

procedure, and the amount of sodium penicillin G was determined. The data from three experiments run in duplicate are given in Table I; the recoveries were 95–97%.

A photograph of a developed chromatogram containing standards of sodium penicillin G, commercial disodium carbenicillin, and commercial disodium carbenicillin with additional sodium penicillin G after ammonia treatment and spraying with starch iodine is shown in Fig. 1.

In comparison with the electrophoretic method of penicillin separation and subsequent biological assay of the separated penicillin, this method seems to be much simpler and several assays can be performed on the same day.

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PHARMACEUTICAL TECHNOLOGY

Tensile Strength of Compressed Powders and an Example of Incompatibility as End-Point on Shear Yield Locus

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Abstract □ Three methods of measuring tensile strengths of compacted powders are described. These methods include transverse compression using squares and disks and the direct tensile stressing of lightly pressed powder. The transverse compression of squares gave the best overall results. The tensile strength of sitosterols NF was found to be too large to be compatible with its use as the end-point of the shear yield locus. However, a Warren-Springs-type equation can be used to describe the yield locus if the tensile strength is replaced by a smaller internal cohesion. A method of estimating both the internal cohesion and the exponent of the Warren-Springs equation from shear cell data is described.

Keyphrases □ Tensile strength, compressed powders—determined by transverse compression of squares and disks and direct tensile stressing, incompatibility as end-point on shear yield locus, internal cohesion estimated, Warren-Springs-type equation, relevance to yield locus □ Powders, compressed—tensile strength determined by transverse compression of squares and disks and direct tensile stressing, incompatibility as end-point on shear yield locus, internal cohesion estimated, Warren-Springs-type equation, relevance to yield locus □ Shear cell data—method of estimating internal cohesion and exponential of Warren-Springs equation, tensile strength of compressed powders □ Yield locus—testing of compressed powders, tensile strength role reevaluated

Tensile strength measurements of powders compacted to various degrees provide a direct measurement of the bonding potential¹ of a given solid mate-

rial. This information is useful to the formulator in the selection of excipients. An excessively strong bond may prevent rapid disintegration and concomitant dissolution. Very weak bonding characteristics may limit the selection and/or quantity of lubricant that may be added to a formulation. In addition to these obvious practical uses of tensile strength information, the tensile strength has been used in characterizing flow properties. Specifically, the tensile strength has been designated as: (a) a point on the shear failure yield locus (1–3), and (b) a limiting factor to the extension of the yield locus (4). The magnitude of the tensile strength played an important role in the evolution of a third position presented herein—*viz.*, the tensile strength is not a point on the yield locus and is not predictable from the yield locus of shear failure. This interpretation is a departure from commonly accepted practice and is believed to be an important conclusion of this research.

THEORY

The tensile strength of powders is an important measurement for characterizing the interaction between solid particles. The strong interactions are at the true contact areas. The extent of the true area of contact between particles after elastic recovery is dependent on the magnitude of the maximum stress applied and the amount of plastic deformation that has occurred. These concepts are basic to the discussion of the results of the experimental work reported here.

Experimentally, tensile strength is not always a readily mea-

¹ Conditions in the compaction process must be controlled to produce maximum values if the true bonding potential is to be observed experimentally.

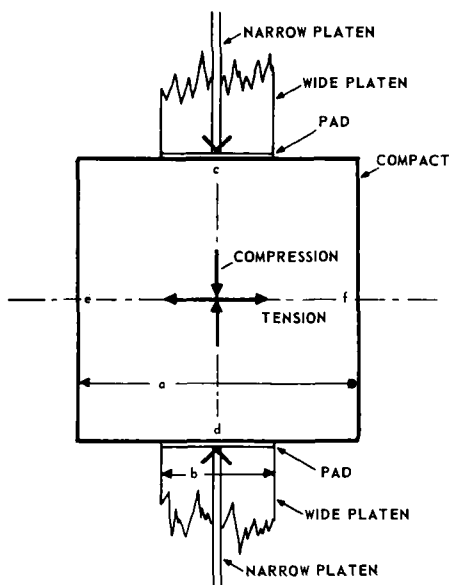


Figure 1—Transversely compressed square. Key: *a*, compact width; *b*, platen width; *c-d*, vertical bisector; and *e-f*, horizontal bisector. Planar diagram does not show the thickness, but platen must extend across entire thickness of compact. Only one set of platens is used. The two narrow platens represent one case and the two wide ones represent another case.

sured property because stress concentration and brittle fracture with crack propagation may cause failure at much lesser mean values of applied stress than the true tensile strength. Also, some methods of determining tensile strength produce compression, shear, and tension stresses simultaneously in different directions within the solid. In these cases, it is necessary to distinguish between shear and tensile failure to assure that the stress at failure is a measure of tensile strength.

Three methods of determining tensile strength are described. Two of these are transverse compression methods: the diametral compression and the compressed square methods. Both use intact compacts removed from the die after compression. They differ from each other only in the geometry of the compact and the relative area of the stress application. The third method is a direct tensile measurement using much smaller compressive loads than would be required to make compacts of sufficient strength to be removed from a die.

Transverse Compression Methods—It is assumed that many scientists interested in pharmaceutical formulations have not

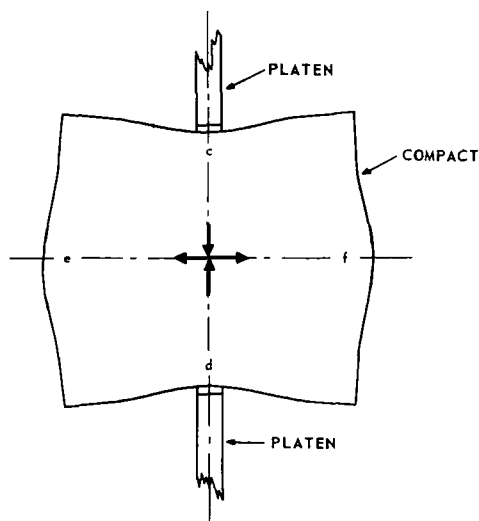


Figure 2—Exaggerated elastic distortion of a square compact under transverse compression.

