Pharmaceutical Research, Vol. 11, No. 5, 1994

Research Article

Hardness Anisotropy of Acetaminophen Crystals

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Received August 17, 1993; accepted December 3, 1993

The anisotropy of acetaminophen hardness was demonstrated using both Vickers and Knoop indentation hardness measurements. Based on a model of Knoop hardness anisotropy proposed by Brookes *et al.* (1), it was concluded that plastic flow in acetaminophen crystals occurs primarily as a result of slip in the (010)⟨001⟩ system. This conclusion was corroborated with the results of the Vickers indentation tests. The apparent brittleness of acetaminophen was rationalized because only one slip system appeared to be operative. Under these conditions generalized plastic flow cannot occur, since this requires the operation of at least five independent slip systems (2). The high stress concentrations that result from flow lead to fracture. Therefore acetaminophen is more precisely classified as being semiductile. When a material deforms plastically as a result of slip in only one slip system, considerable crystal realignment can occur during compaction. This in turn can facilitate capping during decompression and ejection, since the cleavage plane, (010), would become aligned with the direction of highest tensile stress.

KEY WORDS: acetaminophen; hardness; indentation; anisotropy.

INTRODUCTION

The most easily applied methods of evaluating the elastic, yield, and fracture behavior of single crystals usually require large specimens possessing simple geometries. However, large sufficiently flawless pharmaceutical crystalline specimens are extremely difficult to prepare. These materials are inherently brittle, susceptible 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. For these materials, the indentation test is the simplest, and often the only, mechanical test available.

The primary shortcoming of indentation testing is that analytic solutions of the deformation under an indenter require the use of a complex contact geometry. In fact, only approximate solutions have been derived even for the simplest contact behavior, i.e., elastic contact (3). Anisotropy, flow, and fracture complicate the problem immensely. Therefore, although exact solutions are available for the simpler test configurations, calibration factors are required to compare indentation behavior with the results of other tests. While the indentation configuration is not preferred for this reason, if the micromechanics of single-crystal deformation are considered, and if the implications of any assumptions are considered carefully, useful information regarding both flow and fracture may be derived from indentation tests.

Hardness and Plastic Flow

The hardness is a material property which is defined as the mean stress under an indenter giving rise to plastic flow. The mean stress is calculated from the applied load and either the true area of contact or the projected area of contact. A variety of indenter geometries is used. The two most common indenter geometries, the Vickers and Knoop, produce shallow indentations and tend to minimize the amount of surface damage. The Vickers indenter is a four-sided 136° pyramid. The Vickers hardness number (VHN) is calculated from the mean length of the diagonals of an indentation using Eq. (1) and is equal to the mean stress across the true area of contact:

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

where P is the applied load and d is the length of the mean indentation diagonal.

The Knoop indenter produces a long, shallow indentation, which, in an isotropic, ideally plastic material, produces an indentation with length:depth:breadth of 30.53:1:4.29. The Knoop hardness number (KHN) is calculated from the projected area of the indentation using Eq. (2):

$$\text{KHN} = 14.2 \cdot P \cdot l^{-2} \quad (2)$$

where P is the load and l is the length of the long indentation diagonal. Very little recovery of the length of the long diagonal of the indentation occurs after the load is removed (4). Therefore this measurement is an acceptable indication of the projected contact area at maximum load.

Yield Behavior of Single Crystals Determined from Hardness Anisotropy

The plastic yield of single crystals is usually confined to a few slip systems, i.e., slip occurs only on a restricted number of crystallographic planes in a few particular directions.

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Permanent deformation will be observed when the shear stress is sufficient to overcome the energetic barriers to flow on the most favored slip system(s).

During indentation, the load is transmitted to the specimen by each of the indenter facets. The stress applied by each facet can be resolved into normal and shear components along any given slip system. Since the indentation can be produced in many different directions, in general, the shear stress applied by an indenter facet along a particular slip system will vary with the orientation of the indenter. Therefore the hardness tends to vary with direction as well. A complete understanding of the yield behavior of a material requires the elucidation of the slip systems and their flow stresses.

Although the VHN tends to vary from face to face of an anisotropic crystal, it tends not to vary substantially as a function of indenter orientation on any given crystal face because the Vickers indenter is relatively symmetrical. The hardness values determined by asymmetrical indenters such as the Knoop pyramid are much more sensitive to orientation and are often used to investigate and elucidate the origins of flow anisotropy. Hardness anisotropy of crystalline minerals was confirmed during the development of the Knoop test (5–7).

