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The hardness and elastic modulus of some crystalline pharmaceutical materials

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The surface microhardnesses of single crystals of the following materials have been measured: aspirin, hexamine, sodium chloride, potassium chloride, urea, salicylamide and sucrose. A Leitz microhardness tester was used, with indentor loads of 25 g or less, in order to give indentations of less than 50 μm diagonal length and enable measurements to be made on single crystals. The compressive elastic modulus of some of the crystals was also determined using a "Techne" microtensile tester modified to work in compression. When the materials are listed in order of magnitude of Young's modulus, this order is the same as when they are listed in order of magnitude for surface hardness.

The large amount of work done on the compaction of materials to form tablets has shown the importance in this process of the physical nature of the materials themselves. Few measurements have been made of the mechanical properties of pharmaceutical materials, and the present work was initiated to obtain values for the elasticity and surface hardness of a series of crystalline substances in order to explore any relation these might have to the compaction behaviour of the various materials.

There are difficulties in measuring the hardness and elastic modulus of small crystals. Standard hardness testers used in the metallurgical industries are of little value in determining microhardness of crystals of non-metals since the loads applied and the size of the indentations produced are much too large for the very small and (relative to metals) soft particles which comprise pharmaceutical materials. With the development of microhardness testers which need only apply loads as small as 10 g, such measurements become possible.

Many workers have attempted by mechanical, electrical and optical methods to determine the moduli of elasticity of crystalline materials. Unfortunately the value of the modulus of elasticity varies in different crystal directions and is closely linked with the degree of symmetry exhibited by the crystals. The work of Neumann (1954) has shown that for complete expression of the elasticity in different directions of a triclinic crystal, the general case, 21 elastic constants are required. This number reduces in stages, some of the constants becoming equal, as the amount of crystal symmetry increases.

This complexity provides an interesting mathematical situation, and many mathematicians have produced equations, describing the elasticity, which are often very complicated but do not help to explain practical results. There is, however, in any practical, and particularly any industrial situation, a need for a measurement which may not be very precise but which will nonetheless be useful.

With this in mind a commercial micro-tensile testing machine for testing metal whisker crystals, described originally by Marsh (1961) was modified to make

compressive tests on crystals of various materials. The results are subject to inaccuracy due to crystal defects, misorientation, slip and cracking under load, but the averaged values so obtained do enable some conclusions to be reached.

EXPERIMENTAL

The aspirin used was B.P. grade from Laporte Industries Limited. All the other materials used were B.P. grade chemicals from B.D.H. Limited, except sucrose, which was Analar grade. They were not treated in any way beyond sieving, and orienting on the testing machines as described below.

The microhardness tester (Leitz Ltd., London) used can be considered as a microscope fitted with a movable carrier which enables a pyramidal-ended diamond to be pressed into a specimen. The size of the resultant impression is then accurately measured under high magnification. Various weights between 5 and 2000 g can be placed on the loading disc on the top of the diamond holder. The diamond for Vickers hardness tests has a square pyramidal point of 136° angle which is slowly brought into contact with the specimen at a rate controlled by a hydraulic damper. It produces an indentation which appears square in shape, with diagonals, when viewed from above. Illumination is by normal or polarized light shining onto the specimen surface through the objective itself. By measuring the lengths of the diagonals using the measuring graticule, the Vickers hardness of the specimen can be found.

Crystals were mounted by pressing lightly with another slide into heat-softened picene wax on a mounting slide, thus ensuring that the upper surfaces of the crystals were horizontal. The mounting slide and the crystals were then placed on the testing table of the hardness tester ready for indentation.

It was not possible to determine the orientation in many of the samples and a random positioning of the indentations was carried out whilst avoiding obvious irregularities of the surface.

The deformation of crystals under load was determined using a microtensile testing machine (Techne Ltd., Duxford, Cambridge). Normally the specimen is glued between two silica anvils, and a tensile force applied to it by means of a torsion wire capable of providing a load of up to 400 g. As the specimen extends, one anvil moves. It is connected to an inclined-mirror system, through which two images of a slit are projected. A micrometer allows the anvil movement to be cancelled out, as indicated by superpositioning of the two slit images. The micrometer, driving through a 100:1 reduction arm, combined with the sensitivity of the null-point mirror detecting system, is claimed to be capable of measuring length changes down to 50 Å.

The anvils, the use of tensile force, and the specimen mounting system were not suitable for three reasons: (*a*) the adhesive may affect the surface and hence the properties of the crystal; (*b*) it may form a collar and support the crystal; and (*c*) the machine measures tensile properties, whereas compressive behaviour is more relevant in tabletting work.