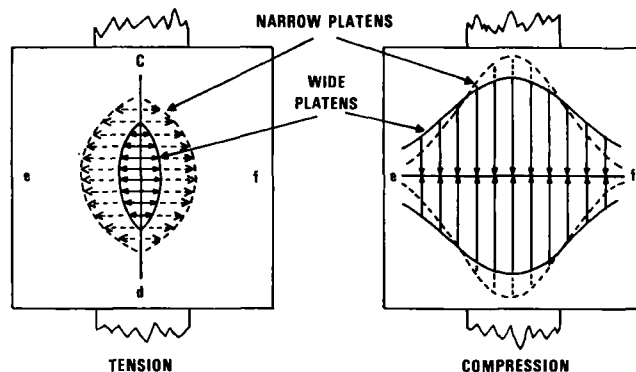


Figure 3—Diagrammatic representation of stresses along bisectors of the compact: tension stresses along *c-d* on the left and compression stresses along *e-f* on the right. Solid lines are for case with platen widths about 0.4 of the width of the compact, and dashed lines are for platen width of about 0.1 of the width of the compact. Relative length of arrows indicates the approximate relative magnitude of the stresses.

been involved in stress analysis problems. In the absence of such a background, the relationship between compression in one direction and a resultant tension may not be obvious, the tension being in a direction normal to the compression. Therefore, a somewhat oversimplified discussion of concepts is presented in the discussion of the transverse compression of square wafers.

Compressed Square—Figure 1 illustrates the case of the square. If a compressive load is applied at the edge of the compact through the very narrow platens (indicated by wide arrows), the shear stresses would be very large at these edges and would cause failure in shear. However, temporarily it is convenient to ignore the shear stresses and consider the compressive and tensile stress distribution within the compact.

When pressure is applied vertically across the center, elastic deformation occurs. The grossly exaggerated elastic distortion of the square after compression would be somewhat like that shown in Fig. 2. The compressive force causes displacement of molecules, and this displacement is transmitted from one molecule to the next. The resistance to compression of molecules to the left and right of the compressed bisector region results in an imbalance of forces which produces tension horizontally in the central region of the compact. The curves in Fig. 3 show diagrammatically the distribution of these stresses along the vertical and horizontal bisectors. The solid curves describe the case of wider² platens, and the dashed curves are for narrower platens. If the platens are as wide as the compact ($b/a = 1$), no tension develops and the compressive stress is a constant across the compact. Based on Fig. 3, the narrower platens would appear to be desirable. However, shear stresses also are present; they are not shown in Fig. 3. Berenbaum and Brodie (5) used photoelastic methods to evaluate the stresses and concluded that the maximum shear stresses occur at the edges of the platens. With very narrow platens, these shear stresses usually exceed the shear strength before the tensile stress exceeds the tensile strength at any region of the compact. Thus, failure in shear occurs instead of tensile failure. However, the shear stresses at the platen edges may be reduced by distributing the compressive load over a somewhat larger surface area. Also, stress concentration may be reduced by using padded platens³. The pads are sufficiently deformable to avoid excessive stress concentration at surface irregularities. Figure 4 shows examples of failure patterns. Wider platens also reduce the tensile stress that develops at the center of the compact, fortunately, at a different rate from the accompanying reduction in shear stress. Thus, with the proper choice of platen widths, the ratio of the shear stress to tensile stress can be minimized. This is the optimum condition attainable for producing tensile failure. Berenbaum and Brodie (5) reported that the ratio of shear stress

² The platen width will be expressed as a fraction of the compact width (fraction b/a in Fig. 1). The platens extend completely across the thickness of the compact.

³ In the authors' laboratory, pads are made from ink blotters. Double-sided adhesive, pressure-sensitive tape is used to fasten the blotter to the platen and to laminate the blotter to prepare double-thickness pads.

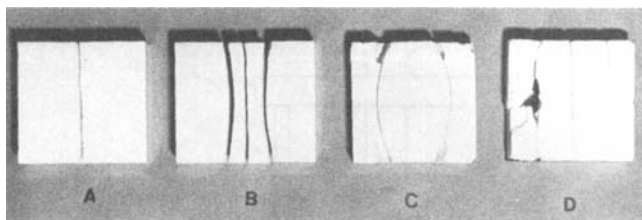


Figure 4—Photograph of square compacts broken by transverse compression. Tensile failure occurs when compact breaks in a central vertical line. Platen width/compact width = 0.4. Key: A, tensile failure; B and D, tensile failure accompanied by secondary failures; and C, shear failure.

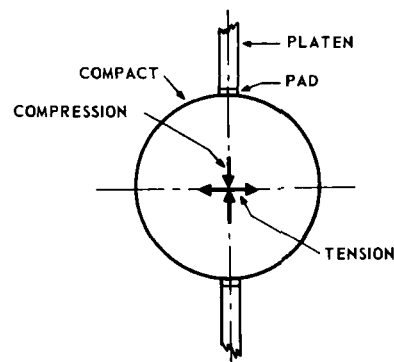


Figure 5—Diametrically compressed disk.

at the platen edge to the tensile strength at the compact center is a minimum when the b/a ratio is about 0.4. This b/a ratio gives a maximum tensile stress equal to 0.16 times the mean compressive stress. Furthermore, if the applied stress (*i.e.*, pressure, not total load) at the platen surface is kept constant as the b/a ratio is varied, the maximum tensile stress occurs when $b/a \approx 0.4$. Therefore, optimum conditions for tensile failure exist when the value⁴ of $b/a \approx 0.4$. When tensile failure occurs, the fracture initiates at the point of maximum tensile stress, the center of the compact, and propagates vertically to the platens⁵.

Because compacts made by compressing powders are not of uniform density throughout, the photoelastic evaluation made with a homogeneous model material only approximates the stress distributions in the powder compact. However, in the absence of a better value, the 0.16 factor will be used to calculate the tensile strength. As noted later, this 0.16 factor, obtained by photoelastic methods, appears to give tensile strengths comparable to those obtained with circular disks. Values for disks are not dependent on the photoelastic evaluation of models.

Diametrically Compressed Disk—Much of the same discussion could be presented for the stress distribution in the disk in Fig. 5 as for the square wafer. Very narrow platens would produce shear failure. The load may be distributed by using padded platens of finite width. Sometimes limited crushing occurs under the platens. Since crushing changes the geometry of the system, the ratio of the tensile stress to the applied load also may become unknown. Some investigators recommend that the platen width be limited to 0.1 of the diameter of the compact to minimize the changes in the effective width of the platens.

