DRUG DEVELOPMENT AND INDUSTRIAL PHARMACY, 11(1), 131-146 (1985)

RELATIONSHIP BETWEEN STRESS, INTERACTION AND THE MECHANICAL PROPERTIES OF SOME PIGMENTED TABLET COATING FILMS

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ABSTRACT

The mechanical properties of pigmented free films of hydroxypropyl methylcellulose in combination with either polyvinyl alcohol or polyethylene glycol 1000 and cast from aqueous systems, were measured using a stress-strain method. The pigments incorporated were two types of talc (differing in average particle size) and two types of titanium dioxide (one of which was surface-treated). Specific surface area data for the pigments and the pH of the aqueous solution or suspension of the film components were determined in order to understand the factors affecting the mechanical properties of pigmented films.

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0363-9045/85/1101-0131$3.50/0

INTRODUCTION

In a recent study[1], data were presented in order to show that the acid-base (electron donor-acceptor) concept[2] can be employed to explain the effects of filler-polymer interactions on the mechanical properties of filled films. The need to acquire a deeper understanding of the effects of particulate solids on film properties has become greater in view of the increasing use of fillers (e.g. talc and magnesium stearate) and colouring pigments (e.g. F.D. & C. pigments) in film coatings for solid dosage forms. One of the undesirable consequences of pigmentation is the formation of localised flaws or micro cracks around pigment particles in a film[3]. These flaws not only could propagate under stress, leading to cracking or edge splitting of film coats, but may also profoundly alter the permeation characteristics of controlled release film coatings.

Funke et al[4] have placed the various effects of filler on film properties in two main categories: (a) hydrodynamic effects, due largely to the size, shape, volume concentration and orientation of the pigment particles; and (b) reinforcing effects, due to strong physical and/or chemical bonding of the filler to the polymer phase. Hydrodynamic factors as well as the degree of filler-polymer interaction may influence the magnitude of the internal stress associated with the localised flaws at the pigment-polymer interface. Inoue[5] observed that while spherical titanium dioxide and zinc oxide pigments increased the internal stress of benzylcellulose with increase in pigment concentration, talc and aluminium powder which had flaky particles had little or no effect on internal stress.

In this paper, the relationship between internal stress, filler-polymer interactions and the mechanical properties of aqueous-based films of hydroxypropyl methylcellulose containing either polyvinyl alcohol or polyethylene glycol 1000, and filled with talc and titanium dioxide, have been examined.

MATERIALS

Hydroxypropyl methycellulose U.S.P. (Pharmacoat 606) and polyvinyl alcohol (Poval PA-5) were manufactured by Shin-Etsu Chem. Co.Ltd., Japan. Polyethylene glycol 1000 was obtained from BDH Chemicals Ltd., Poole, U.K. Two polymer systems were examined: hydroxypropyl methylcellulose (HPMC) in combination with either polyethylene glycol (PEG) 1000 or polyvinyl alcohol (PVA). In each case, the content of the polymer additive (PEG 1000 or PVA) was 20wt% based on that of HPMC.

Two types of talc, differing in average particle size (Talc 4053NM and Talc 4053, Richard Baker Harrison Ltd., U.K.), and two types of titanium dioxide, one of which is surface-treated (Tioxide A-HR, BTP Tioxide Ltd., U.K. and Bayertitan RC-K-20, Bayer (UK) Ltd) were incorporated in the polymer systems as fillers. These fillers are designated talc A, talc B, TiO_2A and TiO_2B, respectively, and their main features are listed in Table 1.

METHODS

Aqueous polymer formulations were prepared from 10%^{w}/v aqueous solutions of the polymers. The filler particles were dispersed in the aqueous film formulations for thirty minutes using a mixer/emulsifier (laboratory model, Silverson Machines Ltd., London). The rotating cylinder technique[6] was employed in casting the films. Cross-sections of the films showed even distribution of filler particles when examined under the microscope.

The tensile strength at break, Young's modulus and elongation at break of the films were determined from stress-strain measurements as detailed in a previous study [6]. A total of twelve dumb-bell shaped specimens (six cut perpendicular to, the axis of rotation of the casting substrate) were examined and the mean of the results was taken in all cases.

