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Mechanical properties of pigmented tablet coating formulations and their resistance to cracking
I. Static mechanical measurement

S.H.M. Gibson [1], R.C. Rowe [2] and E.F.T. White [1]

[1] *Department of Polymer Science & Technology, University of Manchester Institute of Science & Technology, Manchester (U.K.)*
and [2] *I.C.I. Pharmaceuticals Division, Macclesfield, (U.K.)*

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Summary

The mechanical properties of a number of films of hydroxypropyl methyl cellulose containing iron oxide, lake, titanium dioxide and talc pigments were measured in conventional tensile tests. The Young's modulus, and to some extent, the tensile strength of the films was found to depend on the shape of the pigment particles and the presence of interactive forces between the polymer and the pigments. In most cases, the mechanical property data can be used to explain the incidence of edge-splitting in pigmented tablet coatings. The main exception to this were talc-filled films.

Introduction

Pharmaceutical tablets are often coated for protection, masking of taste and for aesthetic reasons (Rowe, 1984a). The traditional sugar coating is now being superceded in many cases by a polymeric one, in which a thin film of polymer is deposited by applying a polymer solution and evaporating the solvent under controlled conditions. These coatings may contain additives such as plasticisers to improve their mechanical properties and pigments which are added to provide opacity and therefore protection from light and which also greatly aid in identifying the tablets. These pigments must be toxicologically acceptable and special grades of metal oxides and food-approved lakes of organic dyes are the most commonly used (Rowe, 1984a). Unfortunately the inclusion of such pigments in polymeric film coating formulations has been shown to cause splitting and cracking of the dry coating, which is not only unattractive but, more importantly, results in the protective advantages of the coating being lost (Rowe, 1982).

It has been suggested by Rowe (1981) that these defects are due to the stress which builds up within the coating on drying, and which may reach high levels which exceed the mechanical strength of the coating. This stress arises because the coating, applied as a solution by spraying,

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

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loses solvent as it dries, and thus it must shrink as the volume of solvent evaporates. Since the coating is applied as a continuous film around a solid tablet core, the amount of shrinkage allowed in the plane of the coating is restricted. When the solvent concentration has been reduced to a certain level, the coating loses its ability to flow and the continued tendency of the film to shrink around the tablet core leads to mechanical stress in the coating. Also, because the coatings are dried above room temperature, a thermal stress arises as the coated tablets cool due to the higher thermal expansion coefficient of the polymeric film compared with that of the tablet substrate.

The mechanical properties of the coating material determine its response to these stresses and hence its resistance to rupture. The most commonly measured mechanical properties are the Young's modulus, tensile strength, fracture energy and extension required to break the sample.

This work describes the evaluation of the fundamental mechanical properties of hydroxypropyl methyl cellulose films containing iron oxides, titanium dioxide, aluminium lake pigments and talc. The results are related to the behaviour and integrity of these materials when applied as coatings on an inert tablet substrate. The results are also examined in the light of evidence of interactions between the pigment particles and the polymer within the films in order to explain and predict the effect of solid additives on the mechanical behaviour of polymeric films.

Materials and Methods

The polymer used was hydroxypropyl methyl cellulose (HPMC, Pharmacoat 606 supplied by Shinetsu Chemical Co. (Japan)) and has been described in previous work (Rowe, 1983).

A plasticiser, polyethylene glycol of mol. w. 200, was added to some films at a concentration of 20% by dry weight of polymer. The pigments used and their physical properties are shown in Table 1. Their density was measured by helium pycnometry; the surface area calculated from BET nitrogen adsorption measurements. The particle size and shape data are those given by the manufacturer and were confirmed by scanning electron microscopy.

Film preparation

A solution of HPMC was prepared by dispersing the required amount of polymer powder in distilled water at 60–70 °C by vigorous shaking. When the dispersion had cooled, methanol (laboratory reagent grade) was added to give a solvent composition of 60% water, 40% methanol, and the mixture was allowed to stand until the polymer dissolved. The solution volume was then

TABLE 1

Pigment characteristics

Pigment	Particle shape	Particle size (μm)	Density (g/cm^3)	Specific surface area (m^2/g)
Red iron oxide	spherical	0.32	5.41	7.56
Yellow iron oxide	acicular	0.5–1	4.32	13.07
Black iron oxide	cubical	0.5–1	4.98	3.84
Titanium dioxide	rounded	0.2	3.78	7.60
FD & C aluminium lake yellow 6	irregular	> 1	1.80	93.10
FD & C aluminium lake red 3	irregular	> 1	2.07	68.20
Talc A	lamellar	70% < 10 90% < 20 100% < 30	2.71	2.99
Talc B	lamellar	85% < 5 95% < 10 100% < 20	2.71	14.33

made up to the correct volume with solvent mixture to give a concentration of 5% w/v. Finally, the solution was filtered, if necessary, through a glass fibre filter.

The incorporation of pigment into the formulation was achieved by ball milling the measured amounts of polymer solution and pigment powder together with glass beads in small jars on a small laboratory mill for 3 h at a slow speed. After this time, about 13 cm^3 of the dispersion was withdrawn from below the surface of the mixture by syringe and transferred to a glass plate (previously treated with dichlorodimethylsilane solution) bounded by a 10 cm-diameter nylon ring. The film was then dried overnight on a level surface in an air oven at 60 °C. The films were allowed to cool in a desiccator.

The films were cut into 10 mm wide strips using a standard parallel edge sample cutter in a fly press. Almost the whole of the circular films was used so orientation effects, if present, cancelled out because particle orientation at the edges of the film would differ from that found in the central portion. The samples were labelled, and stored horizontally exposed to the atmosphere at 20 °C and 50 relative humidity in an air-conditioned room for one week prior to testing.

The tensile stress–strain behaviour of the film samples was measured using an Instron 1121 materials testing instrument interfaced with a Hewlett Packard HP85 microcomputer via a HPIB interface bus and a "Data System Adapter" supplied by Instron Ltd. No extensometer was used for strain measurement because it was considered that the attachment of such a device could cause enough damage to these very thin samples to produce premature breakage. Instead, the strain was calculated from the crosshead speed and the time of movement, measured precisely in ms by the HP85's internal clock. The test conditions were: initial gauge length = 25 mm, crosshead speed = 10 mm/min, full scale load = 50 N. The tests were carried out in an air-conditioned room at 20 °C ± 1° and 50 ±2% relative humidity. Six samples of each type of film (cut from the same film) were extended until they broke, and for each sample the load, stress, strain and energy at peak load and at break were calculated and stored by the computer for statistical analysis. The secant Young's modulus of the samples was calculated as the slope of a straight line drawn between the stress intercepts of 5 and 8 MPa.

