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Predicting mixing performance using surface energy measurements

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Abstract

Surface energy data determined by contact angle studies were useful in predicting interactions in binary and tertiary systems. The binary systems used were mixes of iron oxide with either microcrystalline cellulose (MCC), magnesium stearate or titanium dioxide. The spreading coefficients as determined from the harmonic mean equation provided an indication as to which powder would predominantly spread over the other in the binary mix. The predicted spreading behaviour was compared with actual performance based upon visual inspection and scanning electron micrographs of the mixes. The ternary systems studied consisted of the above binary mixes and glass. Surface energy data obtained from contact angle studies on the mixes were more accurate than estimates derived from the surface energies of the individual powders at predicting spreading of the mixes onto glass. This work provides a model to predict the mechanism of spreading and mixing of binary and ternary powder mixes. © 1997 Elsevier Science B.V.

Keywords: Contact angle; Surface energy; Spreading; Powder mixing

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1. Introduction

In one of a series of articles Rowe (1989a) demonstrated the surprising fact that the spreading of coloured powders over each other could be modelled on the basis of solubility parameters. In most other reports utilising spreading coefficients to probe interactions, the interactions involve a liquid phase, thus making the concept of spreading rather easier to understand. Examples include film coating (Rowe, 1988a), granulation (Rowe, 1988b, 1989b; Zajic and Buckton, 1990), aqueous (Young and Buckton, 1990) and non-aqueous suspensions (Parsons et al., 1992).

It is more common to calculate solubility parameters from molecular structure fragments than to measure them for the actual system that is being studied. This offers a significant advantage if the calculated values are a good indication of

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the surface nature of the real system. Solubility parameters for solid materials are related to an idealised value of the surface energy. However, it is known that the nature of real solid materials (especially powders) is such that their surfaces are heterogeneous. Measured values for the surface properties of powders are (at best) a weighted mean of various regions with different surface energies (crystals with edges, defects, faces with different proportions of functional groups, etc.) and as such reflect the surface heterogeneity of the materials. Therefore, it seems advantageous to measure, rather than predict, the surface nature of the materials which are being used to test the concept that solid–solid interactions can be modelled using spreading coefficients. The aim of this study is to test whether the predictions based on solubility parameters for mixing of coloured powders (Rowe, 1989a) can be obtained by data obtained from contact angles measured on the actual powders which are being studied. Furthermore, the subsequent spreading behaviour of the powder mixtures has been considered in order to extend the model to ternary mixes.

2. Materials and method

The materials used were red iron oxide (Aldrich), microcrystalline cellulose (MCC) (ex-Wellcome), magnesium stearate (BDH) and titanium dioxide (Aldrich).

2.1. Contact angles

Contact angles were measured by the Wilhelmy plate method using a Cahn Dynamic Contact Angle Analyser. The powders were first stuck to a glass cover slip (26 × 22 mm) by coating the glass with Spray Mount adhesive (3M) and then brushing the powder on the surface. Any non-adhering powder was displaced by brushing. Contact angles were measured with formamide and diiodomethane. Surface energies and their polar and dispersive components were determined using the harmonic mean equation (see for example Parsons et al., 1992).

$$\gamma_{lv}^{Tot}(1+\cos\theta) = 4\left[\frac{\gamma_s^d \cdot \gamma_l^d}{\gamma_s^d + \gamma_l^d} + \frac{\gamma_s^p \cdot \gamma_l^p}{\gamma_s^p + \gamma_l^p}\right]$$

where γ_s^d and γ_s^p are the dispersion and polar components of the solid (s); the subscript (l) represents the liquid and γ_{lv}^{Tot} is the surface tension of the liquid.

2.2. Mixing

The powders were added in 50:50 weight ratio to clear glass wide mouth jars and tumbled for 20 min in a Turbula mixer (T 2C).

The mixed blends were assessed in terms of colour and amount adhering to the wall of the bottle. The mixes were also examined by scanning electron microscopy (Philips XL20).