While it is generally agreed that hardness is a function of the stress applied to the individual facets of the indenter and of the critical resolved shear stress of the most active slip system, there appears to be considerable dissent regarding the form of this function. No model adequately explains the behavior of every material (1). This should not be surprising, since the deformation behavior of materials varies so greatly. The models may be placed into three major categories: those which assume that the deformation arises from the shear stresses at the face of the indenter (1,8,9), those which assume that it arises from the stress normal to the facets of the indenter (10,11), and those which consider both possibilities (12,13).

These models may be subdivided further into those which use a hypothetical elastic constraint factor and those which do not. When a blunt indenter such as the Vickers or Knoop is employed, the elastic interaction between the material which is yielding and the surrounding material causes the hardness to exceed the uniaxial yield stress by a multiplicative "constraint factor" (4,14). Other studies have shown that acetaminophen behaves in an elastic/plastic manner (15) so it is logical to prefer models that take such constraint into account.

Such is the case with the model employed below (1) to explore the hardness anisotropy and to determine the slip systems responsible for the plasticity of acetaminophen crystals.

MATERIALS AND METHODS

Crystal Preparation

To obtain a large crystal of acetaminophen for indentation testing, a flawless small crystal was suspended in a cold, saturated pure acetone solution on unwaxed dental floss. As the acetone slowly evaporated, the solid was deposited onto the seed crystal surface and a large, clear, and well-formed crystal resulted after about 2 weeks (Fig. 1). After all indentations were made and measured, the crystals were etched with acetone. The etch pits were then counted using the microscope of the microindentation hardness tester.

Microindentation Testing

Microindentation testing was performed using a Tukon hardness tester and both the Vickers and the Knoop indenters. The temperature at which the tests were performed was 23 ± 3°C. Single large crystals were mounted onto glass slides using plasticene (Canada Games Co., Downsview, Ontario) to immobilize the specimen in the orientations being studied so that the surface to be indented was normal to the indentation direction. This was achieved (i) by maximizing the intensity of light reflected from the surface when the crystal was viewed under the microscope attachment and (ii) by ensuring that the focus was constant in the entire visual field at maximum magnification. Plasticene is recommended as a mounting material if the indentation site remains sharply in focus during the indentation procedure. This was verified in the present tests.

The indenter was lowered hydraulically onto the crystal surface by a cantilever device and maximum force (10 g) was maintained for 10 sec, after which the load was removed automatically. Vibrations, which could give rise to false low hardness values (4), were avoided throughout the testing procedure.

Hardness Anisotropy

The magnitude of flow and fracture anisotropy were determined in the following way.

1. (1) Vickers indentations (≥10 per face) were made on all prominent faces of the as-grown acetaminophen crystals.
2. (2) Knoop indentations were made on the (100), (001), and (010) faces at 30° intervals through 180° (≥6 replicates per angular orientation). Observations which may be useful in assessment of slip system behavior, such as those of indentation shape, the presence and

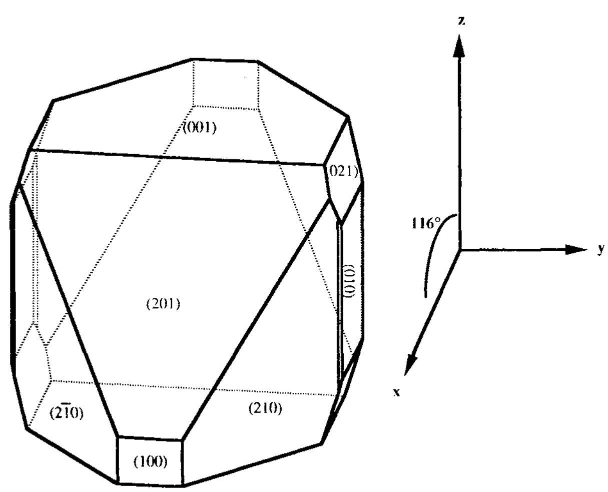

Fig. 1. Illustration of a typical monoclinic crystal of acetaminophen, with the most important faces labeled with Miller indices and the crystallographic axes indicated.

orientations of cracks, and any evidence of slip, such as the presence of slip lines, were made at the time of measurement. Because hardness can vary across a large crystal surface, regions covering the entire crystal surface were sampled for each orientation of the indenter.

The crystal was mounted and oriented to the long axis of the indenter with reference to a crystallographic direction. At least six "clean" indentations were measured for each indenter orientation. A "clean" indentation is one in which the following conditions were noted.

