

Stress crack resistance of some pigmented and unpigmented tablet film coating systems

AUGUSTINE O. OKHAMAFE† AND P. YORK*

Postgraduate School of Studies in Pharmacy, University of Bradford, Bradford, BD7 1DP, UK

Stress crack resistance parameters—tensile strength: Young's modulus ratio, relative surface energy, and toughness index—have been examined for unpigmented free films of hydroxypropyl methylcellulose containing polyvinyl alcohol, and polyethylene glycols 400 and 1000, as well as similar film systems pigmented with either talc or titanium dioxide. Incorporation of either polyvinyl alcohol or polyethylene glycols 400 and 1000 in hydroxypropyl methylcellulose film coatings eliminated the incidence of edge splitting in the coated tablets. Increase in pigment concentration generally led to a decrease in the crack resistance of pigmented films. There was a relation between the stress crack resistance of pigmented free films and the incidence of edge splitting of corresponding film coatings applied to aspirin tablets—generally, the higher the crack resistance the lower the incidence of edge splitting. A similar relationship applied to the unpigmented films only when the tensile strength: Young's modulus ratio was considered.

Stress-strain data such as tensile strength, Young's modulus and elongation, on their own, are of little practical value as a guide to the actual performance of film coatings when applied to solid dosage forms. A plasticized film will probably possess lower tensile strength and modulus than the unplasticized film and yet show a lower incidence of film defects such as cracking when applied to tablets. Similarly, while pigmentation could enhance film stiffness, the incidence of film defects may also rise. This is largely due to the critical role of the internal stresses in film coatings.

Rowe & Forse (1981) and Rowe (1981, 1982) have observed that tablet film coating defects such as cracking, edge splitting, peeling and bridging of intagliations are usually manifestations of high internal stresses in a film. Rowe (1981) proposed that the incidence of edge splitting of a film can be estimated from the tensile strength: Young's modulus ratio—the larger the ratio the higher the incidence of edge splitting. Thus this ratio can be used for predicting the stress crack resistance of film coatings.

It is intended in this paper to evaluate some stress crack resistance parameters—tensile strength: Young's modulus ratio, relative surface energy and toughness index—for some filled and unfilled free films, and to attempt to relate these parameters to the performance of film coatings applied to tablets.

† Present address: Dept. of Pharmaceutics & Pharm. Tech., University of Benin, Benin City, Nigeria.

* Correspondence.

MATERIALS AND METHODS

Hydroxypropyl methylcellulose U.S.P. (Pharmacoat 606) and polyvinyl alcohol (Poval PA-5) were manufactured by Shin-Etsu Chem. Co. Ltd, Japan. The plasticizers, polyethylene glycols 400 and 1000, were supplied by BDH Chemicals Ltd, Poole, UK. Four polymer systems were examined: hydroxypropyl methylcellulose alone as well as in blends with either polyvinyl alcohol or the polyethylene glycols. For the pigmented films, the content of the polymer additives (polyvinyl alcohol and the polyethylene glycols) was 20 wt% of hydroxypropyl methylcellulose.

Two types of talc (talc 4053 NM and talc 4053, Richard Baker Harrison Ltd, Ilford, UK) and two types of titanium dioxide (Tioxide A-HR, BTP Tioxide Ltd, UK; and Bayertitan RC-K-20; Bayer (UK) Ltd) were employed as fillers or pigments, and are designated as talc A, talc B, TiO₂ A and TiO₂ B, respectively, with specific areas of 1.34, 1.81, 7.89 and 8.42 m² g⁻¹. Talc A has a larger average particle size than talc B. TiO₂ A is anatase and of pharmaceutical grade, while TiO₂ B is rutile, surface-treated with alumina and an undisclosed organic material, and water-repellent. Dispersion of the pigment particles in the aqueous polymer formulations was achieved using a mixer-emulsifier (laboratory model, Silverson Machines Ltd, London) for 30 min. Films were cast from 10% w/v aqueous formulations on the inside of a rotating lipped Perspex cylinder as described in a previous study (Okhamafe & York 1983). The free films were conditioned at 20 °C, 58% rh for one week before test.

