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Contact angles of powder mixtures consisting of spherical particles

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Summary

The contact angles of mixtures of powders consisting of spherical particles have been measured using the h-ϵ technique and penetration studies. The use of spherical powders allows a constant powder bed structure to be maintained throughout the range of mixtures. The results show that the hydrophobic component dominates the contact angle of the mixture, although this dominance is reduced as the particle size of the mixture is reduced.

Introduction

The wetting of pharmaceutical powders is a necessary step in several manufacturing processes, and is a preliminary step in the dissolution of drugs from solid dosage forms. The contact angle is used as a measure of the wettability of a solid, and determinations have been made on pharmaceutical powders by: (1) direct measurement on a compact of the powder (Harder et al., 1970; Zografi and Tam, 1976); (2) the h-ϵ method (Kossen and Heertjes, 1965; Lerk et al., 1976); and (3) liquid penetration (Carli and Simioni, 1977; Hansford et al., 1980). A reasonable degree of correlation was established between results from a direct measurement and the h-ϵ method (Fell and Efentakis, 1979) and between a direct measurement and a penetration method (Liao and Zatz, 1979).

All these methods have limitations, but for a given system provide reproducible results. In a review of the methods, Neumann and Good (1979) considered penetration to be the most satisfactory, and the technique does closely resemble the conditions pertaining in practice.

Pharmaceutical powder systems and dosage forms invariably consist of mixtures of materials. Lerk et al. (1976) studied the wetting of a two-component mixture (acetylsalicylic acid and dicalcium phosphate dihydrate) by the h-ε method, and found that the hydrophobic component was dominant when the particle size of the materials was large, but there was a linear relation between the cosine of the contact angle and the proportion of the materials for a fine particle size. Liao and Zatz (1979) using a direct measurement technique found that for mixtures of phenacetin and microcrystalline cellulose of fine particle size, the hydrophobic component dominated the wetting of the system.

In both these studies, the area fractions of the solids exposed to the liquid were calculated assuming spherical particles, and hence the values may in error. In addition, when using penetration studies, varying proportions of the materials will give rise to differing powder bed structures, or one material may coat the other. These problems can be overcome using spherical particles, and this paper reports the results of studies on the wettability of mixed systems of such particles.

Materials and Methods

Two polymer powders whose particles were spherical were used for the study. Polyethylmethacrylate was obtained from Cole Polymers (Croydon, U.K.). A vinyl chloride, vinyl acetate copolymer (Corvic C47/488) was obtained from I.C.I. The materials were sieved to obtain 53–90 μm size fractions which were washed with water and dried prior to use.

In addition to these materials, mixtures of hydrophilic and hydrophobic glass beads were used. The beads were of two particle sizes, 80–105 μm (Jencons, Hemel Hempstead, U.K.) and approximately 15 μm (obtained by fractionation using an Alpine Zig Zag Classifier, Alpine Process Technology, U.K.). To prepare the hydrophilic sample, the beads were: (1) washed with water; (2) washed with methyl alcohol; (3) washed with water and filtered; (4) left in chromic acid for 24 h; then (5) washed 10 times with water, filtered and dried. The hydrophobic glass beads were prepared by: (1) washing with distilled water; (2) washing with methyl alcohol; (3) washing with toluene; (4) allowing the beads to stand in a 5% solution of dichloromethyl silane in toluene for 12 h; (5) rinsing with methyl alcohol; then (6) washing with toluene, filtering and drying.

The liquids used were methanol, ethanol, toluene, acetone, hexane and cyclohexane (all Laboratory Reagent Grade, B.D.H.) and glass distilled water with a surface tension of not less than 70 mNm^{-1} at 20°C. The h-ε method for determining contact angles was used as described previously (Lerk et al., 1976; Fell and Efentakis, 1978). Distilled water was used as the measuring liquid.

Penetration studies were carried out using the apparatus shown in Fig. 1. The apparatus allowed a small constant pressure to be applied to the system permitting penetration of water into the more hydrophobic materials. The materials were packed down to a constant porosity and readings of volume of penetration against time were taken.

