

Effects of paraffin coatings on the tensile strength of lactose

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Measurements have been made of the tensile strength of lactose at different temperatures after coating it with up to 10^{-4} mol of various paraffin hydrocarbons g^{-1} of powder. Providing the coating is in a liquified form, either as a result of the ambient temperature or because of the localized high pressure at the points of true contact between the particles, there is a correlation between the tensile strength of the powder and the thickness and viscosity of the coating layer.

A powder bed is composed of particles bonded to each other by van der Waals', frictional, surface tension and other forces which operate at the surfaces of the particles. Physical contact between neighbouring particles occurs at the minute protrusions or asperities on their surfaces. Any modification of these asperities will be expected to alter the magnitude of the bonding forces between the particles.

Bowden & Tabor (1957) have shown that, when pressure is applied to surfaces, elastic and plastic deformations occur at the contact points causing an increase in the area of contact and hence the adhesion between the surfaces. Recent studies have also shown that, in addition to the elastic and plastic deformation, melting of asperities occurs at these contact points when the powder bed is subjected to elevated temperatures and/or to high pressures (Jayasinghe et al 1969; York & Pilpel 1972). On cooling or when the applied pressure is removed, the previously molten material resolidifies and forms solid bridges between the particles thus causing an increase in the tensile strength of the powder bed.

Modifications to the surface asperities can also be produced by coating the powder with another material. This may or may not react chemically with the surface. Work has been reported on the effects produced on the tensile strengths of powders by coating them with moisture (Eaves & Jones 1972) and with pharmaceutical excipients such as fatty acids (Pilpel & Hopher 1977; Malamataris & Pilpel 1980).

Paraffins as well as other lubricants such as magnesium stearate and stearic acid are frequently used in the compression of pharmaceutical powders into tablets (Strickland 1959; Little & Mitchell 1963). They range from liquids to soft solids, and exhibit

marked changes in viscosity when the ambient or processing temperature is altered.

The purpose of the present study has been to see whether by coating lactose powder with increasing amounts of a series of paraffins whose physical properties vary in a regular manner with their molecular weights, it is possible to establish relationships between the tensile strengths of the powders and the viscosity and thickness of the coating layer.

MATERIALS AND METHODS

The materials used in this investigation were: lactose powder B.P. from Whey Products Ltd.; light liquid paraffin B.P.C. and liquid paraffin B.P. from Macarthy Ltd; white soft paraffin B.P. and yellow soft paraffin B.P. from Evans Medical Ltd, paraffin wax B.P. from Hopkins and Williams Ltd and diethyl ether (analytical reagent from Fisons.)

The lactose was milled in an Apex mill, classified into a narrow size fraction ($10\ \mu\text{m}$ – $30\ \mu\text{m}$) on a Microplex zig-zag Classifier, dried in a hot air oven at $60\ ^\circ\text{C}$ for 48 h and then stored in sealed jars over silica gel. The mean molecular weight of each of the paraffins was determined by the Viscosity method using Staudinger's equation (Weissberger 1960) and the value was confirmed by the Freezing Point Depression method (Standard Methods 1958). The relevant physicochemical properties of the paraffins are listed in Table 1, the range of values indicating that they were commercial products conforming to B.P. standards, but not exactly identifiable mixtures of particular hydrocarbons.

Coating

Samples of the dried lactose were coated with between 0.5 and 10.0×10^{-5} mol g^{-1} of the different paraffins by mixing 250 g of the powder with 0.45 litre of diethyl ether containing the appropriate

* Correspondence.

