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Tensile strength of some pharmaceutical compacts and their relation to surface free energy

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Summary

The time-dependent nature of plastic flow, of 7 pharmaceutical powders, and its effect on the tensile strength of their compacts after consolidation is reported. Magnesium stearate compact showed no change in strength with time. For plastic materials a ln–ln plot of tensile strength versus time resulted in a straight line. The obtained visco-elastic slope, v, is a measure of plasticity. The more pronounced the plastic flow the greater the slope.

After 30 min from compaction, the values of tensile strength obtained were correlated quantitatively to the surface free energy of the materials studied. High surface free energies were associated with higher tensile strength. A constant, k, which relates the surface free energy of materials to the tensile strength of compacts is defined. Plastic materials exhibit the same k value which was greater than that obtained for magnesium stearate.

Introduction

The compression of solids to produce a compact is a complex process. Several simultaneous mechanisms are involved in the consolidation and bonding of particles. These mechanisms can be summarized as packing of particles by diffusion into void spaces, fracture and plastic deformation. This latter mechanism results from the crushing or fracturing of particles or by plastic flow. Plastic flow in some pharmaceutical materials has been determined by comparing their stress relaxation data under constant strain (Shlanta and Milosovich, 1964; Cole et al., 1975).

The effect of plastic flow on tablet tensile strength was investigated by David and Augsburger (1977) who reported that increasing the overall compression cycle and the duration of the maximum compression force resulted in greater tensile strengths. The decay curves for the maximum compressive force with time were then analyzed using the Maxwell model.

Changes in the mechanical properties of compacts with time after compaction has also been observed. Rees and Shotton (1970) reported that during the first hour, the strength of sodium chloride compacts increased by approximately 100% as compared with their initial value.

Despite some clear indications that the nature of solid surfaces does play a role in a variety of pharmaceutical processes (Hiestand, 1966; Zografi, 1968; Rees and Shotton, 1970), it is nevertheless true that the surface effects have been ignored in investigations of plasticity for pharmaceutical materials.

Based on the Griffith fracture theory, which was extensively used to determine the surface free energy of solids (Linford, 1972), a test called the brittle fracture propensity (BFP) was devised (Hiestand, 1977) to measure the ability to relieve stresses by plastic deformation. The BFP value was defined as an inverse measure of localized stress relief and was used to indicate the tendency of a compact to laminate.

The purpose of this study was to investigate the effect of plastic flow or shear relaxation, that occurs after consolidation of pharmaceutical powders, on the tensile strength of compacts. Since the surface free energy of the material and the tensile strength of compacts depend on the bonding strength, a relationship between these two different properties is developed.

Materials and Methods

Materials

The following materials were used: aspirin (B.P. 68); griseofulvin (Cairo Pharmaceuticals); indomethacin (B.P. 80, Fabrica Italinna Lintetici L.P.A.); magnesium stearate (Merck, Darmstadt); phenacetin (Monsanto); potassium chloride (Merck, Darmstadt), and sodium chloride (Merck, Darmstadt). Descriptions of the materials are given in Table 1 and Fig. 1.

A vibratory sieving machine was used to obtain 63–80 μm size fraction of the different samples. All materials were oven-dried at 60°C for 4 h and stored in a desiccator over silica-gel until required. The apparent bulk-density of each material was determined by pouring the dried powder at an angle of 45° into a 100 ml tared cylinder and tamped a given number of times from a uniform height.

Tablet compression

A Carver press [1] was used to form compacts without the addition of excipients. For each material, tablet weights were adjusted carefully to produce compacts with

[1] Carver Laboratory Press, Fred S. Carver INC., U.S.A.