(1) Opposite halves of the indentation were equal in length, indicating that the crystal face of interest was normal to the load.
(2) Accurate measurement of the indentation is certain, not made questionable by chipping at both ends of the indentation (at least one end of the axis is sharp and can be measured unambiguously from the centreline of the indentation).
(3) If a clean indentation could not be obtained after several tries, the instrument load was reduced. The geometry of the resultant indentation is also noted. Fig. 2 shows typical artifacts produced by anisotropic elastic recovery when a Knoop indenter is used. When the indenter diagonals are oriented 90° to the slip lines, pincushioning results, while barreling is seen when the diagonals are 45° to the slip lines. These effects can make measurement of the diagonals somewhat uncertain.

RESULTS

Vickers Hardness Anisotropy

The dislocation density, as measured by counting etch

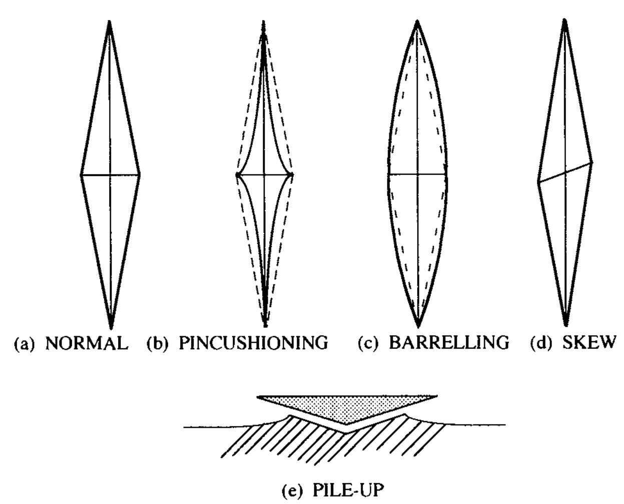

Fig. 2. Illustration of indentation artifacts due to material behavior such as anisotropy when utilizing a Knoop indenter: (a) normal indentation symmetry with standard ratio of axes lengths; (b) pincushioning which occurs when the indenter axes are normal to slip planes in the crystal; (c) barreling which occurs when the indenter axes are 45° to the slip planes in the crystal; (d) skew; (e) pileup around the edge of an indentation due to displacement of material from the bulk of the crystal to the surface as result of slip system operation.

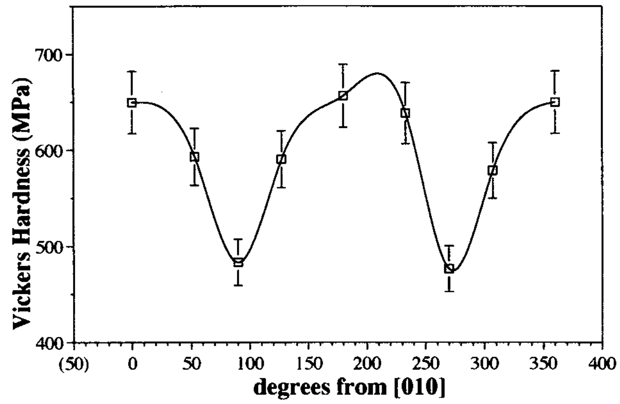

Fig. 3. Plot of VHN for faces around the ⟨100⟩ axis of a typical acetaminophen crystal with respect to the indenter orientation.

pits, is a measure of the relative perfection of the crystals. The number of etch pits observed varied from face to face, but on average the dislocation density ranged from 10^5 to 10^6 cm^{-2}. The quality of the Vickers indentations varied from face to face, as did the measured hardness values. The face that proved to be the most difficult to indent was (010), the cleavage plane of acetaminophen. Cracking almost always occurred; however, on the (010) face, the lateral fracture and chipping were often bad enough to obscure the features of the indentation. For the purpose of illustrating the systematic manner in which hardness varies with direction, the results were plotted in circuits rotating around the three crystal axes (Figs. 3–5).

Knoop Hardness Anisotropy

(100) Face (Fig. 6)

This face provided the best reliability in measurement as evidenced by the lowest standard deviations for all faces ($n \geq 7$). Only a few indentations had unsatisfactory width dimensions as a result of fracture. There was occasional pincushioning associated with the 30, 60, 120, and 150° orientations.

