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The mechanical properties of pigmented tablet coating formulations and their resistance to cracking
II. Dynamic mechanical measurement

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Summary

The stress relaxation properties of hydroxypropyl methylcellulose films containing iron oxides, titanium dioxide, lakes, or talcs as pigments were measured. Talc was shown to enhance the ability of the films to relax and this was related to the lower incidence of cracking of tablet film coatings containing talc compared with those pigmented by other materials.

Introduction

The rupture of film coatings is a problem which is exacerbated by the inclusion of certain types of pigment in the coating formulation (Rowe 1982). The background to this problem was explained in the first part of this paper (Gibson et al., 1988a) in which we presented static mechanical data on hydroxypropyl methylcellulose (HPMC) films containing pigment particles of various shapes and sizes, and showed how the mechanical properties were influenced by the shape, size and concentration of these particles and by pigment – polymer interaction. These results were related to the incidence of defects in tablet coatings composed of these materials. When a film is extended, part of the applied stress can be dissipated by the deformation of the viscoelastic components of the polymer structure. This reduction in stress as extension is held constant is known as stress relaxation and in this paper it was measured for some tablet film coating formulations in order to relate it to the incidence of edge splitting and cracking on coated tablets.

Materials and Methods

The polymer, HPMC, and the pigments (iron oxides, talcs – two sizes A and B, lakes), together with the method of sample preparation were all described in part I (Gibson et al., 1988a). The

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plasticiser, polyethylene glycol, was also described, but in this work a 6000 mol wt. grade was used in addition to the 200 grade.

The Instron tensile testing machine and Hewlett Packard computer used in that study were also used to measure stress relaxation. The samples were extended at a controlled speed until the stress (calculated from the initial cross-sectional area of the sample and the applied load) reached 10 MPa. This extension was maintained for 2 min, during which time the load was monitored continuously. The samples were then quickly returned to their original length.

An initial upper stress limit of 10 MPa was selected because we found that this was the minimum stress for which reproducible results could be obtained. At higher stresses, there was evidence that the samples were permanently deformed. Some experiments involved varying the extension rate of the samples and this was achieved simply by selecting different crosshead speeds of 1, 10, and 100 mm/min. The standard crosshead speed used for the pigment comparison experiments was 10 mm/min.

The tests were carried out in controlled conditions of 50% relative humidity at 20 °C. The samples were allowed to condition in this atmosphere for one week prior to the test. In one set of experiments the effect of conditioning was examined by storing a second set of samples in a desiccator over silica gel and then testing conditioned and desiccator-stored samples at intervals up to 1 month. This experiment was carried out for samples containing yellow 6 lake, red iron oxide and the coarse talc A, at 5% pigment volume concentration, and also unfilled plain film. The results from 4 samples of each formulation at each time interval were averaged.

Results

The results are discussed in terms of their relative stress, i.e., the ratio of the stress at a time after the attainment of the initial load (σ_t) to the stress at the initial load (σ_0). The S.D. of the average relative stress values was in most cases less than 0.02. The times were precise to within 0.5 s at longer times, and within 0.1 s at times less than 7 s.

The speed of the initial elongation had a marked effect on the pattern of the relaxation of the films. This is because relaxation begins as soon as the stress is applied and so at low rates of extension far more of the stress has been dissipated before the target elongation has been achieved than at high extension rates. A fast extension rate (100 mm/min) was useful to show the differences between the behaviour of different films, but the initial stress attained varied somewhat because of the response time of the instrument. For this reason a rate of extension of 10 mm/min was used as standard. At all speeds, however, the films containing the coarse talc A showed an additional mode of relaxation compared with the other films, the onset of which is directly proportional to the rate of initial elongation (shown on a log (t) scale in Fig. 1). The films were retested after two minutes, but the subsequent log time plots did not show talc to be different from the others apart from in the magnitude of the relaxation.

Some films were retested 2 min after the end of the first test to estimate the recovery of the samples. Most of these had a very similar relaxation the second time, with the exception of the coarse talc A-filled films which relaxed considerably less than the first time, i.e. they had recovered less.

The effect of pigment type on stress relaxation

Fig. 2a shows the stress relaxation curves given by the films containing the iron oxide pigments and titanium dioxide at a concentration of 5% v/v. The unfilled, plain film curve is also plotted for comparison. There is very little difference between the behaviour of the iron oxide-containing films but the titanium dioxide causes less relaxation than is shown by the plain film.

Stress relaxation curves given by films pigmented with both sizes of talc and the red and yellow lakes are shown in Fig. 2b. It is clear that whilst the lakes cause a similar amount of relaxation to those films containing the iron oxide pigments, the coarse talc A-filled film relaxes a greater proportion of the initial stress than any of the other films.