Tensile data and Young's modulus were determined from stress-strain measurements on twelve specimens (six cut perpendicular to, and six parallel to the axis of rotation of the casting substrate) as detailed previously (Okhamafe & York 1983). The mean of the results was taken and employed in determining tensile strength: Young's modulus ratios and the relative surface energy values. Analysis of the areas and the shape of the stress-strain curve enabled the toughness indices to be calculated. (Further details and relationships are given in Results and Discussion.)

Flat-faced aspirin tablets (diameter = 13 mm) containing 5 wt% each of Avicel PH 105 (FMC Corporation) and potato starch (BDH Chemicals Ltd) were directly compressed at 122 MPa in an instrumented single punch tablet machine (type E-2, Manesty, Liverpool). The tablets were coated with 10% w/v filled (with talc B and TiO₂ B) and unfilled aqueous film formulations in a 15.1 cm Wurster column to produce 3.2 wt% of film coat per tablet. The coated tablets were stored for one month at 20 °C, 37% rh and the percentage of tablets showing any visual signs of splitting of film coat at the tablet edge for one hundred tablets taken from each batch of coated tablets was recorded as the incidence of edge splitting.

RESULTS AND DISCUSSION

Cross-sections of the free films showed even distribution of filler particles when examined under the scanning electron microscope. This indicates that the rotating cylinder technique employed is adequate for casting solids-loaded free films.

In order to aid forecasting of film coat failure, several relationships have been proposed to provide data on the internal stress and/or stress crack resistance of coating films. Rowe (1981) suggested that the overall internal stress, P , in a film coat applied to a tablet substrate can be represented as in equation (1).

$$P = \frac{E}{1-\nu} \left[\frac{\phi_s - \phi_r}{3(1-\phi_r)} + \frac{\Delta\alpha\Delta T}{1+\nu} \right] \quad (1)$$

where E is the Young's modulus of the film, ν is its Poisson's ratio, ϕ_s is the volume fraction of the solvent at the point when the liquid coating formulation first behaves like a solid, ϕ_r is the volume fraction of solvent remaining in the dry film at ambient conditions, $\Delta\alpha$ is the difference between the thermal linear expansion coefficients of the coating and the tablet, and ΔT is the difference between the

glass transition temperature of the coating and the ambient temperature.

More recently Rowe (1983) has reappraised this equation so that internal stresses due to film shrinkage in a direction perpendicular to its length are taken into account. The modified relationship also incorporates the concept of a cubical (or volumetric) expansion coefficient ($\Delta\alpha$ (cubic)) which can be more readily determined than the $\Delta\alpha$ (linear) term. The new equation is:

$$P = \frac{E}{3(1-\nu)} \left[\frac{\phi_s - \phi_r}{1-\phi_r} + \Delta\alpha \text{ (cubic)} \Delta T \right] \quad (2)$$

Sato (1980) proposed that cracking will occur if P is greater than or equal to the tensile strength, σ , of the film, i.e.,

$$P \geq \sigma \quad (3)$$

Combining and rearranging equations (2) and (3), equation (4) is obtained

$$\frac{\sigma}{E} \leq \frac{1}{3(1-\nu)} \left[\frac{\phi_s - \phi_r}{(1-\phi_r)} + \Delta\alpha \text{ (cubic)} \Delta T \right] \quad (4)$$

thus σ/E serves a measure of the level of internal stress in a film if the right hand side of equation (4) is assumed to be constant. The larger its value, the higher the crack resistance of a film.

Another relation that has been used (Broutman 1965, Jackson & Caldwell 1967) to assess stress crack resistance is based on the modified Griffith (1920) equation:

$$\gamma = (\sigma^2\pi C)/2E \quad (5)$$

where γ is the surface energy of the film, σ is the tensile strength, E is the Young's modulus and C is the flaw or crack size before the initiation of the failure process. The surface energy (γ) is a measure of the resistance of the film to the initiation of the fracture process. Since the flaw size (C) is difficult to measure, $\sigma^2/2E$ (relative surface energy) provides an estimate of crack resistance if C and π are ignored.

