

IJP 00758

Effect of solids–polymer interactions on the properties of some aqueous-based tablet film coating formulations. II. Mechanical characteristics

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(Received February 10th, 1984)

(Modified version received July 11th, 1984)

(Accepted August 14th, 1984)

Summary

The effects of filler–polymer interactions and stress concentrations on the mechanical properties of plasticized and unplasticized hydroxypropyl methylcellulose films (HPMC) filled with two types of titanium dioxide (one of which is surface-treated) and two types of talc (different specific surface areas), respectively, have been examined. The plasticizer was believed to interact more strongly than the film-former (HPMC) with the fillers, a behaviour with dramatic consequences on the tensile strength, Young's modulus and elongation of the plasticized films. Talc, due to its plate-like particle shape, induced more stress in the films but also appeared to have interacted more effectively with the polymers. Some of the filler–polymer interactions have been explained, in part, using the acid–base concept.

Introduction

The various factors which influence the behaviour of particulate solids in coating films were mentioned in the first part of this study (Okhamafe and York, 1984). Funke et al. (1969) have classified these factors into two main types: (i) hydrodynamic effects, due largely to the size, shape, volume concentration and orientation of the filler particles; and (ii) reinforcing effects, due to strong physical and sometimes, chemical bonding of the pigment to the polymer matrix. The hydrodynamic effects

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of the filler will enhance Young's modulus because of the ability of the rigid particles, by their mere presence, to restrict or hinder physically the polymer matrix. The hydrodynamic influence on tensile strength and elongation is considerably less but the reinforcing effect increases Young's modulus and tensile strength with increasing filler content while decreasing elongation (Funke et al., 1969).

Elm (1953) reported that zinc oxide (an 'active' pigment) decreased the elongation and increased the stiffness of paint films more sharply than titanium dioxide (an 'inactive' pigment). The author attributed this behaviour to the greater interaction between zinc oxide and the polymer phase. Studies by Funke et al. (1969) also indicate that the degree of filler-polymer interaction has very pronounced effects on the mechanical properties of films. These workers as well as Lipatov (1966) have observed that improved filler-polymer interaction could minimize accumulation of water at the solid-polymer interface and solvent-polymer interaction.

Most of the investigations on the effects of pigments on the mechanical properties of pharmaceutical film coatings (e.g. Porter, 1980; Rowe, 1982, 1983) have concentrated on the hydrodynamic aspect and the role of internal stress. Since the surface chemistry of the various particulate solids (e.g. talc, titanium dioxide and F.D. & C. pigments) often incorporated in pharmaceutical coating films is likely to be different, the effect of pigment-polymer interaction should not be ignored. This aspect, along with the effect of internal stress, has been examined in filled films similar to those considered in the first part of this work (Okhamafe and York, 1984).

Materials and Methods

The test specimens were cut from portions of the cast films used in the first part of this study (Okhamafe and York, 1984). Cutting, conditioning and measurement of the stress-strain properties (using an Instron tensile tester) of the film specimens followed the procedures employed in a previous investigation (Okhamafe and York, 1983). A total of 12 specimens was employed in each test and in most cases, coefficient of variation did not exceed 12%.

Results and Discussion

Since for each film type the specimens cut parallel to, and perpendicular to, the axis of rotation of the casting substrate did not differ significantly at 95% confidence level, the mean of the two sets of results (parallel and perpendicular) were employed in this study.

A useful method of assessing the effect of filler-polymer interactions on the mechanical properties is to compare the experimental results with predicted data. The predicted data (shown as broken curves), plotted along with the experimental results in Figs. 1-6, are based on models taken from among the various types proposed by Bueche (1960), Nielsen (1966) and Marmo et al. (1976). For tensile

strength this was:

$$\sigma' = \sigma(1 - f^{2/3})S \quad (1)$$

where σ' and σ are the tensile strengths of the filled and unfilled films, respectively, f is the volume fraction of the filler and S is a stress concentration factor. S has a maximum value of 1.0 which implies that there is no internal stress in the film attributable to filler presence. This is unlikely; for most practical situations S will be less than unity. For the purpose of this study, however, S is considered to be unity. Predicted Young's moduli were obtained from Eqn. 2,

$$E' = E(1 - f) \quad (2)$$

where E' and E , respectively, are the Young's moduli of the filled and unfilled films. The elongation model used was

$$\epsilon' = \epsilon(1 - f^{1/3}) \quad (3)$$

where ϵ' and ϵ are elongations of the filled and unfilled films. All the models assume that in each case the property being measured is a function only of the volume fraction of the filler and does not take into account the effects of stress concentrations, particle shape, and orientation and aggregation of the filler particles. The elongation model alone assumes maximum filler-polymer interaction but interaction is considered not to play a role in the other two models.