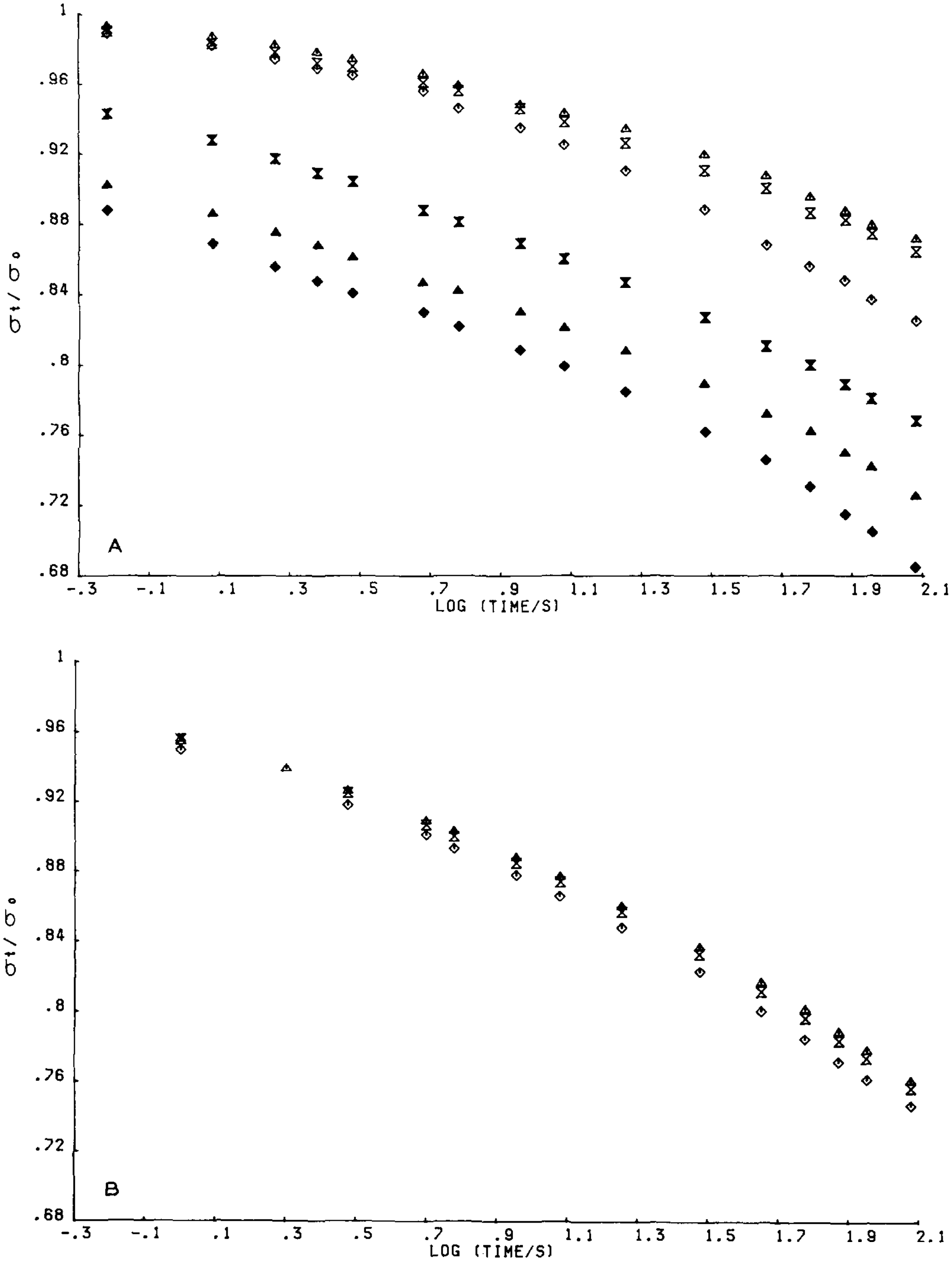

Fig. 1. Relative stress vs log(time) using various extension rates. △, ▲ plain film; ◇, ◆ coarse talc A (5%); ⧖, ⧗ yellow 6 lake (5%). A: open symbols, 1 mm/min; closed symbols, 100 mm/min. B: △, ⧖, ◇ 10 mm/min.

