Surface free energy and polarity effects in the granulation of a model system

R.C. Rowe

ICI Pharmaceuticals, Macclesfield, Cheshire (U K)

Summary

The interfacial works of cohesion and adhesion, the interaction parameter and the spreading coefficients of one phase on the other have been calculated for a model system consisting of untreated and surface-treated glass granulated with a number of polymeric binders using literature values of surface free energies In general the predictions made regarding film formation, granule morphology, failure processes and granule strength are consistent with literature data

Introduction

Powders are often formulated as granules with binding agents to enhance flow and compaction characteristics. Krycer et al. (1983) concluded that significant determinants for optimum granulation are the wetting of the substrate by the binder, binder–substrate adhesion and binder cohesion. Recent attempts at calculating these factors using literature values of both the partial solubility parameters (Rowe, 1988) and surface free energies (Rowe, 1989) of a variety of substrates and binders used in pharmaceutical granulation have demonstrated the applicability of using a simple model based on the summation of interactive forces to predict trends in binder–substrate interactions. In this study the surface free energy approach has been applied to a model system consisting of glass (both untreated and pretreated with dimethylsilane) granulated with a variety of polymeric binders as originally used by Cutt et al. (1986).

Theoretical considerations

If γ_1 and γ_2 are the surface free energies of the binder and the substrate, respectively, then it is possible to calculate not only the work of cohesion (W_c) of each of the two components, but also the interaction parameters (ϕ) and the work of adhesion between the two components (W_a) and the spreading coefficients (λ) of each component on the other (Wu, 1973; Rowe, 1989) i.e.

$$W_{c_1} = 2\gamma_1 \tag{1}$$

$$W_{c_2} = 2\gamma_2 \tag{2}$$

Correspondence R.C. Rowe, ICI Pharmaceuticals, Alderley Park, Macclesfield, Cheshire SK10 2TG, U.K.

$$W_a = 4\left[\frac{\gamma_1^d \cdot \gamma_2^d}{\gamma_1^d + \gamma_2^d} + \frac{\gamma_1^p \cdot \gamma_2^p}{\gamma_1^p + \gamma_2^p}\right] \quad (3)$$

$$\lambda_{12} = W_a - W_{c_1} \quad (4)$$

$$\lambda_{21} = W_a - W_{c_2} \quad (5)$$

$$\phi = 2\left[\frac{x_1^d \cdot x_2^d}{x_1^d \cdot g_1 + x_2^d \cdot g_2} + \frac{x_1^p \cdot x_2^p}{x_1^p \cdot g_1 + x_2^p \cdot g_2}\right] \quad (6)$$

where γ^d and γ^p are the non-polar and polar contributions of the surface free energy and x^d and x^p are the fractional non-polarity and polarity, respectively, of each component; i.e.

$$x_1^d = \frac{\gamma_1^d}{\gamma_1} \quad (7)$$

$$x_2^p = \frac{\gamma_2^p}{\gamma_2} \quad (8)$$

g_1 and g_2 are defined by:

$$g_1 = \frac{\gamma_1}{\gamma_2} \quad (9)$$

$$g_2 = \frac{\gamma_2}{\gamma_1} \quad (10)$$

Results and Discussion

Numerical values of the surface free energies of untreated and treated (silanised) glass as well as those for a number of polymeric binders are given in Tables 1 and 2, respectively. It is important to note that these values are representative literature

TABLE 1

Surface energy data on glass (Westerlind and Berg, 1988)

	γ (mN m^{-1})	γ^d (mN m^{-1})	γ^p (mN m^{-1})
Untreated glass	70.5	23.0	47 5
Treated glass	41.5	27 5	14.0

TABLE 2

Surface energy data on polymeric binders (Rowe, 1989)

	γ (mN m^{-1})	γ^d (mN·m^{-1})	γ^p (mN m^{-1})
Hydroxypropyl methylcellulose	48 4	18 5	29.9
Methyl cellulose	50 0	22 0	28.0
Polyvinyl pyrrolidone	53 6	28 4	17.2
Acacia	50 6	21.6	29 0
Starch	58.7	29 0	29 7

values and have not been measured on the actual batches of material used by Cutt et al. (1986). For instance, the values for the two glasses were actually measured using fibres (Westerlind and Berg, 1988) and the values for the binders were calculated from actual measurements (Rowe, 1989). Unfortunately no data exist for the hydrolysed gelatin used by Cutt et al. (1986). However, from a consideration of its solubility spectrum as compared with acacia, hydroxypropyl methylcellulose and polyvinyl pyrrolidone (Table 3) it would appear that it will have properties similar to acacia and hydroxypropyl methylcellulose.

The results of calculations using the literature values of surface free energy are given in Table 4. The relevance of these results can be best discussed under the headings of firstly, film spreading and granule morphology and, secondly, failure processes and granule strength.