3. Results and discussion

3.1. Visual appearance

In essence the mixes can be described as follows:

1. Iron oxide spreads over MCC leaving a red powder and a clean glass bottle (i.e. the white MCC powder is totally enrobed and the mixture does not adhere to glass) (Fig. 1).
2. Magnesium stearate spreads over iron oxide leaving a mottled appearance and a substantial coating on the glass bottle (Fig. 1).

Fig. 1. Powder mixes, A (iron oxide and MCC) with clear glass wall, B (iron oxide and magnesium stearate) and C (iron oxide and titanium dioxide) coating the glass walls of the containers.

Fig. 2. Spheroids formed in mix C containing iron oxide and titanium dioxide.

3. Iron oxide and titanium dioxide do not spread over each other. The mix is seen to form what appear to be spheroids (Fig. 2), with a pink surface. When spread with a spatula, the spheroids contained unmixed white powder, rather than a uniform mix. The glass bottle has some powder adhering to it (Fig. 1).

3.2. Predictions from solubility parameters

Based on the solubility parameters of Rowe (1992) (Table 1), it would be expected that iron oxide would spread over MCC, magnesium stearate would spread over iron oxide and that iron oxide would spread over titanium dioxide. The first two mixtures performed in accordance with these predictions, however, the iron oxide and titanium dioxide system is a little harder to describe in simple terms. Our observation was that this mixture formed aggregates of powder with a pink coating. The reasons for the formation of the aggregates seen in Fig. 2 are not obvious from the solubility parameter data.

3.3. Predictions of powder–powder interactions from surface energy data

The contact angle data and the surface energy terms that were calculated are shown in Table 2. The errors associated with contact angle determinations for powdered systems are now well known. The effect of surface roughness on the error in measured perimeter has been studied and a factor of 1.78 was determined as appropriate to correct the underestimated perimeter and hence the contact angle measured (Buckton et al., 1995). For comparison purposes, the values of the spreading coefficients of the powders are shown prior to and after correction of the perimeter by a factor of 1.78. Furthermore, it should be noted that the materials were used ‘as received’ in order to attempt correlations with mixing performance of the materials in that state. It is likely that the powders, especially the oxides, will have significant amounts of surface adsorbed material, which will result in surface energy values which are much lower than those expected for clean oxide surfaces. For example, literature surface energy values for titanium dioxide measured at 0 K were found to be 1060 mJ m^{-2} and at 2273 K, 720 mJ m^{-2} (Vatolin and Timofeev, 1988). Compared with the surface energy value measured in this

Table 1
Solubility parameter data from Rowe (1992)

Material	Adhesive strength	Cohesive strength
MCC	207.3	386.1
Magnesium stearate	121.8	82.3
Titanium dioxide	237.5	295.8
Iron oxide		196.0

All data in MPa; adhesive interaction data is between the named material and iron oxide. Spreading will occur in cases where the adhesive interaction is greater than either of the cohesive interactions for the two components. The material with the low cohesive interaction will be the one which spreads over the other.

Table 2
Contact angle data on the powders and powder mixtures and calculated surface energies

Material	Contact angle (degrees) (S.D.)		Surface energy (mJ.m^{-2})	
	Formamide	Diiodomethane	Polar	Dispersive
Iron oxide	60.2 (3.4)	57.4 (3.7)	5.4	31.7
MCC	16.6 (2.0)	31.9 (3.9)	13.2	43.6
Titanium dioxide	63.8 (2.7)	48.6 (3.1)	2.4	36.1
Magnesium stearate	89.6 (0.6)	90.3 (2.5)	3.4	16.8
Iron oxide/MCC mix	24.6 (4.6)	14.9 (0.7)	8.7	49.1
Iron oxide/magnesium stearate mix	89.6 (0.2)	88.9 (2.4)	3.0	17.3
Iron oxide/titanium dioxide mix	38.6 (1.9)	53.6 (2.6)	13.1	33.6

study i.e. 29.1 mJ m^{-2}, there is a difference of almost two orders of magnitude. Further, the literature value referred to experimental conditions of 0 K and 2273 K whereas the temperature used in this study was controlled to 275 K.