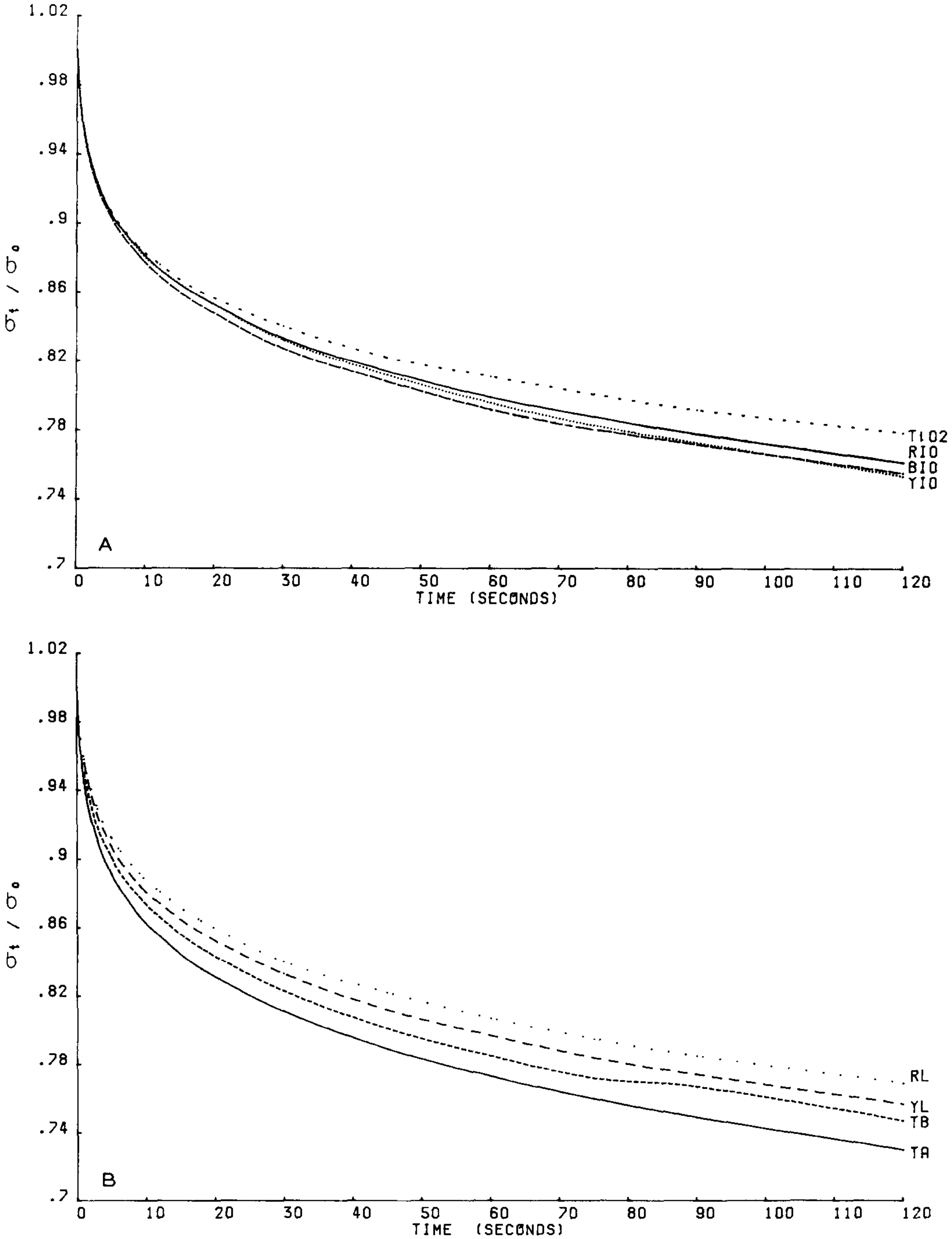

Fig. 2. Relative stress vs time for HPMC films containing 5% pigment. A: RIO, red iron oxide; YIO, yellow iron oxide; BIO, black iron oxide (BID); TiO2, titanium dioxide. B: TA, coarse talc A; TB, fine talc B; YL, yellow 6 lake; RL, red 3 lake.

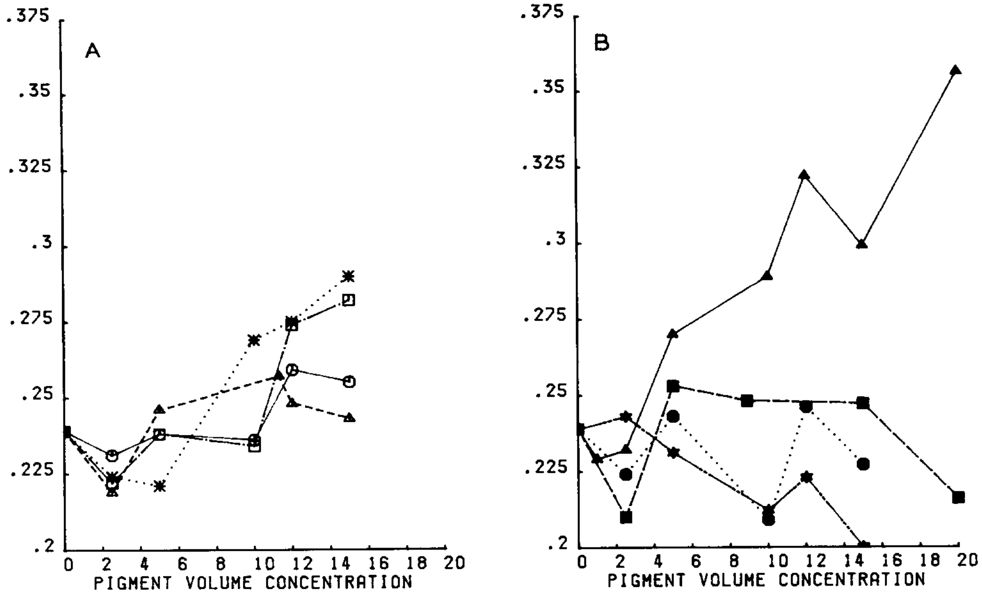

Fig. 3. Relaxation (1 – relative stress) at $t = 120$ s. A: ○------○, red iron oxide; △------△, yellow iron oxide; □——□, black iron oxide; * · · · · · · *, titanium dioxide. B: ▲——▲, coarse talc A; ■------■, fine talc B; ● · · · · · ●, yellow 6 lake; * · · · · · · *, red 3 lake. The lines do not indicate definitive trends and are only included to aid the interpretation of the data.