Results and Discussion

All results are shown as their normalised form, which is the ratio of the value of the measured property of the filled film to the value for the unfilled film. This permits comparison of these data with that of other workers, because in this way the variations in test methods, sample preparation etc. can be accounted for.

Young's modulus

The normalised Young's modulus (E/E_0) vs pigment volume concentration (PVC) plots are shown in Figs. 1 and 2. The Young's modulus of plain HPMC film was found to be 2149 MPa. This is relatively high for a polymer and is indicative of the brittleness of these films. The addition of pigment to the films caused the Young's modulus (E) to rise in almost every case, with the values at 2.5% volume concentration often disproportionately large.

It can be seen, from Fig. 1, that the greatest increase in the Young's modulus of the films is caused by talcs and yellow or black iron oxide, with red iron oxide, titanium dioxide and red and yellow aluminium lakes producing progressively less effect on the modulus in the order listed. The very small effect of the aluminium lake pigments was unexpected as it is in marked contrast to the results obtained for similar materials by Aulton et al. (1984), who found that 3 FD&C aluminium lake pigments tested raised the Young's modulus of HPMC film by about 250% at 15% pigment volume concentration. There is a well-defined maximum Young's modulus in the case of talcs A and B, and the red 3 lake pigment occurring at about 20%, 12% and 12%, respectively. This may be an indication of the critical pigment volume concentration of the pigment/HPMC systems. This maximum is not seen clearly in the results of the other pigments, but both black iron oxide and

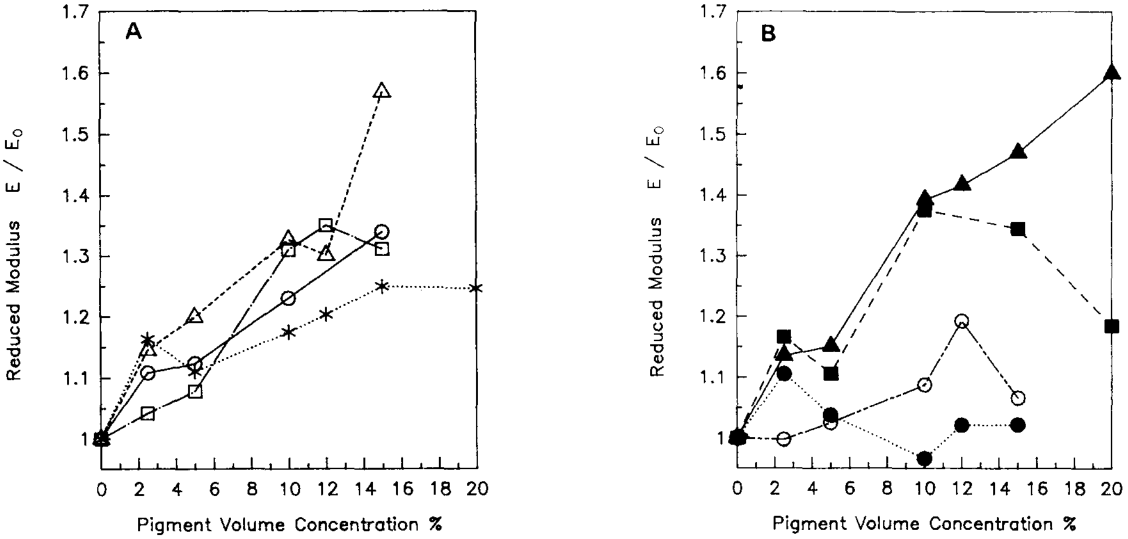

Fig. 1. Reduced Young's modulus values vs pigment volume concentration for HPMC films containing various pigments. A: ○, red iron oxide; △, yellow iron oxide; □, black iron oxide; *, titanium dioxide. B: ▲, talc A; ■, talc B; ●, yellow 6 aluminium lake; ○, red 3 aluminium lake.

titanium dioxide values remain fairly constant at concentrations above 10 and 15%, respectively.

Fig. 2 shows the Young's modulus results for the plasticised materials, which have a mean coefficient of variation of 7%. The behaviour of these materials is rather more complex than that of the unplasticised films. Talc increases the modulus of plasticised HPMC, although at a concentration of 5% the increase is barely noticeable. The aluminium lake yellow 6 enhances the modulus when present at concentrations of 2.5 and 5%, thereafter decreasing the modulus below that of the unfilled film. The initial effect of titanium dioxide, on the other hand, is to decrease modulus considerably, although at higher concentrations the modulus increases. The normalised Young's moduli of films containing titanium dioxide compare well with the values reported by Aulton et al. (1984), Okhamafe and York (1984) and Delporte (1981). Delporte also found a maximum E for films containing 17–25% of pigment. The data for talc-filled films is in good agreement with that of Okhamafe and York for similar grades of talc. The normalised modulus of cellulose acetate phthalate films containing red iron oxide (Porter 1980), and normalised data from Rowe (1983b) are similar to those reported here.

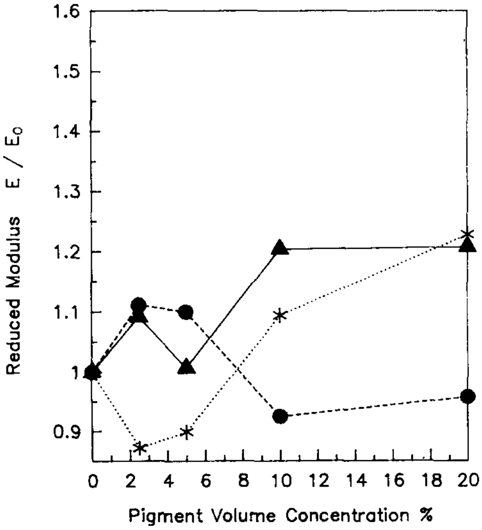

Fig. 2. Reduced Young's modulus values vs pigment volume concentration for plasticised HPMC films containing various pigments, *, titanium dioxide; ▲, talc A; ●, yellow 6 aluminium lake.

For plasticised systems, Okhamafe and York (1984) find that titanium dioxide lowers the modulus of the films initially, but the modulus rises as more pigment is included. Their results for talc show that it raises the modulus fairly steadily.