TABLE I

PROPERTIES OF 63–80 μm FRACTIONS OF POWDERS

Material	Density ($g \cdot cm^{-3}$)			Porosity
	Bulk	Particle	Packing	$\varepsilon = 1 - P_B/P_P$
	P_B	P_P	P_B/P_P	
Aspirin	0.404	1.38	0.292	0.708
Griseofulvin	0.296	1.45	0.204	0.796
Indomethacin	0.387	1.35	0.287	0.713
Magnesium stearate	0.188	1.04	0.181	0.819
Phenacetin	0.511	1.25	0.409	0.591
Potassium chloride	0.914	1.97	0.423	0.578
Sodium chloride	0.8182	2.15	0.381	0.619

the same thickness of 0.30 ± 0.01 cm. The fractions 63–80 μm were carefully introduced in a circular, flat-faced punches 1.4 cm in diameter. All tableting was conducted at a compaction pressure of 90 MNm^{-2}. The compacts were immediately removed from the die, weighed, their diameter and thickness were measured using a micrometer and stored in a desiccator over silica-gel until used.

Compact tensile strength

The tensile strength was determined by application of the diametral-compression test. Materials were compressed diametrically on a modified Erweka hardness tester [2]. In order to minimize the shear and compressive stresses below the loading area, the platen width is limited to 1/10 of the diameter of the compact (Hiestand and Peot, 1974). The motor was operated to apply an increasing force to the tablet at a rate of 0.68 $kg \cdot s^{-1}$. When the compact failed, the tester stopped automatically and the failure load in kg was recorded on the scale. Then force readings were converted to tensile strength in the manner of Fell and Newton (1970). The tensile strength (σ_0) is given by:

$$\sigma_0 = \frac{2F}{\pi Dt} \tag{1}$$

where F is the force applied diametrically at fracture; D is the diameter of the compact; and t is the thickness of the compact. The mode of failure was determined visually by checking the shape of the fragments after fracture. If the compact splits into two equal halves, tensile failure has occurred. All tensile strengths reported are based on 10 determinations. Photographs were taken for the different behavior of compacts after fracture.

[2] Erweka-Apparatebau, Frankfurt, F.R.G.

Surface free energy data

Based on the assumption that no highly specific interaction and orientation of molecules occurs at the solid–liquid interface, Zografi and Tam (1976) used the contact angle measurements to estimate the solid surface free energy (γ). The values of γ for aspirin, griseofulvin, indomethacin, magnesium stearate and phenacetin were obtained from Zografi and Tam (1976).

For potassium chloride, an average value of γ was calculated from data reported by Westwood and Hitch (1963). Whereas the average value of γ for sodium chloride was obtained from Wiederhorn et al. (1970), who used the double cantilever cleavage technique.

Results and discussion

The crystal habit and particle shape of materials may influence the properties of the produced compacts. Photomicrographs of the materials used indicated differences in the appearance and shape of crystals (Fig. 1). Some physical properties of these pharmaceutical powders are illustrated in Table 1.

Compacts that laminate or are too fragile to determine their tensile strength were considered as unsatisfactory as in the case of phenacetin and griseofulvin. However, other powders studied yielded satisfactory compacts; phenacetin compact fractured in the die before ejection. The capping behavior of phenacetin is well documented (Hiestand et al., 1977; Shotton and Obiorah, 1975). Phenacetin crystals do not adequately relieve local stresses by plastic deformation, and fracture in shear occurs across the entire compact (Hiestand et al., 1977). Recently, the problem of phenacetin capping was overcome by using a die with a flexible wall (Amidon and Hiestand, 1981).

The different modes of failure are illustrated by the photographs of compacts subjected to diametral compression test (Fig. 2). In the case of griseofulvin, failure occurred by compression and/or shear, where the specimen fractured in an irregular way resulting in several irregular fragments, Fig. 2b (Fell and Newton, 1970).

For materials that produced satisfactory compacts, only the fracture forces were recorded when compacts failed in tension. This was visually checked by their uniform splitting into two equal halves along the loaded diameter (Fig. 2a). Potassium chloride produced the strongest compact. For aspirin compact, the tensile strength was relatively low and this may be related to the rapid increase in the specific surface area of aspirin particles (Higuchi et al., 1954). For magnesium stearate compacts, too many tensile strength determinations were required to obtain an average of 10 normal tensile failure for each reading.

