The mechanical enhancement of physical aging

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The effect of physical aging on the tensile creep properties of rigid PVC and PMMA was investigated at three temperatures between the glass transition temperature T_g and room temperature. The results confirm Sternstein's claim that mechanical stresses may enhance aging, but also our previous conclusion that such effects occur only at strains larger than 0.3–0.5%. It is further shown that the term 'enhancement' should, preferably, be avoided.

INTRODUCTION

We have discussed previously the effect of physical aging on the mechanical creep behaviour of amorphous glassy polymers[1–5]. Aging was shown to be a spontaneous phenomenon, occurring in the material irrespective of whether it is tested for creep or not (cf pp 166–167 of ref 4 or p 12 and *Figures 6* and *7* of ref 5). Only for high stresses, producing creep strains greater than 0.3–0.5%, was aging found to be influenced by mechanical stress (cf ch. 8 of ref 5).

The spontaneous nature of physical aging is further supported by the fact that its influence on dielectric relaxation[6–9] is very similar to the influence on mechanical creep at small strains.

Yet, Sternstein's results[10–12] appeared to raise some doubts concerning our interpretation. He claimed that much of the aging observed in tests with strains around 0.5% is due to a mechanical enhancement of a spontaneous aging process that is, in itself, rather unimportant. In view of the apparent discrepancy with our results, we investigated this point in somewhat more detail than before, viz. by performing creep/aging tests on rigid PVC and PMMA at a number of temperatures below their T_g.

EXPERIMENTAL

The materials studied were the PVC No. 3 and PMMA No. 24 of tables B1 and B2 of ref 5 (pp. 210–213); in order to reduce possible internal stresses, they were pre-annealed as described previously (see p. 201 of ref 5). The tests were made with the automatic tensile creep tester of Appendix A5 of ref 5 according to the procedure described in ch. 3 of ref 5.

RESULTS

Small-strain creep data

The results of the small-strain tests, which compare with those of ch. 4 of ref. 5, are summarized in *Figures 1–3* (PVC) and *Figures 4–7* (PMMA).

The samples were tested at three temperatures, one close to T_g, the second around room temperature and the third in between these limits. For each measuring temperature T, the sample was quenched three times from a temperature T_0 somewhat above T_g to T. After each quench, we measured the creep properties for a number of aging times, t_e, using the test routine shown in the insert of *Figure 1*; it is identical to that described in ch. 3 of ref 5. For the first two quenches, the creep tests were made at values of t_e of 0.35, 0.75, 1.5, 3, 6 and 12 h. These two aging tests were simply duplicates, made to check the reproducibility. For the third quench, we omitted the creep tests at t_e = 0.35, 0.75 and 1.5 h and only measured the creep at t_e = 3h. By comparing the results of the third quench with those of the first two quenches, we can find out immediately whether the creep at t_e = 3 h is influenced by the execution of the tests at 0.35, 0.75 and 1.5 h; such influence should be observed when mechanical enhancement of aging occurs.

Figures 1–3 show that the tests on PVC are well reproducible. For PMMA, the reproducibility is somewhat less,

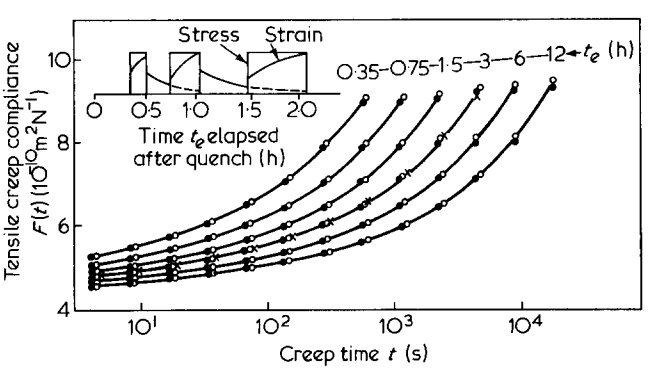

Figure 1 Small-strain tensile creep (σ = 1.8 MN m^{-2}, strain $\epsilon < 0.17\%$) of rigid PVC quenched from 90°C (i.e. about 10°C above T_g) to 60°C. The different curves were measured for different values of the time t_e, elapsed after the quench. The sequence of creep and recovery tests used is given in the insert; the corrections for recovery effects were made as described in ch. 3 of ref. 5 and in the Appendix here. All tests were made with one sample. ○, first quench; ●, second quench (the results show that the data are reproducible); X, third quench; only the creep at t_e = 3 h was measured. The results show that the tests at t_e = 0.35, 0.75 and 1.5 h do not influence the creep at t_e = 3 h