The effect of pigment concentration on the stress relaxation

For each film the value of $1 - (\sigma_t/\sigma_0)$, which is a direct measure of the amount of relaxation, at $t = 120$ s, i.e. the final value in each experiment, was plotted against pigment volume concentration. The results are shown in Fig. 3. The iron oxide pigments generally promote stress relaxation as their concentration in the films is increased. However, when yellow iron oxide was used, the relaxation increased initially but reached a relatively stable value at concentrations greater than 2.5%. Titanium dioxide also increased the stress relaxation of the films, but only at higher levels of concentration, and then more so than the iron oxide pigments.

The two grades of talc differ in their effect upon the HMPC films. Talc B, which is the finer grade, gives very similar results to yellow iron oxide pigment, i.e. increasing the relaxation to a value of $1 - (\sigma_t/\sigma_0)$ of about 0.25 at 120 s, at 5% concentration and remaining relatively stable up to a concentration of 20% when a reduction in relaxation occurs. The coarse talc A, on the other

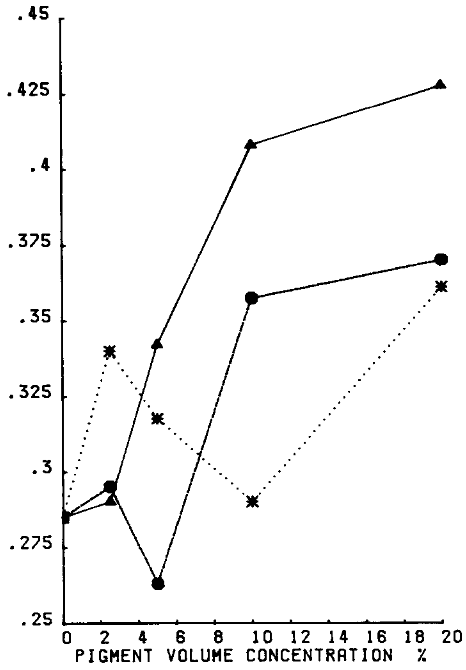

Fig. 4. Relaxation (1 – relative stress) at $t = 120$ s for plasticised films. ▲——▲, Coarse talc A; * · · · · · · *, titanium dioxide; ●-----●, yellow 6 lake. The lines do not indicate definitive trends and are only included to aid the interpretation of the data.

hand, increases the value of $1-(\sigma_t/\sigma_0)$ almost linearly as the concentration of talc is increased.

The films containing the yellow 6 aluminium lake pigment show no consistent change in their stress relaxation behaviour with increasing pigment concentration. The red 3 aluminium lake differs from all of the other pigments in that it causes a reduction in the stress relaxation properties of the filled films as its concentration is increased.

Plasticised films

As expected, the addition of plasticiser to the HPMC enhanced the stress relaxation properties of the material as shown in Fig. 4. The PEG 6000, which is a waxy solid, was much less effective in this respect than the PEG 200. This is not surprising, since the PEG 200 has been found to be the superior plasticiser for HPMC (Sakellariou et al., 1986).

The inclusion of the coarse talc A in the plasticised material in increasing amounts caused the relaxation to increase almost linearly at concentrations up to about 10%, after which the change in relaxation with pigment concentration slowed down. Both titanium dioxide and the lake pigment produced rather different behaviour; the relaxation remained at the same level or was slightly reduced until a certain concentration of pigment was present. Above this concentration (which was 5% for the lake and 10% for titanium dioxide) the relaxation increased to a reasonably high level.