Effect of time on tensile strength

The concept of the time-dependent flow involved in the consolidation processes, has been extensively investigated. Shlanta and Milosovich (1964) measured the stress relaxation of various pharmaceutical powders, and reported that the compression stresses are relieved with time. David and Augsburger (1977) showed that increasing

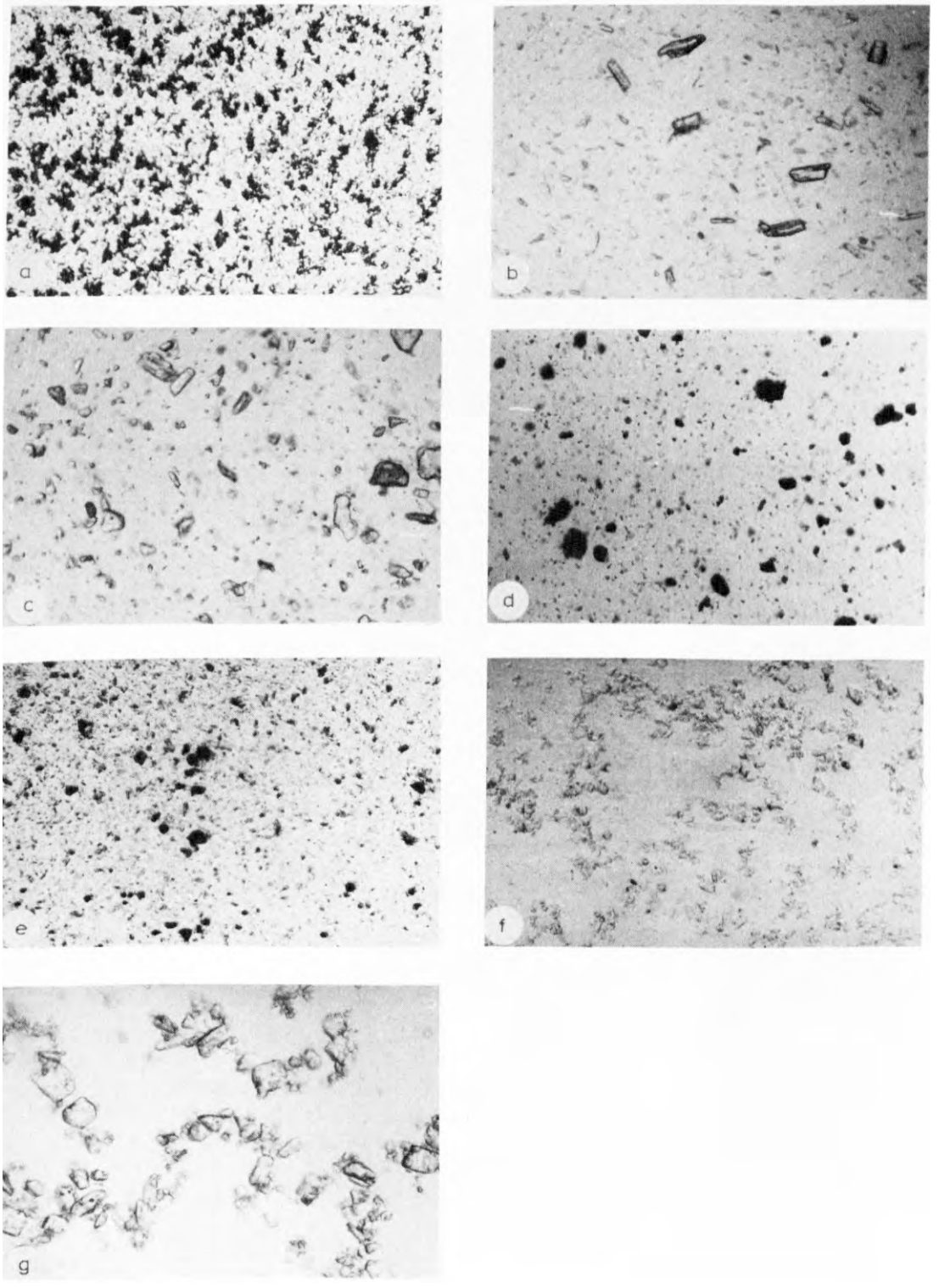

Fig. 1. Typical photomicrographs (×31) of the materials used (63–80 μm) (a) Griseofulvin; (b) aspirin; (c) phenacetin; (d) magnesium stearate; (e) indomethacin; (f) potassium chloride; (g) sodium chloride.