(010) Face (Fig. 7)

While chipping and fracture prevented reliable measurement of almost all indentation widths in any orientation, the

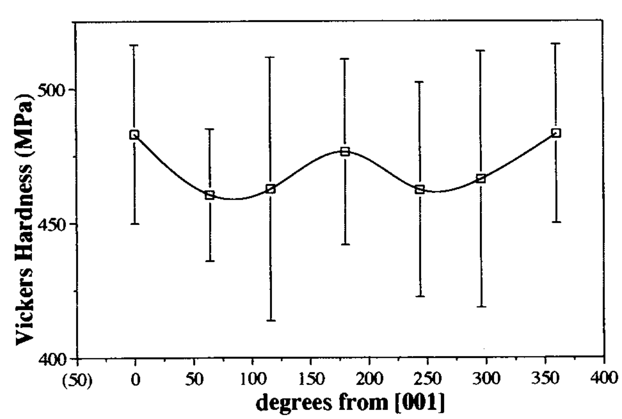

Fig. 4. Plot of VHN for faces around the ⟨010⟩ axis of a typical acetaminophen crystal with respect to the indenter orientation.

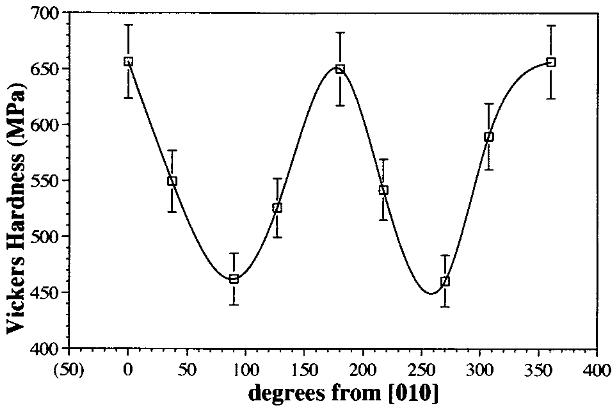

Fig. 5. Plot of VHN for faces around the ⟨001⟩ axis of a typical acetaminophen crystal with respect to the indenter orientation.

worst orientations appeared to be the 30 and 150° directions. One indentation at 150° created a massive fracture. The 30 and 90° angles indented so poorly that only two and four indentations were measurable, respectively (otherwise $n \geq 7$). Of those at the 90° orientation, most were chipped or exhibited very exaggerated pincushioning. The most ideal indentations were found at the 120° alignment. One of the indentations in this orientation exhibited very clear slip lines. On average, the (010) face was harder than the other faces.

The experimental values are offset from the predicted values for critical resolved shear stress on the x axis in Fig. 7 due to the fact that theoretical calculations were made starting from the Cartesian z direction, which is *not* coincident with the crystallographic z direction, but 26° offset from it in this monoclinic crystal.

(001) Face (Fig. 8)

Pileup occurred for all indentations in the 0 and 30° orientations, while chipping was a problem for nearly all indentations at the 60° (preventing any width measurements for this angle) and 120° orientations. Occasional pincushioning was observed in the 30 and 120° alignments. The best results for this face were seen in the 30 and 150° orientations where all indentations had measurable widths. The least satisfactory direction was the 90° alignment, where only two width measurements were possible.

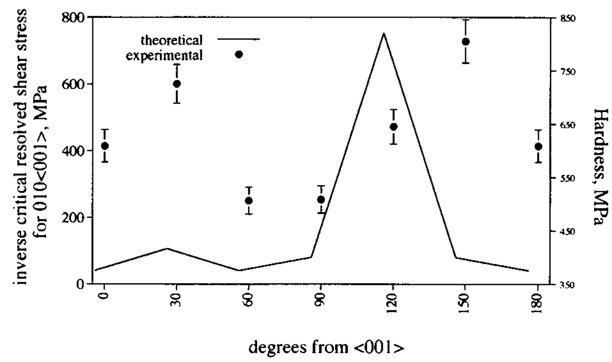

Fig. 7. Plots of inverse critical shear stress calculated for the (010)⟨001⟩ slip system and the experimental hardness of the (010) face of a typical acetaminophen crystal with respect to indenter orientation. The error bars indicate the standard deviation of the measurements.

DISCUSSION

The results of Brookes *et al.* (1), Daniels and Dunn (8), Partridge and Roberts (16), Garfinkle and Garlick (17), Petty (18), and others verify the intrinsic nature of hardness anisotropy in crystalline solids. While all these investigators have developed models based on the hypothesis that dislocation behavior and bulk plastic flow should account for the observed correlation between operative slip systems and the measured anisotropy, that of Brookes *et al.* (1) has been shown to be particularly successful. Its application is rationalized as follows.