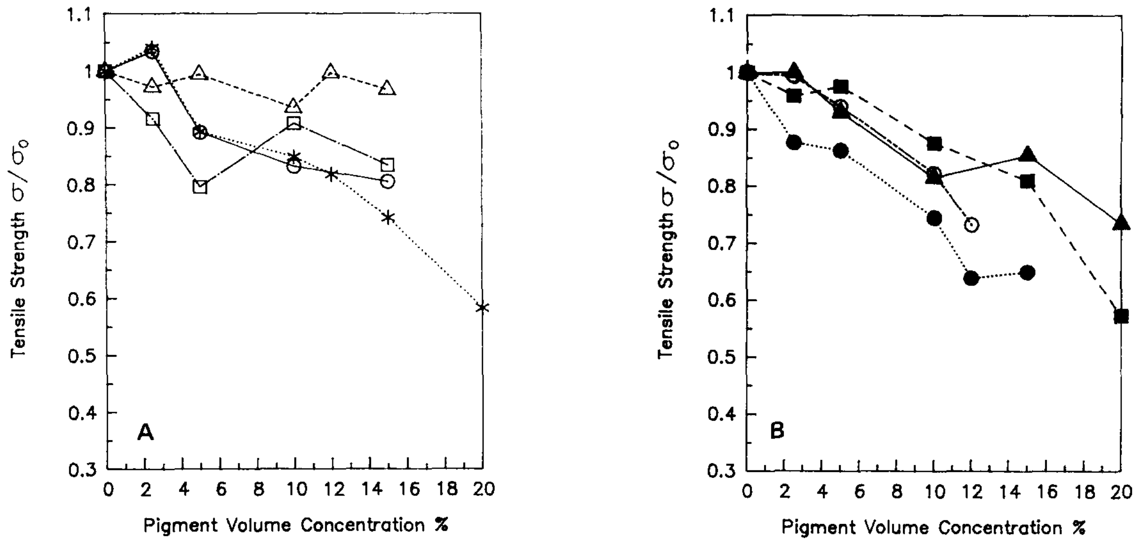

Fig. 3. Reduced tensile strength values vs pigment volume concentration for HPMC films containing various pigments. a: ○, red iron oxide; △, yellow red oxide; □, black iron oxide; *, titanium dioxide. b: ▲, talc A; ■, talc B, ●, yellow 6 aluminium lake; ○, red 3 aluminium lake.

Delporte's films showed no significant reduction in modulus as titanium dioxide was introduced.

Tensile strength

The average coefficient of variation of the tensile strength results was 8%, and these are shown in Fig. 3.

When increased amounts of pigment are included in the HPMC films, the general effect is to reduce continuously the tensile strength of the films, with two exceptions. The first of these concerns yellow iron oxide pigment, which has little or no effect on the tensile strength of HPMC over the full range of concentrations studied. Black iron oxide reduces the tensile strength to about 85% of the unpigmented value, with this figure remaining approximately constant over the range of concentrations. The most rapid reduction of tensile strength is brought about by the aluminium lake pigments, slightly more so with yellow 6 than with the red 3 pigment. Titanium dioxide and red iron oxide both increase the tensile strength of the films very slightly at low concentration (2.5%), further pigmentation causing a decrease in the tensile strength which becomes quite rapid when using titanium dioxide. Talc A reduces the tensile strength of the films at concentrations above 2.5% although the effect is less between concentrations of 10 and 15%. Talc B has little effect below a concentration of 5%, reducing the tensile strength of the films thereafter, and especially rapidly between 15 and 20%. The mean coefficient of varia-

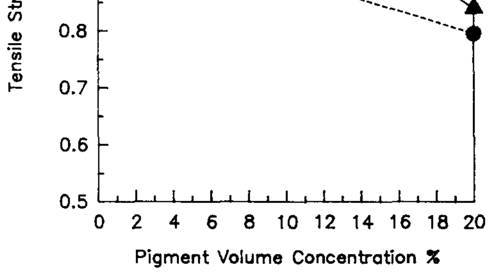

Fig. 4. Reduced tensile strength values vs pigment volume concentration for plasticised HPMC films containing various pigments; *, titanium dioxide; ▲, talc A; ●, yellow 6 aluminium lake.

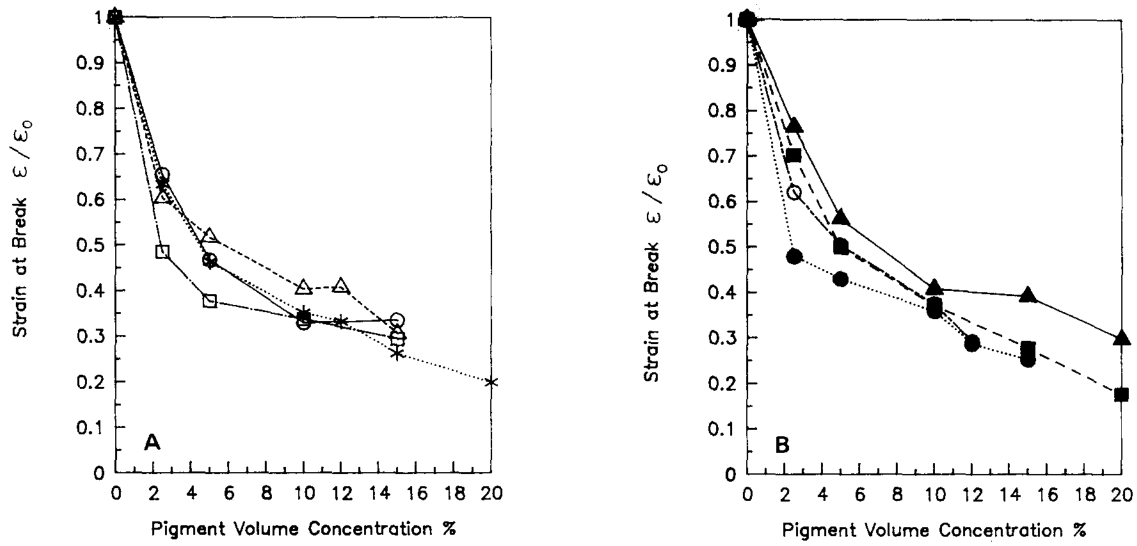

Fig. 5. Reduced strain at break values vs pigment volume concentration for HPMC films containing various pigments. a): ○, red iron oxide; △, yellow iron oxide; □, black iron oxide; ∗, titanium dioxide. b): ▲, talc A; ■, talc B; ●, yellow 6 aluminium lake; ○, red 3 aluminium lake.

