

# Experimental investigation of adhesion between powders and surfaces

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The adhesion between two pharmaceutical powders (poly (ethylene glycol) 4000 and Sta-Rx 1500) and various metal and polymer substrates has been investigated. The powders were either deposited on the substrates with negligible force or forced on by spinning in a centrifuge. The force required to remove the particles was then evaluated by spinning the substrate-powder samples in a centrifuge and counting the remaining powder after rotation at various speeds. The median adhesive force between the powders and various substrates was similar in the case of particles deposited with negligible force, with the exception of adhesion to PTFE, which was about one-third of the force. After the powders had been forced on to the substrate surface the median adhesive force increased. This increase was approximately five-fold for the Sta-Rx 1500 and up to thirty-fold for the PEG 4000. Differences in the adhesion between each powder and the various substrates were now evident with, for example, Sta-Rx 1500 adhering to stainless steel with a force of  $1510 \times 10^{-9}$  N, but to Dural with a force of  $2380 \times 10^{-9}$  N.

Adhesion between powders, either of the same or different materials and between powders and surfaces, plays an important role in the handling and processing of pharmaceutical materials. There are several different mechanisms that cause adhesion, such as van der Waals' forces, electrostatic forces, liquid bridges and contact melting (Rumpf 1977). In some instances the adhesion is desirable, for example in the formation of a compressed tablet or in forming a powder plug to fill a capsule. In other circumstances the adhesion is undesirable, for example in cohesive solids where free flowing properties are needed or between a tablet and the punches from which it was formed.

The process by which adhesion occurs in pharmaceutical systems is complex, usually involving both compression and shear of one surface with the other. In process equipment, such as capsule filling machines, repeated powder contact with metal parts also leads to the formation of a thin layer of powder molecules on the metal. This build-up can markedly affect the performance of such machines (Jolliffe & Newton 1983).

To simplify the system that was studied, the effect of shearing powders over the substrates was eliminated. This allowed the study of adhesion either with or without the effect of a compressive force. To examine such a system several techniques have been developed. Rogers & Reed (1984) presented a new

model which described the adhesion of a particle to a surface following an elastic-plastic impact. A technique for experimental testing of the model was described: this involved determining the impact velocity of small particles on a prepared surface by high-speed cine photography. An impact separation method was used by Otsuka et al (1983) to measure the force of adhesion of powdered organic materials to a glass substrate. The acceleration generated by bringing a swinging hammer to rest was used to detach a powder from a surface. Krupp (1967) developed a centrifuge technique to determine the adhesive forces between a plain metal substrate and adherent spherical particles. The substrate was held vertically in a modified centrifuge tube and the separating force was governed by the speed of rotation of the centrifuge. The number of particles still adhering to the substrate after rotation was noted and the substrate then spun at a higher speed. From this a graph of percentage still adhering against applied separating force was plotted to give a measure of adhesion.

A modification of Krupp's technique has been used in this work to determine the adhesive forces between pharmaceutical powders and substrates of various materials, to provide an initial approach to the problem.

## MATERIALS AND METHODS

### *Adhesion cell*

A specially constructed centrifuge tube was used to hold the test substrate parallel to the axis of rotation of the centrifuge. This is shown in Fig. 1. It was

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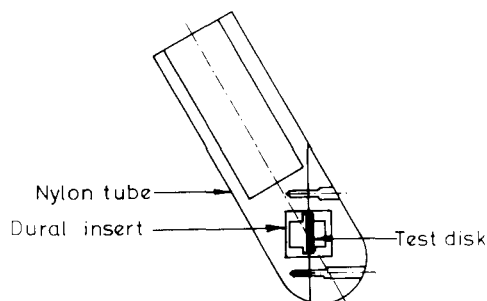


FIG. 1. Centrifuge tube constructed to hold test specimen parallel with the axis of rotation.

constructed from Nylon with the exception of the specimen holder which was of Dural. The tube was placed in the fixed angle rotor of an MSE Superspeed 18 centrifuge ( $8 \times 50$  mL head) and counterbalanced by an identical tube in the opposite tube-hole. The accelerations achieved at the surface of the test disks, at various spin speeds, are given in Table 1.