TABLE 3

Solubility spectra of polymeric binders

HPMC = hydroxypropyl methylcellulose, PVP = polyvinyl pyrrolidone. + = soluble, – = insoluble; * = data not available

	HPMC	Acacia	Gelatin	PVP
Water	+	+	+	+
Ethanol	–	–	–	+
Methanol	–	–	–	+
Glycerol	–	+	+	–
Propylene glycol	+	*	+	–
Acetone	–	–	–	+
Dichloromethane	–	–	–	+
Chloroform	–	–	–	+

TABLE 4

Calculations based on data in previous tables

HPMC = hydroxypropyl methylcellulose; MC = methyl cellulose, PVP = polyvinyl pyrrolidone

	HPMC	MC	PVP	Acacia	Starch
W_c (mN·m^{-1})	96 8	100 0	107.2	101 2	117.4
W_a (mN·m^{-1})					
Untreated glass	113.6	115 0	115 4	115.6	123.1
Treated glass	82 4	85.4	91 9	86 2	94.5
λ_{12} (mN·m^{-1})					
Untreated glass	+16 8	+15 0	+8.2	+14.4	+5 7
Treated glass	−14.2	−14.4	−15 3	−15 0	−22.9
λ_{21} (mN·m^{-1})					
Untreated glass	−25 4	−24 0	−23 6	−23 6	−15.9
Treated glass	−0.6	+2 4	+8 9	+3 2	+11 5
ϕ					
Untreated glass	0.93	0.94	0 92	0 94	0 95
Treated glass	0 91	0 93	0 95	0 92	0 93

Film spreading and granule morphology

The positive values of the spreading coefficient λ_{12} for the untreated glass imply good film formation in the order: hydroxypropyl methylcellulose > methylcellulose > acacia > polyvinyl pyrrolidone > starch with the negative values for the treated glass implying poor film formation for all binders. This is consistent with Cutt et al. (1986) for hydroxypropyl methylcellulose, hydrolysed gelatin and polyvinyl pyrrolidone on untreated glass and polyvinyl pyrrolidone on treated glass where there was an absence of a continuous film but the presence of patches of polymer. Such an effect can be predicted by examination of the spreading coefficient, λ_{21} (i.e. the spreading of the substrate over the binder), since it can be clearly seen that, although all the binders showed negative values for the untreated glass, all with the exception of hydroxypropyl methylcellulose showed positive values, albeit very small with the treated glass. In fact the value for polyvinyl pyrrolidone is almost identical to that for the spreading coefficient of the same polymer over untreated glass implying that granules will be formed in both cases.

Recently Rowe (1988) has advanced the hypothesis of two distinct granule morphologies. In the case where λ_{12} is positive and there is a strongly adhering continuous film of binder around the substrate, a strong dense granule will be formed since there will always be a bond at all points of contact between the substrate particles. However, in the case where λ_{21} is positive and there is no continuous film, a porous open granule will be formed since bonds will only occur through isolated patches of polymer. These differences can be clearly seen on close examination of the scanning electron photomicrographs of granules prepared with polyvinyl pyrrolidone presented by Cutt et al. (1986).

Failure processes and granule strength

The value of the interaction parameter, ϕ, is important since it provides information on the possible mode of failure of the system, i.e. interfacial or adhesive, or cohesive within the weaker component. If the interaction parameter is unity, then interfacial failure in a perfectly bonded system will not be possible because the interfacial bond strength would be greater than the tensile strength of the weaker component. If the interaction parameter is significantly less than unity then interfacial failure will always occur. The values generated in Table 4 imply the presence of both types of failure in all systems. Although Cutt et al. (1986) state categorically that granules formed with hydroxypropyl methylcellulose undergo adhesive failure while those formed with polyvinyl pyrrolidone undergo cohesive failure, the scanning electron photomicrographs presented by these

authors show evidence of both types. In a more recent paper on the granulation of glass with polyvinyl pyrrolidone, Mullier et al. (1987) presented scanning electron photomicrographs showing adhesive or interfacial failure in this system. All the previously discussed factors will influence granule strength although, as previously stated (Rowe, 1989), a complete analysis of granule strength must also include rheology and fracture mechanics. Despite this proviso, certain generalisations can be made based on the results given in Table 4. Firstly, all the granules prepared from treated glass will be weaker and more friable than those prepared from untreated glass; and secondly, based on the relative works of cohesion and adhesion between untreated glass and the two polymers hydroxypropyl methylcellulose and polyvinyl pyrrolidone, granules prepared from the latter should be less friable. In addition, if acacia is regarded as a good model for gelatin then the properties of granules prepared from gelatin should be intermediate between those prepared from the other two polymers. These predictions are consistent with the data generated by Cutt et al. (1986).

The data presented here, in addition to that presented earlier (Rowe, 1989), clearly shows the applicability of this approach in the prediction of binder/substrate interactions leading to statements regarding film formation, granule morphology, fracture processes and granule strength.

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