The surface areas of the pigments were measured with a surface area and pore volume analyser (model 2100, Micromeritics Intr.Corp., U.S.A.). The pH of a 10%^{w}/v aqueous suspension of each filler as well as those of 10%^{w}/v aqueous formulations of the individual polymers and the mixed polymer systems were obtained using a microprocessor pH/millivolt meter (model 811, Orion Research Inc., U.S.A.).

RESULTS AND DISCUSSION

To facilitate a better understanding of the mechanism by which the mechanical behaviour of films are influenced by particulate fillers, predicted data based on previously proposed models (equations (1) - (3))[7,8,9] were obtained. These data (indicated as broken lines) are plotted together with the experimental results in Figs. 1 - 6.

$$\sigma' = \sigma\ (1 - \phi_f^{\frac{2}{3}}) S_c \qquad (1)$$

$$E' = E\ (1 - \phi_f) \qquad (2)$$

$$\varepsilon' = \varepsilon\ (1 - \phi_f^{\frac{1}{3}}) \qquad (3)$$

where σ', E' and ε' are the tensile strength, Young's modulus and elongation respectively, of the filled films while σ, E and ε represent the same parameters for the unfilled systems. ϕ_f is the volume fraction of the filler and S_c is a stress concentration factor which indicates the level of internal stress induced in the films as a result of pigmentation. S_c has a value less than unity since a maximum value of 1.0 indicates absence of filler-induced stress. In the present study, S_c is considered to be unity for reasons of simplicity. While the elongation model assumes maximum filler-polymer interaction, this phenomenon is not a factor in the other two models.

Tensile Strength

As Figs. 1 and 2 indicate, pigmentation initially resulted in a sharp decrease in tensile strength. In film systems containing titanium dioxide, further increase in pigment concentration resulted in either a slight increase in, or unchanged, tensile strength. The tensile strength of the talc-filled films showed a downward trend as filler content was further raised, with the exception of the plasticised system containing talc B where no change in tensile strength occurred.

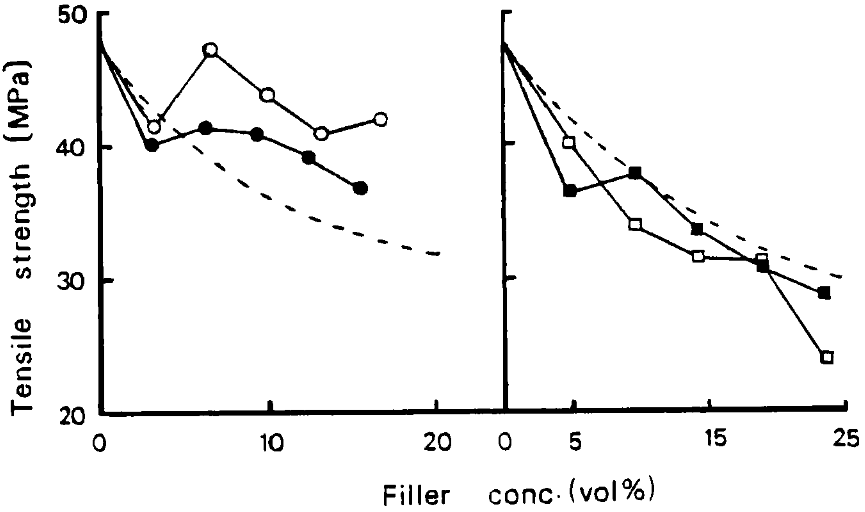

FIGURE 1

Tensile strength of HPMC/PVA film versus filler content at 20°C, 60% R.H. (Note: talc A = □ ; talc B = ■ ; TiO_2A = ○ ; TiO_2B = ● ; broken line = predicted data).

