Creep and recovery of unvulcanized natural rubber

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The creep and recovery behaviour of unvulcanized natural rubber, both filled and unfilled, is investigated under low stresses in tension at room temperature. A method based on the Boltzmann superposition principle has been used to predict the creep function from measurements of its recovery after release from a range of constant loads each held for various lengths of time (t_1). For both gum and carbon black-filled rubbers of a given Mooney viscosity, the technique resurrects a master creep curve which is found to be independent of t_1. Although this has the same general shape as the experimental creep curve the two differ significantly, except for the filled rubber at small stresses. The discrepency is ascribed to non-linear effects mainly associated with the tendency of the unvulcanized rubbers (especially the gum rubber) to flow at high applied tensile stresses and long times. Under such conditions the superposition principle is no longer valid. This non-linear effect due to flow can be approximately corrected for by substracting the experimentally measured permanent set from the creep and recovery data before treating the remainder with the Boltzmann superposition principle. This method of correction yields good agreement between the revised experimental creep and the derived creep compliances for gum rubbers up to $\sigma = 0.50$ kg cm^{-2}, and for black-filled rubbers up to $\sigma = 0.78$ kg cm^{-2}.

INTRODUCTION

The flow and recovery behaviour of unvulcanized rubbers is of relevance to the processing characteristics of such materials. This behaviour is generally complicated and non-linear viscoelastic effects are frequently of significance. However, there may be regions where essentially linear viscoelastic theory would be of help in treating flow and recovery measurements. The most appropriate approach would seem to be the Boltzmann superposition principle, which may be considered the fundamental theorem of linear viscoelasticity.

Considering the importance of this principle, rather little work has been done to check its direct applicability to the materials of present concern. As the flow and recovery of the material are of particular interest, the relatively simple method of loading under constant force for a given time in simple extension was adopted, followed by the measurement of the recovery with time after removal of the load. Previous studies along these lines have been carried out by, for example, Leaderman[1], Jordan[2], and Becker[3]. More recently, a study of the recovery of unvulcanized rubbers has been carried out by Djiauw and Gent[4], where a specimen of rubber is subjected to partial stress relaxation in simple extension at stretch ratio λ_0 and then cut to allow it to retreat. These last workers found that in all cases the delayed recovery followed a simple empirical time function:

$$R(\%) = 100[1 - \exp\{-0.85(t/t_s)^{0.42}\}]$$

where t_s is the period of prior deformation. This relation, however, is not easily applicable in terms of the superposition principle, and the applicability of the principle was not discussed. Their experiments were not designed with this interpretation in mind; results obtained from their technique of using a constant extension (with a consequently decreasing force) followed by recovery under zero load, do not readily lend themselves to analysis based on the principle. They analysed the recovery behaviour in terms of a two-network (both neo-Hookean or Gaussian) model[5] in which the original ('old') entanglement network is partly replaced by a 'new' network whose strands are in their equilibrium distribution of configurations in the state of strain λ_0, while the total number of network strands remains constant. This recovery after partial stress relaxation technique has been extended by Taylor and Ferry[6] to the study of the non-linear stress relaxation of polyisobutylene, where it is found that the old network in extension is best described by a Mooney–Rivlin formulation and the new network in compression by a neo-Hookean. This paper will mainly concern the creep and recovery of unvulcanized natural rubber, both filled and unfilled, in tension at room temperature.

THEORY

For a linear viscoelastic material, the stress σ and the strain γ may be connected by a relation based on the Boltzmann superposition principle. The stress σ at time t is given by:

$$\sigma(t) = \int_{-\infty}^{t} G(t - t_1)\dot{\gamma}(t_1)\mathrm{d}t_1 \qquad (1)$$

where $\dot{\gamma} = \mathrm{d}\gamma/\mathrm{d}t$ is the strain rate, $G(t)$ is the relaxation modulus, and the integration is carried out over all past times t_1 up to the current time t.

An alternative relation can be written to express the strain in terms of the stress history in the form:

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$$\gamma(t)=\int_{-\infty}^{t} J(t-t_1)\dot{\sigma}(t_1)\mathrm{d}t_1 \qquad (2)$$

where $\dot{\sigma}=\mathrm{d}\sigma/\mathrm{d}t$ and $J(t)$ is the creep compliance.

In a creep experiment where a constant stress σ is applied to the material for the period $t=0$ to $t=t_1$ and then removed, the strain at a subsequent time can be considered to arise from the superimposed effect of $+\sigma$ applied at $t=0$ and a stress of $-\sigma$ applied at $t=t_1$. Thus the rate of deformation will change sign at time t_1, and the body gradually return to its initial state. The remaining deformation at time t is, by applying equation (2):

$$\gamma(t)=\sigma[J(t)-J(t-t_1)] \qquad (3)$$

Rewriting this in terms of the time after unloading, x, gives:

$$\gamma(t)=\sigma[J(t_1+x)-J(x)] \qquad (4)$$

where $t=t_1+x$.