Again, the experimenter must check the shape of the fragments after fracture to determine the mode of failure (8). If the compact splits into two equal halves, tensile failure has occurred. Because the relative platen width is limited by the circular geometry, the shear stresses may be too large in a given material and fracture along a shear plane often occurs⁶. (It is the authors' experience that this same material may fracture in tension when the compressed square is used. Thus, the latter is believed to be the preferred method for general application.)

The diametral compression case has yielded to mathematical evaluation. The tensile strength (8) is given by:

$$\sigma_E = \frac{2F}{\pi Dt} \quad (\text{Eq. 1})$$

where σ_E is the tensile strength, F is the load applied diametrically at fracture, D is the diameter of the compact, and t is the thickness of the compact.

Equation 1 applies to knife-edge loading but is not significantly

in error as long as the platen width is not larger than 0.1 of the specimen diameter (8). Again, for real compacts, the lack of uniform density introduces some error. Thus, tensile strength data, obtained by transverse compression methods, are at best good estimates of the correct value. In practice, the results may be the best estimates obtainable by methods requiring only a reasonable experimental effort.

Simple Tensile Failure Measurements—Conceptually, the simplest method of measuring tensile strength is to measure the force needed to pull an object apart. However, the practical problem proves to be very difficult because, when brittle materials are used, stress concentration and crack propagation cause premature failure. Stress concentration may occur because of the difficulty of attachment of the instrument to a compact in a manner that will pull uniformly on all parts of the compact. Also, the nonuniformity of the internal density of the compact distorts the stress pattern internally so that it is difficult to determine the point of origin of catastrophic failure. Ideally, elongated dumbbell shapes should overcome some of these difficulties. However, it is somewhat impractical to produce these shapes by the compression of powder; furthermore, uniform density may not be achieved. Objects cast from melts cannot be used to characterize the tensile strength of objects produced by a compression-elastic recovery cycle because the factors determining the true area of contact are quite different in the two processes. Therefore, a method was selected that uses compacts of simple shape and requires only very limited compression forces. This method uses forces of compression of the same order of magnitude as are used in the shear cell studies done in these laboratories.

An instrument⁷ for determining the tensile strength of powders after subjecting them to small compression loads has been described (10, 11). The cell consists of two lengths of cylindrical tubing that serve as a split die (Fig. 6). These are placed end-to-end in a third, aligning cylinder which may be moved away after the loose compact is formed. The compact is compressed so that it extends across the junction of the other two cylinders. After compaction, the top punch is removed; the aligning cylinder is moved away from the top cylinder, and then the force required to lift the top cylinder and fracture the loose compact is observed. By repeating this process with different amounts of powder in the die, one may prepare a plot of the logarithm of the observed tensile strength *versus* the height of powder above the fracture plane. This semilog plot is then extrapolated to zero height. The extrapolated value is assumed to be the tensile strength at the applied load. Similar plots are prepared by using different loads and repeating the same process for each load. Since the scatter is very large, at least five values for each point on a line were needed, and several points were desired for obtaining a line. The results provide a plot of tensile strength *versus* compaction stress. Obviously, the amount of effort to obtain usable data makes this approach very unsatisfactory. Furthermore, only a few materials gave sufficiently good results to be acceptable. Sitosterols were the most satisfactory.

Obviously, the theoretical considerations are simple unless one attempts to evaluate the effects of lack of uniform powder density in the failure plane. For practical reasons, no consideration was

⁴ Efforts to obtain analytical solutions for the stresses during transverse compression of squares (indentation test) have been based on various assumptions (6, 7). The results suggest that the photoelastic results give somewhat high tensile strength values when b/a is less than 0.25. The authors have elected to accept the experimentally determined values of Berenbaum and Brodie (5) instead of results calculated for a hypothetical model case.

⁵ Since failure along the bisector leaves two independently stressed fragments between the platens, the stress distribution in each fragment determines whether a second failure with further fragmentation occurs. Even when secondary failure occurs, the measurement of the force required to produce tensile failure still is valid.

⁶ In a sufficiently rigid apparatus, progressive shear failure may occur at least with concrete, before fragmentation occurs (9). This suggests that tensile failure may not occur if the rate of supplying energy to the compact is too slow after a critical stress has been attained.

⁷ One of these instruments was built at Parke, Davis and Co. Dr. Joseph Samyn kindly loaned the cell components to the authors.

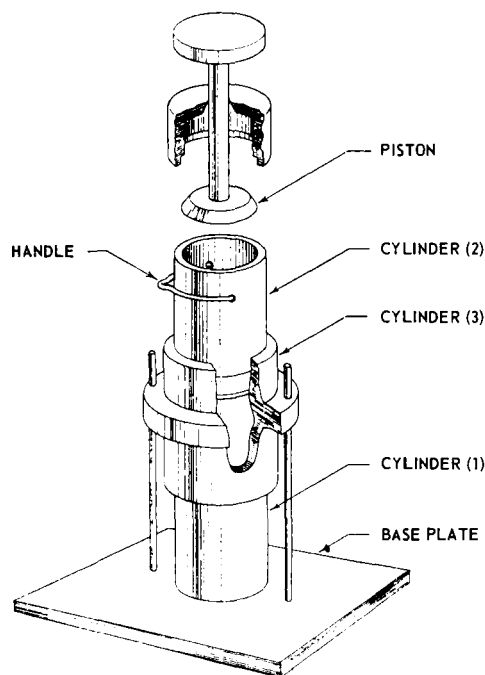


Figure 6—Cell for direct tensile strength test. (Reproduced, with permission from the American Chemical Society, from Ref. 11.)

given to this complication and the observed values were accepted *prima facie*.

EXPERIMENTAL

The same procedures were used for both transverse compression methods. A motorized hydraulic jack was used to apply the compressive load (Fig. 7). The lower platen is supported on a piece of brass tubing to which are bonded the wires of a strain gauge. The output of the strain gauge drives a recorder and provides the needed information for calculating the tensile strength. Interchangeable platens permit the selection of the desired platen width. The pressure surfaces of the platens are covered with a double layer of blotter paper which serves as the pad.

A compact is made in a die by compression with a hydraulic press⁸. The maximum compression force is held constant for 1 min. The compact is removed and placed on edge between the platens. The jack motor is started and the hydraulic jack pressure increases until the compact fractures. By preparing a series of compacts at various compression loads, one obtains the data for a plot of tensile strength *versus* compaction stress.