tion of the tensile strength results given by plasticised HPMC, shown in Fig. 4, was 4%. Both talc and titanium dioxide have a tendency to decrease the tensile strength of the plasticised films. The aluminium lake pigment increases the strength at low concentrations, but further addition of pigment causes a continuous reduction in strength. The normalised tensile strength results generally agree with the trends reported in the literature (Okhamafe & York, 1984; Delporte, 1981), except that the aluminium lake pigments cause a greater reduction in the tensile strength of the films than found by Aulton et al. (1984). Porter's films (1980) seem to be rather more affected by this type of pigment. The tensile strength of the plasticised films appears to agree loosely with the trends found for these systems in the papers previously referred to, i.e. the breaking stress of plasticised films is only slightly reduced by pigmentation.

Elongation

The elongation to break (ϵ), or breaking strain of the materials was one of the least reproducible of the properties measured. Nevertheless, the average coefficient of variation was 14% which is quite satisfactory. The elongation to break of the unplasticised plain film was 6.3%. Normalised results for unplasticised films are shown graphically in Fig. 5. The presence of pigment has a very marked effect in reducing the breaking strain to only about 60–70% of its original value at the lowest pigment concentration used. Talc A had least ef-

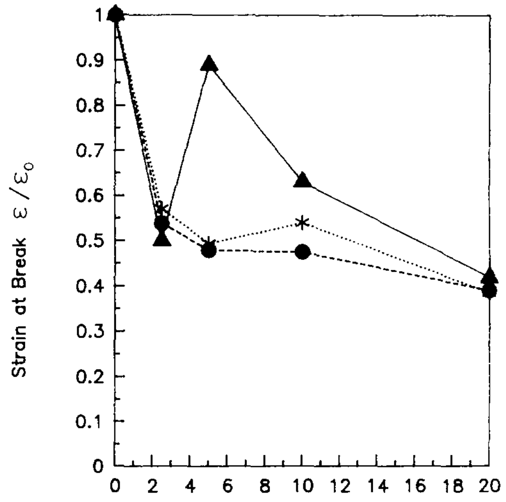

Fig. 6. Reduced strain at break values vs pigment volume concentration for plasticised HPMC films containing various pigments; ∗, titanium dioxide; ▲, talc A; ●, yellow 6 aluminium lake.

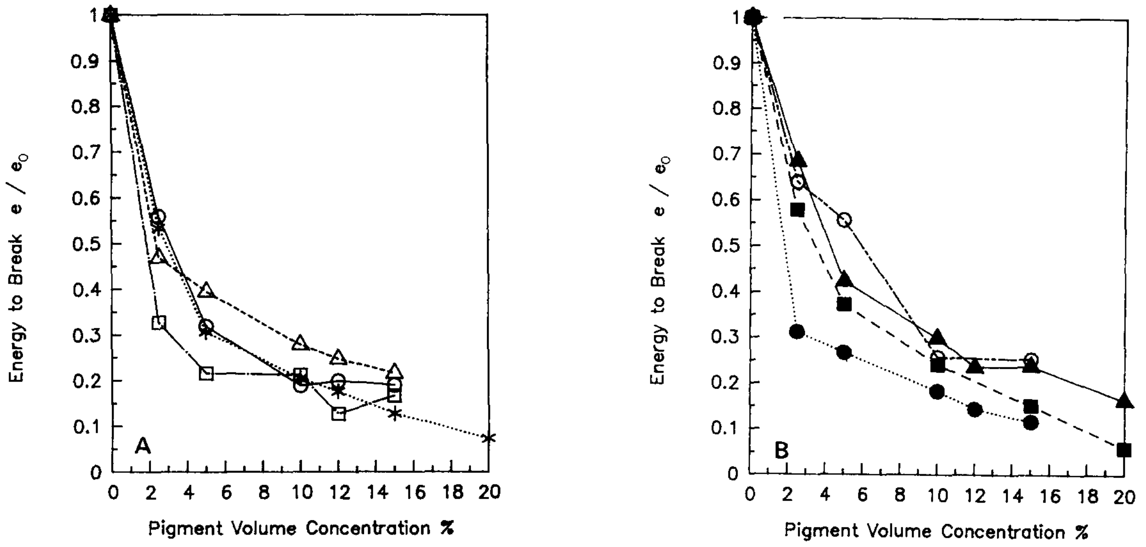

Fig. 7. Reduced energy to break values vs pigment volume concentration for HPMC films containing various pigments. a): ○, red iron oxide; △, yellow iron oxide; □, black iron oxide; *, titanium dioxide. b): ▲, talc A; ■, talc B; ●, yellow 6 aluminium lake; ○, red 3 aluminium lake.

fect, and black iron oxide and the lakes cause the most rapid reduction in elongation.

The plots of normalised breaking strain vs. pigment volume concentration for plasticised films are shown in Fig. 6. Their mean coefficient of variation was 12%. The plasticised unpigmented film yielded at about 3.1% strain, and broke at 5.9% strain, compared with 6.3% for the unplasticised film. Films containing 5 and 10% talc A also yielded at about 3% strain, but their breaking strain was much greater than that of films containing the other pigments. Where yielding did not occur, the elongation to break was, of course, considerably reduced relative to the unpigmented film. An increase in the concentration of pigment resulted in further slight reductions in the elongation values.

It is generally found that the inclusion of titanium dioxide in the films reduces the elongation to break considerably. Okhamafe and York (1984) found that increasing the concentration had little effect, whereas most studies, including this one, find that the elongation is continuously reduced. The reported effects of talc are in better agreement with this work than are Aulton's (1984) aluminium lake film results.

Generally, the results found for plasticised films are similar to those reported here, but Delporte's (1981) values show a more gradual reduction in breaking strain with pigment concentration.