Crack resistance of coating films may also be determined by measuring the energy absorbed per unit volume of film under stress. This quantity is generally regarded as a measure of the toughness of plastic materials. It is provided by measuring the area under the stress-strain curve. Marin (1965) has proposed some simple equations for estimating this parameter, depending on the material and the shape of the stress-strain curve. For stiff brittle materials, the toughness index (T_d) is given by the area of a triangle. Hence,

$$T_d = \sigma\epsilon/2 \quad (6)$$

where σ is the tensile strength of the film and ϵ is the elongation. For very plastic materials, the area under

the curve is approximately that of a rectangle. Therefore,

$$T_d = \sigma \epsilon \quad (7)$$

when the initial part of a stress-strain profile is curved, the area is best approximated by a quadratic parabola. Hence

$$T_d = \frac{3}{2} \sigma \epsilon \quad (8)$$

thus the shape of the experimental stress-strain curves were examined and categorized and toughness indices estimated from the areas under the curve according to equation 6, 7 or 8.

Table 1 shows the stress crack resistance parameters calculated (according to the relationships outlined above) for the unpigmented (or unfilled) free films. The larger the values of the parameters the higher the resistance of the films to cracking and hence, indirectly, the lower their internal stress. Both the toughness and relative surface energy of

while the toughness and surface energy data indicate that the polyethylene glycols will lower crack resistance, σ/E results predict an improvement in crack resistance by the additives.

Consideration of the crack resistance of the pigmented films (see Tables 2 and 3) shows the existence of a large degree of agreement among the three parameters. Generally, there was a fall in the crack resistance of all the films with increase in filler content, irrespective of the filler type. Crack resistance appeared to be lower in talc-filled films than in the corresponding films containing titanium dioxide. This can be attributed to the difference between the particle shape of the fillers. The filler-polymer interfacial bonding, which is most probably of the dipole-dipole type, is weaker than the mainly hydrogen bonds holding the molecular segments of the polymer matrix together. Thus the filler-polymer interface constitutes stress locations or flaws from

Table 1. Stress crack resistance of hydroxypropyl methylcellulose (HPMC) films containing polyvinyl alcohol (PVA), and polyethylene glycols 400 and 1000 (PEG 400 and PEG 1000) at 20 °C, 60% rh.

Conc. of polymeric additive (wt%)	Toughness index (kJ m^{-3}) $\times 10^3$			Relative surface energy $\sigma^2/2E$ ($\pi \text{Cm-MPa}$) $\times 10^2$			$\sigma/E \times 10^{-2}$		
	HPMC/PVA	HPMC/PEG 400	HPMC/PEG 1000	HPMC/PVA	HPMC/PEG 400	HPMC/PEG 1000	HPMC/PVA	HPMC/PEG 400	HPMC/PEG 1000
0 (HPMC alone)	8.14	8.14	8.14	1.42	1.42	1.42	5.22	5.22	5.22
10	8.89	5.36	6.51	1.48	0.99	1.62	5.74	5.30	6.44
20	7.56	5.64	4.67	1.31	0.89	1.21	5.48	6.76	7.57
30		3.73	2.38		0.73	0.83		7.94	7.19
40	6.10	2.48		1.23	0.57		5.39	8.15	
60	2.22			0.71			5.51		
80	0.92			0.46			4.51		
100	0.33			0.28			3.56		

hydroxypropyl methylcellulose films generally exhibited a downward trend with increase in the concentration of the polymeric additives (polyvinyl alcohol and the polyethylene glycols). For hydroxypropyl methylcellulose/polyvinyl alcohol blends, these parameters increased initially at polyvinyl alcohol content of 10 wt% and then began to fall when the level of polyvinyl alcohol was further raised. The relative surface energy of hydroxypropyl methylcellulose also rose at 10 wt% level of polyethylene glycol 1000 before a decreasing trend commenced with further increase in the content of the plasticizer. In contrast, the parameter, σ/E , of hydroxypropyl methylcellulose films rose with increase in the concentration of the plasticizers. Up to 60 wt% of polyvinyl alcohol content, σ/E values of hydroxypropyl methylcellulose films were generally higher than that of the film-former alone. Therefore

