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Surface energetics of powders before and after compaction

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Summary

Contact angle determinations have been carried out on an insoluble polymer powder consisting of spherical particles to provide as simple a system as possible. The methods used were penetration rates into powder beds and compressed discs and the maximum height of a liquid drop on a compressed disc (h-ϵ method). The results show differences between the static and dynamic methods, but not between the two penetration methods. Differences may be due to the velocity of the liquid penetration. Surface energy calculations show that although the absolute values are different between the methods, the proportion of the polar and dispersions components are comparable.

Introduction

The contact angle of a liquid on a material in powder form normally must be measured indirectly. The powder may be compressed into a compact and a static angle determined or alternatively, a liquid penetration method may be used to determine a dynamic angle. Compressing a powder could conceivably change the surface energy and results may not be a true reflection of the uncompressed powder (Buckton and Newton, 1986). The aim of the work reported in this paper was to compare results obtained from static and dynamic methods using a polymer consisting of spherical particles to give more reproducible packing and obviate the need for saturated solutions.

Determination of the contact angle from liquid penetration techniques uses the Washburn equation (1921):

$$l^2 = r\gamma_{\mathrm{LV}}\frac{\cos\theta t}{2\eta} \tag{1}$$

where l is the length of penetration, r is the capillary radius, γ_{LV} is the liquid surface tension, η is the liquid viscosity, t is time and θ is the contact angle. Comparison of the test liquid with one which is perfectly wetting (Studebaker and Snow, 1955) leads to

$$\cos\theta = \frac{\gamma_{\mathrm{LV}_1}}{\gamma_{\mathrm{LV}_2}}\frac{\text{gradient}_2}{\text{gradient}_1} \tag{2}$$

where subscripts 1 and 2 refer to the perfectly wetting and the test liquid, respectively, and the gradient is that of a plot of l^2 vs t.

Contact angles on compressed powders may be determined from the maximum height of a liquid

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drop formed on a saturated compact and applying the following equations (Witvoet, 1971; Lerk et al., 1976):

$$\cos\theta = 1 - \frac{2}{3(1-\epsilon v)}Bh^2 \quad \text{for } \theta < 90° \tag{3}$$

$$\cos\theta = -1 + (2 - Bh)^2 - \frac{2}{3(1-\epsilon \mathrm{v})} \quad \text{for } \theta > 90° \tag{4}$$

Materials and Methods

Materials

The polymer used was Corvic 47/488 (I.C.I. Polymer Div., U.K.). The material was sieved to give a 180–250 μm size fraction. The liquids used were formamide (B.D.H. Ltd., U.K.), polyglycol E200 (Dow Chemicals), cyclohexane, methanol, ethanol and propanol (Fisons Ltd). Water was glass-distilled and gave surface tension readings of not less than 70 mNm^{-1} at 20 °C. Formamide and polyglycol E200 were chosen as test liquids which would give finite contact angles and allow surface energies to be calculated. The organic solvents provide a range of liquids one or all of which should be perfectly wetting. Relevant liquid properties are shown in Table 1.

Liquid penetration

The method used was that described by Van Kamp et al. (1986) which essentially measures the weight loss of liquid from a container on an electronic balance, the container being connected to the material under test. The weight of liquid penetrating with time was measured either into powders packed to give a constant porosity in glass tubes terminating in a porosity-1 glass filter or 1.27-cm-diameter flat-faced tablets prepared at 224 $\mathrm{mN/m^2}$ on an instrumented single-punch tablet machine.

TABLE 1

Relevant properties of the test liquids

Liquid	η ($\mathrm{mNm^{-2}s}$)	γ_{LV} (mN/m)	$\gamma_{\mathrm{L}}^{\mathrm{d}}$ (mN/m)	$\gamma_{\mathrm{L}}^{\mathrm{p}}$ (mN/m)
Water	1	72.8	20.7	52.1
Formamide	3.3	58.2	32.1	26.1
E-200	58.1	43.0	30.0	13.0
Methanol	0.59	22.6	15.4	7.2
Ethanol	1.22	22.1	17.8	4.3
Cyclohexane	1.02	27.8	26.9	0.9
Propanol	2.4	20.8	16.2	4.6

h-ε method

The maximum height of a liquid drop on a 5.1 cm diameter compact prepared at 58 $\mathrm{mN/m^2}$ on a hydraulic press was measured using a cathotometer. Eqns. 3 or 4 were used to determine the contact angle (Lerk et al., 1976).

Results and Discussion

The use of Eqn. 2 to estimate the contact angle requires data from a perfect wetting liquid. In common with the work of Buckton (1985) and Buckton and Newton (1985) no such liquid could be found when using the criteria of Studebaker and Snow (1955), i.e., if any two liquids yield a value of 1 from Eqn. 2 they are more likely to be perfectly wetting than partially wetting to the same extent. Hence, the approach of Buckton (1985) and Buckton and Newton (1985) to use the best wetting liquid (propanol in this case) was adopted and results were calculated against this. The correct choice of wetting liquid is critical, the selection of either propanol or methanol (the poorest of the "wetting" liquids) giving rise to a 2.7-fold difference in cos θ. What difference this makes to the contact angle will depend on its value. For example, the water contact angle using propanol as the best wetting liquid is 87°, which is changed to 78° using methanol as the best wetting liquid, whereas the formamide contact angle is changed from 80° to 62°.