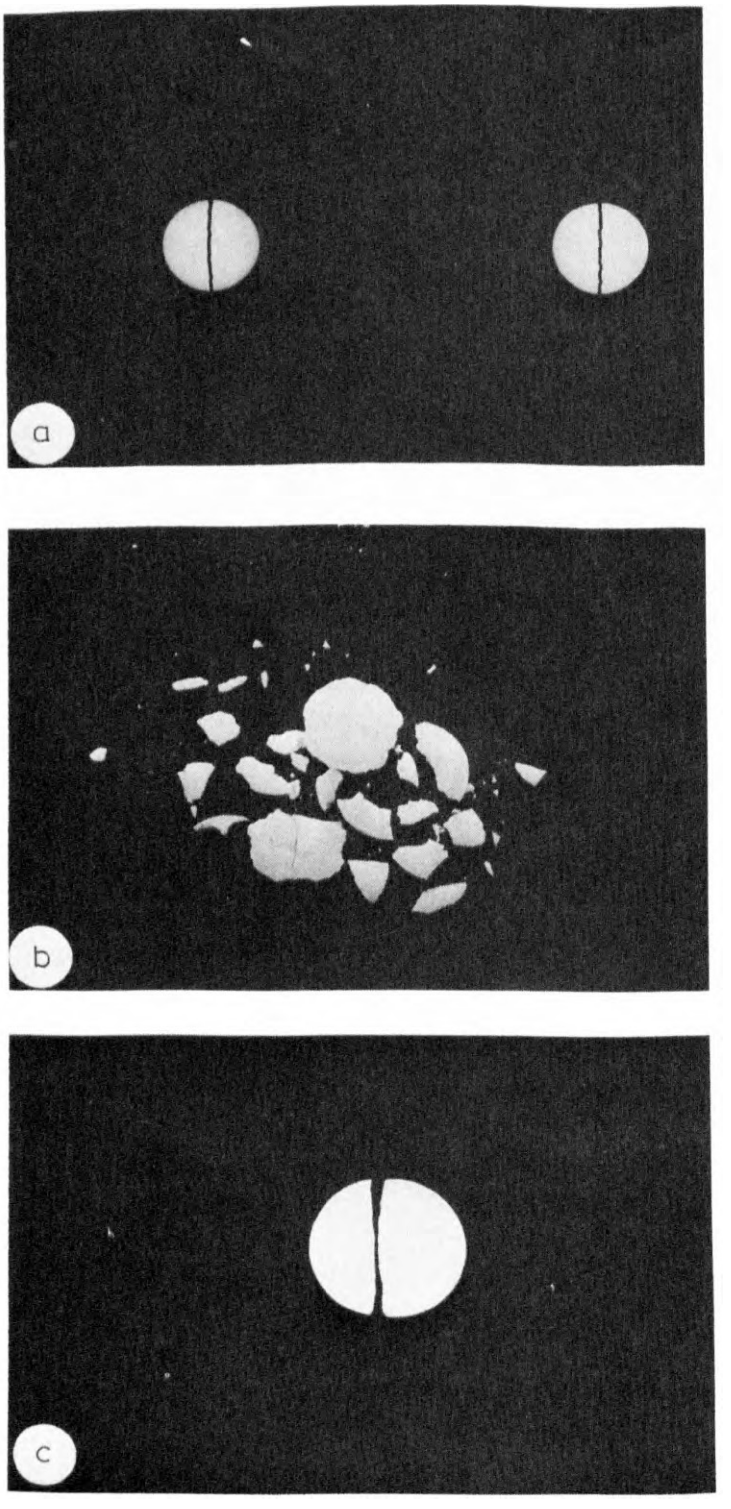

Fig. 2. Fractured compacts after diametral compression. (a) Normal tensile failure; (b) shear and compressive failure; (c) rejected tensile failure.

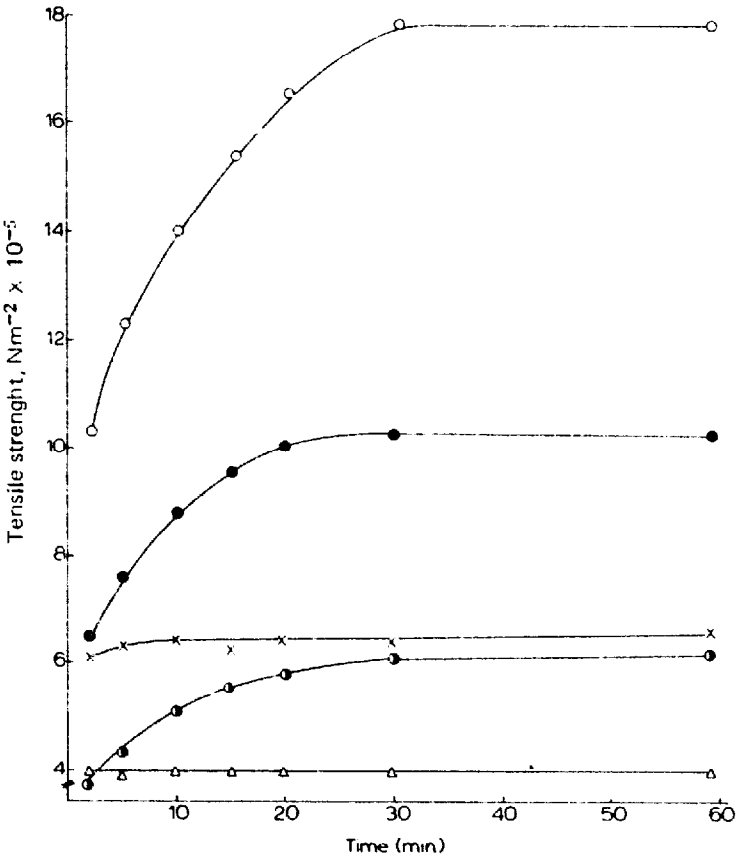

Fig. 3. Effect of time on the tensile strength of compacts. Each coordinate represents the mean of 10 determinations. ○———○, potassium chloride; ◑———◑, indomethacin; ●———●, sodium chloride; △———△, magnesium stearate; ×———×, aspirin.

the duration of the maximum compressive force resulted in significantly greater tablet strengths. Hiestand et al. (1977) confirmed the results obtained by Shlanta and Milosovich (1964) and proved that the incidence of fracture is also a time-dependent phenomena. Rees and Shotton (1970) showed that stress relaxation, for sodium chloride, continues after the compact has been ejected from the die.

In our study, compacts were prepared at a compaction pressure of 90 MNm^{-2}. At selected time intervals, their tensile strengths were determined. A plot of tensile strength versus time is presented in Fig. 3. Statistical treatment for data obtained from Fig. 3 showed significant differences (5% level) for all compacts except for magnesium stearate (Table 2).