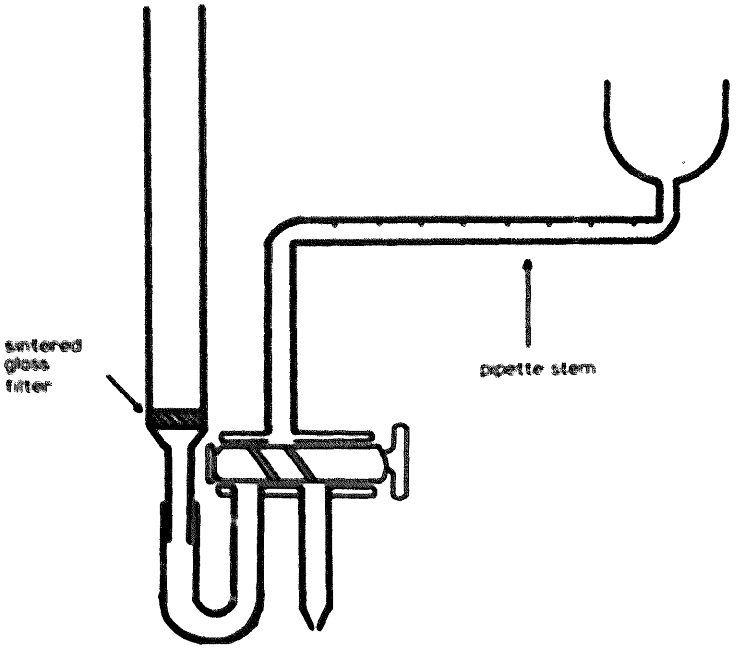

Fig. 1. The apparatus used for the penetration studies. The tube containing the sintered glass filter can be detached and used under zero external pressure.

Results and discussion

The contact angle of a heterogeneous surface has been expressed by Cassie (1948) as:

$$\cos\theta = Q_1 \cos\theta_1 + Q_2 \cos\theta_2$$

where θ is the contact angle on the heterogeneous surface, Q_1 is the fraction of surface having a contact angle θ_1 and Q_2 is the fraction having a contact angle θ_2. Johnson and Dettre (1969) analyzed an idealized model of a heterogeneous surface, and showed that deviations from Cassie's equation occurred, but the angles approached those predicted by the equation as the size of the heterogeneities became smaller. Because the polymers employed had limited particle size distributions, a common particle size of 53–90 μm was selected to give appropriate amounts of material. The conclusions drawn from this size fraction, however, may not necessarily be applicable to very fine particle sizes.

The contact angles of the mixtures of polymers are shown in Fig. 2. Calculation of the contact angles from the h-ε method was achieved using the equations described previously (Witvoet, 1971; Lerk et al., 1976). Contact angles from the penetration studies were determined as follows. Plots of the square of the volume of penetration against time were linear in accordance with the Washburn equation for penetration

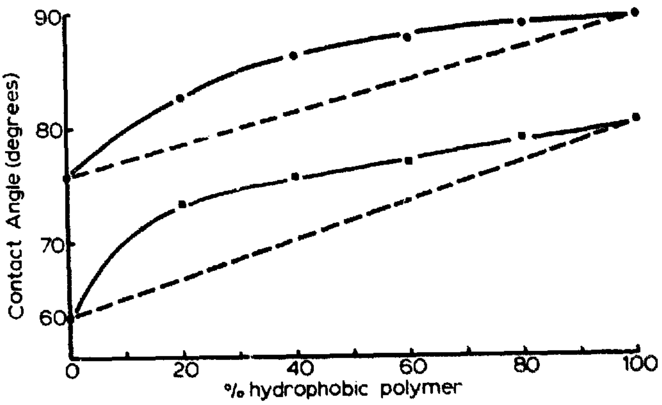

Fig. 2. The relation between the component percentage and the contact angle for the polymer mixtures. ●, contact angles determined by penetration; ■, contact angles determined by the h-ε method; - - - - - -, theoretical curve from Cassie's equation.

of liquid through a capillary:

$$\frac{V^2}{t} = \frac{r^2}{4\eta}\left(\frac{2\gamma}{r} \cdot \cos\theta + \Delta p\right) \qquad (1)$$

where V = the volume of penetration, t = time, r = capillary radius, η = liquid viscosity, γ = liquid surface tension, Δp = external pressure = ρ.g.h where ρ = liquid density, g = acceleration due to gravity, h = head of liquid. To obtain a value for r, several liquids which were suspected of having zero contact angle against the materials were run at equivalent porosities but without the use of external pressure. The following equation then applies:

$$\frac{L^2}{t} = \frac{\gamma \cdot \cos\theta \cdot r}{2\eta} \qquad (2)$$

where L = the distance of penetration. Letting $\cos\theta = 1$, r can be calculated and when more than one liquid gave an identical value of r, those liquids could be taken as having $\cos\theta = 1$ against the materials, and the value of r so calculated used in Eqn. 1.

The results presented in Fig. 2 show for both methods of measurement a deviation from the Cassie equation (1948) and a dominance of the more hydrophobic material contained in the mixture. This confirms the earlier observations of Lerk et al. (1976) and Liao and Zatz (1979) who used less well defined systems. The difference in absolute values of the contact angle between the two methods of measurement is not surprising in view of the large differences in technique, and also, in the h-ε method, a static angle is being determined, whereas penetration measures a dynamic angle.