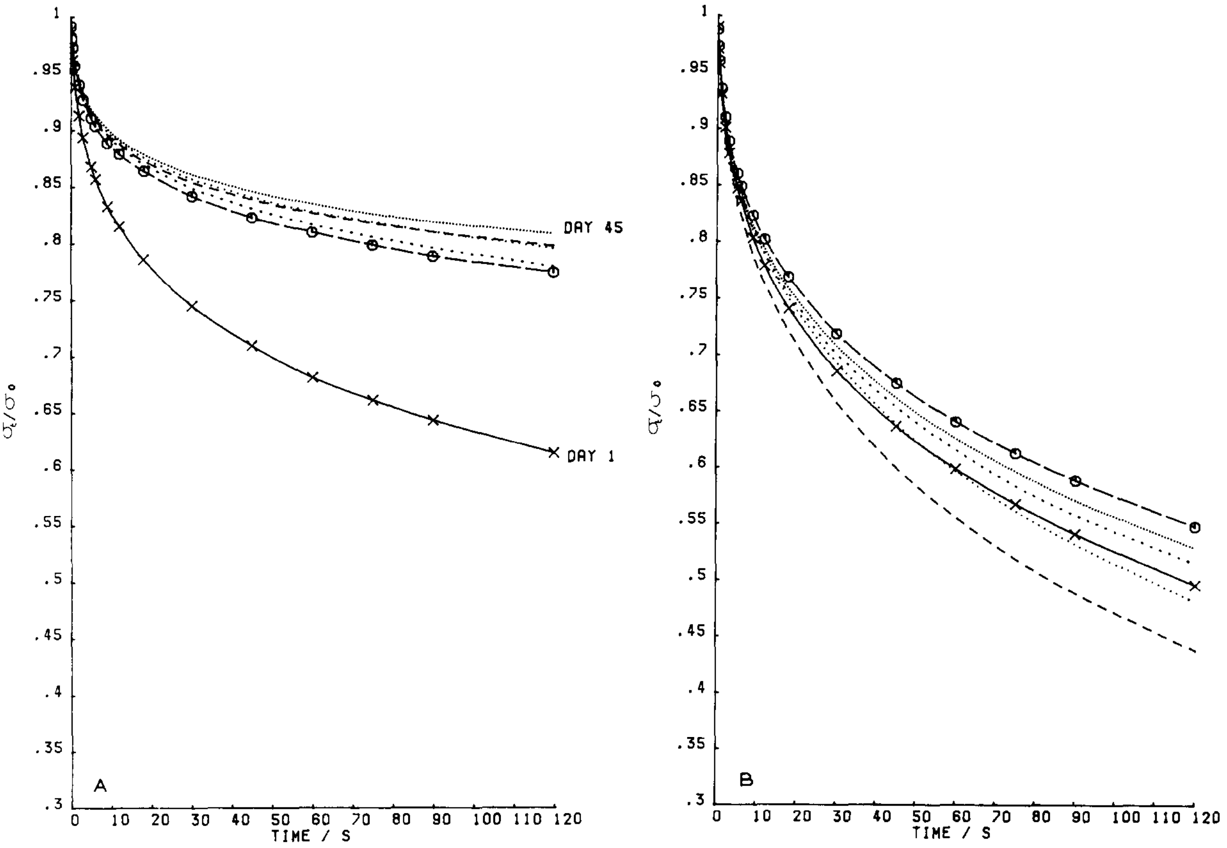

Fig. 5. Effect of conditioning on stress relaxation. × ——— ×, day 1; ○— — —○, day 2; - - - - -, day 4; – – –, day 8; · · · · ·, days 15–20; ·····, days 43–45. A: plain film stored at 20 ° C, 50% relative himidity. B: plain film stored over silica gel at 20 ° C. C: red iron oxide (5%)-filled HPMC stored over silica gel at 20 ° C. D: coarse talc A (5%)-filled HPMC stored over silica gel at 20 ° C. Actual experimental points are only included for two systems. The rest are omitted for clarity.