Table 1. Some physicochemical properties of the paraffins.

| Properties | Light liq. paraff. | Liq. paraff. | Yellow soft paraff. | White soft paraff. | Paraff. wax |
|---|--------------------|--------------|---------------------|--------------------|-------------|
| Mean mol. wt | 215 | 226 | 296 | 304 | 335 |
| Density (g ml ⁻¹) | 0.83-0.86 | 0.87-0.90 | 0.82-0.86 | 0.82-0.86 | 0.90 |
| Mean solidifying/ m.p. (°C) | -2 to -4 | 3 to 5 | 44 to 46 | 47 to 49 | 50 to 53 |
| Viscosity in. poise at 20 °C (± 2 c.p.) | 34 | 39 | 72* | 78 to 84* | 99 to 105* |
| 70 °C (± 1 c.p.) | 13 | 15 | 22 | 24 | 27 |

* Estimated by extrapolation from higher temperatures on the assumption that since the plots given by equation 1 were linear, they would remain approximately so across the boundary of phase change (Pilpel & Hephher 1977).

amount of paraffin in a 2 litre-flask. One batch of lactose was treated with the same amount of ether alone to provide a 'blank' (in fact it was found to have virtually the same tensile strength as the untreated sample). The ether was recovered by distillation while stirring continuously on a water bath at 40 °C. The coated lactose was then resieved to break down aggregates (as confirmed by microscopy) and was stored over silica gel in air tight containers.

Tensile tests

The apparatus consisted of a split nickel-plated cell of the Warren Spring type (Ashton et al 1964) which could be used at both low and elevated temperatures, thus enabling controlled alterations to be made to the viscosities of the paraffin coatings on the lactose (Fig. 1) (Britten & Pilpel 1977).

RESULTS

Fig. 2 shows the variation of the viscosity of the paraffins with temperature confirming that they followed the Andrade-Guzman relationship (Varshni & Srivastava 1959)

$$\eta = Ae^{b/T} \quad (1)$$

where η is the viscosity, T is the absolute temperature, e has a numerical value of 2.718, A and b are constants.

The viscosities and molecular weights of the paraffins which had been determined experimentally fitted the Fox and Loshaek equation (Porter & Johnson 1960),

$$\text{Log } \eta = A^1 \text{ Log } M - B \quad (2)$$

where η is the viscosity, M is the molecular weight, A^1 and B are isothermal constants. This is shown in Fig. 3.

The tensile strength results for all the samples at all the temperatures investigated (corresponding to