Table 1. Acceleration (in multiples of  $g$ ) at various spin speeds.

| Spin speed (rev min <sup>-1</sup> ) | Acceleration ( $g$ ) |
|-------------------------------------|----------------------|
| 1 000                               | 98                   |
| 3 000                               | 885                  |
| 5 000                               | 2 459                |
| 7 000                               | 4 820                |
| 9 000                               | 7 968                |
| 11 000                              | 11 903               |
| 13 000                              | 16 625               |
| 15 000                              | 22 133               |
| 17 000                              | 28 429               |

The substrates studied were mild steel, stainless steel, brass, Dural, PTFE and Perspex. Two small disks of each material were prepared having a rectangular grid marked over one face. One disk had a polished surface and the other had a surface which was untreated after lathing from a larger specimen.

The surface roughness of the disks was evaluated using an electrically indicating stylus instrument (Talysurf 4, Rank Taylor Hobson, Loughborough). This produces a magnified recording of the surface undulations from which the  $R_a$  value is calculated. The  $R_a$  is calculated as the sum of the areas of the profile above and below a reference line per unit length of surface measured, i.e. large values of  $R_a$  indicate rough surfaces (see Talysurf manual).

#### Powders

Samples of poly(ethylene glycol) 4000 (PEG 4000) (Hoechst AG) and Sta-Rx 1500 (Colorcon, USA) were sieved on an Alpine Air Jet Sieve (Alpine,

Augsburg), to remove particles of less than  $32 \mu\text{m}$ . The remaining powder was separated on 8 inch ASTM E11 sieves. The fraction in the size range  $45\text{--}53 \mu\text{m}$  was resieved on  $45$  and  $53 \mu\text{m}$  sieves to remove undersize and oversize particles, and it was this fraction which was used in the experimental programme. Fig. 2 shows SEM pictures of each sample.

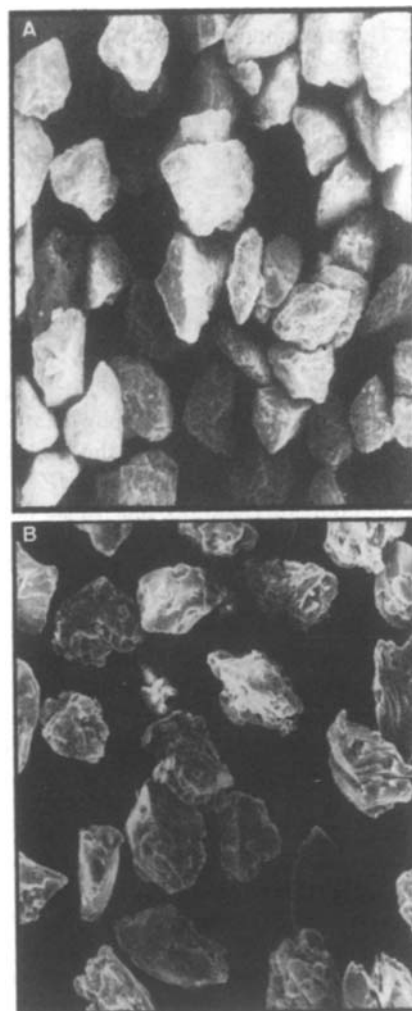


Fig. 2. Scanning electron micrographs of (A) poly(ethylene glycol) 4000 and (B) Sta-Rx 1500. Magnification  $\times 200$ .

The mean particle mass was determined using a Perkin Elmer Autobalance AD-2 (sensitive to  $0.1 \mu\text{g}$ ). A sample of each powder was weighed, a small fraction transferred to a microscope slide and the remaining powder reweighed. The number of particles removed, which was between 3000–6000, was counted and their total weight derived from the difference between the two weights.