In this particular system, the contact angles of the two materials are relatively close together. To examine a system in which the contact angles are very different,

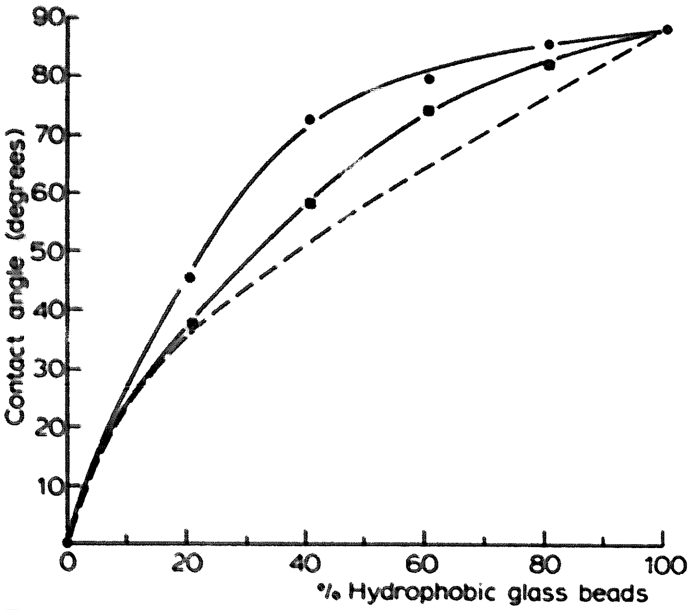

Fig. 3. The relation between the component percentage and the contact angle for mixtures of glass beads. ●, experimental points (80–105 μm); ■, experimental points (15 μm); - - - - - -, theoretical curve from Cassie's equation.

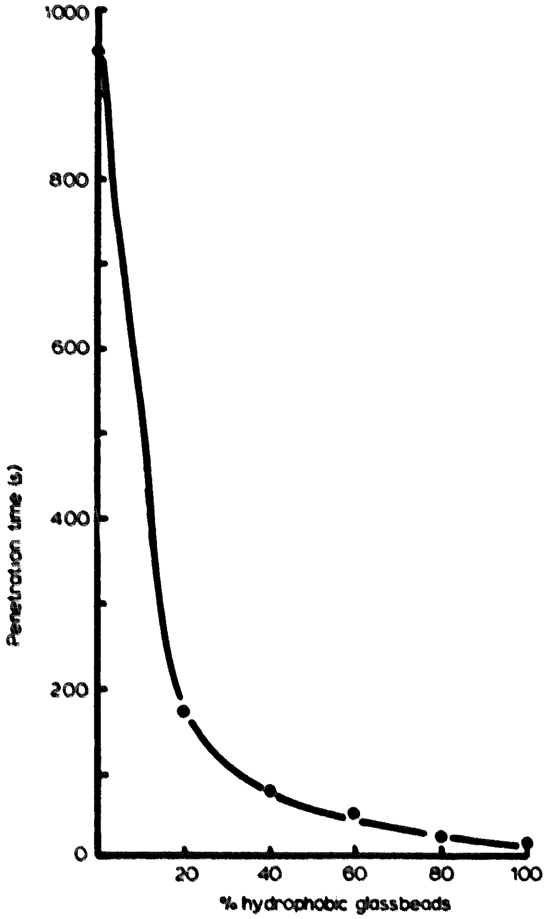

Fig. 4. The relation between time of penetration of 0.5 ml of water and the component percentage for mixtures of glass beads.

mixtures of untreated and silicone-treated glass beads were used. This system was only amenable to study by penetration, and the results are shown in Fig. 3. For the larger size glass beads, the dominance of the hydrophobic portion of the mixture can again be noted. However, for the finer beads, the results, although again showing dominance of the hydrophobic material, lie much closer to the theoretical line. This is in keeping with the theoretical work of Johnson and Dettre (1969).

The use of a model system of spherical particles enables more general conclusions to be drawn on the wettability of mixtures as the proportions of the materials can be changed without varying other factors. Previous results could have been specific for the mixture employed for the reasons given in the introduction. The results confirm that for simple two-component mixtures, the hydrophobic component of the system dominates but this dominance is reduced as the particle size of the component is reduced.

Hence, a greater amount of the hydrophilic material may be required to achieve a given reduction in contact angle. However, as the rate of penetration is proportional to the contact angle, large changes in penetration rate are obtained for small changes in contact angle, when the contact angle is high. This is shown in Fig. 4 for the large glass beads system. Although the addition of 20% hydrophilic beads only reduces the contact angle from 89° to 85°, the time of penetration (for 0.5 ml) is reduced from 950 s to 175 s.

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