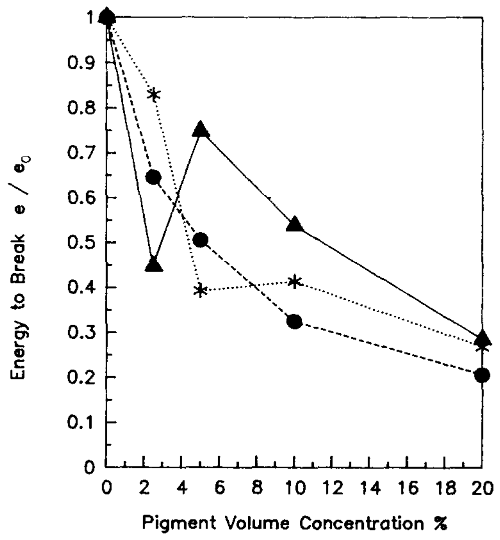

Fig. 8. Reduced energy to break values vs pigment volume concentration for plasticised HPMC films containing various pigments; *, titanium dioxide; ▲, talc A; ●, yellow 6 aluminium lake.

Energy to break

The energy required to break the samples, measured as the area under the stress–strain curves and expressed as the mean of the energy to break/initial cross-sectional area of sample, varied considerably between samples of the same film. The average coefficient of variation of these results, shown graphically in Figs. 7 and 8, is 22.7% which is rather high. This is mainly because of the unpredictable elongation of the samples, i.e. some yielded and some did not. However, although the actual values are reported with limited confidence, the trends shown are of interest. Predictably, the energy to break the materials followed much the same trends as the elongation results. At low concentrations, the difference in toughness produced by the pigments was very pronounced; at higher concentrations it is less so. Generally, talc had the least detrimental effect on the toughness of the samples, with yellow iron oxide performing well at higher concentrations, presumably because of the relatively high tensile strength of films containing this pigment.

Generally the presence of pigment did not reduce the toughness of plasticised films to the same extent as with the unplasticised films. The results resemble those of unplasticised materials in that the differences between the pigments are much greater at small concentrations than at large concentrations. The film containing 2.5% talc, which did not yield, reduced the energy to break more than the other pigments at this concentration. When the talc concentration was increased, however, the films yielded and the energy to break was greatly improved. Titanium dioxide performed particularly well at a concentration of 2.5%; this film required 83% of the energy supplied to the plain film to break it. At higher pigment concentrations, the toughness of these films was halved. Addition of aluminium lake pigment in increasing concentrations caused a continuous reduction in the energy required to break the films.

Theoretical considerations

It is useful to compare the measured mechanical properties with theoretical prediction in order to assess how these systems correspond to theoretically ideal situations. Many of the relationships for filled polymeric systems have been derived from Einstein's (1906) fundamental equation which describes the viscosity of a suspension of rigid, spherical particles in a fluid.

$$\eta/\eta_0 = 1 + 2.5c \qquad (1)$$

where
η = the viscosity of the suspension,
η_0 = the viscosity of the suspending matrix,
c = the volume fraction of dispersed spheres.

This relationship is only valid for extremely low concentrations of particles, because it assumes that the particles do not interact with each other, and this condition is not satisfied in concentrated dispersions. Solvation or aggregation of the particles includes some of the suspending matrix in the dispersed phase, thereby increasing the effective value of c and thus the viscosity of the suspension.

Since a very large number of equations have been proposed to describe suspension viscosities, many of them empirical extensions of Einstein's work. They have been collected and categorised by Rutgers (1962), who recommends the equation of Mooney (1951), which is valid for all concentrations of c, as the most useful.This is:

$$\ln(\eta/\eta_0) = 2.5c/(1 - sc) \qquad (2)$$

where s is a self-crowding factor, $= 1/\Phi$, and Φ is the concentration of particles corresponding to maximum packing. For random loose packing of spherical particles, s is 1.66. Adsorption of material onto the particles affects their packing behaviour, and so changes the s factor. Mooney's equation was the basis of a relationship derived by Brodnyan (1959) for interacting, non-spherical particles.

These are all hydrodynamic theories, in that they are based on the principle that the presence of rigid particles in a fluid restricts flow, thus increasing the viscosity of the fluid. Apart from particle shape, the properties of the particles are not considered.

The Einstein constant for rod-shaped particles is given by Burgers (1938). Nielsen (1974) tabulated the effect on Einstein's constant of using a matrix having a Poisson's ratio of less than 0.5.

This modified Einstein equation was shown to be a fairly good fit for the yellow iron oxide and talc particles, although generally the theories developed to describe the viscosity of concentrated suspensions of interacting particles all predict values which are higher than the measured Young's modulus values of the pigmented films. The theory which predicts values closest to those found here is Einstein's relationship. Possibly, this is because the particles are dispersed in a rigid matrix which reduces the effect of interparticle interactions, so the modifications to the fundamental theory would not be applicable to these systems.

Hashin (1962) developed theoretical expressions for the bulk and shear moduli of a composite material consisting of spherical particles of an isotropic elastic material dispersed in a continuous matrix of a second isotropic elastic material. This theory is based on a consideration of the change in strain energy in the matrix caused by the addition of the spherical particles.

Using these equations, the Young's modulus and Poisson's ratio of the composite can be calculated from simple elastic relationships.

$$K^*/K_m = 1 + \left\{3(1-\nu_m)(K_p/K_m - 1)c\right\} \times \left\{2(1-2\nu_m) + (1+\nu_m) \times \left[K_p/K_m - (K_p/K_m - 1)c\right]\right\}^{-1} \quad (3)$$

$$G^*/G_m = 1 + \left\{15(1-\nu_m)(G_p/G_m - 1)c\right\} \times \left\{7 - 5\nu_m + 2(4-5\nu_m) \times \left[G_p/G_m - (G_p/G_m - 1)c\right]\right\}^{-1} \quad (4)$$

$$E = \frac{9KG}{3K+G} \quad (5)$$

$$\nu = \frac{E}{2G} - 1 \quad (6)$$

Where

K^*, G^* = the bulk or shear modulus of the composite,

K_m, G_m = the bulk or shear modulus of the matrix,

K_p, G_p = the bulk or shear modulus of the inclusion,

c = the volume fraction of the inclusions,

ν_m = Poisson's ratio of the matrix.