The creep compliance of rubbers and other materials is often found to approximate to a linear dependence on the logarithm of the time, viz:

$$J(t)=J_0\left(1+A\log\frac{t}{t_0}\right) \qquad (5)$$

where J_0 is the compliance after some reference time t_0 and A is a parameter indicative of the rate of increase of $J(t)$. Using this relation and equation (4), the set at a time x after unloading is given by:

$$\gamma(t)=\sigma J_0 A\left[\log\frac{t_1+x}{t_0}-\log\frac{x}{t_0}\right]$$

$$=\sigma J_0 A\log\left(\frac{t_1}{x}+1\right) \qquad (6)$$

It is interesting to note that $\gamma(t)$ is strictly a function of (t_1/x) only if the creep compliance is of the form in equation (5). Then equation (6) follows, giving the precise functional dependence on (t_1/x). Djiauw and Gent[4] concluded that the recovery in their experiments was a function of (t_1/x), but the form proposed was not equation (6). However, their experiments were conducted under conditions of constant extension (rather than constant load) followed by recovery under zero load, so that unequivocal conclusions are difficult to draw.

Provided the logarithmic form of equation (5) applies, a plot of $(\gamma/\sigma J_0)$ against $\log[(t_1/x)+1]$ should be a straight line through the origin of slope A. However, equation (5) is not always a good representation of the behaviour of the materials with which we are concerned, and so the applicability of equation (6) may not be appropriate. We have adopted a somewhat different approach.

If the dependence of the recovery upon the time under load is known, the superposition principle enables the time dependent creep compliance to be predicted. This may then be compared with the directly observed creep compliance. The agreement between the two relations is thus a test of the applicability of the principle.

The method of resurrecting the creep compliance is as follows. From equation (4), the 'reduced set' may be defined as:

$$S(t_1, x)\equiv\frac{\gamma(t)}{\sigma}=J(t_1+x)-J(x) \qquad (7)$$

$S(t_1, x)$ is the set at time x after release of a load applied for a time t_1. If, for example, $t_1=10$ and $x=1$ units of time, we have:

$$S(10,1)=J(11)-J(1)$$

which gives the creep that would have occurred between 1 and 11 units of time. Similarly, for $t_1=10$ and $x=11$:

$$S(10,11)=J(21)-J(11)$$

so that $S(10,1)+S(10,11)=J(21)-J(1)$, the creep between 1 and 21 units of time. In general, the creep between 1 and $(2n+1)$ units of time can be obtained from the sum of the set for $t_1=n$, $x=n+1$ and for $t_1=n$, $x=1$:

$$S(n, n+1)+S(n,1)=J(2n+1)-J(1) \qquad (8)$$

where n is a positive integer.

In addition we may obtain the creep at short times (e.g. 1 to 10 s) by plotting the differences in the set in the early stages of recovery for test-pieces held extended for long periods of time, provided the rate of change of compliance with time is small at long times: these can be calculated from equation (7). For $t_1 \gg x$, $J(t_1+x)$ will not change significantly with x when x is small. For example, from equation (7) the set at 1 s is given by:

$$S(t_1,1)=J(t_1+1)-J(1) \qquad (9)$$

and that at 5 s is given by:

$$S(t_1,5)=J(t_1+5)-J(5) \qquad (10)$$

By subtracting equation (10) from equation (9) we have:

$$S(t_1,1)-S(t_1,5)\simeq J(5)-J(1) \qquad (11)$$

as $J(t_1+1)$ and $J(t_1+5)$ are effectively equal if t_1 is sufficiently large.

Hence by taking various values of t_1 and x the creep curve can be derived from the set data. It should be noted that the creep at any particular time can be calculated in a number of ways depending upon the values of t_1 and x selected.

EXPERIMENTAL

The polymer was an uncrosslinked natural rubber with characterization data given in *Table 1*.

For creep and recovery experiments, the test sheets were prepared by moulding for 1 h at 100°C and then cooling to ambient temperature under pressure. In order to eliminate the residual moulding strains, all test sheets were annealed at room temperature for 2–3 days before use. Test-pieces were die stamped in the form of a dumb-bell about 2.0 mm thick. They were gripped between two clamps of the simple extensometer[7] shown in *Figure 1*,

Table 1

Rubber	Mooney viscosity V_r	Intrinsic viscosity $[\eta]$ (dl/g)	Number-average molecular weight $\bar{M}_n$
Gum	60	2.95 ± 0.24	(197 ± 13) x 10^3
	40	2.35 ± 0.24	(164 ± 13) x 10^3
Black-filled (50 phr HAF)	87	–	–