Consider a cylindrical crystal deforming under an applied unidirectional tensile stress. During the early phase of plastic deformation, the crystal becomes elliptical in cross section due to slip in the primary slip system by the rotation of slip planes about an axis lying in those planes and normal to the slip direction. The crystal tends to deform plastically as the resolved shear stresses behave according to the Schmid and Boas (19) relationship:

$$\tau = (F/A) \cos\lambda \cos\phi \tag{3}$$

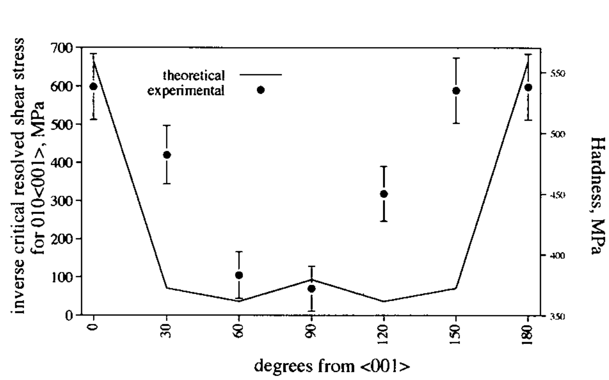

Fig. 6. Plots of inverse critical shear stress calculated for the (010)⟨001⟩ slip system and the experimental hardness of the (100) face of a typical acetaminophen crystal with respect to indenter orientation. The error bars indicate the standard deviation of the measurements.

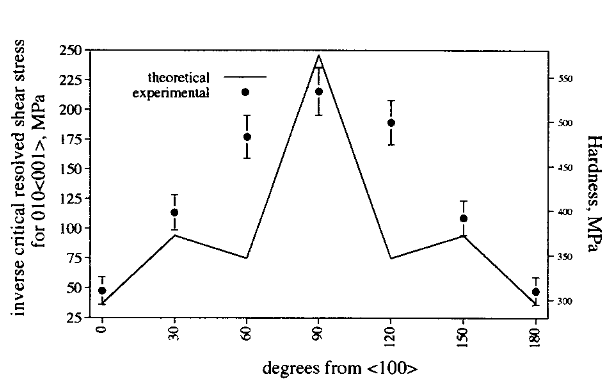

Fig. 8. Plots of inverse critical shear stress calculated for the (010)⟨001⟩ slip system and the experimental hardness of the (001) face of a typical acetaminophen crystal with respect to indenter orientation. The error bars indicate the standard deviation of the measurements.

where τ is the resolved shear stress, F is the applied force, A is the cross-sectional area of the specimen, λ is the angle between the stress axis and the slip direction, and ϕ is the angle between the stress axis and the normal to the slip plane.

The evaluation of hardness anisotropy requires the consideration of several other points.

(1) The angle between the axis of the deformation stress and the indentation surface must be calculated, thus permitting calculation of values for λ and ϕ for a given orientation.

(2) The deformation stress is assumed to be a tensile force parallel to the line of steepest slope on the individual indenter facets as proposed initially by Daniels and Dunn (8).

(3) The slip planes are constrained elastically during indentation so that the specific selection of slip systems will be affected by the interaction of the indenter and the elastically deforming material immediately beneath the indented region. As indentation occurs, the material beneath the indenter is displaced from within the bulk to the specimen surface. This means that a slip system permitting rotation about an axis parallel to an adjacent indenter facet would be better oriented for slip than one whose axis is normal to the facet. The rotation of the slip planes is constrained by the cosine of the angle ψ between the face of an adjacent facet and the rotational axis for any given slip system. When the axis of rotation is parallel to the indenter facet, rotational constraint is minimal, $\psi = 0$, and constraint is unity. When $\psi = 90$ degrees, the constraint is maximized and, since slip plane rotation is not possible, slip does not occur. These considerations by Daniels and Dunn (8) resulted in the following effective resolved shear stress equation:

$$\tau_e = (F/A) \cos\lambda \cos\phi \cos\psi \quad (4)$$

Although F and A cannot be specified using unequivocal values from a hardness test, the relative magnitude of the resolved shear stresses can be found from the product of the cosines of the angles for indentations in any direction on a given plane of a crystal. The highest hardness values should be found to be coincident with those directions experiencing the lowest effective resolved shear stress.