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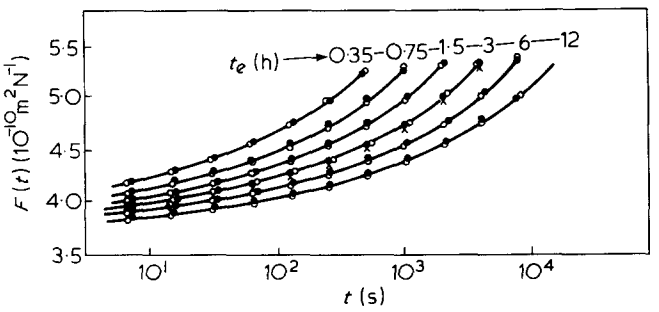

Figure 2 As for *Figure 1*, but now for a quench from 90° C to 40° C; σ = 3.4 MN m^{-2}; ϵ < 0.19%

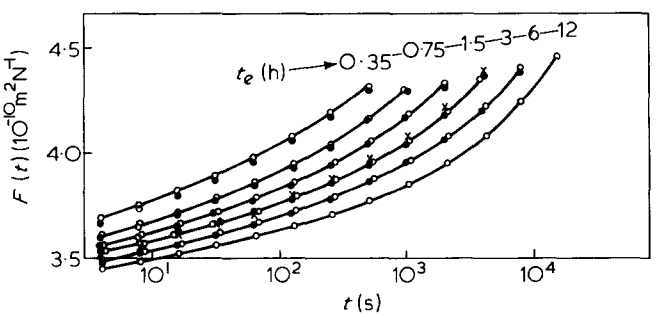

Figure 3 As *Figure 1*, but now for a quench from 90° to 20° C; σ = 4.9 MN m^{-2}; ϵ < 0.22%

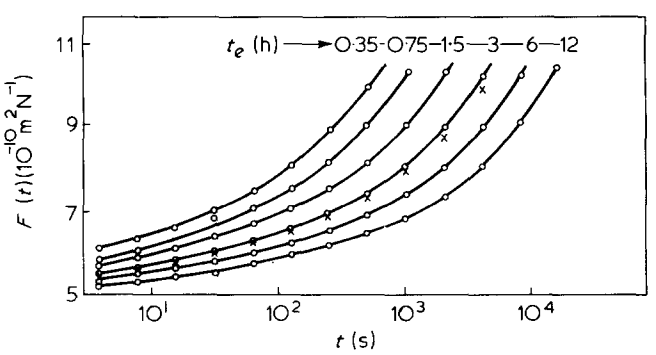

Figure 4 As *Figure 1*, but for PMMA, quenched from 115° to 90° C; σ = 1.55 MN m^{-2}; ϵ < 0.16%; the data for the second quench are omitted for reasons explained in the text

but still reasonable. In order to avoid overcrowding in *Figures 4–6*, we have omitted the results of the second quench in these diagrams. An impression of the non-reproducibility of the PMMA data can be obtained from *Figure 7*. We observe a systematic shift between the creep curves obtained after the two quenches; however, this shift is much smaller than that produced by the change in aging time from 0.35 to 6 h. The origin of the non-reproducibility of the PMMA data is unknown.

Figures 1–6 show that *at small strains* (the amount of strain is given in the legends to *Figures 1–6*), *there is no effect of mechanically enhanced aging*; in all cases, the test at t_e = 3 h is not influenced by the execution of the three earlier tests at t_e = 0.35, 0.75 and 1.5 h. This agrees with our ealier findings (cf *Figures 6* and *7* of ref 5), and shows that there is nothing wrong with our earlier small-strain data nor with the interpretation of the aging effects.

High-strain creep data

To detect the alleged mechanical enhancement of aging, the small-strain tests were repeated at high strain levels.

