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A new approach for determination of powder wettability

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Abstract

Based on the work initiated by Shanker, R.M., Baltusis, P.J. and Hruska, R.M. (Development of a new technique for the assessment of wettability of powders. *Pharm. Res.*, 11 (Suppl) (1995) s243 (abstract)) and Dove, J.W., Buckton, G. and Doherty, C. (Comparison of wetting behaviour of theophylline and caffeine using various contact angle measurement methods and inverse gas chromatography. In *15th Pharm. Technol. Conf.*, 19–21 March 1996, Oxford, UK), this study has focused on the determination of effectively wet perimeters during Wilhelmy plate immersion experiments of powder stuck on glue. Data generated from extrapolated immersion loads of plates in two different apolar liquids, enable a measure of powder wet perimeter. Such perimeters are used to derive contact angles of reference liquids on the particular powder. Two powders were taken as models: starch and ketoprofen. © 1997 Elsevier Science B.V.

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Powder wettability assays are often criticised, as their frequent prerequisite is compaction. The energy transmitted to the native powder, is liable to induce polymorphic changes and, regardless of the accuracy of the test, the results can be biased (Buckton and Newton, 1995). Assays that avoid preliminary compaction, like liquid penetration experiments or microcalorimetry, are time-consuming, and liquid penetration of powder beds is particularly product-consuming. Recently, Shanker et al. (1995) and Dove et al. (1996), have investigated a new approach to the determination of powder wettability, working with the native powder, on a measurement derived from the Wilhelmy plate method. In this work, we present a way of effectively measuring powder wet perimeters, the key variable of the test (Chawla et al., 1994).

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Table 1
Surface tension decompositions of reference liquids given in literature and measurements

Measurements (mN/m)	$\gamma_{\mathrm{Lmeas.}}$	Two parameter model (Rowe, 1989)			Three parameter model (Good, 1992)			
		γ_L	γ_L^d	γ_L^p	γ_L	γ_L^{LW}	γ_L^+	γ_L^-
Methylene iodide	50.4	50.4	50.4	0	50.8	50.8	0	0
Dodecane	24.6	—	—	—	—	—	—	—
Water	71.9	72.0	23.2	48.8	72.8	21.8	25.5	25.5
Glycerol	63.6	63.7	32	31.7	64	34	3.92	57.4

The surface tension of dodecan is assumed to be only apolar: $\gamma_L = \gamma_L^d = 24.6$ mN/m.

The test powders are pregelatinised maize starch: starch 1500™ (Roquette) and ketoprofen™ (Rhône Poulenc Rorer). The reference liquids are bidistilled water, methylene iodide 99.0% (Aldrich), glycerol 99.9% (Aldrich) and dodecane (Prolabo). Surface tensions of all liquids are checked prior to use, with the Wilhelmy plate method on a (Lauda TD1) microbalance. Measured values of reference liquid surface tensions and decompositions used for calculations are given in Table 1.

In order to determine immersion load values on powder, the powder is fixed on a plane substrate. For this purpose, Guilspray™ (Guilbert) adhesive spray, is sprayed on a hot (70–80°C) sodocalcic glass 25 × 1 mm section slide, leading to coating of the slide with an even, smooth layer of transparent glue. No naked glass patches, nor external rugosity was found through microscopic examination. After cooling, the exact dimensions of the slide are measured with a Mitutoyo micrometer. Glue-coated slides are then covered with the test powder, shaken in a flask containing a small (10 g) amount of powder. Particles that do not adhere, are removed under pressurised air flow.

The test consists in the immersion of a slide in a reference liquid. The load is recorded as a function of the imposed displacement in and out of the liquid at a speed of 10 mm/min. The apparatus used for such recordings is an Instron rheometer, equipped with a 2.5 N static load cell (Fig. 1).

If viscous forces are neglected, owing to slow displacement of the slide, the two forces that act on the slide are the Archimedean pressure and the capillary force resulting from the liquid surface tension. A typical trace obtained from load displacement measurements is shown in Fig. 2. The slopes of the graphs are related to the Archimedean pressure which increases linearly during immersion, as slide section is constant. According to observed coating of some slides with 'good wetting' liquids, emersion values were not used to derive any contact angle as the force recorded during emersion, might well imply cohesional breakage of the reference liquid and spare the solid/liquid interface. The load value at contact during immersion, is hence the measurement on which the test is based. This load value equilibrates the vertical componant of the capillary force: $\gamma_{LV}\, p$, where p is the effective wet perimeter of the slide.