which crack propagation leading to a film coat failure could originate. Reference to Van Krevelen's (1976) proposition, which states that the stress at the tip of a flaw (such as the filler-polymer interface) is multiplied by a factor of $(L/r)^{1/2}$ (where L is the length of the flaw and r is its tip radius), indicates that talc, which is plate-like, would be more likely to create greater stress (and hence lower crack resistance) in the films than spherical titanium dioxide. An identical explanation can be applied to the generally slightly lower crack resistance of films loaded with talc A when compared with talc B-filled films. The flaw size term, L , in Van Krevelen's (1976) relation would be larger for talc A as a result of its greater average particle size. Crack resistance was also slightly higher in films pigmented with TiO_2 A than in those filled with TiO_2 B. This may be due to the surface treatment of TiO_2 B which could have hindered filler-polymer

Table 2. Stress crack resistance of talc-filled films at 20 °C, 60% rh.

Filler content (wt%)	Toughness index (kJ m ⁻³) × 10 ³				Relative surface energy $\sigma^2/2E$ (π Cm-MPa) × 10 ²				$\sigma/E \times 10^{-2}$				
	HPMC	HPMC/ PVA	HPMC/ PEG 400	HPMC/ PEG 1000	HPMC	HPMC/ PVA	HPMC/ PEG 400	HPMC/ PEG 1000	HPMC	HPMC/ PVA	HPMC/ PEG 400	HPMC/ PEG 1000	
Unfilled	0	8.14	7.56	5.64	4.67	1.42	1.31	0.89	1.21	5.22	5.48	6.76	7.57
Talc A	10	3.00	3.79	2.00	2.44	0.97	1.00	0.38	0.49	4.31	4.98	4.13	4.35
	20	2.00	2.03	1.45	1.81	0.68	0.67	0.42	0.43	3.51	3.95	4.17	3.85
	30	0.85	0.88	0.65	0.65	0.54	0.55	0.31	0.35	3.12	3.48	3.39	3.65
	40	0.71	0.72	0.42	0.37	0.48	0.47	0.21	0.21	2.98	3.03	3.09	3.01
	50	0.42	0.50	0.21	0.28	0.30	0.34	0.12	0.18	2.55	2.83	3.03	3.23
Talc B	10	3.12	3.01	2.50	2.67	0.91	0.76	0.53	0.60	3.99	4.19	4.60	4.83
	20	2.75	2.35	1.90	2.11	0.91	0.81	0.40	0.50	3.77	4.27	3.96	4.40
	30	1.09	0.96	0.74	0.91	0.74	0.59	0.35	0.45	3.13	3.51	3.61	4.15
	40	0.98	0.77	0.71	0.71	0.66	0.49	0.35	0.36	2.81	3.17	3.55	3.35
	50	0.63	0.60	0.57	—	0.46	0.42	0.32	—	2.52	2.92	3.22	—

interaction and thereby increased the size of the filler-polymer interface.

Overall, the rate of change of crack resistance with increase in either polymer additive or pigment concentration is highest with the toughness index and lowest with the σ/E parameter. One factor that is common to all three parameters is the tensile strength of film. This clearly emphasizes the role of film strength in the fracture process. However, only the toughness index incorporates film elongation as a positive contributor to crack resistance. The Young's modulus term in the relative surface energy $\sigma^2/2E$ and σ/E parameters is a negative factor in crack resistance but is not taken into account by the toughness index. Apparently, therefore, there is substantial similarity between σ/E and the surface energy parameter, but judging by the sensitivity of each of the parameters to changes in crack resistance and the degree of agreement among them (see Tables 1, 2 and 3), the surface energy parameter may actually be closer to the toughness parameter.