These equations were solved to find theoretical values of E/E_0 at a number of pigment volume concentrations for HPMC filled with red and black iron oxides. The values of the elastic constants used in the equations were those given by Simmons and Wang (1971). These were:

	E/GPa	ν_m
Haematite (red iron oxide)	210	0.14
Magnetite (black iron oxide)	231	0.26

It should be noted that many of the hydrodynamic

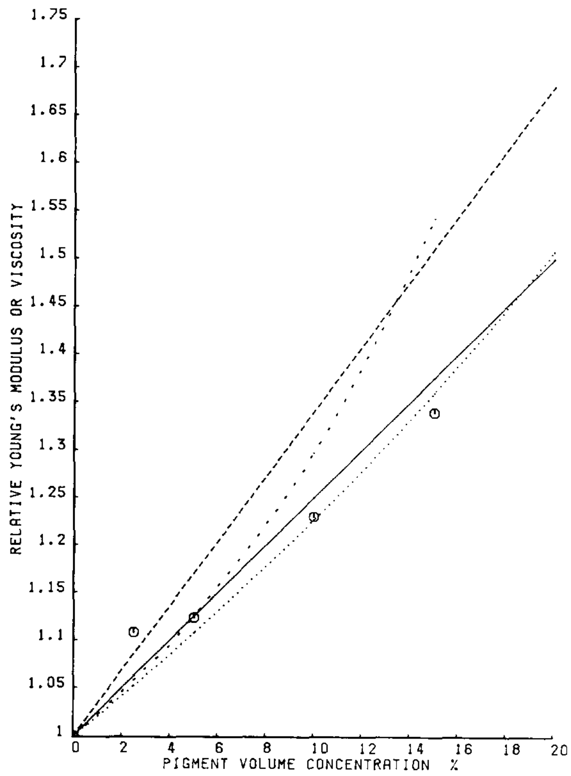

Fig. 9. Calculated theoretical values for reduced Young's modulus vs pigment volume concentration. ———, Einstein (Eqn. 1) $k = 2.5$; - - - - - -, Einstein, $k = 3.4$ (rods of aspect ratio 1:5); - - - -, Mooney (Eqn. 2), $k = 2.5$, $s = 1.66$; ······, Hashin (Eqn. 3, 4); ○, red iron oxide experimental points.

theories assume that the Young's modulus of the particles is very much greater than that of the surrounding medium, although, in this case they differ only by a factor of 100.

The resulting curve is included in Fig. 9. The theoretical reduced modulus at each concentration was evaluated for red and black iron oxide separately, but the values were not significantly different from each other. The theoretical curve is a close fit to the reduced modulus values found for both iron oxides, except that the black oxide gives more scattered results. The elastic constants necessary to evaluate Hashin's expression for the other pigments were not readily available, but from the two examples given it would be expected that the resulting curves would differ very little from that shown.

In a previous paper (Gibson et al., 1988a), we presented heat of immersion and glass transition temperature results which indicated that there is little or no interaction between the iron oxide or talc pigments and the HPMC polymer. These pigments therefore provide an excellent opportunity for estimating the effect of particle shape on the mechanical properties of these filled coating films.

Pilpel (1969) has described particles in terms of shape factors and sphericity. He states that the flatness of the particles has a greater effect on the shape factor than the length/breadth ratio. Accordingly, the sphericity of a particle would decrease in the order spherical > cubic > acicular > lamellar. This order is apparent in the Young's modulus values of pigmented films; talc increases the modulus most, red iron oxide least. This is consistent with the predicted effect of shape of filler particles upon the magnitude of modulus increase produced.

It is clear from Figs. 1 and 2 that titanium dioxide and aluminium lake pigments do not produce the expected increase in Young's modulus when included in a film formulation, in that they show negative deviations from the theories of modulus enhancement. The rounded titanium dioxide particles should, on the basis of particle shape and size alone, produce an effect similar to that of red iron oxide. Any deviation from the spherical shape would, of itself, produce a greater modulus increase than predicted for spheres. The modulus of these films does increase as pigment is added but there must also be a plasticising effect which counteracts this increase, producing the overall effect of a small modulus increase and we believe that this is caused by adsorption of the polymer onto the pigment whilst in solution.

We have shown (Gibson et al., 1988a) that there is strong evidence of specific interactions between hydroxypropyl methylcellulose and titanium dioxide and so adsorption of the polymer onto the pigment particles may be expected to take place in this case. According to Kipling (1965), when polymers are adsorbed from solution, the high-molecular-weight fractions are preferentially adsorbed because the smaller molecules are more soluble. This leads to a reduction of the average molecular weight of the bulk polymer and so decreases the Young's modulus of the film overall. Both of the FD&C aluminium lake pigments show a dramatic negative deviation from the theoretical reinforcing behaviour of fillers. The effects of these two pigments also differ widely. Whilst the red 3 lake produces a continous increase in Young's modulus, which reaches a maximum at a concentration of 12%, the yellow 6 lake raises the modulus of the films initially, but has little or no effect thereafter.

These pigments are distinguished by their porous, irregular structure, which gives rise to their large specific surface area, and also by the strong affinity for water of the alumina hydrate base material. These pigments probably exist as stable aggregates, even when dispersed in the films. The loose particle aggregates may rupture or be compressed under the applied tensile strain, giving them a low effective Young's modulus which in turn would decrease the overall modulus of the film. In addition it was found, using thermogravimetric analysis, that films containing aluminium lake pigment had a larger proportion of loosely bound water than the other films. The inclusion of such "wet" pigments may cause plasticisation of the matrix by the loosely bound water, which would decrease the Young's modulus of the material.

The different behaviour of the films containing red 3 lake from those containing yellow 6 lake is very marked. The differences may be partly explained by the results of Prillig (1969), who observed that the solubility of HPMC in both water and gastric juices was reduced by the presence of erythrosine (red no. 3) dye.This implies that there is some cross-linking interaction between the dye and the polymer which could also raise the modulus of the pigmented film. This cross-linking effect would occur in addition to the reinforcing effect of the particles themselves and the modulus decreasing effect of the aggregates or associated water giving the nett result shown in Fig. 1. In the laboratory, it was easily observed that the red 3 lake was less bleed-resistant than the yellow 6, indicating an affinity for water. This bleeding of the dye would accentuate the different behaviour of the red lake.

An appraisal of published work suggests that no mode of behaviour completely describes the tensile strength of filled materials. Often, the tensile strength of a material is reduced by the inclusion of a filler, but in certain cases the filler has the effect of increasing the strength of the composite. This behaviour is often attributed to the quality of bonding between the filler and matrix molecules.

Neilsen (1966) suggests that where there is good adhesion between filler and polymer, the following simple relationship for the elongation to break may apply:

$$\epsilon/\epsilon_0 = 1 - \varphi_F{}^{1/3} \tag{7}$$

where φ_F is the volume fraction of the filler.