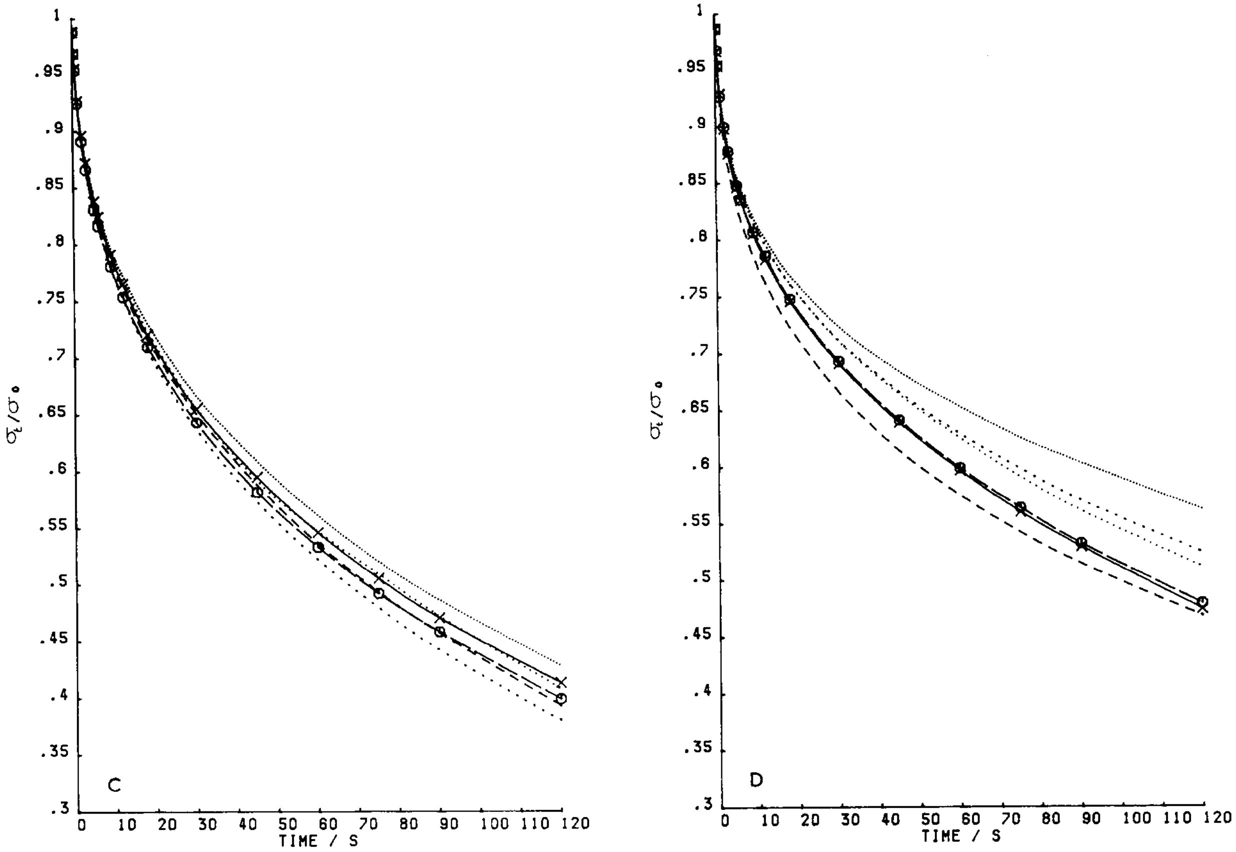

Fig. 5. (continued).

The effect of storage time and conditions on stress relaxation

Fig. 5 shows some of the relaxation curves given by the conditioned and desiccator-stored films. The stress relaxation behaviour shown by the desiccator-stored samples was rather scattered. This is probably because of small differences in the amount of time that each was exposed to the testing conditions of 20 ° C, 50% RH. It was demonstrated, by weighing, that the samples take up moisture rapidly during the first minute or two after removal from the desiccator. Generally, the conditioned samples relaxed to between 0.54 and 0.67 of the applied stress on the first day, depending on the time allowed to condition them. Subsequent tests usually gave very similar results of 0.73 to 0.78, the exception being the red iron oxide-filled film which gave an intermediate result on day two.

The relaxation of the desiccator-stored films generally remained high, but some films, and the talc and lake filled films especially, seemed to show less relaxation after longer storage times. The red iron oxide-filled films gave the most consistent set of results and, together with the lake, the most relaxation. This, coupled with their behaviour as conditioned samples, leads to the conclusion that they are less likely to change their behaviour on contact with moisture than the others.

The effect of combining talc with other pigments

In order to examine the effect of talc on films containing one of the other pigments, films containing 5% of red or yellow iron oxide or lake yellow 6, and, in addition, a further 5% of the coarse talc A were tested. The inclusion of talc in both the yellow and red iron oxide-filled films enhanced the stress relaxation properties to a small extent, whilst the lake-filled film seemed to be unaffected by the talc. None of the films relaxed as much as the one containing 5% of the coarse talc A alone.

The coarse talc A-filled films were conspicuous for their very high stress relaxation, believed to be connected with the lamellar shape of the particles. In order to study this effect more closely, a film containing 5% of graphite was made and tested. "Ceylon" graphite was chosen for this purpose from several grades which were examined by scanning electron microscopy, because it was the most similar in form to the talc A particles. This film was found to show similar relaxation properties to the coarse talc A filled film.

Discussion

Tobolsky (1960) gave a method for deriving a series of discrete relaxation times for materials in the rubbery flow region of the viscoelastic spectrum. This is essentially a curve-fitting technique based on the existence of different modes of relaxation which contribute to an overall relaxation at various times. Thus:

$$E_r(t) = E_{r_1}e^{-t/\tau_1} + E_{r_2}e^{-t/\tau_2} \ldots E_n e^{-t/\tau_n} \qquad (1)$$

By plotting log $E_r(t)$ against t, one can find E_n from the intercept and τ_n from the slope of the straight line part of the graph. Subtracting these values from $E(t)$ and repeating the plot gives various values for E_n. Since each relaxation modulus and relaxation time represents a particular mode of relaxation, it should be possible to relate the number of modes of relaxation to various relaxation processes within the material.