### Method

Before use, the substrates were cleaned by immersion in acetone within an ultrasonic bath with the exception of Perspex which was cleaned in ethanol. No attempt was made to remove any chemically or physically bound impurities from the surfaces.

The powders were deposited on the surface of the test disks so that each particle was separated from its neighbour by at least one particle diameter. This was achieved by sprinkling the particles onto an aluminium plate and inverting this over the test disks and tapping the back of the plate with a spatula to dislodge the particles. The particles would be deposited with a negligible force after their drop of about 10 mm.

The disks, having been prepared, were then mounted in the modified centrifuge cells. Two types of experiment were performed: (i) the force of adhesion was measured when the particles were deposited with negligible force, as described above. In this case, the disks were mounted in the tubes with the powder on the outer surface; (ii) the powder was forced onto the substrate surface by mounting the disks with the powder facing inwards and then spinning in the centrifuge at a known speed and hence force. In the second case the disk was turned round (so that the powder was now on the outer face).

In both types of experiment the loss of powder particles was monitored by counting the particles remaining after centrifuging at an initially low speed using a binocular microscope. The disks were then replaced in the centrifuge cells and spun at a higher speed and the counting repeated. This was continued until there was less than 20% of the particles still adhering.

The effect of a lubricant, stearic acid, was studied by depositing a thin film of it on the substrate surface. This was achieved by wiping a 5% w/v solution in chloroform over the substrate before depositing the powder.

### RESULTS

The force ( $F$ ) applied by spinning in the centrifuge, either to pull a particle off the substrate or to force it on to the substrate, can be calculated from the equation

$$F = Mr\omega^2 \quad (1)$$

where  $M$  is the particle's mass,  $r$  is the distance from the axis of rotation to the particle and  $\omega$  is the angular velocity.

The mean particle mass of the PEG 4000 was  $4.98 \times 10^{-2} \mu\text{g}$  and that of the Sta-Rx 1500  $8.14 \times$

$10^{-2} \mu\text{g}$ . Typical adhesion profiles of percentage of particles still adhering against applied force can be plotted as in Fig. 3, where the adhesion of PEG 4000 to smooth brass and smooth PTFE is shown, after depositing the powders with negligible force. The data shown in Fig. 3 and subsequent Figures were calculated from five replicate experiments. The error bars represent a spread of  $\pm$  one standard deviation, and were usually less than 5% of mean value.

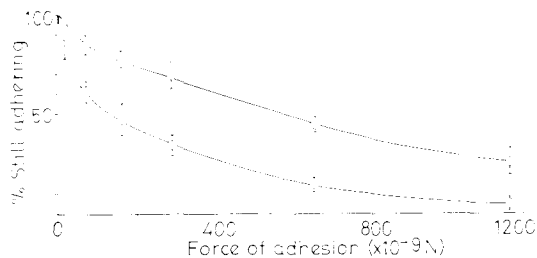


FIG. 3. Adhesion profiles of PEG 4000 to smooth brass  $\circ$ , and smooth PTFE  $\square$  (deposited with negligible force).

From these profiles the value of the median adhesive force was calculated. Also a measure of the spread of adhesive forces was determined: this was calculated as half the difference between the force above which 25% of the powder still adhered and the force above which 75% of the powder still adhered expressed as a percentage of the median adhesive force. This was termed the 'adhesional spread'.

Table 2 shows the median adhesive forces and adhesional spreads for PEG 4000 and Sta-Rx 1500 with the test substrates.