The polar (superscript *p*) and dispersive (superscript *d*) surface energy data were used to calculate spreading coefficients (λ) using the following equations:

$$\lambda_{1/2} = 4\left[\frac{\gamma_1^d \cdot \gamma_2^d}{\gamma_1^d + \gamma_2^d} + \frac{\gamma_1^p \cdot \gamma_2^p}{\gamma_1^p + \gamma_2^p} - \frac{\gamma_1}{2}\right]$$

$$\lambda_{2/1} = 4\left[\frac{\gamma_1^d \cdot \gamma_2^d}{\gamma_1^d + \gamma_2^d} + \frac{\gamma_1^p \cdot \gamma_2^p}{\gamma_1^p + \gamma_2^p} - \frac{\gamma_2}{2}\right]$$

where subscripts *1* and *2* represent two different samples; $\lambda_{1/2}$, the spreading coefficient of sample *1* over *2*; γ^d, the dispersion component; γ^p, the polar component and γ, the total surface energy of the sample.

The spreading coefficient approach has always been used with systems for which at least one component is a liquid. With liquid-based systems, the physical concept of spreading is an easy one to understand at a molecular level; however, this is not the case for a system in which all the materials are in the solid state. As such there are inherent difficulties in understanding why this approach should work for predicting the mixing of two powdered systems. The data have been treated in this way as a means of testing the approach proposed by Rowe (1989a) i.e. assuming that spreading coefficient may relate to solid–solid interactions on a macroscopic level, only in the current study, measured surface energies are used instead of solubility parameters.

From Table 3, it can be seen that both sets of spreading coefficients data determined using measured and corrected values of contact angle show the same trend and that iron oxide should spread over MCC, magnesium stearate should spread over iron oxide and spreading is not favoured for the iron oxide–titanium dioxide system. These predictions are in keeping with the observations reported above. Indeed the magnitudes of the spreading coefficients are also in keeping with the observations, the largest positive value being for iron oxide over MCC, which gives a red powder with no sign of white material. The next largest spreading coefficient is for magnesium stearate over iron oxide, and this yields a mix with a pink mottled appearance (in keeping with spreading of magnesium stearate over the iron oxide to a considerable extent). Finally the iron oxide/titanium dioxide mix is seen to form aggregates of unmixed powder (this is observed by crushing the aggregates with a spatula which reveals that the contents are not a pink mix, but a single colour). This observation, which is unusual as the other mixes do not form aggregates, is in keeping with the negative spreading coefficients (i.e. the works of cohesion of both the individual components are greater than the work of adhesion between the two). The overall pink colour of the mix can be regarded as an equal contribution from both the red iron oxide and white titanium dioxide.

Table 3
Spreading coefficients calculated from surface energies (mN/m)

Material 1	Material 2	Experimental values as measured		Corrected values	
		Spreading 1 over 2	Spreading 2 over 1	Spreading 1 over 2	Spreading 2 over 1
Iron oxide	MCC	14.6	−25.0	7.1	−10.0
Iron oxide	Mg stearate	−22.0	11.9	−10.2	7.1
Iron oxide	Titanium dioxide	0.0	−2.8	−0.1	−0.8
Iron oxide/MCC mix	Glass	−12.4	−10.2	−4.3	−1.5
Iron oxide/Mg stearate mix	Glass	15.0	−57.5	9.7	−22.1
Iron oxide/titanium dioxide mix	Glass	6.3	−13.4	2.3	−3.8
Iron oxide	Glass	7.2	−31.9	4.0	−10.6
MCC	Glass	−5.5	−5.0	−2.5	0.0
Titanium dioxide	Glass	−0.3	−36.6	1.4	−12.6
Mg stearate	Glass	15.6	−57.4	10.0	−22.0

3.4. Prediction of adhesion tendencies of powder mixes to glass

A visual inspection of the mixes showed that the three mixes used adhered to the glass walls of the containers to different extents. Surface energy data were applied to predict the behaviour of the mixes and the findings compared with the surface energy data of individual powders over glass. Contact angles of the mixes were obtained using samples prepared in a similar manner to that of the individual powders.