If the internal processes leading to the cracking or failure of film coatings are considered, it appears that the toughness index might be the most satisfactory of the three parameters for monitoring the crack resistance of pigmented films. The origin of film

failure is usually a flaw such as a micro-crack, void, filler-polymer interface or other similar defects. Under an applied stress, the flaw grows in a direction perpendicular to the applied stress, but the polymer deforms in order to stop the growing flaw, and in the process absorbs energy. Increasing deformation eventually leads to the severance of the bonds linking the polymer segments together, and film failure ensues. The deformability of a polymer is enhanced by an increase in elongation, but is frequently accompanied by a reduction in tensile strength and Young's modulus. Thus it is apparent that the flaw factor (size, shape and/or number of flaws) is taken into account in the toughness index, but not necessarily in the other two parameters. If the flaw factor, C , were included in the surface energy parameter (see equation (4)) then the sensitivity of this parameter would probably have moved closer to that of the toughness index since the magnitude of the flaw factor in the filled films would rise with increase in filler concentration.

Correlation between free and applied films

Although it was not possible to use more than 100 tablets in each assessment of the incidence of edge splitting of the coated tablets, the results obtained, in

Table 3. Stress crack resistance of TiO₂-filled films at 20 °C, 60% rh.

Filler content (wt%)	Toughness index (kJ m ⁻³) × 10 ³				Relative surface energy $\sigma^2/2E$ (π Cm-MPa) × 10 ²				$\sigma/E \times 10^{-2}$				
	HPMC	HPMC/ PVA	HPMC/ PEG 400	HPMC/ PEG 1000	HPMC	HPMC/ PVA	HPMC/ PEG 400	HPMC/ PEG 1000	HPMC	HPMC/ PVA	HPMC/ PEG 400	HPMC/ PEG 1000	
Unfilled	0	8.14	7.56	5.64	4.67	1.42	1.31	0.89	1.21	5.22	5.48	6.76	7.57
TiO ₂ A	10	3.31	4.83	4.08	5.24	1.11	1.22	0.56	0.75	4.81	5.88	5.75	6.37
	20	2.11	3.19	2.01	2.11	1.07	1.30	0.55	0.55	4.40	5.52	5.05	4.76
	30	1.73	2.85	1.59	1.91	1.11	1.03	0.44	0.46	4.39	4.77	4.49	4.03
	40	1.72	2.42	1.23	1.34	0.92	0.89	0.52	0.49	3.88	4.34	4.83	4.02
	50	1.32	1.73	0.99	1.08	0.81	0.90	0.53	0.54	3.52	4.28	5.17	4.51
TiO ₂ B	10	3.68	4.46	4.63	4.23	1.04	1.01	0.45	0.54	4.33	5.06	4.88	5.26
	20	2.25	2.32	1.34	2.14	1.08	1.00	0.37	0.56	4.36	4.87	4.29	4.99
	30	2.78	2.51	1.53	1.78	1.12	0.90	0.45	0.51	4.34	4.42	4.36	4.74
	40	1.54	1.57	1.19	1.10	0.93	0.83	0.43	0.45	4.01	4.23	4.05	4.05
	50	1.17	1.18	0.96	0.80	0.64	0.72	0.33	0.34	3.39	3.94	3.98	3.82

which the incidence of edge splitting was 12% for hydroxypropyl methylcellulose alone and 0% when in combination with polyvinyl alcohol or polyethylene glycol 400, were considered acceptable for examining general trends in edge splitting (Fig. 1).