In these experiments, the round compacts were 4.29 cm in diameter and the square ones were 3.81 cm on a side. Since a constant weight of powder was used, the thickness of the compacts varied with the compression force; the thickness was estimated by averaging five values determined with a micrometer. Four measurements were made equally spaced radially near the edge and one was made in the center of the compact.

The direct tensile test apparatus shown in Fig. 6 has the general features already described. Certain modifications were made⁹ in the mechanical linkage for pulling the two sections apart. The top cylinder was attached to three fine wires whose opposite ends were attached to a pivot, needle-bearing support. (This assembly replaced the bail handle shown in Fig. 6.) Thus, the tension on the three wires was equalized. The needle bearing was supported from the probe of a strain-gauge assembly¹⁰. The output of the strain gauge was connected to a recorder.

The base of the cell was clamped to a motor-driven table that moved up and down on ways. This permitted stress to be applied to produce fracture.

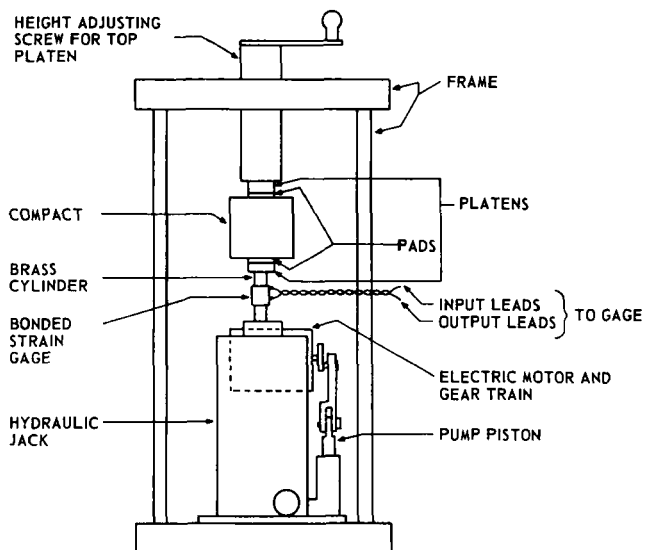


Figure 7—Schematic diagram of instrumented jack for compression testing of tensile strength.

RESULTS

Figure 8 compares the results of the two transverse compression tests for powdered sucrose. In both cases, the fracture clearly was tensile failure. These data indicate that the 0.16 factor is approximately correct. This comparison is the primary reason for including these data. Figure 9 shows similar results for sitosterols. With sitosterols, the diametral test was questionable because the compact disintegrated into many fragments. The square compacts made at smaller compression forces failed in tension and yielded strength values greater than those of the diametral compression case. Thus, it appears that in the diametral case, stress concentration caused shear failure to occur. When square sitosterols compacts were made at higher compression forces, the square compacts failed in shear also. This was established by the shape of the fragments.

Figure 10 and the insert in Fig. 9 show the results for sitosterols with the direct tensile method¹¹. Figure 10 shows the scatter of the data used to extrapolate to zero height. The slope of the insert graph in Fig. 9 is compared to the slope of the extrapolated curve. As expected, the former is somewhat larger than one would expect from the extrapolation. Since the extrapolation is over such a large distance, the extrapolated slope is of questionable value. However, it is less than the slope experimentally determined at low relative density.

Figure 11 shows the same tensile strength data as in Figs. 8 and 9, but here the abscissa is the mean relative density of the compact, where the mean relative density is the apparent density of the compact divided by the absolute density of the pure compound. The data obtained by the direct tensile strength measurements are not included in Fig. 11 because the column of powder is far from uniform in density and the density at the fracture plane is unknown. It is obvious from Fig. 11 that the same compaction stress does not produce identical relative density compacts in both the round and square dies. These plots provide an alternative comparison of the data obtained with the round and square dies.

When considering the tensile strength and shear cell data together, Fig. 8 is of greater interest than the relative density plot in Fig. 11. This is because the relative density is not determined in the shear cell procedure used in the authors' laboratory. While relative density data are used with some other shear cells where the powder bed is much thicker, the problem of producing a known uniform density in the entire shear cell becomes formidable. The authors' cell uses a very thin layer of powder to mini-

⁸ Model 341-20, Loomis Engineering and Manufacturing Co., Caldwell, N.J.

⁹ In the Upjohn laboratories.

¹⁰ No. 7035, G1 8-350, 8 oz, 12V, Statham Instruments Inc.

¹¹ Both the highest values observed and the average values observed with the direct tensile test are shown in Figs. 9 and 10. Since errors in tensile strength observations are expected to cause less than true strength values to be observed, it was decided to show both results.

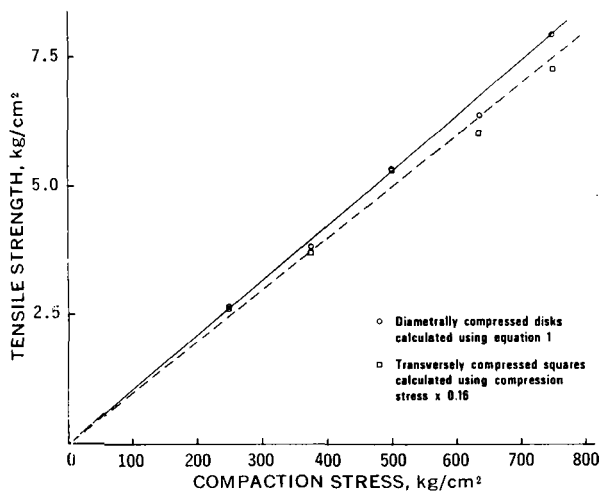


Figure 8—Comparison of tensile strength of sucrose powder compacts as determined by diametral compression of a disk and transverse compression of a square; confirms 0.16 factor for squares.

mize this problem. Some results of shear strength measurements are shown in Figs. 12 and 13. The experimental procedures for obtaining these data will not be described, because they are identical to the procedures described earlier (4). Tensile strength data for powders of aspirin USP and calcium carbonate USP (precipitated, extra light) are shown in Fig. 14.