For PVC, the measurements were made at 20°C, for PMMA at 30°C. The results are shown in *Figures 8* and *9*; the creep data are presented as curves of the 'apparent creep compliance' $F(t) = \epsilon(t,\sigma)/\sigma$ *versus* time.

The tests were carried out at stress levels of 10, 20 and 30 MN m^{-2}, resulting in creep strains of roughly 0.4, 1.0 and 1.8%. The data show that mechanical enchancement of aging is still negligible for σ = 10 MN m^{-2} (i.e. at strains up to 0.4%). The enhancement only appears for stresses of 20 and 30 MN m^{-2} (i.e. for strains of 1.0–1.8%) and is still very modest at 1% strain (σ = 20 MN m^{-2}). *The present*

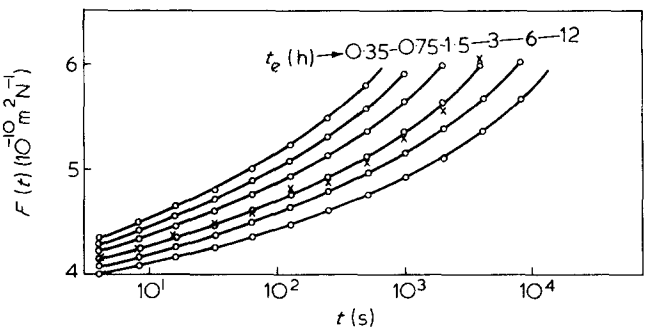

Figure 5 As *Figure 4*, but for PMMA quenched from 115° to 60° C; σ = 2.8 MN m^{-2}; ϵ < 0.17%

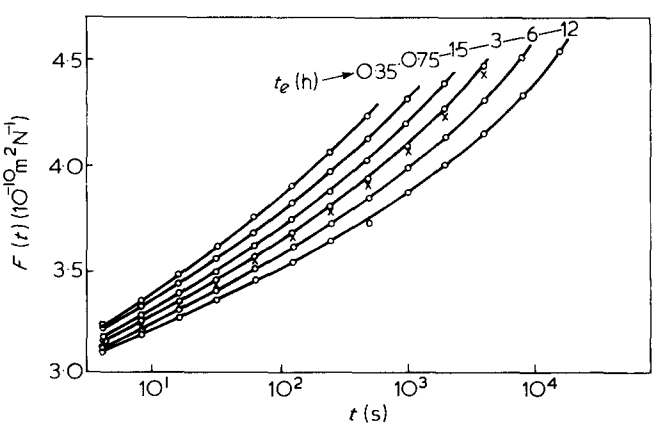

Figure 6 As *Figure 4*, but for PMMA quenched from 115° to 30° C; σ = 4.9 MN m^{-2}; ϵ < 0.22%

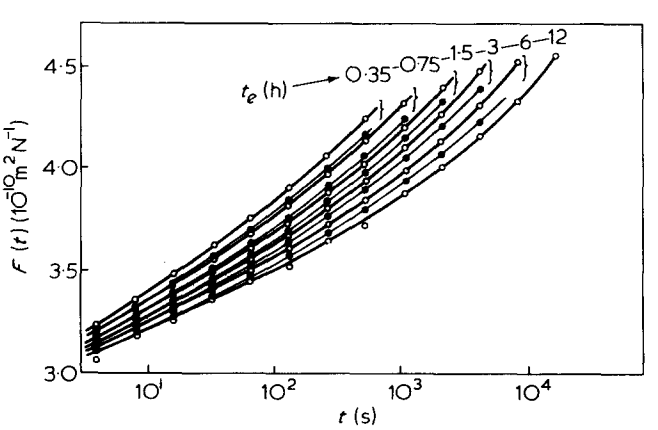

Figure 7 As *Figure 6*, but now only the results obtained after the first two quenches are given; for the second quench, the creep test at 12 h has not been performed