(4) Brookes *et al.* (1) showed that the maximum constraint is *not* defined by $\psi = 0$ *alone*. The consideration of the relationship between the slip direction in a given plane and an adjacent indenter facet revealed that the maximum constraint is found only when the slip direction (s.d. in Fig. 9) and an axis parallel to a specific indenter facet (**HH**) are coincident ($\gamma = 0$) and ψ is automatically 90°. When γ is greater than zero, then even though $\psi = 90°$, rotation of the slip plane occurs. However, if the axis of rotation, (a.r. in Fig. 9) and **HH** are coincident (γ must be 90°), the minimum constraint is found. Brookes *et al.* (1) thus modified the effective resolved shear stress due to rotational constraint to ½ ($\cos\psi + \sin\gamma$), and the complete equation was changed to

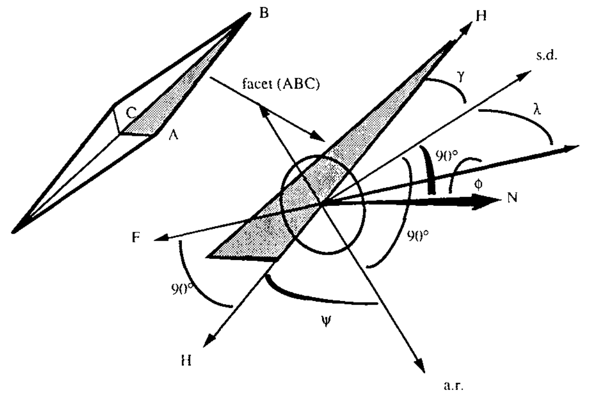

Fig. 9. Diagram illustrating the geometric relationships in the Brookes–O'Neill–Redfern model.

$$\tau_e' = \tfrac{1}{2}(F/A) \cos\lambda \cos\phi (\cos\psi + \sin\gamma) \quad (5)$$

An illustration of the model giving all the relevant angles is shown in Fig. 9. The significant point is that there will always be a finite resolved shear stress on crystal slip systems regardless of the crystallographic nature of the indentation. Brooks *et al.* (1) applied the theory to many systems (metallic and nonmetallic; hardness range, 13 to approx. 10^4 kg/mm^2), achieving good agreement with experiment.

The critical resolved shear stresses resulting from indentation on the (100), (010), and (001) faces of acetaminophen were calculated for the six most probable slip systems, i.e., (100)⟨010⟩, (100)⟨001⟩, (010)⟨100⟩, (010)⟨001⟩, (001)⟨100⟩, and (001)⟨010⟩. Values for each Knoop indenter facet were evaluated at 30° intervals through 180° degrees using a Microsoft Excel spreadsheet. Finally, the inverse critical resolved shear stress values were summed for all indenter facets to provide a relative estimate of the apparent hardness value for the given indenter orientation. Plots of these values, given as a function of orientation and slip system, are shown for the (100) face in Fig. 10.

In the simplest case, one would inspect the data to find the single slip system or combination of slip systems that (a) have the lowest critical resolved shear stress *on each face* and (b) have the appropriate variation with indenter orientation *on each face*. As shown in Fig. 10, one might consider the (100)⟨001⟩ or (001)⟨100⟩ slip system because they both appear to mirror the experimental hardness of the (100) face. However, these slip systems do not predict the hardness behavior of the (010) and (001) faces. In fact, the only single slip system that predicts the hardness of all faces is (010)⟨001⟩, and that, only approximately.

At this stage, it is usual to consider combinations of slip systems. In the least complicated case, one simply considers the lower envelope of two or more critical resolved shear stress curves. For example, the combination of the (010)⟨001⟩ and (001)⟨100⟩ slip systems would produce an envelope of the correct shape for the (100) face with lower mean critical resolved shear stress values overall. At a slightly more complex level, this procedure is carried out *for each indenter facet* prior to summing.