The resulting theoretical curve was compared with the elongation to break values (Figs. 5 and 6) and was found to predict values which were generally too high. Nielsen also suggested that this equation could be used to predict breaking stresses from a knowledge of the Young's modulus of the material and Hooke's law. However, since the modulus of these films decreases quite rapidly towards the breaking point, the values calculated using the secant Young's moduli would bear little resemblance to the measured values.

Davidge and Green (1968) stated that for crystalline material embedded in glass, the following factors are significant in determining the strength of the composite: (1) the difference between the thermal expansion coefficients of the filler and the matrix, (2) the volume fraction of the dispersed phase, (3) the size of the particles, (4) the elastic properties of the materials. They observed that the particle size of the filler affects the strength of the composite only when greater than a certain critical size. This critical flaw size can be estimated by the method given in this paper if Poisson's ratio, modulus, thermal expansion coefficients and surface energy data are known or assumed. They also state that if the coefficient of thermal expansion of the dispersed phase is less than that of the matrix, then the surrounding matrix cracks radially with respect to the particles. These cracks can join up when stress is applied and so the strength of the composite is greatly reduced. Equations 8 and 9 are from the paper by Davidge and Green (1968) and were used to calculate the critical flaw size for red iron oxide in HPMC.

$$P = \frac{\Delta\alpha\, \Delta T}{(1+\nu_1)/2E_1 + (1-2\nu_2)/E_2} \tag{8}$$

$$R_c \geq \frac{8\gamma_s}{P^2((1+\nu_1)/E_1 + 2(1-2\nu_2)/E_2)} \tag{9}$$

where: P = pressure experienced by a spherical particle in the matrix as a result of differences in thermal expansion coefficients between the particle and the matrix, R_c = the critical flaw radius of the system, $\Delta\alpha$ = the difference in thermal expansion coefficients of matrix and particle, ΔT = change in temperature of material, ν_1, ν_2 = Poisson's ratio for matrix and particle, E_1, E_2 = Young's modulus of matrix and particle, γ_s = surface energy of the matrix.

The critical flaw size for red iron oxide in HPMC, calculated by the method of Davidge and Green, is about 5×10^{-15} m, assuming: $\Delta\alpha = 2.76 \times 10^{-4}$ (average assumed from Rowe 1982); $\Delta T = 40$ (because films cast at 60°C); $\nu_1 = 0.35$ (Rowe 1980), $\nu_2 = 0.14$ (Simmons and Wang, 1971); $E_1 = 2149$ MPa (measured data), $E_2 = 210$ GPa (Simmons and Wang, 1971); $\gamma_s = 50$ mNm^{-1} (average surface tension value from manufacturer's literature). This calculated flaw size is obviously very much smaller than the size of any of the particles studied here.

Fracture occurs in a material when an applied stress overcomes the cohesive strength of the material. However, the applied stress is magnified by cracks or flaws in the material so that the local stress, e.g. at the end of a crack, may be sufficient to cause local fractures and crack propagation when the apparent applied stress is much less than the cohesive strength of the material. The stress concentration factor, K_σ, for a crack with a length $2c$, very much greater than its height, is given by:

$$K_\sigma = 2\sqrt{c/\rho} \qquad (10)$$

where ρ is the crack tip radius (Tetelman and McEvily, 1967). The maximum stress at the end of a crack is then $K_\sigma \sigma$.

The Griffith theory states that the total energy within a material in which fracture is taking place remains constant, so a crack will grow if the increase in free surface energy caused by the creation of new crack surfaces is compensated for by the reduction in elastic potential energy within the material.

Rowe (1981) showed that microscopic cracks do indeed exist within HPMC films even when no pigment is present, so the theoretical strength of the material could never be attained.

In filled films there are an abundance of cracks due to the presence of filler particles, in addition to those which would normally be present as imperfections in the polymer matrix. These cracks would be large and so the stress concentration factor would be greater than that normally encountered in unpigmented films, so their effective tensile strength would be lower. Okhamafe and York (1985) considered the effect of flaws in the matrix of HPMC films, originating from the presence of pigment particles, upon the fracture mechanism of the pigmented films. They concluded that the greater the length and smaller the crack tip radius of the flaws (based on the shape of the filler particles), the smaller would be the stress crack resistance of the material leading to a reduction in tensile strength.

A close examination of the results shown in Figs. 3 and 4 reveals distinct similarities in the ways that certain pigments affect the breaking strength of HPMC. The breaking stress of films containing red iron oxide pigment is almost identical to those containing titanium dioxide at each concentration. These pigments have very similar particle sizes and shapes. It would appear that the "indirect plasticisation" of the HPMC by titanium dioxide discussed earlier does not affect the breaking stress of films. This may be because the failure of the films is initiated by small cracks around the pigment particles and not by an overall weakness in the matrix material.

The presence of yellow iron oxide pigment does not cause any significant change in the breaking stress of HPMC. Since it differs from the other iron oxide pigments most markedly in particle shape, it is likely that this behaviour is a function of the needle-shaped particles. It has been shown (Gibson et al., 1988b) that these particles are randomly orientated within the film. Under tensile stress, the particles could interfere physically with one another, restricting the elongation of the material and thus placing less stress on the polymer matrix. Another explanation of these results lies in the compressibility of the tangled masses of yellow iron oxide particles. When the film is cooled down and the matrix contracts, exerting a compressive force on the particles, some of the stress could be

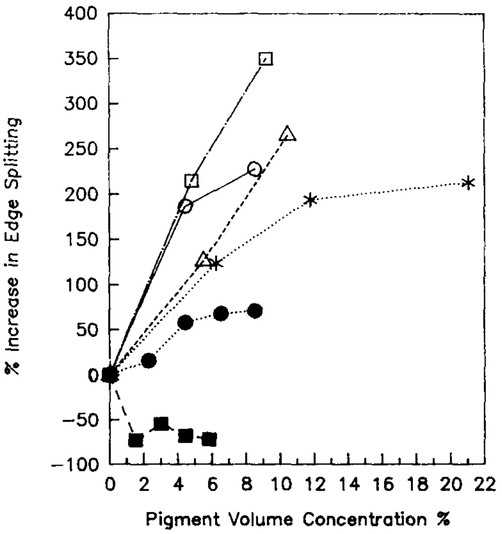

Fig. 10. The increase in the incidence of edge splitting in tablet coatings vs pigment volume concentration: ○, red iron oxide; △, yellow iron oxide; □, black iron oxide; *, titanium dioxide; ■, talc B; ●, yellow 6 aluminium lake.

relieved by the relative movement of particles over one another, so the matrix in the vicinity of the particles would be less likely to crack.