Reversing the direction of torsion wire twist, replacing both chuck assemblies by flat-faced compression anvils and adding a spring to maintain contact between the carriage and the coarse strain micrometer enabled the machine to be used with specimens in compression instead of in tension.

For compressive tests, crystals devoid of cracks and with flat, uniform and parallel faces were selected from a batch without subjecting them to extra stress. A manipulating device was used consisting of a hypodermic needle with its point ground flat attached by flexible plastic tube to a vacuum pump. The crystal was held onto the needle by pump suction, the vacuum pressure being controlled by covering or uncovering a small hole in the tube.

A low-power projection microscope arrangement was constructed for crystal measurement, the area over which the load was applied in the subsequent compressing experiments, as well as the length of the specimen, being found from the projection diagrams obtained.

After area measurements the crystal, still held on the hypodermic needle, was placed between the compression anvils, and a load just sufficient to deflect the mirror (0·01 g) was applied. The crystal was thus supported by the friction between it and the anvils and the holding device could be removed. The load was increased at a uniform rate in twelve increments and after each load application the strain micrometers were adjusted to return the optical detection system to the null position. The specimen was observed through a microscope during the test to detect cracks or slipping.

RESULTS AND DISCUSSION

Surface microhardness

The results of many determinations are given in Table 1. The limits of error are usually larger for the softer materials since in general the definition and quality of the indentation decline as the load which can be applied diminishes: to obtain a precise indentation under reasonable loading a hard material is needed.

Table. 1. *The Vickers hardness of crystalline materials*

	Indentation						
	Length (μm)	Depth (μm)	Load (g)	s.d.	No. of indentations	Hardness value (kg/mm^2)	Limits of error (P=0·05)
Steel	18·0	2·6	100	0·23	25	565	0·01
Sodium chloride	49·2	7·0	25	1·30	60	21·2	0·7
Aspirin ..	46·4	6·6	10	3·13	325	8·7	0·9
Sucrose.. ..	27·0	3·9	25	1·63	30	63·6	4·8
Hexamine ..	37·3	5·3	10	1·32	25	13·3	0·9
Urea	45·1	6·4	10	1·43	25	9·1	0·7
Salicylamide ..	35·1	5·1	10	1·41	25	15·1	1·1
Potassium chloride ..	51·8	7·4	10	1·52	25	17·7	0·9

Previous work on the microhardness of non-metals is sparse except in two fields. In crystallography large pure or doped crystals, especially sodium chloride and other electrovalent compounds have been prepared and tested by Matkin & Caffyn (1963) and other workers. In geology the microhardness of single crystals of minerals has been studied with a view to their identification by e.g. Mitsche & Onitsch (1948), who also investigated factors which could influence mineral crystal microhardness values.

Of the materials tested, aspirin was by far the most difficult, conchoidal cracking and flaking obscuring most of the indentations. Sucrose crystals also showed

this effect, though clearer indentations were obtainable than with aspirin. Although urea and salicylamide did not show the cracking, definition was not ideal. Hexamine and potassium chloride produced clear indentations, provided a flat natural surface could be found.

For sodium chloride, the measurements were made at several loadings, since it had previously been suggested (Meyer, 1909) that hardness could be a function of applied load. Sodium chloride is the only material tested here for which literature results are available (Hofer, 1962).

This author found that with a non-symmetrical indentor there appeared to be a variation of hardness with orientation for sodium chloride, although he was unable to measure any difference, even on different faces of the crystal, using a symmetrical indentor. Our hardness results for sodium chloride agree well with Hofer's, and our value of n, the Meyer exponent, of 1·9 may be compared with his value, 1·89, obtained for loadings below 60 g. A Meyer exponent of 2 means that hardness is independent of applied load: this is very nearly true for sodium chloride. The hardness value from the present work, 21·2, agrees with Hofer's value and also with that of Matkin & Caffyn (1963) who measured the change in hardness of sodium chloride when calcium chloride was incorporated into the lattice by fusion and re-crystallization.

For the other materials it was not possible to use a series of different loads, the load used being restricted to the value producing the clearest and most convenient size of indentation relative to the size of the specimen. In these cases the indentor load and indentation depth must be stipulated for each hardness value quoted.