Tensile strength

Figs. 1 and 2 show the tensile strength plots. Overall, the solid-loading of the

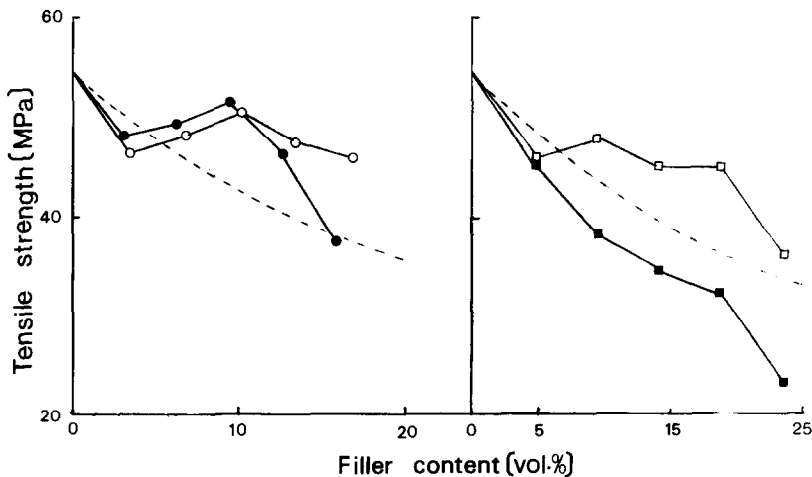


Fig. 1. Tensile strength of HPMC film against filler concentration at 20°C, 60% R.H. (Talc A = ■; Talc B = □; TiO₂A = ○; TiO₂B = ●; broken line = predicted curve.)

films had a detrimental effect on the tensile strength of the films with the largest fall occurring at a filler concentration of 3.0–4.5 vol. %. Thereafter tensile strength increased slowly or remained largely unchanged until at some filler level (presumably the critical pigment volume concentration or CPVC), a downward trend commenced. The exception is HPMC loaded with talc A which showed a continuous fall in tensile strength with increase in filler concentration. The behaviour of the fillers suggests disruption of some of the bonds (mainly hydrogen bonds) holding the polymer chains together. Since titanium dioxide and talc are polar in character some form of interaction, mostly of the dipole–dipole type, will occur between the filler and the polymer matrix; but these bonds are considerably weaker than the inter-segmental hydrogen bonds of the polymer. In addition, the filler–polymer interfaces constitute stress locations or concentrations, represented by S in Eqn. 1, which will contribute further to lower film strength. As filler level rises, filler–polymer interaction increases and so does stress concentration. If the former increases faster than the latter, film strength increases, and vice versa. Above CPVC, the polymer phase is unable to bind all the pigment particles and the resulting voids (stress concentrations) then lead to a continuous decrease in tensile strength.

The important role played by stress is indicated by Van Krevelen's (1976) observation that the stress at the tip of a flaw (in this case, a filler–polymer interface) is increased by a factor of $(L/r)^{1/2}$ where L is the length of the flaw and r is the tip radius. Since talc is plate-like and titanium dioxide spherical, stress concentration will be much greater in talc-filled films than in titanium dioxide-filled films. This may account for the slightly superior tensile strengths of the latter, rather than greater filler–polymer interaction. If the larger specific surface area of titanium dioxide (about 4 times that of talc B) and the stress concentration factor are taken into consideration, it seems possible that talc may have interacted more effectively

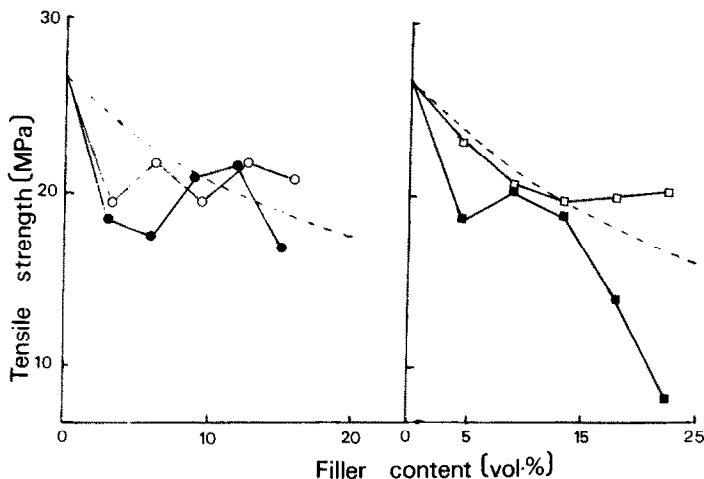


Fig. 2. Tensile strength of HPMC/PEG 400 film against filler concentration at 20°C, 60% R.H. (Talc A = ■; Talc B = □; TiO₂A = ○; TiO₂B = ●; broken line = predicted curve.)