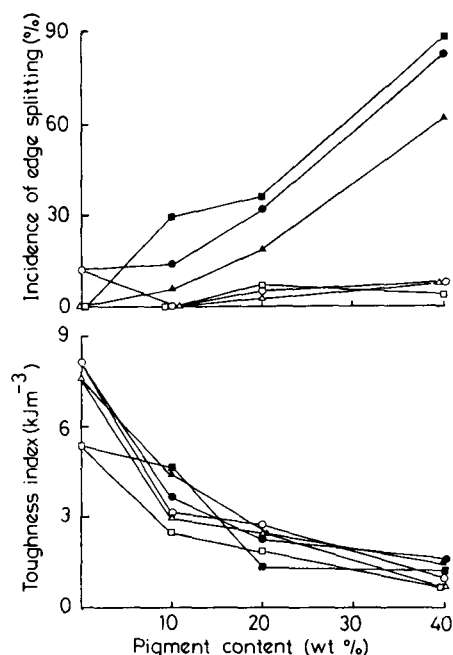


FIG. 1. Relation between the stress crack resistance (toughness index) of pigmented free films of hydroxypropyl methylcellulose alone (○, ●) and in combination with either polyethylene glycol 400 (□, ■) or polyvinyl alcohol (△, ▲), and the incidence of edge splitting of equivalent films applied to aspirin tablets. (Note: open symbols = films pigmented with talc; closed symbols = films pigmented with titanium dioxide.)

Addition of either polyvinyl alcohol or polyethylene glycol 400 to hydroxypropyl methylcellulose completely eliminated edge splitting. Of the three crack resistance parameters, only the σ/E ratios accurately reflect this observation. This suggests that, σ/E may be the parameter of choice for predicting crack resistance in unpigmented film systems. The plots of stress crack resistance (toughness index) and the incidence of edge splitting of the pigmented films against pigment concentration (Fig. 1) clearly indicate that the incidence of edge splitting rose as the crack resistance of the films containing titanium dioxide fell. A similar but less pronounced trend was observed for talc-filled films, with the exception of hydroxypropyl methylcellulose films where the unfilled film coating appeared to show a

higher incidence of edge splitting than those loaded with talc. To a large extent, therefore, stress crack resistance data based on free films may be used to forecast edge splitting of applied film coats containing pigments. This is probably due to the generally higher internal stresses in filled films than in unfilled films, as well as the sharp changes in internal stress when filler content is varied.

However, the considerably greater incidence of edge splitting of titanium dioxide-filled films than those of films containing talc could not have been predicted from the crack resistance data. Related observations by Rowe (1982) suggest that Inoue's (1943) explanation in terms of the particle morphology of the fillers may be applicable to the results obtained in this study. Inoue (1943) indicated that the internal stress of benzylcellulose film remained largely unchanged when filled with talc or aluminium powder because the plate-like particles of the fillers were orientated parallel to the surface of the substrate and consequently, volume shrinkage of the film was restrained parallel to the plane of the film. It seems likely that a number of other factors may also be involved. For example, the film preparation technique could influence the degree of filler-polymer interaction as well as film morphology. The internal stress of a free film cast by a pouring technique can be expected to be different from that of an equivalent sprayed film.

Nonetheless, considerable benefits can be derived from crack resistance data on free films partly because the equivalent data on applied film coats are difficult to obtain. For example, the term, ϕ_s , volume fraction of solvent at the solidification point (see equation (2)), is not easily determined. It will also be necessary to evaluate the term, $\Delta\alpha$ (see equation (4)), for various types of tablet cores. Crack resistance data based on free films are thus useful for screening and predictive purposes.

CONCLUSIONS

Stress crack resistance parameters (tensile strength: Young's modulus, relative surface energy and toughness index) for filled and unfilled free films based on hydroxypropyl methylcellulose and derived from aqueous systems have been evaluated.

Film systems corresponding to some of the free films were applied to aspirin tablets and the incidence of edge splitting of the film coatings determined. Crack resistance of the films decreased as filler content increased. The addition of either polyvinyl alcohol or polyethylene glycols 400 and 1000 to hydroxypropyl methylcellulose eliminated

the incidence of edge splitting in the film coated tablets.

There was a relation between all three stress crack resistance parameters of free films and the incidence of edge splitting of equivalent film coatings applied to aspirin tablets for filled systems, but a similar correlation was only found for unfilled systems when the tensile strength:Young's modulus ratio was considered.

Toughness index was thought to be the most suitable of the parameters for predicting crack resistance of pigmented systems while the tensile strength:Young's modulus ratio was considered most adequate for unpigmented films.

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