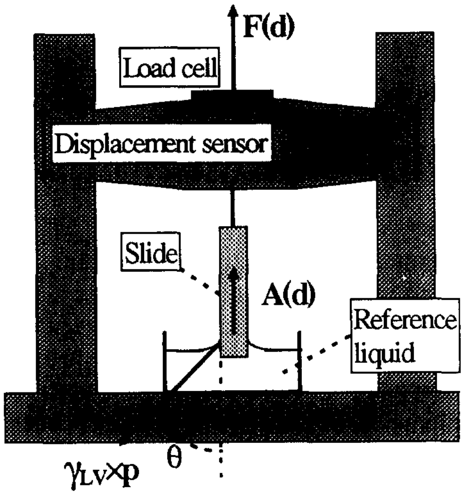

Fig. 1. Measurement of dynamic contact angle at immersion of slides. Instron equiped with 2.5 N static load cell ΔF_i.

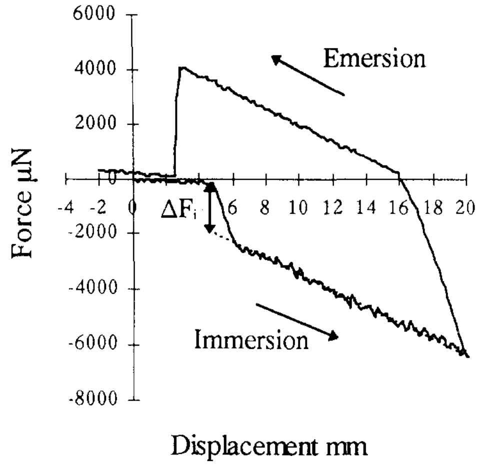

Fig. 2. Immersion/emersion cycle of sodocalcic glass vs. water. Speed of displacement 10 mm/min.

$$\Delta F_{meas.} = \gamma_{LV} p \times \cos \theta \quad (1)$$

with θ the contact angle of the liquid on the slide (Fig. 1).

When the slide contacts the liquid, the lower section disappears, and the adhesional wetting occuring at this stage, disturbs the recording. Furthermore, the corners of the slide can cause the liquid meniscus to deform without breaking, as in Fig. 2. During the 2–3 mm displacement required to break the meniscus, the load value does not reflect the actual effect of capillary forces on the particular surface under test. We therefore advise to extrapolate the load value at contact, from the late recording of the buoyancy slope, or work with very fine slides, so as to minimise disturbances.

Dynamic immersion contact angles on sodocalcic glass and glue covered slides for water, methylene iodide, and glycerol are reported in Table 2, and surface tension decompositions according to Good (1992), are given in Table 3, for both these surfaces. Good's three parameter model of surface tension divides tension in a dispersive componant γ^{LW} and in acid γ^{+} and basic γ^{-} components.

Table 2
Cosine of contact angles of water, methylene iodide and glycerol on glass and glue-covered slides

Surface	Sodocalcic glass	Glue-covered slide
Cos θ_{Water}	0.853 ± 0.06	-0.439 ± 0.03
Cos $\theta_{\mathrm{Methylene\ iodide}}$	0.641 ± 0.04	0.154 ± 0.07
Cos $\theta_{\mathrm{Glycerol}}$	0.283 ± 0.1	-0.478 ± 0.05

Standard deviations are calculated from a minimum of six values of $\Delta F_{\mathrm{immersion}}$.

With powder stuck on glue, the surface is no longer readily defined and the perimeter wet by the liquid can be described as the sum of two perimeters, introducing a Cassie-like law for the measured load. (Cassie, 1948). Such relationship was previously supported by Dove et al. (1996)

$$\Delta F_{meas.} = \gamma_L \times p_{glue} \times \cos \theta_{glue} + \gamma_L \times p_{powder} \times \cos \theta_{powder} \quad (2)$$

This is a three unknown equation, if we consider that contact angles of liquids on the glue, can be directly measured with glue coated slides of known perimeter.

As $\gamma_{LV} \times \cos \theta_{L/S} = \gamma_{SV} - \gamma_{SL}$ (Young, 1805) and $\gamma_{SL} = \gamma_{SV} + \gamma_{LV} - 2 \times (\gamma_{LV} \times \gamma_{SV}^{d})^{0.5}$ (Fowkes, 1964) we can derive the following relationship between contact angles of two apolar liquids on the powder:

$$(\cos \theta_{1\,powder} + 1) = (\cos \theta_{2\,powder} + 1) \times (\gamma_{LV2}/\gamma_{LV1})^{0.5} \quad (3)$$

The system simplifies to a four unknown system of three equations. Two attitudes can be undertaken: either add a third apolar liquid to fully describe the system, the five unknowns beeing p_{glue}, p_{powder}, $\cos \theta_{1\ \mathrm{powder}}$, $\cos \theta_{2\ \mathrm{powder}}$, $\cos \theta_{3\ \mathrm{powder}}$, or neglect the glue perimeter in the case of fine and/or polydisperse powders.