with the polymer system. The higher tensile strength values of talc B-filled films compared with those filled with talc A, may be explained by the greater interaction of talc B (larger specific surface area) with the polymers as well as the greater stress in talc A-filled films (where L is larger because the particle size of talc A is bigger).

A comparison of the predicted and experimental data in both plasticized and unplasticized HPMC films appears to indicate that filler-polymer interaction is greater in the unplasticized system. This may not really be so. Although it is likely that tensile strength will be less adversely affected in the plasticized film (since the effect of stress will be better accommodated as a result of its greater deformability) a situation can be envisaged in which the filler, to varying degrees, interacts preferentially with either the plasticizer (PEG 400) or HPMC. Application of the acid-base concept (Okhamafe and York, 1984) does indeed suggest that in the plasticized system, the fillers ($\text{pH} = 6.35\text{--}9.01$) have probably interacted more with PEG 400 ($\text{pH} = 3.05$) with which they have a larger pH difference than HPMC ($\text{pH} = 7.26$). The strong reactivity of the polyols with titanium dioxide has been reported by Ritter (1973). Since PEG 400 cannot form a coherent film on its own, tensile strength will be lower although the degree of filler-plasticizer interaction is high. Therefore the negative deviation of the experimental results from the predicted values of the plasticized films may not actually indicate a lower filler-polymer interaction in this system.

CPVC is discernible in some of the plots as the filler content at which a downward trend commenced following the preceding rise in tensile strength: 10.1 and 9.4 vol. % for TiO_2A and B, respectively, in HPMC films; 11.9 vol. % for HPMC/PEG 400 films containing TiO_2B ; and 8.9 vol.% for HPMC/PEG 400 filled with talc A.

Young's modulus

Figs. 3 and 4 show that generally the Young's moduli of the films were enhanced when filler concentration increased until CPVC (in cases where it was observed) was reached. TiO_2A seemed to have achieved a slightly higher increase in Young's modulus in HPMC/PEG 400 films than the surface-treated TiO_2B . Modulus was also more effectively enhanced in films loaded with talc B (larger surface area) than in talc A-filled films. Of the fillers used, talc B appeared to be the most powerful modulus enhancer.

Young's modulus is invariably increased when pigments are incorporated in films (Funke et al., 1969; Toussaint, 1973/74; Rowe, 1982, 1983) due to an increase in the stiffness or rigidity of the polymer phase. At least part of the stiffening occurs as a result of physical restriction of the polymer matrix by the hard, rigid filler particles (a hydrodynamic effect). An important hydrodynamic factor is the shape of the filler particles. The shape factor has been defined, by Guth (1945) as the ratio L/d where L is the length of the filler particle and d is its diameter. For titanium dioxide particles which are spherical the shape factor is 1.0 but for talc the factor will be greater than unity because of its plate-like particles. The higher the shape factor the greater its contribution to modulus enhancement. A reinforcing effect also plays a significant role in modulus increase if the filler interacts with the polymer phase. It is

generally accepted that filler-polymer interaction reduces substantially polymer chain mobility at the polymer-filler interface. The decrease in chain mobility is further transmitted down the polymer network resulting in a more rigid film. Kwei (1965) has reported that this effect can extend up to nearly 1500 Å from the pigment-polymer boundary.

If the reinforcing effect alone is considered, it would normally be expected that modulus will be increased more by titanium dioxide than by talc because of the considerably greater specific surface of the former and therefore its greater capacity to interact with the polymer phase.