The two types of talc produce almost the same reduction in tensile strength except at concentrations at and above 20% when the small particles of talc B produce a uniformly weak structure. The electron micrographs of this film (Gibson et al., 1988b) showed a random orientation of the particles and unlike acicular particles, this weakens the film. It is interesting that the black iron oxide pigment results, though variable, show that the addition of this pigment at any concentration weakens the film to the same extent. This behaviour may be analogous to that of yellow iron oxide, described above, since the black iron oxide particles are cubical in shape and a cube can be thought of as a short needle, i.e. having an aspect ratio of 1.

The effect of pigments upon the properties of tablet coatings

It is useful to compare these mechanical data with the results given by Rowe (1982, 1984b) which relate the incidence of edge splitting to the amount of pigment in the coating, using similar materials to those used in this study. Fig. 10 is a plot of the percentage increase in edge splitting caused by the pigments, when compared with unpigmented film, against pigment volume concentration (PVC), using the raw data for Rowe's published results. The talc is a fine grade, which corresponds to talc B in this work. It should be noted that the formulations used in the two experiments differ in two respects: Rowe's tablet coatings contained glycerol as plasticiser and were cast from aqueous solution.

A comparison of the effects of different pigments shows that the iron oxides cause a greater increase in edge splitting than the other pigments, black iron oxide being the worst, especially at high concentrations. Titanium dioxide is slightly less detrimental to film continuity, and the yellow 6 lake causes much less edge splitting than any of the metal oxides. Talc is the only pigment beneficial in this respect, in that it actually reduces the incidence of edge splitting by 67% on average. No trend is evident when the amount of talc in the coating is varied, but the range of concentrations used was not very large.

Okhamafe and York (1985) reported similar effects for titanium dioxide and talc pigments, but the pigments, especially the talcs, were of a different grade.

These results for edge-splitting bear some resemblance to the Young's modulus vs PVC plots in Fig. 1 for the films filled with metal oxides. The apparent advantage of using titanium dioxide instead of iron oxides to counteract the edge-splitting defect is reflected in the lower modulus of these films. However, the reduced modulus values suggest that the yellow iron oxide pigment would give rise to more defective tablets than is the case. The lower incidence of edge splitting given by the lake-filled coatings is echoed by the low modulus of the free films (Fig. 1b) but in terms of modulus alone, one would expect no significant increase in edge splitting from using this pigment. The results for talc are also not consistent with the idea that a high-modulus film produces more defective tablets, since talc raised the modulus of the films most of all but actually decreased the incidence of edge splitting. Talc A and yellow iron oxide were, however, seen to be the least harmful in reducing the strength of the films, on average. One difference between the tensile testing of free films and the situation in a drying tablet coating is that the tensile forces in the tablet coating act in all directions in the plane of the coating. Since the talc particles are lamellar, it is possible that the slight reinforcing effect seen in the tensile testing experiment is enhanced in this multiaxial stress situation relative to the yellow iron oxide needles. The effect of the lake pigment on edge splitting seems more reasonable if the relatively severe effect of the pigment in reducing tensile strength is considered (Fig. 3).

Both Rowe (1981, 1983c) and Okhamafe and York (1985) have demonstrated that the tensile strength to Young's modulus ratio (σ/E) can be a useful guide to predict the incidence of edge splitting in unpigmented tablet coatings. In these cases the edge splitting incidence rose as the σ/E ratio of the coatings decreased. σ/E was calculated from the results given earlier to find out whether the resulting values more accurately reflected the 'in situ' behaviour of the films. If a high σ/E ratio indicates a better resistance to edge splitting, then the values predict that titanium dioxide, yellow 6 lake and yellow iron oxide are the best pigments to use to minimise the defect, but it also predicts that talcs at higher concentrations are the worst.

Of the static mechanical properties it is the energy to break the free films which most closely predicts the relative effects of the pigments on edge splitting, in that films containing talcs or yellow iron oxide required a marginally higher energy input to rupture them than those containing other pigments. These results only partly predict the order of increase of edge splitting given by the pigments because the energy to break the lake pigmented films is low in comparison with the other pigments, which suggests a greater incidence of edge splitting in these films than is actually the case. Generally the inclusion of pigments in plasticised films of HPMC was less harmful than in unplasticised films. The difference between talc and the other pigments, in terms of its effect upon the mechanical properties was greater, and this was most noticeable in the values for elongation at break, where the talc-filled films caused only a gradual decrease in elongation to break at lower concentrations (10% and below). The pigments reduced the energy to break and the tensile strength and increased the Young's modulus less than in the corresponding unplasticised films. The overall effect is that the films are not weakened to the same extent by pigments when they are plasticised.

These results suggest that plasticisers can reduce edge splitting, as was demonstrated by Okhamafe and York (1985). However, it should be noted that whilst the internal stress in plasticised films is probably reduced because of the lower Young's modulus, the tensile strength is also reduced relative to the unplasticised film. The occurrence of edge splitting will therefore depend upon achieving the correct balance between these two properties.

Conclusions

The Young's modulus of the films is raised by pigments to an extent which depends upon pigment shape and which can be predicted by existing theories of viscosity and modulus enhancement. The exceptions are titanium dioxide and the lake pigments which have less of an effect upon the modulus than expected, due to particle–polymer interactions, or, in the case of the lakes, loose particle structure.

The ultimate tensile properties of the films depend mainly on the concentration of the particles added. If the thermal expansion coefficients of the matrix and filler promote premature cracking of the matrix on cooling from the fabrication temperature, then the introduction of the filler in any concentration is detrimental to the ultimate tensile properties of the system. Pigments cause a large decrease in film tensile strength, except in the cases of yellow or black iron oxides, which are not weakened to such a great extent because the shape of the particle allows the growth of flaws to be retarded.

The incidence of edge splitting in pigmented coatings depends upon the nature of the pigment used, but there is no one characteristic of all pigments which determines the likelihood of the defect occurring. For many films, the incidence of edge splitting is directly related to the tensile strength: Young's modulus ratio. The exceptions are films containing talc, and the likely reasons for this are to be dealt with in a companion paper.

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