DISCUSSION

Tensile Strength Measurements—Precise measurements of the tensile strengths of loosely compacted powders are difficult to achieve. Kočova and Pilpel (3) reported tensile strength values for various particle-size fractions of lactose and of calcium carbonate, which are said to be based on: “. . . a best straight line by regression analysis.” However, their reported values are not always linear and no systematic variations with size fractions are obvious. These data were obtained using an apparatus of the design described by Ashton *et al.* (12), which uses a direct tensile stress method of measurement. This apparatus is accepted by various workers using the Jenike shear cell (1, 3). However, the published data obtained with this cell have not been sufficiently precise to motivate the authors to build an apparatus of this design. Appar-

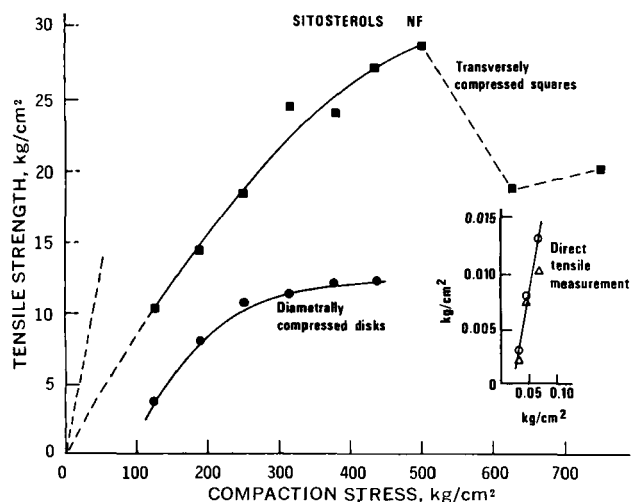


Figure 9—Tensile strength of sitosterols NF (40 mesh) compacts determined by transversely compressed squares (■), diametrically compressed disks (●), and the Nash direct tensile apparatus (in insert graph, Δ indicates average values and \circ indicates the highest values). Insert graph is a magnification of region near origin and shows direct tensile data points. Dashed line with larger slope has same slope as data in insert graph.

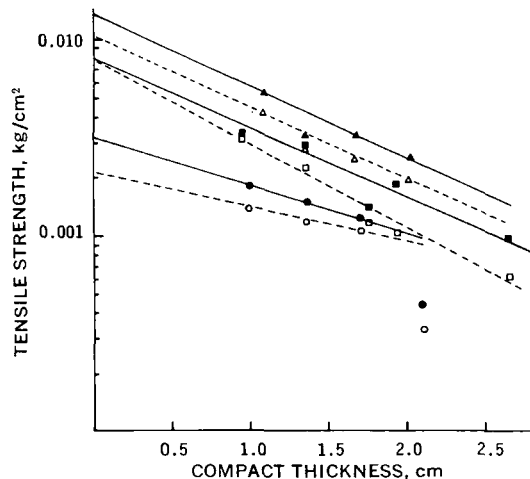


Figure 10—Data used to obtain tensile strength values for sitosterols by extrapolation to zero compact thickness; used only with direct tensile test method. Key: \blacktriangle , 150-g load, high value; \triangle , 150-g load, average value; \blacksquare , 100-g load, high value; \square , 100-g load, average value; \bullet , 50-g load, high value; and \circ , 50-g load, average value.

ently, no existing method using loosely packed powder beds is highly successful.

Use of Tensile Strength as a Point on Shear Yield Locus

Figure 12 is a shear yield locus for sitosterols. Note the tensile strength¹², point X, plotted on the negative side of the σ axis. The table lists values obtained from experimental work with sitosterols. The slope based on the direct tensile measurements is about 3.4 times the slope used to estimate the magnitude of point X. Extrapolation of the insert graph would yield a value for the

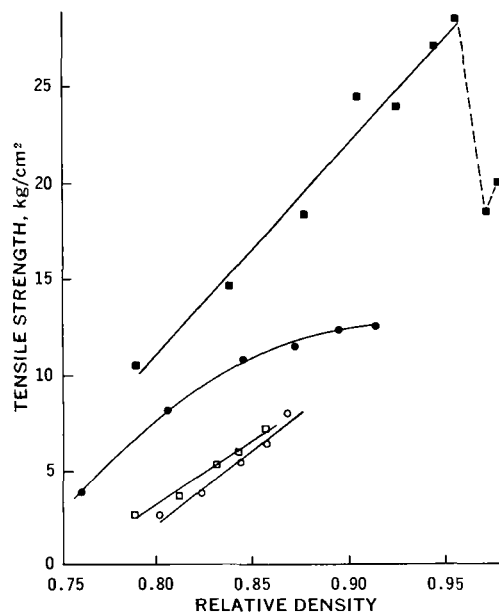


Figure 11—Tensile strength of sitosterols and sucrose as a function of the relative density of the compact (same experimental points as in Figs. 8 and 9). Key: \blacksquare , sitosterols—transversely compressed squares; \bullet , sitosterols—diametrically compressed disks; \square , sucrose—transversely compressed squares; and \circ , sucrose—diametrically compressed disks.

¹² The magnitude of X depends on the resultant principal compressive stress, σ_{pm} , which is the major consolidation stress produced by the normal load and the shear stress; σ_{pm} is obtained by using a Mohr diagram (4). The magnitude of X was obtained by multiplying σ_{pm} by the slope of the line between the origin and the closest point of the tensile strength versus compaction load plot of Fig. 9. As will be noted, this is a very conservative estimate of the tensile strength.

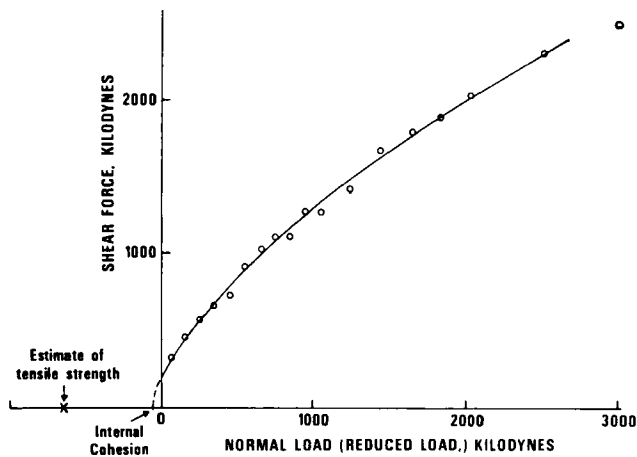


Figure 12—Shear yield locus for sitosterols. Note that extrapolation to the normal load axis cannot be to the tensile strength point, X, as some have suggested (1-3). The X value plotted is estimated from transversely compressed square data. The X value based on direct tensile test would be very far from the origin on this scale.

tensile strength of about 2100 kdynes instead of the 618 shown in Fig. 12. Even the very conservative estimate of tensile strength grossly exceeds the magnitude of any point that could be on the yield locus.