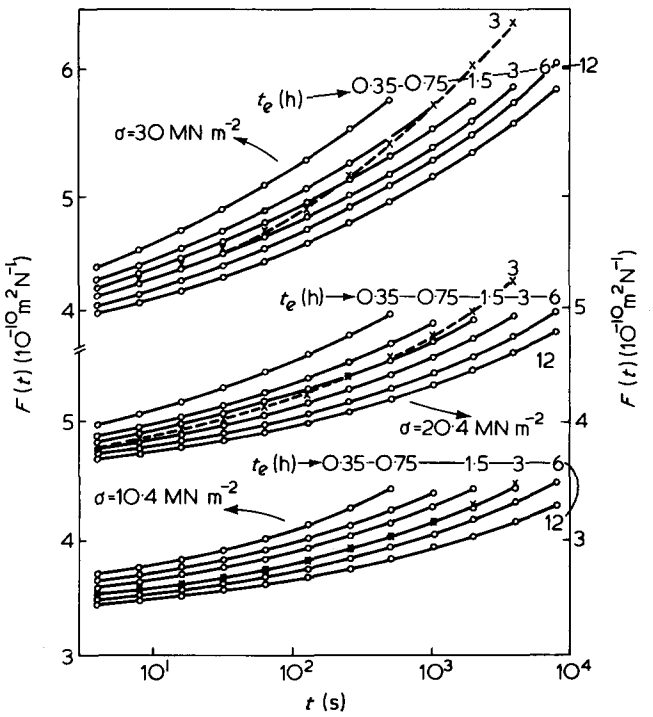

Figure 8 Tensile creep of rigid PVC quenched from 90° to 20°C and subsequently tested at different values of aging time t_e. ○, first quench, according to the procedure outlined in the insert of *Figure 1*; X, second quench with a new sample; the creep tests at t_e = 0.35; 0.75 and 1.5 h were omitted and only the creep at t_e = 3 h was measured. The three families of curves pertain to three different stress levels; the corresponding maximum creep strain amounted to 0.4, 1.0 and 1.8%. Note that for the three stress levels, the vertical scales are shifted

data thus confirm Sternstein's claim that mechanical stresses may enhance aging; however, in creep tests, the effect is only observed at strains above 0.4%.

Actually, the test procedure of *Figures 1–9* is not identical to that of Sternstein. He used an intermittent loading sequence, such that the elapsed time increases in an arithmetic progression. In our procedure (cf *Figure 1*) the t_e values increase in a geometric progression. Therefore, we repeated the tests of *Figure 8*, but now according to Sternstein's procedure. However, the results given in *Figure 10* do not differ from those of *Figure 8*.

DISCUSSION

At first sight, the present conclusion that a high stress may enhance aging seems to contradict the earlier one that a high stress erases the previous aging, i.e. de-ages the sample (see ch. 8 of ref 5). However, this contradiction is only apparent.

To show this, we have summarized in *Figure 11* the experimental findings obtained so far. Two types of aging tests have been used. In the first, type 1, the quench is followed by a sequence of creep and recovery tests (cf insert of *Figure 1*). The result is a family of creep curves for a number of values of aging time t_e. The position on the time scale of these creep curves depends on the magnitude of the stress.

For a low stress (linear viscoelastic behaviour), the creep curves are not influenced by the magnitude of the stress, and the same holds for the aging behaviour. This case is dealt with under *Small-strain creep data* above and in most of our previous work (except ch. 8 of ref 5).

For a high stress, the creep is accelerated, and the creep curves still shift to longer times with increasing aging time t_e (see *Figure 11*, type 1, high stress). This case is dealt with under *High-strain creep data* above.