Table 3
Good's model decompositions for sodocalcic glass and glue slides

(mN/m)	Sodocalcic glass slide	Glue-covered slide
γ_S	62.9	21.3
γ_S^{LW}	33.9	16.8
γ_S^{+}	2.4	1.9
γ_S^{-}	88.8	2.7
Polarity	0.46	0.21

Table 4
Perimeters and contact angles of apolar liquids for starch and ketoprofen (52 mm of apparent slide perimeter)

	Starch	Ketoprofen
Cos $\theta_{\text{powder}}^{\text{Methylene iodide}}$	0.239	0.0832
Cos $\theta_{\text{powder}}^{\text{Dodecan}}$	0.774	0.551
Powder perimeter (mm)	86.40	99.90

The last proposition is retained, as microscopic examination of powder covered glue slides proves a larger amount of powder compared to glue. Experiments are carried out to determine a powder perimeter with two immersion loads of apolar liquids. Results for starch and ketoprofen using methylene iodide and dodecane are given in Table 4. This approach for determination of perimeters, was checked on a plane sodocalcic glass surface of macroscopic 52 mm apparent perimeter (Table 5). The value of the measured 51 mm is in agreement with the apparent perimeter owing to experimental errors. For powder covered slides, the ratio of effectively wet to apparent perimeter is 1.7 for starch and 1.9 for ketoprofen, which is in keeping with the 1.8 value found for similiar gold-coated plates by Buckton and Newton (1995). Although particle size should influence this ratio, values obtained for compacted plates are similar and would account for limited penetration of liquid in compacts, during Wilhelmy plate contact angle measurements.

Table 5
Contact force measured, dynamic immersion angles and derived perimeter for glass slides

	Dodecane	Methylene iodide
$\Delta F_{\text{immersion}}$ (μN)	1330	1130
Standard deviation of 10 measurements (μN)	44	57
Cos $\theta_{\text{immersion}}$	0.438	1.0
Perimeter: 51 mm		

Table 6
Surface tension as expressed from the three parameter Good's model for starch and ketoprofen using water, methylene iodide and glycerol

(mN)	Starch	Ketoprofen
γ_S	23.11	19.05
γ_S^{LW}	19.35	14.79
γ_S^{+}	0.113	0.394
γ_S^{-}	31.28	11.56

In possession of wet powder perimeter measurement, $\theta_{\text{powder}}^{\text{Water}}$ and $\theta_{\text{powder}}^{\text{Glycerol}}$ can be calculated from immersion load values of similar slides in the particular liquids. Starch and ketoprofen surface tension decompositions are given in Tables 6 and 7, for Good's model and Wu's harmonic mean model (Wu, 1973), respectively. For these calculations, wet powder perimeter is assumed to be liquid-independent. This is supported on the one hand, by limited penetration of liquids in powder-covered slides and no observed air entrapment on the slide rough surface. If the same surface is wet for the same displacement during immersion, the effectively wet perimeter should be the same. On the other hand, results in Tables 6 and 7 are shown to disagree. Such discrepancies are well known in the literature. They could be attributed either to different errors in the measurement, or to the model itself (Good, 1992). The dependence of the wet perimeter on the type of liquid used regarding viscosity (Chawla et al., 1994) and surface tension is important. It has not yet been quantified, but capillary rise of the reference liquid along the slide rough surface, should be considered for instance. The two apolar liquids used in this study display similar low viscosities, and should hence give a measure of the higher possible wet perimeter for a particular powder.

This new approach for determination of powder perimeters seems promising although, some points need to be checked, especially whether or

Table 7
Surface tension as expressed from the two parameter Wu's harmonic mean model using H_2O and CH_2I_2

	Starch	Ketoprofen
γ_S (mN/m)	38.49	24.96
γ_S^d (mN/m)	22.63	18.72
γ_S^p (mN/m)	15.86	6.24
Polarity	0.41	0.25

not neglecting the glue perimeter is a valid approach for the slides tested and if, on the contrary, three apolar liquids could yield better results. Wet perimeter dependance on liquids will have to be more fundamentally addressed.

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