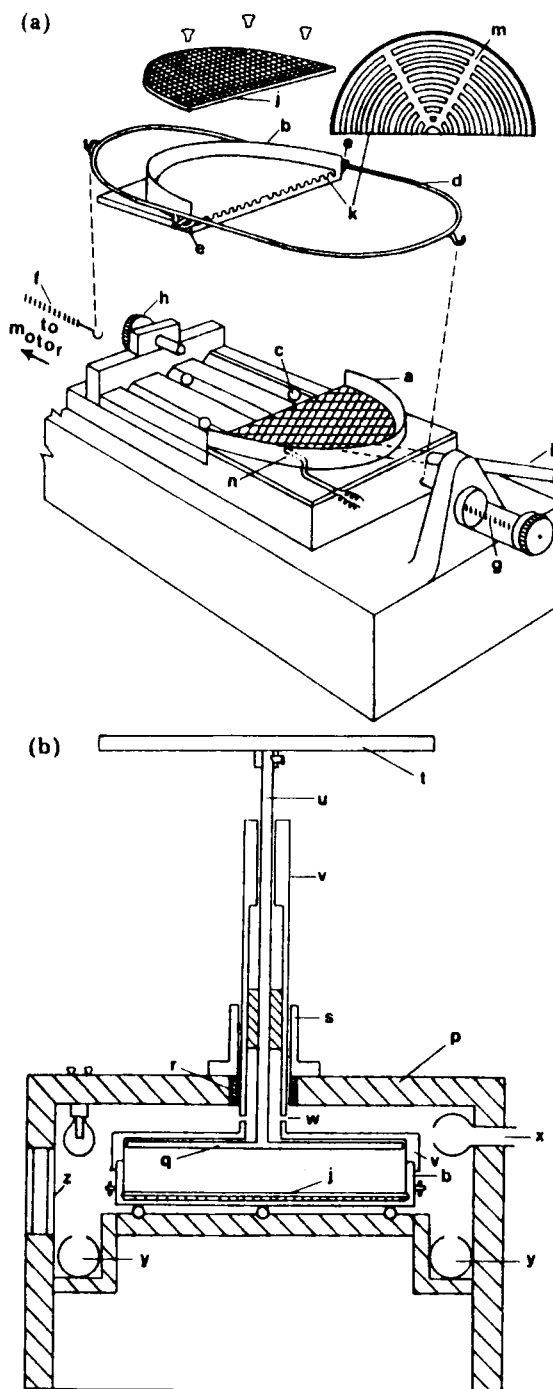


FIG. 1(a,b) Tensile tester. (a) Fixed half-cell. (b) Movable half-cell. (c) Steel ball bearing. (d) Wire loop. (e) Locating pin. (f) Calibrated spring. (g) Zero spring. (h) Clamp screw. (j) Rigid mesh. (k) Annular groove. (l) Gas inlet. (m) Cross channel. (n) Thermistor. (p) Insulating jacket. (q) Plunger. (r) Cork bush. (s) P.T.F.E. guide. (t) Load platform. (u) Graduated scale. (v) Locating piece. (w) Gas outlet. (x) Gas inlet (jacket). (y) Desiccant. (z) Window.

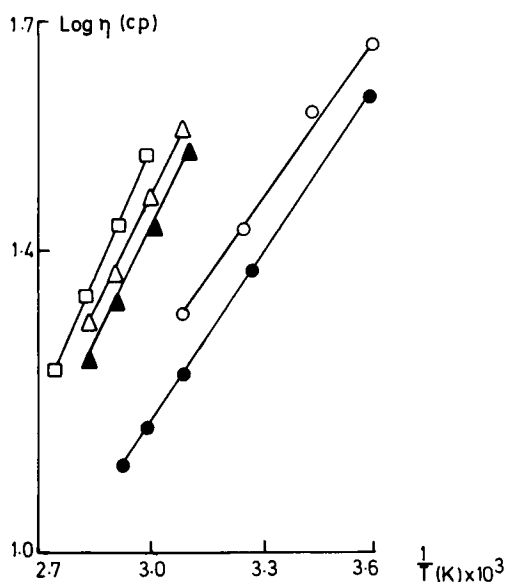


FIG. 2. Log viscosity of paraffins versus reciprocal of absolute temperature. ● Light liquid paraffin. ○ Liquid paraffin. ▲ Yellow soft paraffin. △ White soft paraffin. □ Paraffin wax.

particular viscosities of the coating films) were found to fit the general equation,

$$\log T = A^{11} Pf + B^1 \quad (3)$$

with a correlation coefficient > 0.90 for at least five measurements over a range of packing fraction Pf , from 0.35 to 0.50. T was the tensile strength, A^{11} and B^1 were constants which depended on the nature and amount of the paraffin used and on its viscosity at the temperature employed (all the samples had been subjected to the same consolidation pressures during the experiments in order to eliminate the effects of pressure on viscosity). The values of tensile strength

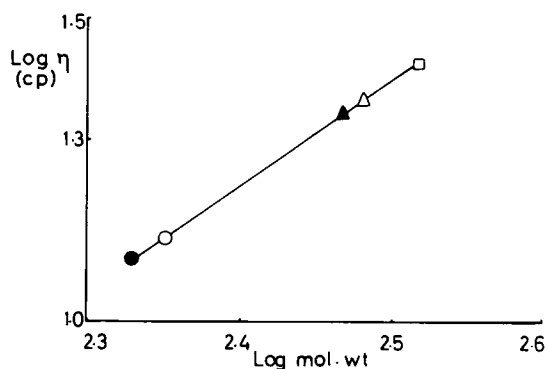


FIG. 3. Log viscosity of paraffins at 70 °C versus log molecular weights. ● Light liquid paraffin. ○ Liquid paraffin. ▲ Yellow soft paraffin. △ White soft paraffin. □ Paraffin wax.

at different temperatures at a fixed Pf 0.41 (selected because it involved minimum extrapolation of the linear plots of $\log T$ vs Pf) were determined. Fig. 4 (a,b) is representative of how the tensile strength at this fixed Pf of 0.41 varied with the paraffin content at 35 °C and 50 °C (The corresponding assumed viscosities (see later) of the paraffin coatings are given in the legends to the graphs. It is not possible to measure these viscosities in situ but it seems not unreasonable to assume that as a first approximation they will be similar to those of the materials in bulk at the same temperature. The curve for yellow soft paraffin was omitted to avoid overlapping with white soft paraffin). The tensile strength initially increased with increase in the amount of paraffins then decreased to a minimum and finally increased again as the paraffin content was further increased.