Table 2. Median adhesive forces ( $\times 10^{-9}$  N) for powders deposited on the smooth and rough test surfaces with negligible force. The adhesional spread (%) is shown in parentheses.

| Substrate       | Powder      |           |           |           |
|-----------------|-------------|-----------|-----------|-----------|
|                 | Sta-Rx 1500 |           | PEG 4000  |           |
|                 | Smooth      | Rough     | Smooth    | Rough     |
| Mild steel      | 306 (306)   | 304 (262) | 250 (329) | 181 (347) |
| Stainless steel | 315 (309)   | 318 (301) | 252 (300) | 246 (327) |
| Dural           | 340 (312)   | 270 (345) | 246 (315) | 239 (254) |
| Brass           | 315 (336)   | 252 (272) | 549 (290) | 477 (279) |
| Perspex         | 366 (258)   | 340 (268) | 303 (339) | 275 (363) |
| PTFE            | 116 (348)   | 237 (284) | 140 (360) | 134 (337) |

In the experiments where the powders were initially forced on to the test surface, the force of adhesion and adhesional spreads are given in Table 3.

The effect of a layer of stearic acid on the adhesion to the test surface was also evaluated. The results are given in Table 4.

Table 3. Median adhesive force ( $\times 10^{-9}$  N) for powders deposited on the test surface at 15 000 rev  $\text{min}^{-1}$ . The adhesional spread (%) is shown in parentheses.

| Substrate       | Sta-Rx 1500 |            | PEG 4000  |           |
|-----------------|-------------|------------|-----------|-----------|
|                 | Smooth      | Rough      | Smooth    | Rough     |
| Mild steel      | 2060 (89)   | 1640 (121) | 6040 (51) | 5860 (39) |
| Stainless steel | 1510 (117)  | 1440 (124) | 6680 (54) | 6640 (54) |
| Dural           | 2380 (116)  | 1800 (119) | 7670 (47) | 6830 (54) |
| Brass           | 2170 (109)  | 2160 (117) | 7800 (52) | 7200 (56) |
| Perspex         | 2560 (109)  | 2470 (98)  | 6630 (55) | 6650 (55) |
| PTFE            | 1210 (162)  | 1140 (150) | 3440 (67) | 3410 (68) |

Table 4. Median adhesive force ( $\times 10^{-9}$  N) for particles on a stearic acid-covered substrate. The adhesional spread (%) is shown in parentheses.

|   | Sta-Rx 1500 |           |
|---|-------------|-----------|
|   | Smooth      | Rough     |
| Mild steel                              |             |           |
| Deposited with negligible force         | 250 (292)   | 166 (292) |
| Spun on at 15 000 rev $\text{min}^{-1}$ | 1210 (99)   | 950 (130) |
| Stainless steel                         |             |           |
| Deposited with negligible force         | 241 (308)   | 208 (319) |
| Spun on at 15 000 rev $\text{min}^{-1}$ | 1060 (115)  | 963 (123) |

Table 5. Surface roughness ( $R_a$ ) for sample disks.

|                 | $R_a \mu\text{m}$ |                    |        |                    |
|-----------------|-------------------|--------------------|--------|--------------------|
|                 | Rough             |                    | Smooth |                    |
|                 | Mean              | Standard deviation | Mean   | Standard deviation |
| Mild steel      | 0.53              | 0.10               | 0.26   | 0.08               |
| Stainless steel | 0.60              | 0.28               | 0.17   | 0.03               |
| Dural           | 0.18              | 0.01               | 0.10   | 0.03               |
| Brass           | 0.41              | 0.07               | 0.11   | 0.04               |
| Perspex         | 0.17              | 0.02               | 0.11   | 0.01               |
| PTFE            | 1.34              | 0.15               | 0.55   | 0.13               |

The  $R_a$  values for surface roughness of the substrates are given in Table 5.

#### DISCUSSION

The adhesion studied in these experiments was far removed from the ideal case of adhesion between a perfect sphere and smooth substrate for which theoretical equations exist (Rumpf 1977). The powders, whilst being almost equi-dimensional, did not have smooth exteriors but rather had angular and rough surfaces. The substrates were also irregular on close inspection. Rumpf (1977) concludes that the predominant forces involved in powder adhesion, by

at least an order of magnitude, are van der Waals' forces, which are only active over a short range. The effect of the roughness of the contacting surfaces is to reduce the area over which the van der Waals' forces are able to act.