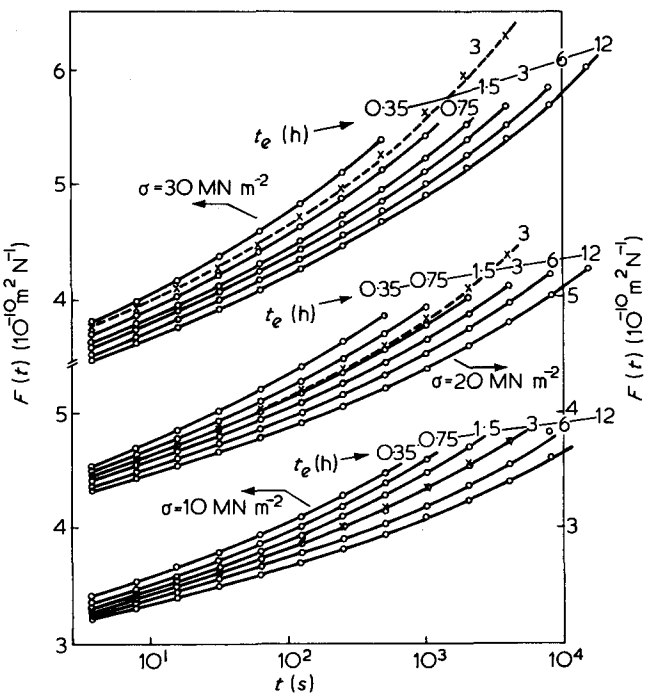

Figure 9 As *Figure 8*, but for PMMA quenched from 115° to 30°C. The stress levels and maximum creep strains are roughly the same as in *Figure 8*

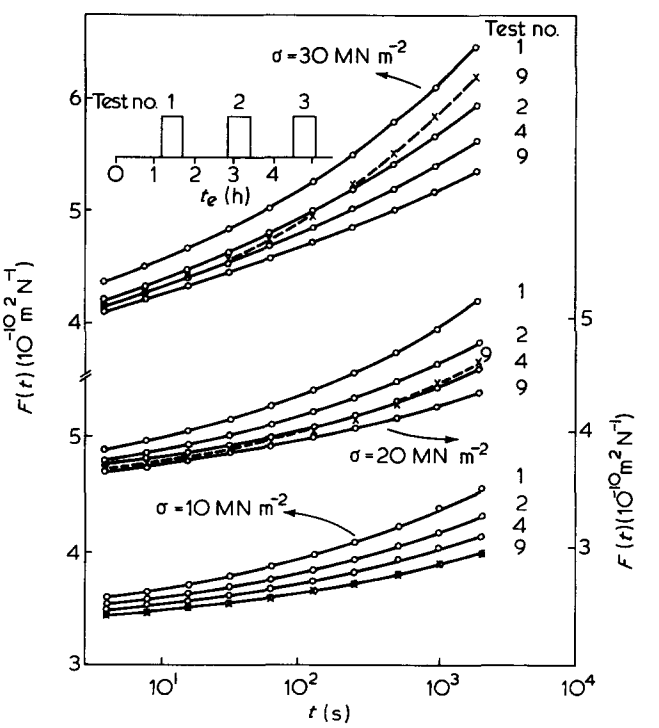

Figure 10 As *Figure 8*, but the creep tests were not made according to the procedure of *Figure 1*, but according to the intermittent loading sequence (4096 s off, 2048 s on, etc.) shown in the insert. ○, first quench; the curves are the results of tests 1, 2, etc.; to avoid overcrowding, the results of the tests 3, 5, 6, 7 and 8 are not shown. X, second quench with a new sample; the tests 1–8 were not performed

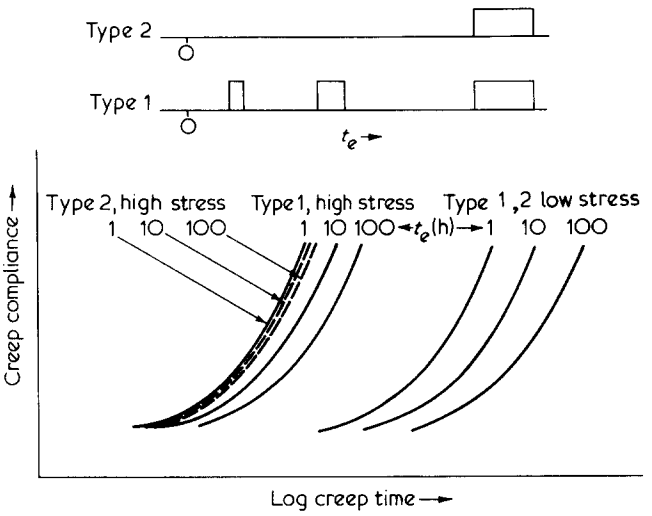

Figure 11 Effect of stress level on the aging behaviour as measured by the two types of creep/aging tests made so far; for details see text