The inherent difficulty of this approach is that one requires some knowledge of the relative strength of the crystal as a function of direction. For highly symmetric ionic or

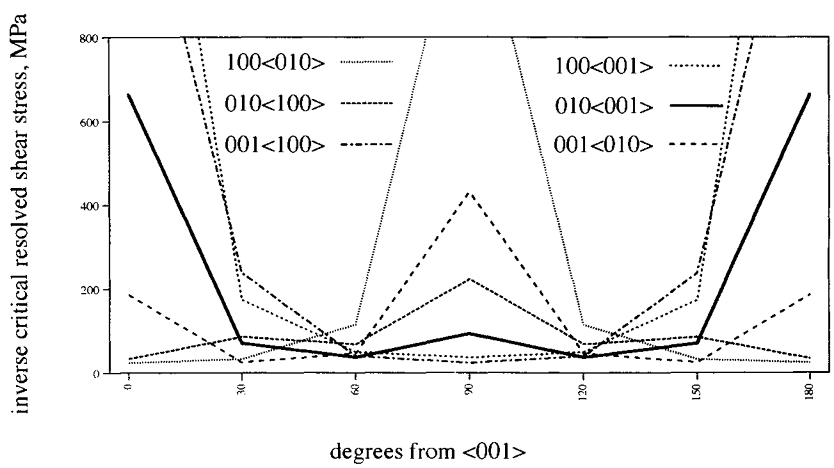

Fig. 10. Plot of inverse critical resolved shear stress values for various slip systems for Knoop indentations on the (001) face.

metallic crystals, it is customary to consider that the interplanar cohesion is influenced primarily by (a) interplanar spacing and (b) slip distance. In primitive cells, slip should be directed only along the shortest lattice translation vectors, the ⟨100⟩ family (20). However, acetaminophen is much more complicated. Its crystals are composed of hydrogen-bonded pleated sheets in the (010) plane, which are stacked in the ⟨010⟩ direction by van der Waals forces (Fig. 11). The directionally varying strength of the three-dimensional lattice that incorporates covalent, van der Waals, and hydrogen bonds can be estimated only on an order-of-magnitude scale. This makes the process of summation highly questionable.

However, given that the (010)⟨001⟩ slip system predicts quite well, it is informative to consider whether this result is consistent with other information about acetaminophen crystals and their hardness.

(1) From consideration of the bonding anisotropy alone, it is expected that the (010) plane would be the one of the most probable operative slip systems and is in fact the one predicted by the Knoop hardness anisotropy data using the Brookes–O'Neill–Redfern model, i.e., (010)⟨001⟩. It may be that steric hindrance or packing strain inhibits flow in the ⟨100⟩ direction or the formation of extra (100) half-planes [the latter required for flow in the (010)⟨100⟩ slip system].

(2) Slip on the (010) plane would be consistent with the variation of Vickers hardness around the x and z axes. For the purpose of illustration, one can approximate the structure and slip behavior of acetaminophen crystals with a pack of cards. Indenting a card face (i.e., in the ⟨010⟩ direction) is intuitively more difficult than indenting the deck on either of its sides (i.e., in either the ⟨100⟩ or the ⟨001⟩ directions). Thus, one would expect the ⟨010⟩ faces to possess a higher Vickers hardness than either the ⟨100⟩ or the ⟨001⟩ faces. As shown in Figs. 3–5, this is the case.

(3) In Fig. 4 it is shown that the (001) direction is harder than the (100) direction. This would be expected if flow occurs in the (010)⟨001⟩ slip system. Flow is more constrained elastically in the ⟨001⟩ direction because it can occur only toward the depth of the crystal. On the (100) face, flow in the (010)⟨001⟩ system can occur laterally and is, thus, relatively unconstrained.

(4) Constrained plasticity often leads to fracture. Therefore, one would expect indentation on both the (010) and the (001) faces to be accompanied by cracking

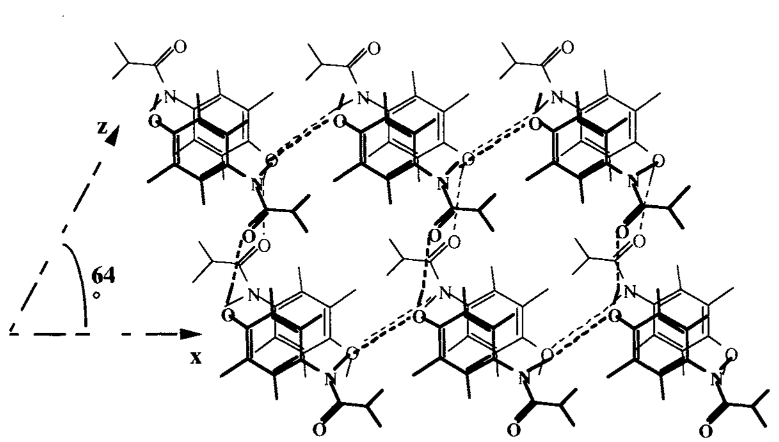

Fig. 11. Illustration of the crystal lattice of acetaminophen, viewed along the y axis.