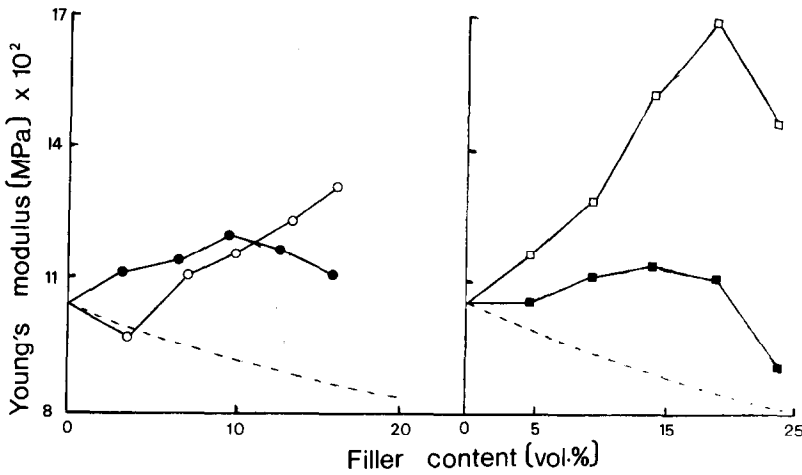


Fig. 3. Young's modulus of HPMC film against filler concentration at 20°C, 60% R.H. (Talc A = ■; Talc B = □; TiO₂ A = ○; TiO₂ B = ●; broken line = predicted curve.)

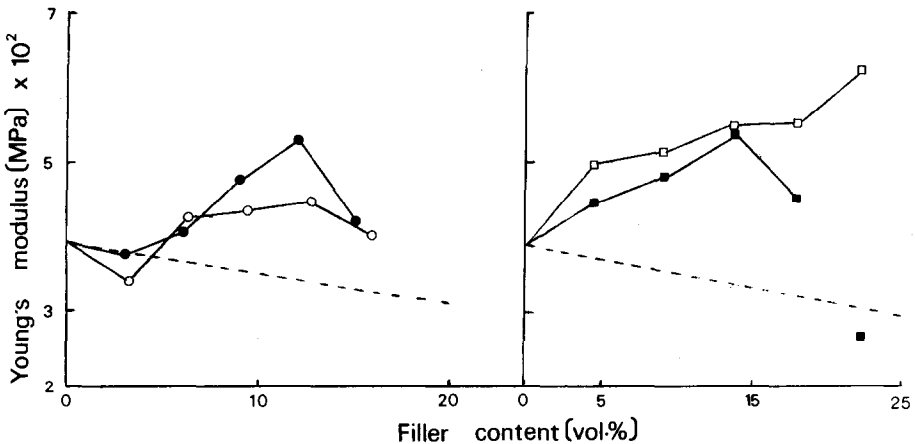


Fig. 4. Young's modulus of HPMC/PEG 400 film against filler concentration at 20°C, 60% R.H. (Talc A = ■; Talc B = □; TiO₂ A = ○; TiO₂ B = ●; broken line = predicted curve.)

On the basis of the available results it is possible to consider which of the two effects—hydrodynamic or reinforcing—played a more critical role. On comparing the moduli of HPMC films filled with talcs A and B, respectively, and taking into account the greater specific surface (and hence greater capacity to interact) of the latter as well as the probable similarity of their shape factors it seems that filler-polymer interaction was the dominant modulus enhancement factor. The much smaller difference between the effects of talcs A and B in HPMC/PEG 400 is probably due, as suggested earlier, to the preferential interaction of the fillers with the plasticizer at the expense of the film-former (HPMC). Since the plasticizer lacks any film-forming ability, filler-polymer interaction has little polymer chain stiffening effect. (This is reflected by the smaller positive deviation of the observed results from the predicted data.) It is apparent, therefore, that in the plasticized systems the hydrodynamic effects of the fillers are mainly responsible for modulus increase. Of the two titanium dioxide fillers, TiO_2B was a weaker modulus enhancer in the plasticized system and this suggests that surface treatment of the pigment adversely affected filler-polymer interaction.

In some films, there was agreement between the CPVCs based on tensile strength and Young's modulus data, respectively, as shown, for example, by the HPMC and HPMC/PEG 400 films, respectively, containing TiO_2B . Other observed CPVCs are 12.7 vol. % TiO_2A in HPMC/PEG 400; 14.1 and 13.3 vol. % Talc A in HPMC and HPMC/PEG 400, respectively; and 18.8 vol. % talc B in HPMC.

Elongation

As indicated in Figs. 5 and 6, filler inclusion in both plasticized and unplasticized HPMC films generally led to a decrease in elongation. These results are consistent with those of Elm (1953) and Funke et al. (1969). Nielsen (1966), Toussaint (1973/74) and Marmo et al. (1976) have also observed that solids-loading usually reduces elongation even if the filler does not interact with the polymer. The two talcs were essentially similar in their effects on elongation as were TiO_2A and B. The talcs, however, lowered elongation more effectively than either of the titanium dioxide pigments.