DISCUSSION

The initial increases in tensile strength in Fig. 4 (a,b) may be ascribed to bond formation between the paraffin molecules and lactose particles. Initially the paraffins form a discontinuous film causing the development of some paraffin-lactose bonds and some paraffin-paraffin bonds, in addition to the lactose-lactose bonds already operating at the true points of contact between the asperities of neighbouring lactose particles. This effect is similar to that produced by addition of very small amounts of moisture or fatty acids (Eaves & Jones 1972; Malamataris & Pilpel 1980). As more paraffin is added, it increasingly coats the surface asperities of the lactose, reducing the number of lactose-lactose bonds by masking the London and van der Waals' forces between the particles. When a continuous monomolecular film has been formed the paraffin now acts as a lubricant, reducing the conventional coefficient of friction between the lactose particles and making it easier for them to slide past each other (Bowden & Tabor 1954, 1964). This produced minima in the tensile strength when approximately $0.5-2.0 \times 10^{-5}$ mole of paraffin was present g^{-1} of lactose. The specific surface of the lactose, obtained by optical microscopy and application of the relevant equations (Esezobo & Pilpel 1977) was $2 m^2 g^{-1}$. Since each g mole of a substance contains 6.23×10^{23} , that is, Avogadro's number of molecules, therefore the total surface area, S_A , of the added paraffins for each molar concentration can be calculated from

$$S_A = M^1 \times A_0 \times 6.23 \times 10^{23} m^2 g^{-1} \quad (4)$$

of lactose

where M^1 is the molar concentration g^{-1} of lactose

and A_0 is the area per molecule of the paraffin calculated on the assumption that the paraffin molecules lie flat on the powder surface and that the C-C and C-H bond lengths are respectively 0.015 nm and 0.011 nm. Dividing the total surface area of the added paraffin by the specific surface of the lactose, the number of layers in the coating was obtained. These are given in Table 2.

The concentration range that produced the minima in tensile strength, $0.5\text{--}2.0 \times 10^{-5}$ mole of paraffin g^{-1} of lactose, corresponds to layers between 1 and 5 molecules thick, when rounded off to the nearest whole number; this procedure compensates for the molecular weight range in each of the paraffins. Addition of more paraffin leads to the formation of a thicker coating which tends to smooth out irregularities on the surfaces of neighbouring particles and increases their area of contact. The coating now begins to act as a binding agent increasing the cohesion between the particles, hence leading to an increase in the tensile strengths.

Table 2. Derived parameters.

| Paraffin concn (mol $\text{g}^{-1} \times 10^5$) | Area mol^{-1} ($\text{m}^2 \times 10^{20}$) | Surface area of added paraffin ($\text{m}^2 \text{g}^{-1}$ lactose) | No. of layers in coating | Conc. for: | |
|---|--|--|--------------------------|--|---|
| | | | | 3 layers ($\text{mol g}^{-1} \times 10^5$) | 11 layers ($\text{mol g}^{-1} \times 10^5$) |
| Light Liquid | | | | | |
| 0.5 | 47.0 | 1.5 | 1 | 2.0 | 8.0 |
| 1.0 | | 2.9 | 2 | | |
| 2.0 | | 5.8 | 3 | | |
| 5.0 | | 14.0 | 7 | | |
| 10.0 | | 29.3 | 15 | | |
| Liquid | | | | | |
| 0.5 | 50.4 | 1.6 | 1 | 2.0 | 7.0 |
| 1.0 | | 3.1 | 2 | | |
| 2.0 | | 6.2 | 3 | | |
| 5.0 | | 15.7 | 8 | | |
| 10.00 | | 15.7 | 16 | | |
| Yellow | | | | | |
| 0.5 | 63.9 | 1.9 | 1 | 1.5 | 6.0 |
| 1.0 | | 3.9 | 2 | | |
| 2.0 | | 7.9 | 4 | | |
| 5.0 | | 19.8 | 10 | | |
| 10.0 | | 39.7 | 20 | | |
| White soft | | | | | |
| 0.5 | 70.6 | 2.1 | 1 | 1.5 | 5.0 |
| 1.0 | | 4.3 | 2 | | |
| 2.0 | | 8.8 | 4 | | |
| 5.0 | | 21.9 | 11 | | |
| 10.0 | | 43.9 | 22 | | |
| Paraffin wax | | | | | |
| 0.5 | 77.3 | 2.4 | 1 | 1.3 | 4.0 |
| 1.0 | | 4.8 | 2 | | |
| 2.0 | | 9.6 | 5 | | |
| 5.0 | | 24.0 | 12 | | |
| 10.00 | | 48.1 | 24 | | |