The shape of the particles can be approximated by superimposing spheres upon each other such that the largest spherical diameter is that of a sphere of the particle's volume, whilst the smallest spherical diameter would illustrate the smallest degree of roughness present. Assuming contact with a flat substrate, the strength of the van der Waals' forces acting at the point, or points of contact is proportional to the radius of the contacting spherical portions. Since the contacting surfaces could have a wide range of curvatures, of radii ranging from nanometres up to about 25 micrometres, this could lead to a large range of adhesive forces.

The adhesive profiles for powders deposited with negligible force (see, for example Fig. 3) exhibit a wide range of adhesive forces, with increasing separating forces removing progressively fewer particles. This results in a large adhesional spread with values around 300%.

Powders that had been forced on to the substrates had a differently shaped adhesion profile. Fig. 4

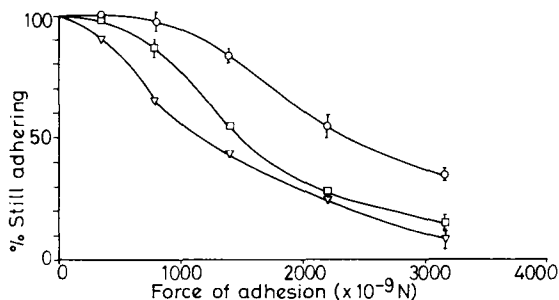


Fig. 4. Adhesion profiles of Sta-Rx 1500 to smooth PTFE  $\nabla$ , Dural  $\circ$ , and stainless steel  $\square$  (spun on at 15 000 rev  $\text{min}^{-1}$ ).

shows the adhesion profiles of Sta-Rx 1500 with smooth PTFE, Dural and stainless steel. They all show an initial section where practically no particles are removed, even by forces which would have removed most of the particles had they been deposited with negligible force. There is then a section where most of the particles are removed while a few particles remain tenaciously adhered even at much higher separating forces. The relative spread in adhesion forces is much reduced by the pressing-on process. The values have decreased from around 300% to about 100–120%. This may have

arisen from plastic flattening of the tiny surface asperities under the applied pressing forces which leads to an increased contact area and hence greater van der Waals' interactions.

The adhesion forces, when the powder is forced on to the surface, exhibit a log-normal distribution which is not seen when the powders are deposited with negligible force (see Fig. 5).

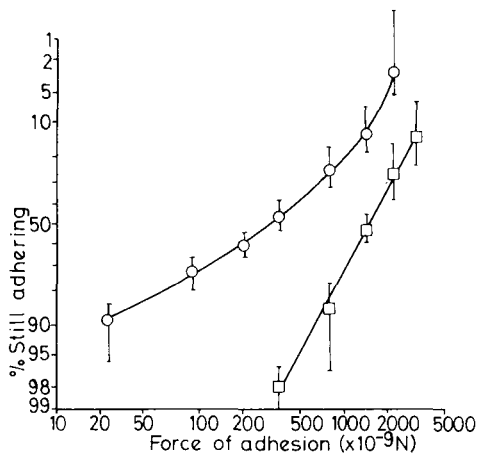


FIG. 5. Log-probability plot of the adhesion of Sta-Rx 1500 to smooth stainless steel.  $\circ$  Deposited with negligible force.  $\square$  Spun on at 15 000 rev min<sup>-1</sup>.

The median adhesive forces for the Sta-Rx 1500 deposited with negligible force on smooth surfaces show little variation between materials, with the exception of the adhesion to PTFE which is about one-third of the other values. The adhesive forces between the smooth substrate surfaces and the Sta-Rx 1500 all lie within the experimental variations of about  $\pm 7\%$  of each other (with the exception of adhesion to PTFE). However, there are some large differences between the adhesion to rough and smooth surfaces of the same substrates, i.e. Dural, brass and PTFE.