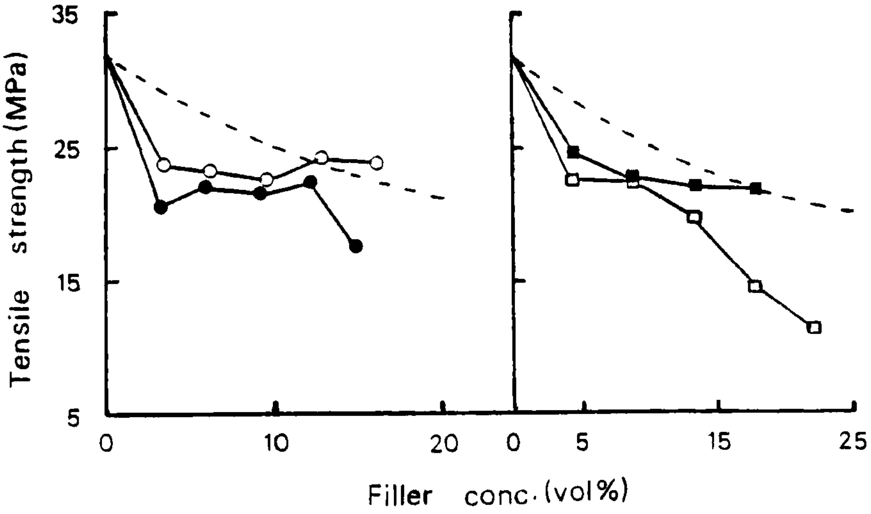

FIGURE 2

Tensile strength of HPMC/PEG 1000 film versus filler content at 20°C, 60% R.H. (Note: talc A = □ ; talc B = ■ ; TiO_2A = ○ ; TiO_2B = ● ; broken line = predicted data).

Two main factors are thought to determine the influence of pigments on the tensile strength of films. These are the internal stress of the films and the degree of pigment-polymer interaction. Incorporation of the pigment particles in a film causes discontinuities in the network of the polymer matrix as hydrogen bonds between adjacent polymer segments are broken. Although pigment-polymer interaction probably occurs by a dipole-dipole mechanism (since both the polymers and pigments used are polar in character) this bonding interaction is weaker than the severed hydrogen bonds. Thus the pigment-polymer interface constitutes a weak link in the structure of the film and may therefore be regarded as a stress concentration (S_c in equation (1)). Hence the internal stress of the films will increase as filler concentration rises, leading to a fall in tensile strength. On the other hand, increasing filler-polymer interaction with increasing filler content enhances tensile strength. In titanium dioxide-filled films, the filler-polymer interaction factor exhibited a slightly dominant effect on the overall strength of the films while the internal stress factor played a far more important role in films loaded with talc.

The differences between the effects of the pigments can be attributed, in part, to their particulate features (see Table 1). Internal stress appears to be greater in the presence of plate-like talc compared with spherical titanium dioxide. This may be explained by Van Krevelen's proposition[10] that the stress at the tip of a flaw (such as a filler-polymer interface) is increased by a factor of $({}^{L}/r)^{\frac{1}{2}}$ where L is the length of the flaw and r is its tip radius. This probably also accounts for

TABLE 1

Specific Surface Area and Particle Features of the Fillers used

Filler	Specific surface area (m^2 g^{-1})	Particle Feature
Talc A	1.34	plate-like, coarse.
Talc B	1.81	plate-like, fine.
TiO_2 A	7.89	spherical, anatase, untreated surface.
TiO_2 B	8.42	spherical, rutile, water-repellant, surface treated with alumina and an undisclosed organic compound.

the greater negative effect of talc A (which has a larger average particle size than talc B) on tensile strength, especially in HPMC/PEG 1000 film. It is also probable that the hydrophobic coating on TiO_2B inhibited filler-polymer interaction and was therefore less effective in enhancing tensile strength than TiO_2A.

On the basis of the acid-base concept employed in a recent paper[1],there should be greater filler-polymer interaction in the film system plasticised with PEG 1000 than in HPMC/PVA films. This is because the pH difference between each filler and HPMC/PEG 1000 (see pH data in Table 2) is larger in each case than that between the

TABLE 2

pH of Aqueous Polymer Systems and Filler Suspensions

System	pH
PVA (10% $^w/v$ aqueous solution)	5.11
PEG 1000 (10% $^w/v$ aqueous solution)	3.30
HPMC (10% $^w/v$ aqueous solution)	7.26
HPMC/PVA (10% $^w/v$ aqueous mixture)	6.70
HPMC/PEG 1000 (10% $^w/v$ aqueous mixture)	6.04
Talc A/water (10% $^w/v$ aqueous suspension)	9.00
Talc B/water (10% $^w/v$ aqueous suspension)	9.01
TiO_2A/water (10% $^w/v$ aqueous suspension)	7.33
TiO_2B/water (10% $^w/v$ aqueous suspension)	6.35

corresponding filler and HPMC/PVA. It is thought, however, that the fillers interact preferentially with the polymer additives (PEG 1000 and PVA) which are inherently lower in strength than the film former (HPMC). As a result, the greater filler-polymer interaction in the plasticised system does not translate to a larger increase in tensile strength than in HPMC/PVA because PEG 1000, unlike PVA, cannot form a coherent film. This is reflected by the greater overall positive deviation of the experimental results from the predicted data for HPMC/PVA films than for the HPMC/PEG 1000 system.