The general increase in tensile strength observed in Fig. 4 (a,b) as the melting/solidifying points of the coatings increased from the liquid paraffins (except for light liquid paraffin) to the paraffin wax may be explained by assuming that under the

consolidation pressure applied during a tensile test paraffin coatings which are solid at room temperature become locally liquified because of the high pressures acting selectively at the points of

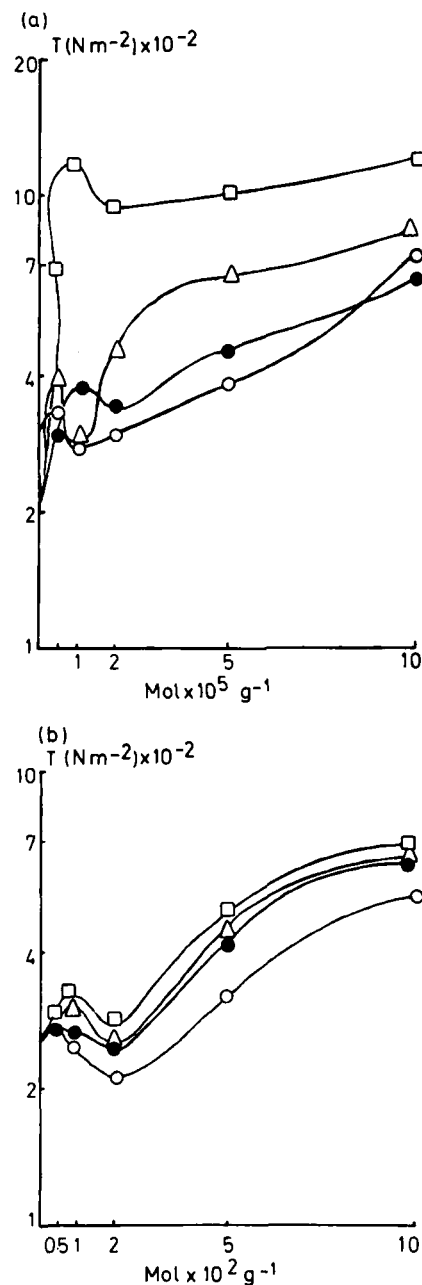


FIG. 4. Tensile strength at Pf 0.41 versus concentration of paraffin at (a) 35 °C and (b) 50 °C. Key with assumed viscosity of coating (cP), at 35 and 50 °C: ● Light liquid paraffin 24, 17. ○ Liquid paraffin 27, 19. △ White soft paraffin 53, 36. □ Paraffin wax 66, 44.

true contact between neighbouring particles of lactose. Under these conditions the Clausius Clapeyron equation does not apply and an increase in pressure will be expected to cause a decrease in melting point instead of an increase (York & Pilpel 1972) with actual melting occurring at the contact points. This occurs to an appreciable extent only when the ambient temperature has been raised to within about 20 °C of the melting point of the coating concerned (Pilpel & Britten 1979). It is possible to deduce the viscosities of these assumed liquid/molten films from the viscosity-temperature data given in Fig. 2 and the values are included in Fig. 4 (a,b).