The increase in strength that occurred with these materials can be attributed to the time-dependent flow or plastic flow which provides stress-relief within the compact. This plastic flow leads to an increase in true contact area between particles. However, compacts made of potassium chloride, sodium chloride and indomethacin exhibited much greater plastic flow than the aspirin compact. For instance, during the first hour after ejection from the die, the strength of potassium chloride compact

TABLE 2

EFFECT OF TIME ON COMPACT TENSILE STRENGTH FOR THE DIRECTLY COMPRESSED MATERIALS

Compact	Time	Tensile strength		
	(min)	$Nm^{-2} \times 10^{-5}$	S.D. [a]	t [b]
Potassium chloride	2	10.35	0.40	–
	30	17.94	0.52	36.6 [c]
Sodium chloride	2	6.47	0.32	–
	30	10.32	0.43	22.7 [c]
Indomethacin	2	3.73	0.26	–
	30	6.07	0.29	19.0 [c]
Aspirin	2	6.06	0.13	–
	30	6.42	0.25	4.06 [c]
Magnesium stearate	2	3.94	0.52	–
	30	4.06	0.60	0.48 [d]

[a] Standard deviation, based on 10 measurements.
[b] Student's t-statistic for difference comparing tensile strength of compact after 2 min with that after 30 min.
[c] Strengths are significantly different, at 5% level.
[d] No significant difference, at 5% level.

increased by approximately 73% compared with the initial value at 2 min (Fig. 3). Whereas the strength of aspirin compact increased by only 9% during the same period. This indicates that plastic deformation is more pronounced for potassium chloride compact than in aspirin compact. This finding is in accordance with the results obtained by Shlanta and Milosovich (1964). They reported that materials giving good tablets by direct compression showed medium relaxation, except for aspirin compacts. They also noted that the relaxation of aspirin was in the same low range as that obtained for powders forming poor tablets.

Potassium chloride compacts exhibited the greatest degree of plastic flow compared to other compacts which could be related to its lower yield strength. Coles et al. (1975) reported that a more rapid reduction in pore volume of potassium chloride

TABLE 3

LEAST-SQUARES FIT PARAMETERS FROM DATA IN FIG. 4

Compact	Viscoelastic slope, ν (min^{-1})	Intercept, $\ln \sigma_0'$ (Nm^{-2})	σ_0' ($Nm^{-2} \times 10^{-5}$)
Potassium chloride	0.204	13.7	8.91
Sodium chloride	0.188	13.24	5.62
Indomethacin	0.177	12.72	3.34

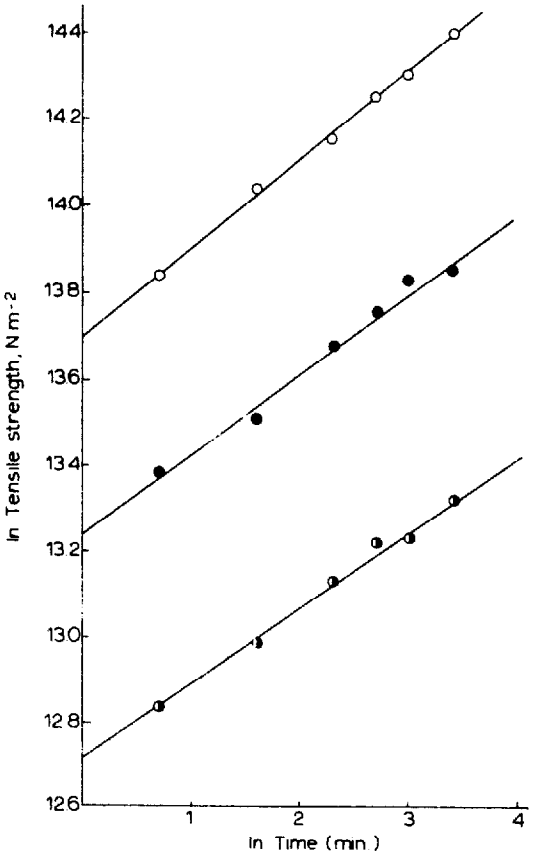

Fig. 4. Data from Fig. 3 treated according to Eqn. 3. O·····O, potassium chloride; ◑———◑, indomethacin; ●———●, sodium chloride.

compact under an increasing load is indicative of a lower yield strength than in sodium chloride compact.