The results as shown in Table 3 confirm the visual observations that the magnesium stearate/iron oxide mix adheres to the greatest extent to glass, followed by the titanium dioxide/iron oxide mix. The relative magnitudes of the spreading coefficients of the mixes onto glass reflected the extents of adhesive forces in the systems. The MCC/iron oxide mix however did not show any tendency to adhere to glass and this observation is supported by negative values for the spreading coefficients of both the mix over glass and glass over the mix.

One hypothesis for the above observations is that the powder which predominantly spreads over the second powder in a binary mix would influence the spreading pattern of the mix over glass. This is true in the case of the magnesium stearate/iron oxide mix where magnesium stearate spreads over the iron oxide, and where magnesium stearate is predicted to adhere to glass (Table 3): the mix adhered onto glass (Fig. 1). In the MCC/iron oxide mix, the MCC particles were completely covered by iron oxide particles but did not show any tendency to adhere to glass. The third mix, in which titanium dioxide and iron oxide aggregates coexist, shows limited adhesion onto glass. This behaviour is predicted from the spreading coefficients of the powder mixtures, but not from the values for the individual powder components. There seems to be some interaction between the two components of the mix resulting in an overall surface energy of the mix being different from that of either component.

3.5. Consideration of factors other than surface energies

It is usual to regard mixing as being influenced by factors such as particle size, shape, roughness, humidity and electrostatic charge. In this study the effect of electrostatic charge has been ignored which has proved reasonable for what seems to be a relatively non-charged system (perhaps due to the use of an inorganic salt as one of the components).

It is generally assumed that small particles can prove difficult to mix, but when they do mix they will spread on larger particles. In order to see if there was any relationship between the observed mixing and the sizes of the powders, the sizes of the materials used in this study were assessed using a calibrated microscope. The median values were: iron oxide 0.6; MCC, 70.0; magnesium stearate 5.9; and titanium dioxide 0.2 microns. Thus, based on the spreading coefficients, there is one case where small particles spread over large (iron oxide over MCC); one where larger particles spread over small (magnesium stearate over iron oxide) and one where very small particles are unable to mix (titanium dioxide and iron oxide). The case where the spreading of small particles over large is favoured resulted in the most homogeneous appearance (pure red colour), whilst that with spreading of larger particles over small resulted in a light pink colour (rather than the pure white which may have been predicted). It can be concluded that the spreading of one powder over another is not dependent upon the respective particle sizes; however, the appearance of the mix may be more uniform if small particles spread over larger ones.

Particle shape, density, and roughness and environmental humidity have not been considered in the current study; however, it is logical that these factors will have a significant role in many mixing processes. The close correlation between predictions based on spreading coefficients and observed mixing behaviour of primary powder mixes and their interactions with glass containers, which is reported here, provides encouragement that surface energetics will aid in the prediction of mixing to a greater extent than was previously thought probable. However, it would be unlikely that all mixing processes could be predicted in this way, thus it becomes important to undertake further research to define the areas in which different factors are dominant during mixing processes.

4. Conclusions

The use of surface energy and spreading coefficients data obtained from contact angle determinations of the powders has proved to be a useful approach in predicting how powders behaved in a binary mix. There is good correlation between theoretical data and visual observations and scanning electron micrographs of the powders. Further, the results are in keeping with and improve upon the findings by Rowe (1989a). The study of the actual surface nature of the materials as compared with solubility parameters gives a better indication of the spreading and mixing tendencies of powders.

Surface energy data have been successfully extended to predict the adhesion of a binary system onto a third component, glass. Substitution of the surface energy data of glass by that of another excipient from a tertiary powder mix seems a promising way of predicting interactions in mixes. Of the numerous factors that determine mixing of two or more powders, surface forces of particles seem to be significant for the systems studied here; however, for other systems it is probable that other factors will dominate. Furthermore, at present it is outside our understanding as to why spreading coefficients for solid–solid interactions give good predictions of macroscopic events such as powder mixing, and as such, further studies are needed before these encouraging data should be taken as proving that all powder/powder interactions can be modelled in such a manner.

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