The PEG 4000, when deposited with negligible force, exhibits similar adhesive forces (to the Sta-Rx 1500) to most of the substrates with the exception of brass to which it adheres with twice the strength. The difference between rough and smooth surfaces is, again, small in most cases although the adhesive forces tend to be slightly less with the rougher surface.

The forcing of the powder onto the substrate caused a marked increase in adhesive forces for both powders and also revealed marked differences

between the powders and their adhesion to the different substrates.

Most of the Sta-Rx 1500-substrate bonds increased between five and seven times in strength, with the exception of the adhesion to smooth PTFE where a ten-fold increase was noted. Differences between metal substrates were now seen, with the Sta-Rx 1500 showing less adhesion to stainless steel than the others. Adhesion to PTFE was still less than to any of the other substrates but was still higher than had been expected, perhaps due to deformation of the substrate as well as the powder. Adhesion to Perspex was stronger than to most of the metals.

Forcing the PEG 4000 on to the substrates caused a much larger increase in adhesion of up to thirty times the force required to remove the particles deposited with no force. In this case the mild steel showed lower adhesive bond strength than any of the other metals. Adhesion to PTFE was roughly half that of the other materials while adhesion to Perspex was on a par with the stainless steel. Brass, to which PEG 4000 was very adherent, when deposited with negligible force, showed the highest values of adhesive force although it was only slightly higher than Dural. Adhesional spread was around 50–60% which was half the value of the Sta-Rx 1500 when forced onto the substrates. The large difference in the increase in adhesion force seen between Sta-Rx 1500 and PEG 4000 may be due to differences in the mechanical properties of the powders. Unfortunately, relevant values for the appropriate mechanical properties are not available in the literature. Intuitively, one would expect PEG 4000 to be more plastic than Sta-Rx 1500, while the latter will be more elastic than the former. In the case of Sta-Rx 1500, the force exerted on the particles will be more likely to be absorbed by elastic straining of the particles. This elastic strain energy will then be lost when the centrifuge slows down.

A stearic acid layer on the mild and stainless steel substrates caused a significant lowering of the adhesion of Sta-Rx 1500. The lowering was between 25–50%.

As in all the experiments the adhesion measured is the force required to pull the particles off the substrate in the normal direction.

This will impose a tensile stress at the substrate-particle junction. The order of magnitude of this stress, and also the compressive stress exerted by spinning the particles onto the substrate, can be arrived at by making the assumption that the area of contact between the powder and substrate is of the order of 1–10  $\mu\text{m}^2$ . This leads to stresses in the region

of 64–640 kPa at a spin speed of 3000 rev min<sup>-1</sup> and to stresses of 1.6–16 MPa at a spin speed of 15 000 rev min<sup>-1</sup>.

The adhesive forces of powders to substrates can be determined using the centrifuge technique perhaps with a view to selecting a material for constructing process plant from, which would reduce the powder adhesion. The forcing of the material onto the substrate has shown up a vast difference between the two powders, which shows that the PEG 4000 would be much more liable to adhere to surfaces during processing than the Sta-Rx 1500. This is borne out in practice during tableting within our laboratories. Sta-Rx 1500 can be formed into tablets using an unlubricated punch and die with ease, but PEG 4000 tends to adhere to the punches. This adhesion of PEG 4000 to punches has been studied by Ritter et al (1978).

#### *Conclusions*

The adhesion of Sta-Rx 1500 and PEG 4000 to

several substrates has been characterized using a centrifuge technique. In these experiments, both the force of adhesion when the particles were deposited on the substrates with negligible force, and the force of adhesion when the particles were forced on to the substrates, were studied. It was shown that while the powders both showed similar adhesion to the substrates when sprinkled on, the PEG 4000 adhered much more strongly after the powder had been pressed on.

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