Young's Modulus

Figs. 3 and 4 show the Young's modulus data obtained. Generally, Young's modulus increased when pigments were added to the polymer

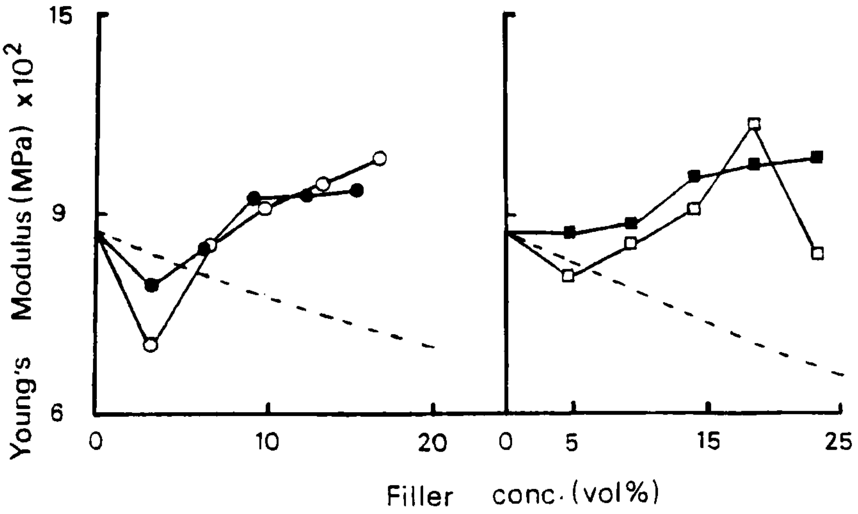

FIGURE 3

Young's modulus of HPMC/PVA film versus filler content at 20°C, 60% R.H. (Note: talc A = □ ; talc B = ■ ; TiO_2A = ○ ; TiO_2B = ● ; broken line = predicted data).

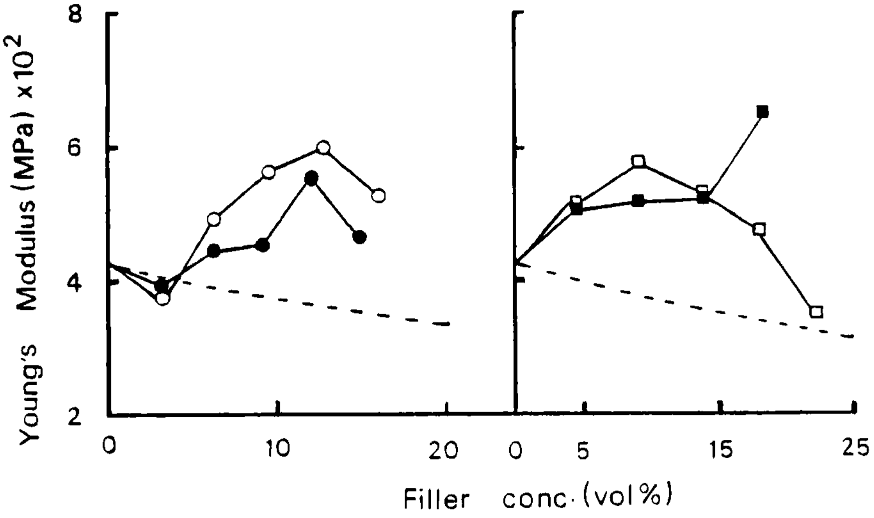

FIGURE 4

Young's modulus of HPMC/PEG 1000 film versus filler content at 20°C, 60% R.H. (Note: talc A = □ ; talc B = ■ ; TiO_2A = ○ ; TiO_2B = ● ; broken line = predicted data).

systems. This is in agreement with findings reported by other workers[4,11]. Increased modulus is usually due to a rise in the stiffness or rigidity of the polymer matrix which may be brought about in two ways. First, the mobility of the polymer phase may be physically hindered by the mere presence of the hard filler particles. This is a hydrodynamic effect. Second, filler-polymer interaction (a reinforcing effect) could stiffen the molecular chains of portions of the polymer matrix at the filler-polymer interface thus reducing segmental mobility. The stiffening effect can be transmitted further the network of the polymer phase as Kwei[12] has noted.

