)	(100)	0.082 ± 0.014	0.093 ± 0.014
(011)	(100)	0.073 ± 0.012	0.079 ± 0.012
(011)	(100)	0.073 ± 0.010	0.079 ± 0.010
(101)	(110)	0.072 ± 0.002	0.080 ± 0.003
(101)	(110)	0.072 ± 0.002	0.080 ± 0.003
(101)	(010)	0.072 ± 0.002	0.079 ± 0.003

[a] The crystals tended to cleave along defined planes.

Early fracture mechanics models were developed by assuming that the fracture energy is required to form new surfaces (1). This suggests that materials which possess a large surface free energy should exhibit the greatest fracture resistance. In fact, the fracture surface energy, which may be calculated from the fracture toughness [Eq. (4)], is often much larger than the surface free energy (1). Under quasi-equilibrium conditions, this discrepancy arises in crystalline materials largely because plastic flow near the crack tip dissipates some strain energy in the fracture process.

The relationship between the fracture surface energy and the surface free energy provides a good definition of brittleness. The more brittle a material is, the closer these two values are. For a plane–strain fracture

$$\Gamma = K_C^2 \cdot (1 - \nu^2)/2 \cdot E \tag{4}$$

Γ = fracture surface energy
K_C = fracture toughness
E = Young's Modulus
ν = Poisson's ratio

The surface tension of sucrose in air at 170°C has been reported to be 62 mJ m^{-2} (31). The fact that this value is comparable to the average fracture surface energy of sucrose (110 mJ m^{-2}) suggests that sucrose behaves in an essentially brittle manner.

The microindentation technique using a Vickers indenter is sufficiently versatile to elucidate the average flow and fracture behavior of single crystals and to explore the anisotropy of these characteristics as well. An even more detailed analysis is possible if other indenters are employed (e.g., the Knoop indenter).

Such a detailed analysis of flow and fracture anisotropy may not be required to characterize the mechanical behavior of most organic materials during normal compaction procedures. The random alignment of crystals in a powder bed generally causes an average behavior. The effects of anisotropy may need to be addressed if large residual stresses arise from the elastic strain mismatch of randomly oriented but highly anisotropic crystals or at higher pressures, when preferred orientations may occur. While the effect of moisture was not considered in this study, its presence or absence can have a substantial effect on flow and fracture. The role of moisture has been studied in detail (21) and will be presented in a later publication.

The parameters determined by microindentation techniques may be used to evaluate the predictive capability of other tests that are used more commonly and are more easily applied. They will be particularly useful if the investigator can employ them to predict the compaction behavior of pharmaceutical materials. Models which predict the uniaxial compaction behavior of both ductile and brittle materials will be presented in a later publication.

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