The results from the talc filled and unfilled plain films were treated in this way and four values of E_r and τ were obtained for each material. This was disappointing since it may have been expected that the talc would introduce an extra relaxation mechanism which could be detected by this procedure. However, this relationship was not proposed for polymers in the glassy state, and Tobolsky states that it is really only meaningful for monodisperse polymers. Nielsen (1974) proposed the following equation which was said to predict the creep compliance of some filled materials relative to the unfilled material.

$$\epsilon_{0(t)}/\epsilon_{1(t)} = E_1/E_0 \qquad (2)$$

where $\epsilon_{1(t)}$, $\epsilon_{0(t)}$ are the creep compliances of the filled and unfilled polymer. Since creep and stress relaxation are closely related, i.e. $\sigma_{(t)} = 1/\epsilon_{(t)}$, the above equation could be rewritten as:

$$\sigma_{1(t)}/\sigma_{0(t)} = E_1/E_0 \qquad (3)$$

All of these parameters have been measured in the course of this work for HPMC combined with many different fillers, and so the relationship can be tested for these materials. For the above equation to be valid for materials which increase in Young's modulus as the filler content increases, the stress at time t in a stress relaxation test would need to be greater for the filled polymer than for the unfilled polymer, i.e. the stress relaxation would decrease with increasing filler concentration. A comparison of the Young's modulus values described in part I (Gibson et al., 1988a) with the stress relaxation measurements in this paper shows that of the filled systems studied, this is only true for the red lake and for the yellow 6 lake in as much as the modulus and stress relaxation are more or less unaffected by the pigment volume concentration. According to Nielsen (1974) the increase in stress relaxation as a result of the presence of rigid fillers probably indicates that the particles have become "dewetted" i.e. where the polymer-pigment interface has broken down under the application of stress, leaving void areas in the film.

Many of the pigments studied here have been shown to increase the amount of stress relaxation in HPMC films subjected to a low to moderate tensile stress as their concentrations within the film are increased. The exceptions are the aluminium lake pigments, whilst yellow iron oxide and the fine talc B have little or no effect. Since the metal oxide pigments do not inhibit stress relaxation in the manner described by Nielsen above, the relaxation probably occurs at the interfaces between the pigment particles and the polymer matrix. As the concentration of the pigment is raised, the amount of interfacial surface increases proportionally as does the capacity for relaxation because the increasing non-interactive interface creates voids in the film on application of stress by the dewetting of the particles.

Tobolsky (1960) said that stress relaxation in amorphous polymers below their glass transition temperature occurs as a result of internal crazing, i.e. microcrack formation within the glassy polymer matrix. In part I the effect of fillers as stress concentrators and crack originators was discussed and the presence of a number of large crack sources in the film would inevitably enhance stress relaxation. However, this alone does not adequately explain the greater effect of the coarse talc A and lesser effects of the fine talc B and yellow iron oxide on stress relaxation. The experimental results show repeatedly that films containing the coarse talc A relax a larger proportion of the applied stress at moderate stresses, and that this enhanced relaxation is not repeatable should the sample be retested after a period of no stress. These observations suggest that in these films a distinct mechanism for the release of stress exists which is uniquely associated with the talc.

The main feature of talc which distinguishes it from the other pigments used is the lamellar shape of its particles. It is the ease with which these particles can slip over one another when oriented (e.g. by mechanical force) which gives talc its well-known lubricating properties. The role of this particular shape of filler in the relief of stress was confirmed by the use of graphite in place of the coarse talc A which showed much the same behaviour.

It is likely that the particles relieve the applied stress by the slippage of the oriented flakes of talc over one another. This mechanism would take effect in addition to the formation of microcracks within the glassy polymer matrix. This mechanism would, of course, apply equally to talc filled plasticised films. If the particles actually slip over one another then this would account for the poor "recovery" of the talc-filled films found earlier, because the structure of the films would have changed irreversibly. The slippage of the talc lamellae is hindered by the presence of other types of pigment in the film.

We have shown (Gibson et al., 1988b) that the fine talc B particles are different from those of the coarse talc A, being much smaller, thinner and unable to orient themselves effectively parallel to the surface of the film. They cannot therefore relieve stress in the film in the same manner as the coarse talc A. Since the fine talc B particles are highly anisotropic and randomly oriented (relative to the coarse talc A particles) one might expect that they would exhibit similar behaviour to yellow iron oxide particles if differences due to particle chemistry are insignificant. This does seem to be the case since neither pigment causes any consistent change in the stress relaxation of HPMC.

An alternative explanation for the behaviour of the two talcs concerns the internal crazing of the matrix as mentioned by Tobolsky (1960). The particle would constitute a flaw or crack in the film and these cracks would, in the case of oriented talc A particles, be in the same plane as the tensile stress. The growth of these cracks would result in decreasing the stress within the sample. In the case of randomly distributed anisotropic particles, i.e. the fine talc B and yellow iron oxide, the cracks would form in various directions, and, on average, only a third of them would be in the plane of the applied stress. Of course at the same volume concentration there would be more of these particles and thus more flaws because they are smaller, but the crack radius would also be smaller and so the effect overall would be less.

The red 3 aluminium lake causes the stress relaxation of the HPMC films to decrease when its concentration is increased. This is interesting because the dye used in the lake pigment has been found to decrease the solubility of HPMC (Prilling 1969) i.e. it interacts in some way with the polymer. In part I (Gibson et al. 1988a) we noted that this interaction can reinforce the material and so may also account for the reduced relaxation of films containing this pigment.