Elongation may be regarded as a measure of the capacity of a film to deform prior to failure. A low deformation capacity implies elongation is small and the film is brittle. When deformation capacity is high, film elongation is large. Usually film failure originates from a flaw (stress concentration) such as that provided by the filler-polymer interface. Under an external or applied stress the flaw propagates but the polymer matrix deforms in order to accommodate the growing flaw or crack until the deformation capacity of the polymer is exceeded and then the film fails. Two factors are therefore of crucial importance: (i) particle shape and size, which determine the flaw size (the size of the filler-polymer interface); and (ii) filler-polymer interaction, which by stiffening the polymer chains (modulus enhancement) reduces the deformation capacity of the polymer phase. An increase in the contribution of either of these factors favours a decrease in elongation. These factors are probably greater in talc-filled films, as indicated earlier in the discussions on tensile strength and Young's modulus. This is also reflected by the larger positive deviations

of the experimental data from the predicted results in these films than in those filled with TiO_2A and B. The similarity of talcs A and B may be explained by the larger flaw size effect of talc A being counter-balanced by the greater filler-polymer interaction of talc B. A similar explanation applies to TiO_2 -filled films since the size of the TiO_2B -polymer interface would be larger than that of films containing TiO_2A (untreated surface) in which filler-polymer interaction is greater.

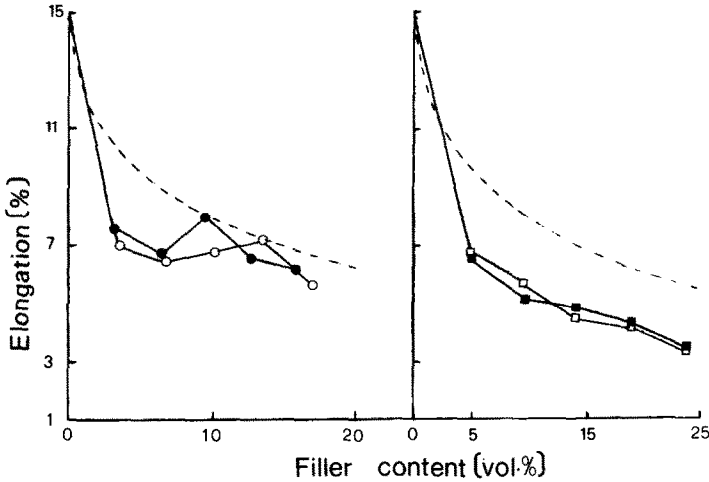


Fig. 5. Elongation of HPMC film against filler concentration at 20°C, 60% R.H. (Talc A = ■; Talc B = □; TiO_2A = ○; TiO_2B = ●; broken line = predicted curve.)

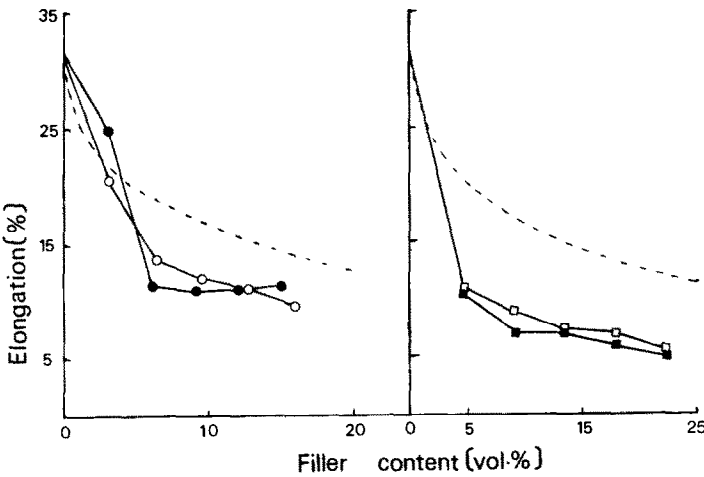


Fig. 6. Elongation of HPMC/PEG 400 film against filler concentration at 20°C, 60% R.H. (Talc A = ■; Talc B = □; TiO_2A = ○; TiO_2B = ●; broken line = predicted curve.)

Comparison of HPMC and HPMC/PEG 400 film systems shows that there is a bigger positive deviation of the experimental data from the predicted results in the latter. The preferential interaction of the pigments with the plasticizer probably leaves the network of the polymer matrix with a lower level of plasticizer, and therefore, a smaller elongation than in the unfilled film.

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