The hydrodynamic effect of plate-like talc on Young's modulus is greater than that of spherical titanium dioxide in view of the larger shape factor of plate-like talc (shape factor has been defined[13] as the ratio $^{L}/d$ where L is the average length of the filler particles and d the average diameter). Titanium dioxide, being spherical, has a shape factor of 1.0. However, TiO_2A and TiO_2B, with specific surface areas 4-6 times those of the two talcs (see Table 1), possess a potentially greater reinforcing capacity since the greater the surface area of the filler the greater the available surface for filler-polymer interaction. The data in Figs. 3 and 4, however, indicate that talc and titanium dioxide had approximately identical effects on the modulus of the films. The application of the acid-base concept suggests greater modulus enhancement by a reinforcing mechanism in the presence of talc than that of titanium dioxide; but the results obtained do not reflect this probably because the polymer chain stiffening effect of the fillers is hindered as a result of the inherently weak nature of the polymer additives, especially PEG 1000. Some support for this hypothesis can be found in a previous study[1] where the large increase in the modulus of HPMC film in the presence of talc B was attributed more to filler-polymer interaction than to hydrodynamic factors.

Elongation

Figs. 5 and 6 illustrate the elongation results. In all cases, there is a fall in elongation with increase in filler concentration. Taking the predicted data into consideration, it would appear that the reduction in elongation was more pronounced in the presence of talc than that of titanium dioxide. The effects of talcs A and B on the elongation of the films were similar, and the same applies to TiO_2A and B in HPMC/PEG 1000 system. However, elongation was more effectively lowered in HPMC/PVA films by TiO_2B than TiO_2A.

It has been reported[8,9] that pigment incorporation in films usually results in a decrease in film elongation even if the pigment does not interact with the polymer phase. However, the greater the degree of filler-polymer interaction the more pronounced is the fall in elongation. In addition to the role played by filler-polymer interaction, the particle shape (a hydrodynamic factor) has a considerable influence on the magnitude of film elongation. As discussed earlier, the filler-polymer interface is a stress concentration; the stress associated with talc, which is plate-like, will be higher than that found for the spherical titanium dioxide. Elongation has been considered as a measure of the deformation capacity (i.e. the ability to deform under stress) of a film[1]. Stress

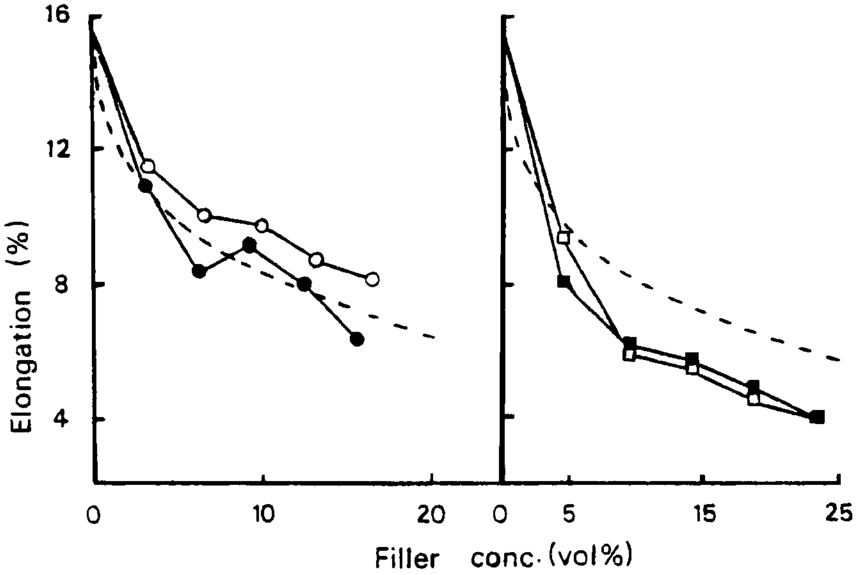

FIGURE 5

Elongation of HPMC/PVA film versus filler content at 20°C, 60% R.H. (Note: talc A = □ ; talc B = ■ ; TiO_2A = ○ ; TiO_2B = ● ; broken line = predicted data).