To emphasize the importance of this observation, it is necessary to discuss the shear yield locus and to develop an empirical equation to describe it. However, before proceeding, supplemental results will be considered. As may be seen in Fig. 13, the data for aspirin are similar to the data for sitosterols. Again the point marked X is estimated from the slope between the lowest transversely compressed square tensile strength value and the origin. Again the estimated value of the tensile strength is too large to fit onto the yield locus for the powder. In this case the tensile strength at low relative density was not determined. Therefore, it is not established that the tensile strength of the lower relative density powder beds would be comparable to the magnitude estimated from the transverse compression data. However, these limited observations are not in conflict with the previous case of the sitosterols. Table I lists the values obtained from shear cell measurements for both materials. The equations in the Appendix were used to estimate n and S from shear cell data.

The area of true contact between particles is established with the application of a shear force in the shear cell and by a compressive force in the tensile strength tests. Therefore, one may question whether the two processes may be compared. Certainly the condition of the powder in the two beds is not identical; however, some shearing occurs in the compression of a powder bed. Therefore, the two processes are not totally different and gross differences of tensile strength of the two differently prepared beds would not be expected. Shearing should increase the true contact

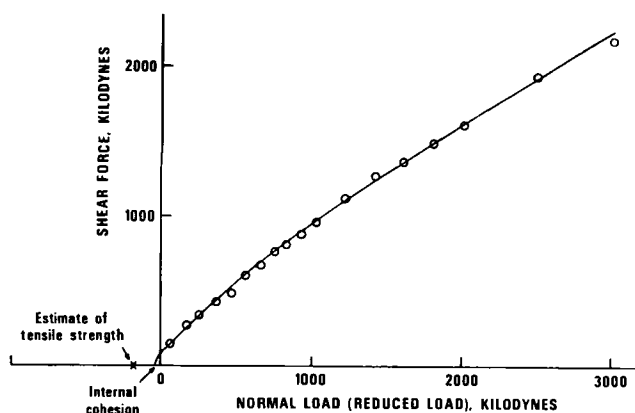


Figure 13—Shear yield locus for aspirin. The X value is estimated from transversely compressed square data.

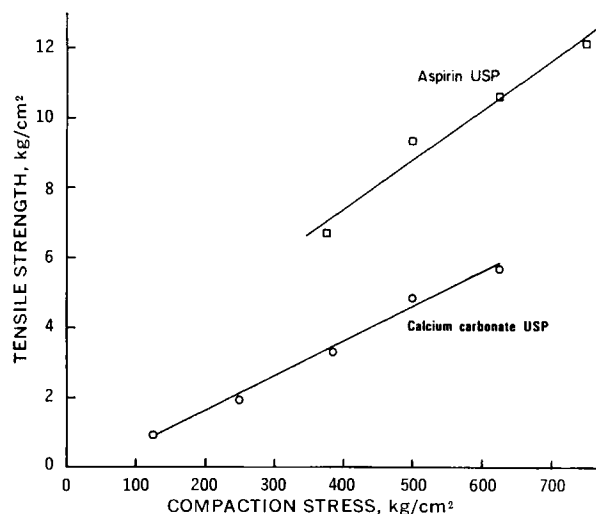


Figure 14—Tensile strength by transversely compressed squares.

area and would be expected to increase the tensile strength. Thus, any difference would be expected to favor a larger tensile strength for a bed prepared by the application of shearing motion. Therefore, any real differences should increase the discrepancies considered herein.

In the interest of brevity, it is assumed in the following discussion of the yield locus that the reader is familiar with shear cell methodology and terminology such as are used in Refs. 1 and 4.

In an earlier publication (4), an empirical expression was used to describe the area of true contact as the applied load stress, σ_r , of a shear cell, is reduced from its maximum value, σ_p :

$$\sigma_r + S = kA_r^n \quad (\text{Eq. 2})$$

where S is the internal cohesive stress and is a function of σ_p , A_r is the true contact area per unit cross section of the powder bed (a dimensionless number), k is a proportionality term, and n is a constant. Obviously at the maximum load conditions (indicated by a subscript p):

$$\sigma_p + S = kA_p^n \quad (\text{Eq. 3})$$

where A_r has its maximum value, A_p , when σ_r has its maximum value, σ_p . Dividing Eq. 2 by Eq. 3 gives:

$$\frac{\sigma_r + S}{\sigma_p + S} = \left(\frac{A_r}{A_p}\right)^n \quad (\text{Eq. 4})$$

It is reasonable to assume that the shear stress at failure is directly proportional to the area of true contact that is sheared. Therefore, Eq. 4 may be used to obtain:

$$\frac{\sigma_r + S}{\sigma_p + S} = \left(\frac{\tau_r}{\tau_p}\right)^n \quad (\text{Eq. 5})$$

where τ_r is the shear strength observed when the applied load is σ_r , and σ_p is the shear strength when the applied load is its maximum value¹³, σ_p . Equation 5 will describe a yield locus. It is equivalent to the well-known Warren-Springs equation, except that in this derivation S is the internal cohesive strength. In the Warren-Springs equation, S is considered to be the tensile strength.

If S is assumed to be the tensile strength, some conceptual problems arise. These are indicated in the following arguments where momentarily S is identified as the tensile strength.

For convenience, a normalized term, S^* , is used where:

$$S^* = \frac{S}{\sigma_p + S} \quad (\text{Eq. 6})$$

¹³ A_p may be estimated if the mean deformation pressure, P , is constant and known.