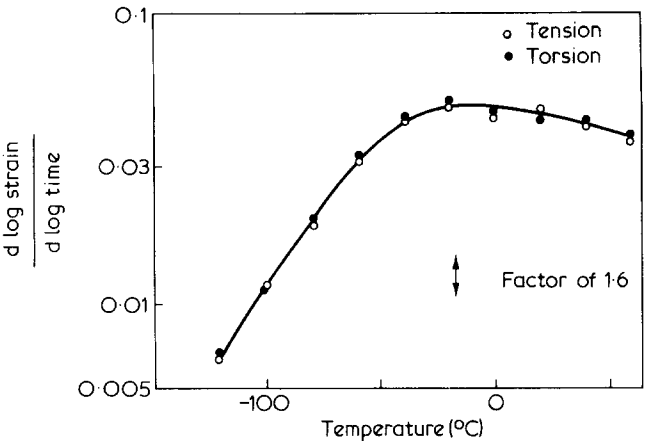

Figure 12 Double-logarithmic creep rates of PMMA at a creep time of 100 s

In the second type of experiment (see *Figure 11*) only a single creep test has been performed after each quench; so, to obtain the creep properties at, say, four values of t_e, four quenches have been performed. This type of test is dealt with in section 8.1 of ref 5; the crosses in *Figures 1–9* have been obtained with this type of experiment. The previous data show that, in this type of test, the aging effects disappear when the stress level is sufficiently high (cf *Figures 59–63* of ref 5). This disappearance of aging is summarized in *Figure 11* by drawing the high-stress creep curves obtained with this second type of test (broken lines) close to one another. At low stresses, the influence of the magnitude of the stress level disappears and the type 1 and type 2 tests give identical results (cf *Figures 1–6*). This has been indicated also in *Figure 11*, which should be considered as an extension of *Figure 63* of ref 5.

We now turn from empiricism to interpretation. First, a remark about Sternstein's interpretation. In our opinion, he has compared the high-stress results of a type 1 test with the high-stress results of a type 2 test, and has therefore concluded that the deformation process is the prime origin of aging (*Figure 11*). This does not appear a reasonable interpretation to us; at very low stress levels, aging is still observed, independent of the previous deformation. In view of this, the term 'mechanical enhancement of aging' is confusing, the more so because, in general, the aging effects are most pronounced even at the lowest stress level. This can be seen in *Figure 8*, but more clearly in *Figure 81* of ref 5, where, in the type 1 tests, the aging effect largely disappears at the stress level of 35 MN m^{-2} (strain ~ 2.5%).

Our second remark concerns the stress levels at which the 'mechanical enhancement of aging' is observed. Our creep data (*Figures 8–10*) suggest that the effects are only significant at strains above, say, 0.5–1.0%. Sternstein's stress relaxation data[11–12] suggest that the effects can be seen already at much lower strains. However, care must be taken in comparing the strain levels in creep and stress–relaxation tests. If, in a stress–relaxation test, a strain of, say, 0.5% is prescribed, the initial stress may be much higher (factor of 2–3) than the creep stress which produces the same strain after, say, 1 h. So, the apparent discrepancies between Sternstein's and our data may be due to the fact that in stress–relaxation tests, the non-linear viscoelastic region is reached at lower strains than in creep.

Another indication for this is found in Sternstein's first paper on this subject[10], in which he reported that, at strains of about 0.5%, the double-logarithmic stress–relaxation rate of PMMA at 30°C is a factor of 1.6 higher in torsion than it is in tension. This is at variance with linear viscoelastic theory[13]. Therefore, we suggest again that the stress–relaxation data suffered from non-linear effects.

We have repeated these experiments by performing small-strain creep tests in torsion and in uniaxial extension on the same PMMA as dealt with in the Results section above. The tensile strains and the maximum shear strains in the surface of the twisted torsion sample were kept below 0.2%.

The creep tests were carried out at −120°, −100°, −80° . . . +40° and +60°C. Before each individual test, the sample was heated to 110°C, next quenched to the measuring temperature, and finally tested after an aging time t_e of 2 h.

From the resulting creep curves, we calculated the shear compliance $J(t)$, the tensile compliance $F(t)$ and the double-logarithmic creep rates d log $J(t)$/d log t and d log $F(t)$/d log t. For a creep time of 100 s, these rates are given in *Figure 12;* obviously, there is no significant difference between the creep rates in torsion and in tension, provided the material is tested in the linear viscoelastic region. According to linear viscoelastic theory, the same must then hold for the double-logarithmic stress–relaxation rates.