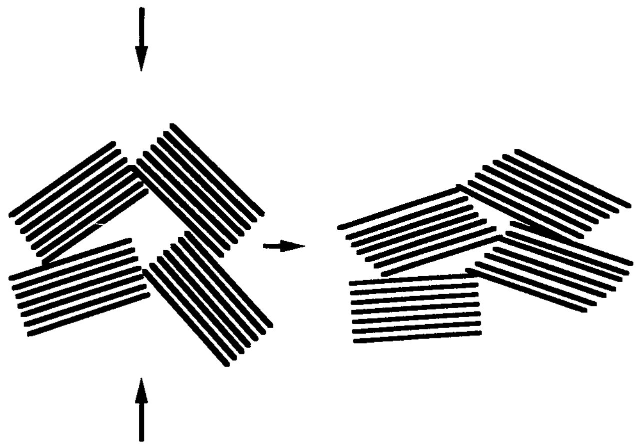

Fig. 12. Illustration of the effect of compaction on the orientation of acetaminophen crystals. Flow on the (010)⟨001⟩ slip system causes the (010) cleavage plane to align with the major tensile stress during decompression.

and chipping since flow in the (010)⟨001⟩ slip system would be constrained on these faces. Conversely, indentations on the (100) face should be relatively flawless. This was found to be the case, with the except of one or two orientations on the (001) face.

Given these considerations, we believe that it is reasonable to suggest that plastic flow in acetaminophen crystals occurs primarily as a result of slip in the (010)⟨001⟩ system. This fact gives rise to considerable anisotropy of plasticity and fracture.

CONCLUSIONS

The anisotropy of acetaminophen hardness was demonstrated using both Vickers and Knoop indentation hardness measurements. Based on a model of hardness anisotropy proposed by Brookes *et al.* (1), we believe that it is reasonable to suggest that plastic flow in acetaminophen crystals occurs primarily as a result of slip in the (010)⟨001⟩ system. Because only one slip system appears to be operative, generalized plastic flow cannot occur, since this requires the operation of at least five independent slip systems (2). The result is the development of high stress concentrations that lead to fracture. As a result, acetaminophen is considered to be brittle, although it may be more precisely classified as semiductile, as is sodium chloride.

The limited ductility of acetaminophen has a significant practical consequence during tablet compaction. When a material deforms plastically as a result of slip in only one slip system, considerable crystal realignment can occur as shown in Fig. 12. In a compact, this will cause the crystals to become mutually aligned with the ⟨010⟩ crystal direction becoming increasingly oriented in the direction of punch travel. Since the (010) plane is also the cleavage plane, this alignment could facilitate capping during decompression and ejection.

ACKNOWLEDGMENTS

Financial assistance to W.D.H., from the Natural Sciences and Engineering Research Council of Canada and the Medical Research Council of Canada, and to A.Y., in the form of a Medical Research Council Summer Studentship, is gratefully acknowledged.

NOMENCLATURE

VHN	Vickers hardness number (load/area)
P	Applied load (g)
d	Length of the mean indentation diagonal (μm)
KHN	Knoop hardness number (load/area)
l	Length of the long diagonal measurement of a Knoop indentation (μm)
(100)	Miller crystallographic indices notation indicating the crystal face which is aligned normal to the *x* axis
(010)	Miller crystallographic indices notation indicating the crystal face which is aligned normal to the *y* axis
(001)	Miller crystallographic indices notation indicating the crystal face which is aligned normal to the *z* axis; however, in this monoclinic system, the *z* axis is 116° from the *x* axis
<100>	Indicates a direction parallel to the *x* axis in the Miller notation
(100)<100>	Indicates, using the Miller indices system, a slip system operating in an *x* plane in the *z* direction
n	Number of indentations measured successfully for each orientation on a particular facet
τ	Resolved shear stress according to Schmid and Boas (19)
F	Applied force
A	Cross-sectional area of the specimen
λ	Angle between the stress axis and the slip direction
ϕ	Angle between the stress axis and the slip plane normal
ψ	Angle between the face of an adjacent indenter facet and the rotational axis of any given slip system
τ_e	Effective resolved shear stress according to Daniels and Dunn (8)
s.d.	Slip direction
a.r.	Axis of rotation
HH	Axis parallel to specific indenter facet
γ	Angle between the slip direction and an axis parallel to a specific indenter facet
τ_e'	Modified effective resolved shear stress according to Brookes *et al.* (1)

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