Table I—Tensile and Shear Failure Values of Various Powders

Material	Slopes of Tensile Strength Data		Shear Strength Values			
	Direct ^a Tensile Squares	Com- pressed ^b Squares	n^c	S^d	σ_{pm}^e	X^f
Sitosterols NF	0.283	0.0834	1.57	0.661	119.5	9.96
Aspirin USP		0.0179	1.30	0.372	109.8	1.96
Sucrose		0.0103	1.61	1.20	119.5	1.23
Calcium carbonate		0.0078	1.26	0.767	125.1	0.976

^a Slope for data in insert graph of Fig. 9. If this value were used to estimate the tensile strength for the sitosterols in the shear cell, the value would be 33.8 instead of 9.96 kdynes/cm². ^b Based on straight line from origin to point at lowest compression stress used with compacts. ^c Estimated using Eq. A5. ^d Kilodynes per square centimeter; obtained by using Eqs. A4 and A6. Internal cohesion in shear cell is obtained by multiplying by the cross-sectional area of cell, 62.04 cm². ^e Kilodynes per square centimeter; major consolidation stress; estimated from a Mohr semicircle drawn tangent to the right end of the yield locus. ^f Kilodynes per square centimeter; $\sigma_{pm} \times$ slope of tensile strength (squares). (This value is not assumed to be an accurate estimate of the tensile strength for powders in the shear cell but is included for comparison. At least for sitosterols, the tensile strength is a larger value than this estimate.)

It is reasonable to assume that the tensile strength, S , is directly proportional to the zero load area of true contact, A_0 , i.e., when $\sigma_r = 0$, $S \propto A_0$. (A different A_0 value would be obtained for each σ_p .) Also, when permanent deformation occurs, and it must occur at any significant applied load, the area of true contact under maximum load is directly proportional to the maximum load applied. Of course, this assumes that the deformation pressure remains constant. This appears to be true for many pharmaceutical materials (13). Therefore, $\sigma_p + S \propto A_p$, and:

$$S^* \propto \frac{A_0}{A_p} \quad (\text{Eq. 7})$$

However, solving Eq. 4, when $\sigma_r = 0$, gives:

$$S^* = \left(\frac{A_0}{A_p}\right)^n \quad (\text{Eq. 8})$$

Obviously, relationships shown in Eqs. 7 and 8 are compatible only when $n = 1$.

The proponents of the Warren-Springs equation reject the case of $n = 1$ because it is argued that the yield locus (Eq. 5) must cross the σ_r axis at right angles to it. If $n = 1$, a plot of τ_r versus σ_r would be a straight line with a slope of $\tau_p/(\sigma_p + S)$, so it does not meet this criterion. These arguments suggest that S in Eq. 5 should not be equal to the tensile strength.

With some materials, the estimate of tensile strength obtained from the transversely compressed squares is not very different from the estimate of S . Because these are high relative density values, the significance is doubtful. The results for calcium carbonate and for sucrose are listed in Table I to illustrate that not all materials are alike. Calcium carbonate and sucrose are known to be harder, i.e., have larger permanent deformation pressures, than sitosterols and aspirin. It seems reasonable to assume that the effect of this resistance to deformation would reduce the true area of contact established by compression and, thereby, account for a diminished tensile strength.

Since sitosterols were the only material for which low relative density tensile strengths were determined, only that case can be considered as strong evidence that the tensile strength is not an end-point on the yield locus. However, the data for the other materials appear useful in providing additional perspective.

Because of the apparent need to accommodate a large tensile strength value, a linear model for the yield locus was used by Hiestand (4). The tensile strength was described by a Mohr circle drawn through the origin (4). While this model was compatible with much larger values of the tensile strength, than was the curvilinear model, the linear model ignored the experimentally observed curvature of the shear failure data. As the precision of these measurements was improved and shear failure stresses were

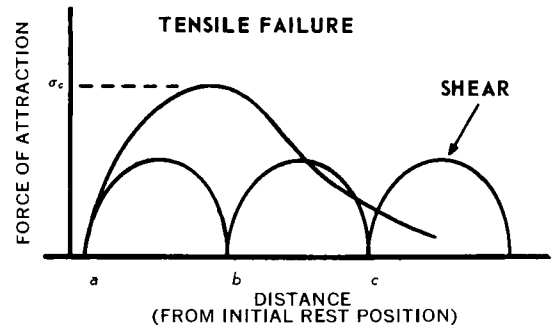


Figure 15—Diagrammatic comparison of attraction between two atoms as they move from a potential energy well in tensile separation and in shear. σ_c is the critical tension at failure. a , b , and c are equal potential energy wells related to the shearing motion. Movement to a new energy well does not necessarily lead to separation.

obtained at smaller reduced loads, it became obvious that the shear cell data are best described by a Warren-Springs-type equation. Therefore, it has been concluded that: (a) the Warren-Springs equation is suitable for describing the yield locus for failure in shear but, contrary to common usage, the S term in the Warren-Springs equation is not the tensile strength but instead is the internal cohesion; and (b) the magnitude of the internal cohesion may be much less than the tensile strength.

The following *a priori* arguments are presented to support these conclusions.

Consider a powder bed of uniform spheres. A force of attraction exists between the particles because of van der Waals' forces. These forces plus the externally applied load, σ_p , produce deformation at the regions of contact. All molecules in the individual particles contribute to the attraction between particles. However, at the regions of true contact, the molecules are closer than their equilibrium separation, where the intermolecular repulsion to the immediate neighbor would be equal to the force pushing them together. Thus, no contribution to the net, at rest attraction arises from attraction between immediate neighbor atoms in the interface. However, in tensile failure, the molecules in the interface are going to be the primary contributors to the strength because they must be moved out of the potential energy well in which their close contact has placed them. Thus, the tensile strength is the result of both the at rest attraction between particles and the maximum attraction produced as molecules in true contact regions are separated.

The attractive stress acting at the initiation of shear also includes the at rest portion of the attractive stress and that portion of the separation stresses necessary to permit shear motion. Since the separation in shear may not reach the critical separation distance, the magnitude may be less than the tensile strength. However, that force arising from the separation is overcome by the shear force and is not contributing to generating areas of true contact. Therefore, S should include only the internal, i.e., the at rest, cohesion and not the attraction arising as a consequence of the separation of interfaces.

The comparison of tensile and shear strengths is shown diagrammatically in Fig. 15, where the relationship between force and displacement of atoms from their true contact position for the two processes, shear and tensile failure, are shown. In tensile fracture, the atoms are moved from their potential energy well until a critical value, σ_c , of attraction is exceeded. Beyond this critical separation, attraction decreases and fracture has occurred. In shear, the movement is from one potential energy well on the interface to the next (illustrated in Fig. 15 by movement from a to b to c , etc.), often without the separation distance becoming large enough to produce permanent separation or fracture. A smaller separation results in a smaller shear force. Because of the particulate nature of the shear plane across the powder, a significant fraction of the molecules will be separated completely even during shear. However, an approximately equal number of molecules at the opposite edges of the particles will be approaching each other. Therefore, the net effect should be small.