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APPENDIX

The small-strain creep tests of *Figures 1–7* were conducted according to an intermittent loading sequence, part of which is shown in *Figure A1*. Owing to recovery effects, the strain during test 2 depends on the loading during test 1, and similarly, all later tests will be influenced by the recovery from the earlier loadings.

To correct for the mutual interference of the different tests, we measured the strain as a function of time over each recovery period. Each recovery curve was then extrapolated over the period of the next creep test (dashed lines in *Figure A1*), and in this way (see third creep test in *Figure A1*), the interference between the different tests was corrected for.

At first sight, this procedure seems rather unreliable, because each creep test lasts about as long as the previous recovery period (*Figure A1*). However, the actual situation is less unfavourable. This is illustrated in *Figure A2* for the special case of the second creep test. Empirically, it appears that the curves obtained when the recovery is plotted *versus* the logarithm of the recovery time are fairly smooth. Actually, the recovery is measured over at least 2.5 decades of time (the minimum recorded recovery time is about 4 s, the maximum 928 s for the first creep test, 1676 s for the second, etc.). The extrapolation over the next creep period adds no more than 1/3 of a decade to the 2.5 decade wide interval (see *Figure A2*), strongly suggesting that the extrapolation cannot be very inaccurate.

The qualitative argument given above can be illustrated by a quantitative example. The creep curves shown in *Figures 1–7* obey the formula (see ref 5):

$$F(t) = F_0 e^{(t/t_0)^m} \; ; m \sim 1/3 \qquad \text{(A1)}$$

Theoretical curves according to this equation are plotted in *Figure A3* for various values of t_0. We compare these curves with the experimental ones of *Figures 1–7*, measured at the shortest t_e value, viz. 0.35 h. *Figure A3* shows that the relative changes in compliance between $t = 4$ and $t = 512$ s increase with decreasing t_0. Comparison with *Figures 1* and *4* show that, in our experiments, t_0 varied from about 1000 s at the highest temperatures (*Figures 1* and *4*) to 3×10^4–10^5 s at the lowest (*Figure 3*). The theoretical recovery after the first creep test is given by:

$$\epsilon(t) = \sigma_0 \{F(t + t_1) - F(t)\} \qquad \text{(A2)}$$

where t = recovery time, $t_1 = 512$ s = first creep time and σ_0 = stress level.

Applying equation (A1), we obtain:

$$\frac{\epsilon(t)}{\epsilon_1} = \frac{F(t + t_1) - F(t)}{F(t_1)} = \frac{e^{(t+t_1/t_0)^{1/3}} - e^{(t/t_0)^{1/3}}}{e^{(t_1/t_0)^{1/3}}} \qquad \text{(A3)}$$

where ϵ_1 denotes the strain at the end of the first creep period. The recovery curves according to equation (A3) are plotted for $t_0 = 1000$ and $t_0 = 3 \times 10^4$ sec in *Figure A4*. Extrapolation of the curves measured up to $t = 928$ s over the period of the second creep test ($t = 928$–1952 s) will be quite accurate. Recovery during the second creep period is only a few per cent of the maximum strain during the first creep test. Consequently, the uncertainty in the extra-

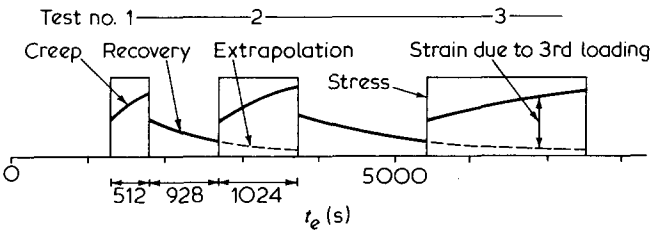

Figure A1 Outline of the intermittent loading sequence and of the way in which the corrections were made for the recovery effects