The plastic flow concept has been treated mathematically as the Maxwell model under constant strain (David and Augsburger, 1977). Applying the same model to our results, straight lines were not obtained by plotting the ln of tensile strengths versus time. Therefore, a simple type of 'parabolic' equation may be used to represent our results, and is given by:

$$\sigma_0 = \sigma_0' t^v \tag{2}$$

And the ln of this equation:

$$\ln \sigma_0 = \ln \sigma_0' + v \cdot \ln t \tag{3}$$

where σ_0 is the observed tensile strength at time t and v is the visco-elastic slope.

The plots of ln σ_0, as a function of ln t, for potassium chloride, sodium chloride

TABLE 4

RELATION BETWEEN THE OBSERVED TENSILE STRENGTH (AFTER 30 MIN) AND THE SURFACE FREE ENERGY OF THE VARIOUS COMPACTS

Compacts	Surface free energy ($Erg \cdot cm^{-2}$)	Observed tensile strength ($Nm^{-2} \times 10^{-5}$)	K (cm)
Aspirin	67.5	6.42	1.1×10^{-5}
Griseofulvin	62.2	–	–
Indomethacin	61.8	6.07	1.1×10^{-5}
Magnesium stearate	23.0	4.06	5.6×10^{-6}
Phenacetin	58.3	–	–
Potassium chloride	181.0	17.94	1.1×10^{-5}
Sodium chloride	110.0	10.32	1.1×10^{-5}

and indomethacin are illustrated in Fig. 4. The lines are linear, i.e. the parabolic equation holds for these plastic materials. A linear regression analysis was performed to obtain the best estimate for the slopes and intercepts (Table 3). The intercept, ln σ_0', represents the ln tensile strength of compact at t = 1, while v is the visco-elastic slope and is a function of the porosity of the compact.

Surface free energy

Solid must bond together to give a cohesive mass. Particle–particle bonding during consolidation depends upon attraction forces developed between particles. These forces could be physical, e.g. surface, size and shape, or chemical. In turn, the chemical forces could be ionic, as in case of sodium chloride, or molecular as in most drugs. The magnitude of the attraction forces depends upon the pressure applied, and the surface free energy.

Since the surface free energy of a solid is related to the porosity, which is also related to the tensile strength, it was reasonable to correlate both parameters.

The surface free energy, γ, for the materials which produced satisfactory compacts are listed in Table 4. A comparison with the results obtained for the tensile

TABLE 5

MOLAR AREA A_m OF MOLECULES AT THE SURFACE, SURFACE FREE ENERGY, γ, AND SURFACE FREE ENERGY PER MOLE, γ_m

Material [a]	A_m (cm^2/mol) $\times 10^{-9}$	γ (Ergs/cm^2)	γ_m (Ergs/mol) $\times 10^{-9}$
Phenacetin	2.32	58.3	135
Griseofulvin	3.22	62.2	200
Indomethacin	3.46	61.8	214

[a] Data are obtained from Zografi and Tam, 1976.

strength, σ_0, of compacts showed that a direct relationship may exist. The higher the surface free energy, the stronger the compact. Therefore,

$$\gamma = \sigma_0 \times k \quad (4)$$

where k is a constant with the unit of cm, and may represent the distance at which the atomic attraction forces operate. Materials exhibiting plastic flow have the same k, and this was greater than that for magnesium stearate, which did not show any plastic flow (Table 4). Thus, materials with a tendency for plastic flow will attain an extensive contact area when compacted and strong bonds would be obtained.