The reasons for the reduced relaxation of talc-filled films containing additional pigments, compared with the coarse talc A alone, probably lie with the particle sizes and shapes. It has already been shown that lamellar talc particles are good at relieving stress and so the inclusion of talc in the films should result in an increase in relaxation. It is likely that the highly irregular massive structure of the lake particles hindered the formation of any kind of layer structure in the film, so the talc relaxation mechanism would be unable to operate. The much smaller iron oxide particles would not inhibit the talc lamellae to the same extent. It might have been expected that the presence of a mixture of lamellae and spheres in the film would be more conducive to stress relaxation than lamellae alone because the spheres could act as "rollers" between the talc layers. However, it seems that this is not the case; the small particles restrict the larger flaky particles, probably because they are fixed within the matrix.

The "recovery" of the materials, as determined from consecutive relaxation tests on the same sample, gives an indication of the type of processes which may be taking place within the films when stressed. It is unlikely that the films actually recover to any appreciable extent over a short period of time, but the occurrence of similar relaxation patterns when they are stressed a second or subsequent time arises because the fundamental structure and properties of the material were almost unchanged by the first relaxation experiment. In the case of the coarse talc A, where the slippage of talc particles or catastrophic crack formation had caused irreversible changes to take place in the structure of the film, it responded to the second application of stress in a different way because the talc-specific relaxation mechanism would already have been partially exploited.

The apparent increase in relaxation with increasing speed of initial elongation is simply due to the fact that the films begin to relax the stress as soon as it is felt, and so if it is applied at a slow rate, a significant proportion of the relaxation will have occurred before the measurements actually begin. This is reflected in the changes of rate of relaxation noticable in the plot against log time which occurs at times directly proportional to the rate of initial elongation (Fig. 1). Since the stress decays in an approximately exponential manner, this would seem reasonable and confirm that the changes in the relaxation rate are real phenomena. The irreversible nature of the coarse talc A relaxation mechanism was evident again as the change in relaxation rate after about 30 s did not occur if the sample had been retested previously.

Plasticisation of the polymer encourages stress relaxation because the plasticiser increases the free volume of the polymer, making it less rigid and more able to adapt to the applied stress. This is demonstrated clearly by the fact that the lower molecular weight polyethylene glycol produced the most stress relaxation.

Internal stress and stress relaxation

It is well known that internal stress exists within solvent cast films as a result of shrinkage during solvent loss and differences in thermal expansion coefficients between the film and the substrate. Rowe (1981) examined this phenomenon and estimated the magnitude of these stresses in HPMC films applied to tablets. The differences in stress relaxation behaviour between the films stored in a desiccator and those left in humid conditions demonstrates the relative ease with which the films can relax the internal stress built up during the film-forming process. This is because if stress relaxation has already begun within the sample, it will not relax to as great an extent during the test. During the first couple of days of the experiments at 50% RH and 20 ° C, the measured stress relaxation of the samples became less, indicating that during storage the polymer was adapting to the constant but diminishing internal stress.

That the films stored in a desiccator gave very large amounts of stress relaxation throughout the experiment can only be because the lower humidity of the storage conditions in some way inhibited the relaxation of the internal stress. The unfilled plain and talc-filled films stored at low humidity relax less than the red iron oxide and lake-filled films and this is in contrast to the results at higher humidity. It therefore seems likely that the relief of internal stress by the samples must occur by a different mechanism from that which takes place under applied tensile strain. Since this type of relaxation is moisture-dependent and inhibited by the lake and red iron oxide pigments, the relaxation probably takes place by the slow accommodation of the internal stress by reorganization of the polymer molecules. The presence of moisture would have a plasticising effect on the polymer and so the molecules would be able to move more freely and the relief of the internal stress would proceed more quickly. The talc particles do not impede this action because their potential for slippage provides internal lubrication, but the lake and iron oxide particles do. Inoue (1943) demonstrated that the inclusion of flaky particles does not increase the measured internal stress of benzyl cellulose films, although other pigments cause an increase in internal stress as their concentration is increased.

The relationship between stress relaxation and edge splitting in coatings

In part I (Gibson et al. 1988a), we discussed the influence of pigments on the incidence of edge splitting of coatings on tablets. This showed that the inclusion of talc in a coating actually reduced the incidence of edge splitting, relative to coatings containing the other pigments, or even no pigment at all. This was despite the fact that talc-filled films showed a high Young's modulus, which with all other pigments was severely detrimental to the integrity of the coating.

From the results presented here it is clear that the reason for this effect is that the talc promotes relaxation in the films by virtue of the shape of its particles. This means that the build-up of internal stress to high levels during the drying process is prevented because the stress is relieved by the movement or orientation of the talc particles. Therefore the residual internal stress in the dried coating will be less than otherwise and so the incidence of edge splitting is reduced. The inclusion of plasticisers in the formulation also reduces edge splitting (Okhamafe and York, 1985) and this is also due to the enhanced relief of stress by the increase in polymer free volume which also promotes stress relaxation as shown in Fig. 3

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