Modulus of elasticity

The determination of Young's modulus of elasticity of the materials proved difficult. Crystal inhomogeneities such as cracks or piled-up dislocations played a large part in determining the results and it was not always possible to see these defects during the selection of crystals for testing. Where cracking occurred during the tests it usually revealed itself by a sudden increase in strain without increased stress. However, four crystals of each of the substances sodium chloride, sucrose, hexamine and aspirin and one crystal of salicylamide, all free from cracks or outgrowths, were tested using the modified microtensile tester. The results were corrected as far as possible for machine deformation or specimen slip and the stress-strain curves were plotted (Fig. 1). Each graph shows an initial curved portion, due to the breaking of surface asperities and possibly a slight shifting in position of the crystal between the anvils as compressive force is applied. This initial portion is followed by a straight line, for which Hooke's law applies, the slope being the modulus of elasticity.

Further tests suggested that testing many more samples would yield little more information since the same scatter of results was produced however many tests were carried out.

Sodium chloride crystals behaved well in the machine, little specimen slip occurring. Susceptibility to deformation depends on the crystal structure; materials like sodium chloride, having a face centred cubic lattice, are easily deformed, whilst body centred crystals tend to work harden. Theile (1932) obtained a value of $1{\cdot}8 \times 10^5$ g/mm^2 for the modulus of elasticity of sodium chloride at 20° which compares well under these conditions with the present value of $1{\cdot}9 \times 10^5$ g/mm^2. No literature values were available for the other substances studied.

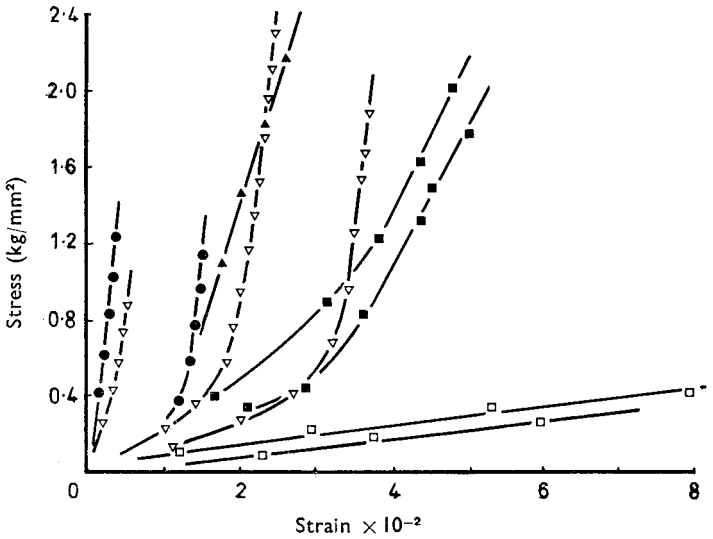

FIG. 1. Some typical stress-strain curves for crystals of five substances: ● Sodium chloride. ▽ Sucrose. ■ Hexamine. ▲ Salicylamide. □ Aspirin. The slope of the straight part of each curve is the elastic modulus. The values are in g/mm²: sodium chloride, $1{\cdot}9 \times 10^5$; sucrose, $2{\cdot}2 \times 10^5$; salicylamide, $1{\cdot}3 \times 10^5$; hexamine, $0{\cdot}9 \times 10^5$; aspirin, $0{\cdot}09 \times 10^5$.

The elastic moduli of urea and potassium chloride were not measured, because satisfactorily-shaped crystals could not be found in the available crystal batches.

Sucrose showed a similar value for the modulus of elasticity to that of sodium chloride. Initially more deformation occurred either due to the breakdown of asperities on the crystal faces to which the load was applied, or to slip in the crushing anvils. Hexamine crystals and the single salicylamide crystal tested showed still greater slip. Aspirin crystals, however, seemed to show cracking throughout the crystal at very low loads, the crystal rapidly showing complete breakdown. The form of the cracks was completely different from that in the other materials: one or two straight cracks occurred parallel to the force axis between the anvils and this different breakdown effect in aspirin produced a very low modulus of elasticity.

A comparison of the surface hardness and modulus of elasticity results shows that the materials lie in the same order whichever property is considered. The hardest material has the highest modulus of elasticity and the softest, aspirin, the lowest. The surface hardness test probably reflects the properties of the bulk material.

This conclusion is supported by the suggestion of Matkin & Caffyn (1963) that surface hardness is a measure of the rate at which dislocations dissipate energy when moving through the crystal lattice. Thus both the modulus of elasticity and the surface microhardness depend on the way the crystal lattice is made up and should reflect the bulk mechanical behaviour of the crystal.

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