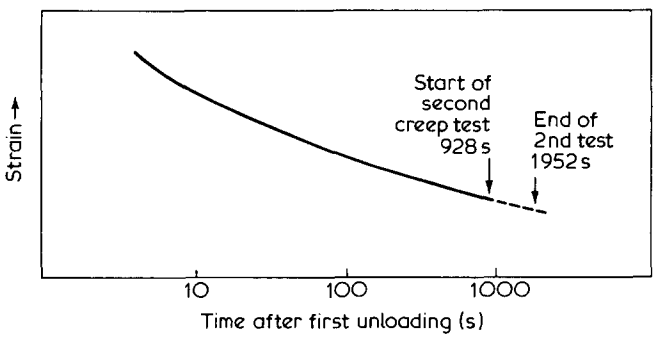

Figure A2 Recovery between the first and second creep test of *Figure A1*; schematic

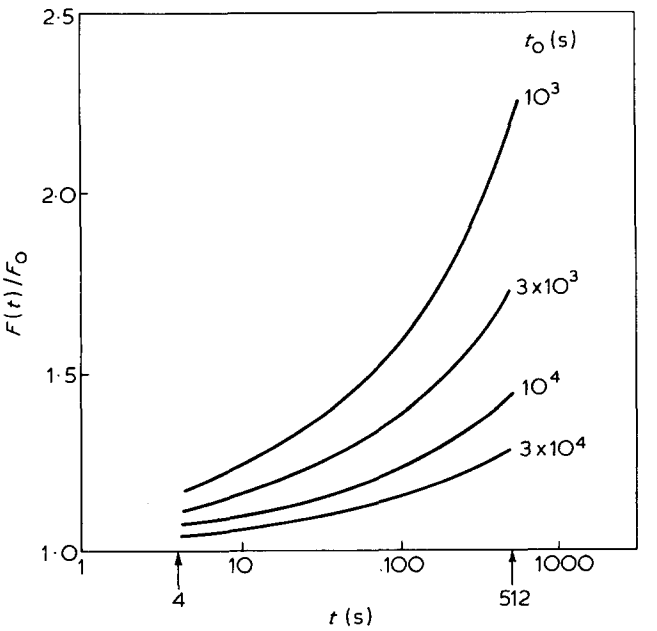

Figure A3 Creep curves according to equation (A1) for various values of t_0; note that the creep times in the $t_e = 0.35$ h tests of *Figures 1–7* varied between 4 and 512 s

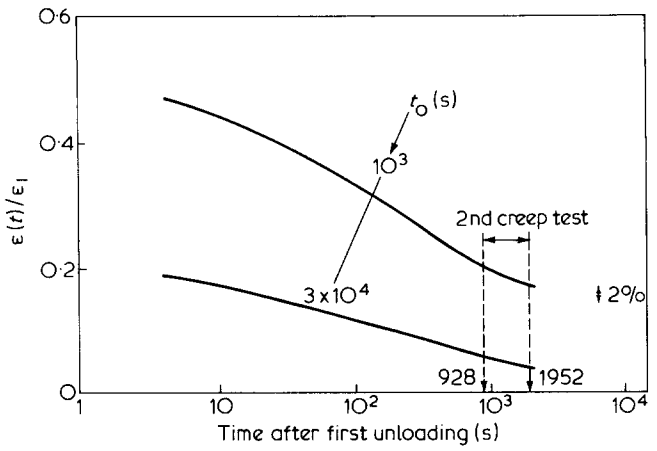

Figure A4 Recovery curves according to equation (A3); for details see text

polation will be less than, say, 1%. Similar results can be obtained for the recovery after the 2nd, 3rd, etc. creep test.

For the *large-strain region* (*Figures 8* and *9*), the deviations from linear viscoelastic behaviour are not very large. The apparent compliances are only 10–40% larger than the small-strain compliances (compare the 10 and 30 MN m^{-2} curves at equal t_e-values in *Figures 8* and *9*). Further, the creep curves are not curved more strongly at the high stress level (30 MN m^{-2}) than at the low one (10 MN m^{-2}). Therefore, for high stress levels, the correction procedure is expected to work just as satisfactorily as for low stresses; experience has confirmed this.

However, it should be realised that the method corrects only for the time-dependent recovery strains. It cannot correct for the changes in material properties induced by tests at high stress levels (cf p 11 of ref 5).