The increase in tensile strength of coated lactose with increase in the assumed viscosity of the coating may be attributed to the formation of liquid/molten bonds between neighbouring particles, the strength of which increased with increase in viscosity of the coating. When tension is applied to the powder bed in the tensile tester, these bonds oppose separation of the particles thus causing an increase in tensile strength. This would agree with the observations of

Bowden & Bastow (1931) that adhesion between surfaces is considerably increased by interposing a viscous liquid between them.

It seemed logical to expect that there might be some connection between the tensile strength of the coated lactose and the thickness and assumed viscosity of the coating layer. Table 3 was therefore constructed. Arbitrarily selecting the coating to be first 3 and then 11 molecules thick, and selecting various fixed assumed viscosities for the coatings (as shown in the Table), the experimental values of the tensile strength were noted when the coatings would have been expected to have had these particular viscosities as a result of the temperature employed. It is seen from the Table (section a and b) that the tensile strengths of the samples were very similar when the paraffin coatings had the same thickness and were of the same assumed viscosity due to temperature. The same conclusion is reached by applying the same treatment to data obtained in a previous investigation on lactose coated with fatty acids (Malamataris & Pilpel 1980). The appropriate values of tensile strengths are given in Table 3c and

Table 3. Tensile strength at fixed number of layers and fixed viscosity of coating.

(a) Paraffin coatings that are liquid at room temperature

| | | Viscosity (cP) | | | | | | | |
|--------------|----------|--------------------------------------|----------------------|--------------------------------------|----------------------|--------------------------------------|----------------------|-----|-----|
| | | 20 | | 30 | | 60 | | | |
| | | Tensile strength (Nm ⁻²) | | Tensile strength (Nm ⁻²) | | Tensile strength (Nm ⁻²) | | | |
| | | For 3 layer coating | For 11 layer coating | For 3 layer coating | For 11 layer coating | For 3 layer coating | For 11 layer coating | | |
| Paraffins | Temp(°C) | | | Temp(°C) | | Temp(°C) | | | |
| Light liquid | 43 | 280 | 510 | 23 | 385 | 635 | -6 | 425 | 690 |
| Liquid | 50 | 260 | 490 | 30 | 380 | 630 | 0 | 420 | 680 |

(b) Paraffin coatings that are solid at room temperature

| | | Viscosity (cP) | | | | | | | |
|--------------|----------|---------------------|----------------------|---------------------|----------------------|---------------------|----------------------|-----|-----|
| | | 45 | | 60 | | 80 | | | |
| | | For 3 layer coating | For 11 layer coating | For 3 layer coating | For 11 layer coating | For 3 layer coating | For 11 layer coating | | |
| Paraffins | Temp(°C) | | | Temp(°C) | | Temp(°C) | | | |
| Yellow soft | 39 | 330 | 500 | 27 | 395 | 700 | 16 | 695 | 935 |
| White soft | 42 | 330 | 510 | 31 | 395 | 710 | 20 | 695 | 930 |
| Paraffin wax | 48 | 325 | 480 | 38 | 390 | 650 | 29 | 695 | 940 |

(c) Fatty acids that are solid at room temperature

| | | Viscosity (cP) | | | | | | | |
|-------------|----------|---------------------|----------------------|---------------------|----------------------|---------------------|----------------------|-----|-----|
| | | 20 | | 40 | | 60 | | | |
| | | For 3 layer coating | For 11 layer coating | For 3 layer coating | For 11 layer coating | For 3 layer coating | For 11 layer coating | | |
| Fatty acids | Temp(°C) | | | Temp(°C) | | Temp(°C) | | | |
| Palmitic | 37 | 320 | 370 | 16 | 351 | 490 | 4 | 390 | 520 |
| Stearic | 43 | 310 | 360 | 22 | 350 | 489 | 10 | 385 | 500 |
| Behenic | 57 | 310 | 380 | 32 | 345 | 500 | 21 | 380 | 530 |

are again seen to be similar for the same thickness and viscosity of the coating.

Conclusions

The conclusions of this work are:

1. That increasing additions of various paraffins to lactose powder produce the same pattern of effects on tensile strength as additions of water and of fatty acids.
2. That the tensile strength of lactose coated with paraffins depends on the viscosity and on the thickness of the coating.

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