Localized cracking around pigment particles in tablet film coatings: a theoretical approach

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The problem of localized cracking around pigment particles in tablet film coatings has been treated as being analogous to stress cracking in two phase ceramics. For this purpose a simple model of a spherical cavity in an infinite isotropic medium has been used. As well as allowing the estimation of the stresses generated by the differences in thermal expansion of the dispersed pigment and the polymer matrix, the model predicts the effect of some formulation variables. The predictions are in agreement with the observed cracking on film-coated tablets.

Solid inclusions in the form of aluminium lakes of water soluble dyes, opacifiers (e.g. titanium dioxide) and various inorganic materials (e.g. iron oxides, calcium carbonate, talc and colloidal silica) are often added to film coatings to improve their colour, opacity and their film forming characteristics (Rowe 1984). An interesting problem with such materials, highlighted by Porter (1981, 1982), is that of localized cracking around individual particles or aggregates of the additive in film coatings applied to tablets. In a comment on this problem, Rowe (1982) suggested that the effect might be due to differences in the thermal expansion of the solid inclusion and the polymer matrix and he presented literature data on the thermal expansion coefficients for some representative materials to support this hypothesis. However, such localized cracking is not limited to pigmented polymer films, but is present in most two phase systems. Kingery (1957) proposed a similar mechanism for localized cracking in two phase ceramic compositions consisting of crystalline phases (e.g. aluminas or silicas) dispersed in glass. Since these systems can be regarded as directly analogous to pigmented polymer films, it would appear logical to consider how the ceramicists have approached the problem.

Equations for the prediction of internal stresses in two-phase ceramics have been derived by Selsing (1961) and are based on the model system of a hydrostatic pressure, P, present in a spherical cavity of radius, R, in an isotropic medium with a modulus of elasticity E_1 and a Poisson's ratio of v_1. If it is assumed that the spherical cavity is a solid particle with a modulus of elasticity of E_2 and a Poisson's ratio of v_2, and that the pressure is caused by the differences in the thermal expansion of the particle and the medium, $\Delta\alpha$, over the temperature range, ΔT, then it can be shown (Selsing 1961) that

$$P = \frac{\Delta T \, \Delta\alpha}{\dfrac{1+v_1}{2E_1} + \dfrac{1-2v_2}{E_2}} \qquad (1)$$

This pressure will then be equivalent to radial and tangential stresses of $-PR^3/r^3$ and $+PR^3/2r^3$, respectively, in the medium at a distance r from the centre of the particle. In this treatment, positive pressures are compressive and positive stresses tensile while negative pressures are tensile and negative stresses are compressive.

Unfortunately, accurate values for all the parameters in the equation are not available for the materials used in film coating. However, it is possible to predict P using estimations based on previously published data. Consider, for example, a film of hydroxypropyl methylcellulose (Pharmacoat 606—Shin-Etsu Chemical Co., Japan) pigmented with red iron oxide. For this example E_1 will be of the order of 2×10^3 MPa (Pickard 1979; see Rowe 1981) with v_1 of the order of 0·35; E_2 and v_2 will be of the order of $2·1 \times 10^5$ MPa and 0·14, respectively (Simmons & Wang 1971) and the coefficients of linear expansion of the polymer and pigment will be of the order of $1·2 \times 10^{-4}$ and $0·08 \times 10^{-4}\,°C^{-1}$, respectively (Rowe 1982). If a cooling range (ΔT) of 40 °C is assumed, then P for this system will be of the order of 13·1 MPa. Although this value of P is only approximately 25% of the tensile strength of this polymer (Rowe 1981) and cracking will occur only when the tensile strength of the polymer is exceeeded, this value of P is significant, especially if the film is subjected to further external stresses, e.g. as a result of the tablet striking a baffle in the coating pan.

As well as allowing the localized stresses produced in a pigmented film to be estimated, the treatment has other implications.