In Eq. 2, the significance of S clearly is the force that must be added to the normal load to produce the true area of contact that

must be sheared. Since S is the force added to σ_p to account for the total normal force acting during the shear motion, the magnitude of S is determined by the at rest attractive forces. Since this force is expected to be less than the tensile force, S must be less than the tensile force.

CONCLUSIONS

Transverse compression methods provide good estimates of the tensile strengths produced by the compression of powdered materials. It is the authors' experience that the method using squares provides tensile failure with more materials than the disk method.

The observed tensile strengths of a plastic material, sitosterols, was too large to be fitted as the end-point on the shear yield locus of the powder. Therefore, it is concluded that an alternative characterization of the end-point of the yield locus should be used. Conceptually, this point is an internal cohesion value and it is so designated. A method of evaluating the internal cohesion from shear cell data alone is presented.

APPENDIX: ESTIMATION OF n AND S FROM SHEAR CELL DATA

If the tensile strength is not used as the value for S , then a method of estimating both n and S is needed. A graphical method is useful. While not limited to simple powders¹⁴, this discussion is directed to these cases.

The simple powder exhibits constant S^* values; therefore, S is a linear function of $\sigma_p + S$. Thus, for a simple powder:

$$\left(\frac{\tau_r}{\tau_p}\right)^n = (1 - S^*)\frac{\sigma_r}{\sigma_p} + S^* \quad (\text{Eq. A1})$$

The graphical method for the evaluation of n assumes that n is a constant for a single yield locus. A plot is made of $\log(\tau_r/\sigma_p)$ versus $\log(\sigma_r/\sigma_p)$. The slope at $\sigma_r = \sigma_p$ and $\tau_r = \tau_p$ is measured from the graph and is designated $1/n'$. Mathematically at this same point¹⁵:

$$\frac{1}{n'} = \frac{d \log(\tau_r/\sigma_p)}{d \log(\sigma_r/\sigma_p)} \Big|_{\sigma_r=\sigma_p} = \frac{\sigma_p}{n(\sigma_p + S)} \quad (\text{Eq. A2})$$

Using Eqs. 6 and A2, one may obtain:

$$\frac{n}{n'} = \frac{\sigma_p}{\sigma_p + S} = 1 - S^* \quad (\text{Eq. A3})$$

Combining Eqs. 5 and 6, one obtains at $\tau_r = 0$:

$$S^* = \left(\frac{\tau_0}{\tau_p}\right)^n \quad (\text{Eq. A4})$$

where τ_0 is the intercept of the yield locus, i.e., the shear stress when $\sigma_r = 0$.

Combining Eqs. A3 and A4 gives:

$$\left(1 - \frac{n}{n'}\right)^{1/n} = \frac{\tau_0}{\tau_p} \quad (\text{Eq. A5})$$

¹⁴ Some investigators (3) gave the designation "simple powder" to materials that exhibit constant S^* and $\tau_p/(\sigma_p + S)$ values.

¹⁵ Equation 5 is rearranged to give:

$$\frac{\tau_r}{\sigma_p} = \frac{\tau_p}{\sigma_p} \left(\frac{\sigma_r + S}{\sigma_p + S}\right)^{1/n}$$

$$d\left(\frac{\tau_r}{\sigma_p}\right) = \frac{\tau_p}{n(\sigma_p + S)} \left(\frac{\sigma_r + S}{\sigma_p + S}\right)^{1/n-1} d\left(\frac{\sigma_r}{\sigma_p}\right)$$

and:

$$\left(\frac{\tau_r}{\sigma_p}\right) d \log \frac{\tau_r}{\sigma_p} = \left(\frac{\tau_p}{n(\sigma_p + S)}\right) \left(\frac{\tau_r}{\sigma_p}\right) \left(\frac{\sigma_r + S}{\sigma_p + S}\right)^{1/n-1} d \log \frac{\sigma_r}{\sigma_p}$$

$$\frac{d \log \frac{\tau_r}{\sigma_p}}{d \log \frac{\sigma_r}{\sigma_p}} \Big|_{\sigma_r=\sigma_p} = \frac{\sigma_r}{n(\sigma_r + S)} \Big|_{\sigma_r=\sigma_p} = \frac{\sigma_p}{n(\sigma_p + S)}$$

Extrapolation¹⁶ of plots such as in Fig. 12, where τ_r is plotted against σ_r , provides an estimate of τ_0 . Thus, in Eq. A5, τ_0/τ_p and n' are estimated graphically and n can be determined by an iterative procedure. Then S^* is calculated with Eq. A4.

For sitosterols, τ_0/τ_p was estimated to be 0.0635 and the n' estimate gave 1.58; $n = 1.56$ was obtained with Eq. A5 and $S^* = 0.0136$ by Eq. A4. From Eq. A3, one can obtain:

$$S = \frac{\sigma_p}{1 - S^*} - \sigma_p \quad (\text{Eq. A6})$$

This gives a value for the data in Fig. 12 of $S = 41$ kdynes for the internal cohesion.

Small changes in the magnitude of n cause the left side of Eq. A5 to change value markedly. Thus, the precision of the determination of n and S^* is limited only by the precision of the graphical determination of n' and τ_0/τ_p .

Some investigators (3) assumed that the $\log \tau_r/(\sigma_p + S)$ versus $\log(\sigma_r + S)/(\sigma_p + S)$ must be linear. Using this criterion, they determined n by using the measured tensile strength for S to prepare the log-log plot from which they obtained an estimate of the slope which is $1/n$. In Eq. A3, one notes that S^* is a small number even when S is relatively large. Therefore, large relative errors in the value of S^* produce only small changes for the value of n . Add to this the insensitivity of a log-log plot and it becomes obvious that the method is not very sensitive to errors in determining S . Possibly this is the reason that the use of the tensile strength for S has not been questioned previously.

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¹⁶ A more general form of Eq. A5 is:

$$\left[1 + \frac{n}{n'} \left(\frac{\sigma_r}{\sigma_p} - 1\right)\right]^{1/n} = \frac{\tau_r}{\tau_p}$$

This form avoids the use of the intercept value, τ_0 ; but the change in magnitude of the left side of the equation with change in n is less rapid when the magnitude of σ_r/σ_p becomes significant.