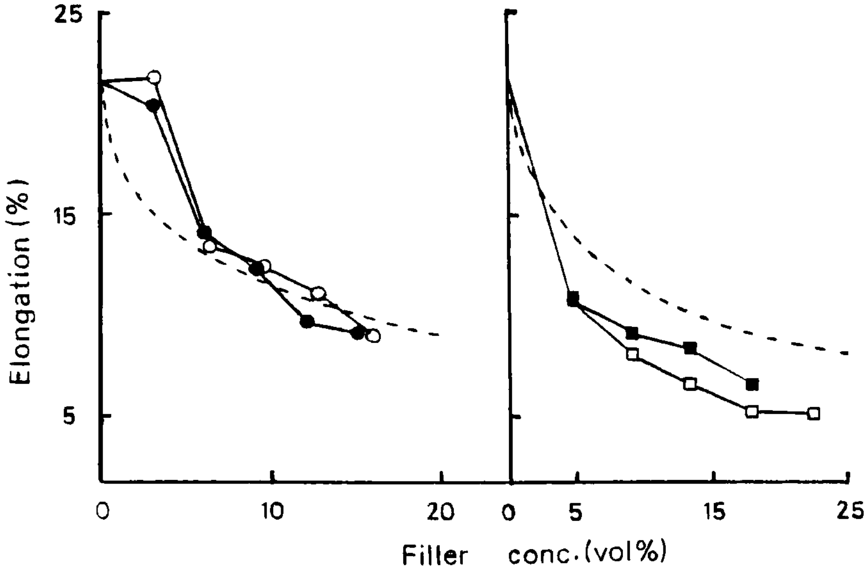

FIGURE 6

Elongation of HPMC/PEG 1000 versus filler content at 20°C, 60% R.H. (Note: talc A = ; talc B = ■ ; TiO_2A = ○ ; TiO_2B = ● ; broken line = predicted data).

concentrations, which in effect are flaws in the film, will enhance film failure and therefore decrease elongation. Filler-polymer interaction decreases polymer chain mobility and hence the deformation capacity of a film. Thus the larger fall in the elongation of talc-filled films may be attributed to a combination of greater filler-polymer interaction (based on the acid-base concept) and higher internal stress.

The larger drop in the elongation of the plasticised system (HPMC/PEG 1000) than that obtained for HPMC/PVA can best be explained in terms of the acid-base concept. PEG 1000 is a plasticiser while PVA is not. Therefore, the plasticised film has a higher deformation capacity (elongation). However, as a result of preferential interaction between the fillers and the polymer additives at the expense of HPMC (see Table 2 for pH data), partial separation of the polymer phase could have occurred, and this would reduce the amount of polymer additives in the HPMC matrix. Elongation fall is therefore greater in HPMC/PEG 1000 films than in HPMC/PVA blends because PEG 1000 is a plasticiser which incidentally also interacts more effectively, than either HPMC or PVA, with the fillers.

CONCLUSIONS

1. The mechanical characteristics of aqueous-based free films of HPMC in combination with either PVA or PEG 1000 and loaded with selected pigments have been measured using a stress-strain method.
2. Attempts were made to relate the stress induced in the films by the pigments, and the degree of pigment-polymer interaction, to the

mechanical properties of the films. Thus although talc created more stress in films (as a result of its plate-like shape) than spherical titanium dioxide, leading to a greater fall in film strength and elongation, application of the acid-base concept indicated talc interacted more effectively with the polymer systems.

3. Hydrophobic surface treatment of titanium dioxide produced reduced film strength probably due to a lower level of filler-polymer interaction.

4. The type of the polymer additive included in a film was found to influence the degree of pigment-polymer interaction and thereby the mechanical properties of films. The polymer additives used (PVA and PEG 1000) were thought to interact more effectively than HPMC with the fillers. Consequently, the reinforcing effects of the fillers on tensile strength and Young's modulus were not fully achieved. In addition, pigmentation led to a sharper drop in the elongation of the plasticised films than would have been expected.

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