The porosity of sodium chloride or aspirin compacted at 90 MNm^{-2} was found to be 18.2% and 5.1%, respectively, which is directly proportional to their obtained tensile strength and their surface free energy.

A molecular surface area approach can be useful to explain many phenomena (Amidon and Samaha, 1978). The surface free energy per mole, γ_m, is given by:

$$\gamma_m = A_m \gamma \quad (5)$$

where A_m is the molecular surface area in cm^2, and γ is the surface free energy in $ergs/cm^2$ (Zografi and Tam, 1976). Although close values were reported for the surface free energy γ, for the 3 powders shown in Table 5, yet only indomethacin produced a satisfactory compact. This finding could be justified at a molecular level, by comparing their surface free energy per mole, γ_m. Indomethacin has a higher γ_m value than both phenacetin or griseofulvin.

To conclude, the results of this study suggest that plastic flow and its effect on the tensile strength of a compact is an intrinsic property of the particulate material, and can be correlated to its surface free energy. High surface free energies are associated with high strength parameters because both depend on the bonding strength.

References

Amidon, G.E., Smith, D.P. and Hiestand, E.N., Rotary press utilizing a flexible die wall, J. Pharm. Sci., 70 (1981) 613–617.

Amidon, G.L. and Samaha, M.W., Functional group additivity in solubility estimation. Paper presented at the Basic Pharmaceutics Section, APHA Academy of Pharmaceutical Sciences, 25th National Meeting, Hollywood, Nov. 12–16, 1978.

Cole, E.T., Rees, J.E. and Hersey, J.A., Relations between compaction data for some crystalline pharmaceutical materials. Pharm. Acta Helv., 50 (1975) 28–32.

David, S.T. and Augsburger, L.L., Plastic flow during compression of directly compressible fillers and its effect on tablet strength. J. Pharm. Sci., 66 (1977) 155–159.

Fell, J.T. and Newton, J.M., Determination of tablet strength by the diametral-compression test. J. Pharm. Sci., 59 (1970) 688–691.

Hiestand, E.N. and Peot, C.B., Tensile strength of compressed powders and an example of incompatibility as end-point on shear yield locus. J. Pharm. Sci., 63 (1974) 605–612.

Hiestand, E.N., Powders: particle–particle interactions. J. Pharm. Sci., 55 (1966) 1325–1344.

Hiestand, E.N., Wells, J.E., Peot, C.B. and Ochs, J.F., Physical processes of tableting, J. Pharm. Sci., 66 (1977) 510–519.

Higuchi, T., Elowe, L.N. and Busse, L.W., The physics of tablet compression. J. Am. Pharm. Ass. (Sci. Edn.), 43 (1954) 685–689.

Linford, R.G., Surface energy of solids. Chem. Soc. Rev., 1 (1972) 445–463.

Rees, J.E. and Shotton, E., Some observations on the ageing of sodium chloride compacts. J. Pharm. Pharmacol., 22 (1970) Suppl., 17S-23S.

Shlanta, S. and Milosovich, G., Compression of pharmaceutical powders I. J. Pharm. Sci., 53 (1964) 562–564.

Shotton, E. and Obiorah, B.A., Effect of physical properties on compression characteristics. J. Pharm. Sci., 64 (1975) 1213–1216.

Westwood, A.R.C. and Hitch, T.T., Surface energy of (100)potassium chloride. J. Appl. Phys., 34 (1963) 3085–3089.

Wiederhorn, S.M., Moses, R.L. and Bean, B.L., Plastic deformation and the fracture surface energy of sodium chloride, J. Am. Ceram. Soc., 53 (1970) 18–23.

Zografi, G., Compilation of symposium papers, 5th National Meeting, APhA Academy of Pharmaceutical Sciences, 1968, p. 190.

Zografi, G. and Tam, S.S., Wettability of pharmaceutical solids: estimates of solid surface polarity. J. Pharm. Sci., 65 (1976) 1145–1149.