The definition of the nature of cracking
The nature of the cracking, if it occurs, will depend on whether the inclusions contract more, or less, than the polymer matrix during cooling (Binns 1962). Where the inclusions contract more than the polymer matrix, P will be negative resulting in a positive (i.e. tensile) radial stress and a negative (i.e. compressive) tangential stress with the final result that cracking will occur circumferentially around the particles. In the opposite case where the polymer matrix contracts more than the inclusion, P will be positive resulting in a negative (i.e. compressive) radial stress and a positive (i.e. tensile) tangential stress with the final result that cracking will occur radially from the particles. In both cases the danger of cracking will be at a maximum at the

inclusion/polymer matrix interface where the stresses are highest. From the literature data on the coefficients of expansion of some representative excipients used in tablet film coating (Rowe 1982), it can be predicted that the latter case is the more likely in pharmaceutical tablet coating. This is indeed the case (Porter 1981, 1982).

The effect of pigment concentration
Ideally the treatment holds only where there is a single cavity in an infinite medium. An examination of the treatment shows that the stresses induced in the medium decrease proportionately to the cube of the distance from the centre of the inclusion. Provided, therefore, an inclusion has a matrix envelope surrounding it of sufficient size that the stresses of the edge of the envelope are negligible and that the distance between inclusions is such that their matrix envelopes do not overlap, then the boundary conditions as used in the treatment should still hold. However, increasing the pigment concentration will cause particles and their matrix envelopes to interact, allowing cracks to link up with other cracks or with other particles, to cause catastrophic cracking. Experience in ceramics has shown that the treatment is applicable for dispersed phase volumes of at least 10% v/v (Selsing 1961; Davidge & Green 1968) and in some cases even higher (Binns 1962). However, even at low pigment concentrations a homogeneous dispersion is assumed; inhomogeneity due to poor dispersion will exacerbate the problem. Such an effect has been reported for tablet film coatings (Porter 1982).

The effect of pigment particle size
Equation 1 shows that the magnitude of the induced stresses should be independent of particle size. However, this condition will only occur when the boundary conditions are as stated. Since the matrix envelope of an inclusion is related to the particle size of the inclusion, and, since inhomogeneity due to poor dispersion is exacerbated by the inclusion of large particles, it would be expected that increasing particle size would have a detrimental effect on cracking. This has been shown to be so in ceramics (Binns 1962;

Davidge & Green 1968) and there is an indication that it is also the case with tablet film coatings (Porter 1982).

The effect of pigment particle shape
The treatment described assumes spherical-shaped inclusions. However, this is not so for most pigment particles. Many are anisotropic and have different coefficients of expansion along different axes. These properties will lead to the development of areas of high stresses, especially at protruding corners, resulting in an increased tendency for crack initiation and propagation. Although observations in ceramics do tend to support this (Binns 1968), no data for tablet film coatings exist.

In conclusion it can be seen that, by the application of a model system for which the stress analysis has already been developed, it is possible not only to estimate the stresses induced by the differences in thermal expansion of a dispersed pigment and a polymer matrix, but also to predict the effect of some formulation variables. From what little literature data there are on this subject (see Porter 1981, 1982) , it would appear that the predictions are in agreement with the observed facts.

REFERENCES

Binns, D. B. (1962) in: Stewart, G. H. (ed.) Science of Ceramics, Vol I, Academic Press, London pp. 315–334
Davidge, R. W., Green, T. J. (1968) J. Mat. Sci. 3: 629–634
Kingery, W. D. (1957) J. Am. Ceram. Soc. 40: 351–352
Pickard, J. F. (1979) Ph. D. thesis. Council for National Academic Awards
Porter, S. C. (1981) Drug and Cosmetic Industry, September, 50–58
Porter, S. C. (1982) Int. J. Pharm. Tech. and Prod. Mfr. 3: 21–25
Rowe, R. C. (1981) J. Pharm. Pharmacol. 33: 423–426
Rowe, R. C. (1982) Int. J. Pharm. Tech. and Prod. Mfr. 3: 67–68
Rowe, R. C. (1984) in: Florence, A. T. (ed.) Materials used in Pharmaceutical Formulation. Critical Reports on Applied Chemistry, 6: 1–36
Selsing, J. (1961) J. Am. Ceram. Soc. 44: 419
Simmons, G., Wang, H. (1971) Single Crystal Elastic Constants and Calculated Aggregate Properties—A Handbook, 2nd Edition, The MIT Press, Cambridge