Table 2 gives the contact angle values determined from penetration into powder beds and tablets and from the h-ε method. There is good agreement between the two penetration studies, but the values are considerably higher than those determined by the h-ε method. The agreement in

TABLE 2

Contact angles on Corvic powder determined by liquid penetration into powder beds and compacts and the h-ϵ method

Liquid	Powder		Tablet		h-ϵ compact θ
	gradient	θ	gradient	θ	
Water	0.07415	87.2°	0.00275	89.9°	71.2°
Formamide	0.06627	80.0°	0.01793	86.5°	60.3°
E-200	–	–	0.00219	80°	36.9°
Methanol	0.3075	68.3°	–	–	0°
Ethanol	0.1898	61.2°	0.109	69°	0°
Cyclohexane	0.3066	58.8°	–	–	0°
Propanol-2	0.1882	0°	0.1455	0°	0°

results between the two penetration studies indicates that compression is not changing the surface energy characteristics of the powder (Fukuoka et al., 1981). Hence, the different values obtained from the h-ϵ method are not due to the powder being compressed.

Liquid penetration is a balance between the interfacial driving force and a viscous retarding force, whereas a static contact angle as determined by the h-ϵ method is determined by the equilibrium of interfacial energies. The movement of liquids at solid–liquid interfaces causes disorientation of molecules at the periphery leading to displacement of interfacial tensions from their equilibrium values. If the molecular relaxation time is τ and the displacement length is L, the natural recovery velocity is $V_n = L/\tau$. If the interfacial velocity is lower than V_n, the molecules will have sufficient time to recover from the displacement and the interfacial tensions will be the equilibrium values. In this case, the dynamic and static angles will be the same. If, however, the interfacial velocity is higher than V_n, the solid–liquid interfacial tension is increased and from Young's equation, Eqn. 5, the contact angle is increased (Phillips and Riddiford, 1972).

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta \tag{5}$$

where the subscripts SV and SL refer to the solid–vapour and solid–liquid interfacial tensions respectively. Methanol, ethanol and cyclohexane exhibit effectively zero angles when measured by the h-ϵ method yet the values are high when estimated by the liquid penetration method. All penetrate rapidly and the high angles may be a consequence of this rapid penetration.

Further problems associated with liquid penetration methods have been detailed by Yang and Zografi (1986). These results are similar in that they show a higher value of the contact angle from penetration studies.

Table 3 gives the surface energies of the powder as calculated from the various liquid pairs using the Wu equation (1971). The surface energy

TABLE 3

Surface energies and their components calculated using various liquid pairs

Liquid–liquid	Powder			Tablet			h-ϵ		
	γ_S^P	γ_S^D	γ_S	γ_S^P	γ_S^P	γ_S	γ_S^P	γ_S^D	γ_S
Water–formamide	17.7	8.2	25.9	19.7	4.8	24.5	22.7	13.7	36.4
Water–E200	–	–	–	18.2	6.1	24.3	19.6	18.7	38.3
Water–methanol	24.9	2.5	27.4	–	–	–	27.3	8.8	36.1
Water–ethanol	19.6	6.3	25.9	19.3	5.1	24.4	23.5	12.7	36.2
Water–cyclohexane	12.9	15.2	28.1	–	–	–	–	–	–
Water–propanol	14.7	12.1	26.7	13.1	12.4	25.5	25	11	36
Formamide–ethanol	21.8	6.2	28	19	5.1	24.1	24.8	12.6	37.4
Formamide–cyclohexane	9.1	15.2	24.3	–	–	–	10.7	25.4	36.1
Formamide–propanol	11.4	12.8	24.2	6.9	14.5	21.4	28.9	10.7	39.6
Formamide–E-200	–	–	–	15.9	6.7	22.6	12.3	23	35.3
E-200–ethanol	–	–	–	24.0	4.9	28.9	–	–	–
E-200–cyclohexane	–	–	–	–	–	–	9.8	25	35.2

Values for γ_S^P, γ_S^D, γ_S are in mN/m.

calculated from the dynamic contact angle is lower than that calculated from the static angle. The surface energy components are variable depending on the liquid pair chosen but these estimates are dependent on the precision of the contact angle values as shown by Luangtana-anan and Fell (1987). Interestingly, if average values are taken, the proportions of the surface energy components are independent of the method of determining the contact angle, all methods giving ca. 70% of the surface energy as polar forces.

All indirect methods of measuring contact angles are open to question due to the degree of complexity of the systems under study. The results obtained from a relatively simple system, presented in this paper, show that there are differences between the values determined from penetration and static methods although the surface energy calculations indicate that the results are comparable on a proportional basis. It is unlikely that there is a method of choice, the values obtained being a reflection of the "in use" condition of the powder.

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