$[\eta]$, $\bar{M}_n$ were measured in toluene at 25°C, and all ± values refer to 95% probability limits

and the gauge length of each measured with a rule. The latter moves in a vertical slot, fine adjustment being obtained by means of the rubber disc drive. The rule is set with its bottom edge (zero) opposite the lower gauge mark of the test piece such that the mark, bottom edge and the image of the pupil of the eye in the mirror (which is situated closely behind the test piece) are colinear. The position of the upper gauge mark is noted in a similar manner and the gauge length read off. Re-zeroing and reading can be carried out quickly for different gauge lengths. A load is applied to the lower clamp for different periods of time, t_1, before it is removed. For each value of t_1 the creep and recovery are measured by recording the gauge length of the test piece at various times after loading and unloading.

Three loadings corresponding to stresses (σ), referred to the unstrained cross-sections, of 0.25, 0.50 and 0.78 kg cm^{-2} were used; higher loadings were restricted (with the present apparatus) by the difficulty of accommodating the substantial creep occurring at these high stresses. This probelm of excessive creep also limited the loading period, t_1, for the gum rubber, for instance, to 20 min at $\sigma = 0.25$ kg cm^{-2}. For carbon black-filled rubber, t_1 could be extended to much longer times as the carbon black stiffened the rubber and hindered its flow to some extent.

RESULTS AND DISCUSSION

Figure 2 shows typical creep recovery curves for gum and carbon black-filled rubbers after releasing from a constant load which has been applied for various times, t_1. The addition of carbon black to the gum stock has greatly stiffened the rubber.

In *Figure 3* we plot the recovery strain $\gamma/\sigma J_0$ against $\log[(t_1/x)+1]$ as suggested by equation (6). The relation does not show proportionality between $\gamma/\sigma J_0$ and $\log[(t_1/x)+1]$, and this indicates that the creep relation (equation 5) used in the derivation of equation (6) is not obeyed. The plot shows, moreover, that recovery is not complete even after long recovery times. This suggests that there is a flow process taking place in the specimen during creep; the plastic flow restricts the recovery at large x. The magnitude of this unrecoverable, residual strain (the 'permanent set') is given in the insert of *Figure 3*. *Figure 3* also shows non-linearity behaviour in that $(\gamma/\sigma J_0)$ is not independent of stress at high stresses ($\sigma \geqslant 0.78$ kg cm^{-2}).

It is evident from the results in *Figure 3* that equations (5) and (6) are not good representations of the creep behaviour of the gum rubber used here. In order to investigate the validity of the superposition principle, the alternative approach discussed in the Theory section must

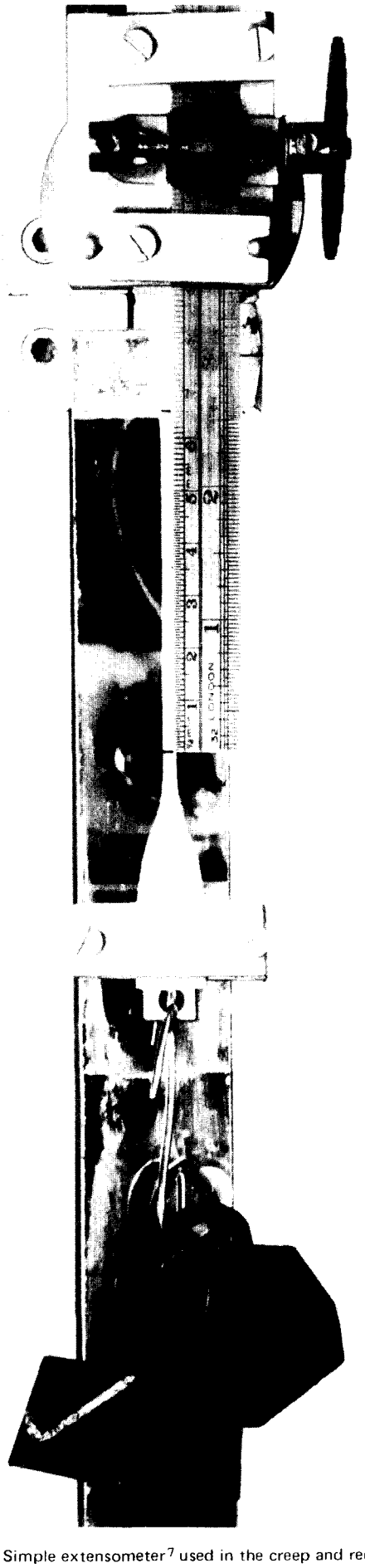

Figure 1 Simple extensometer[7] used in the creep and recovery experiments; the plane mirror is situated behind the test-piece, with the camera lens representing the eye

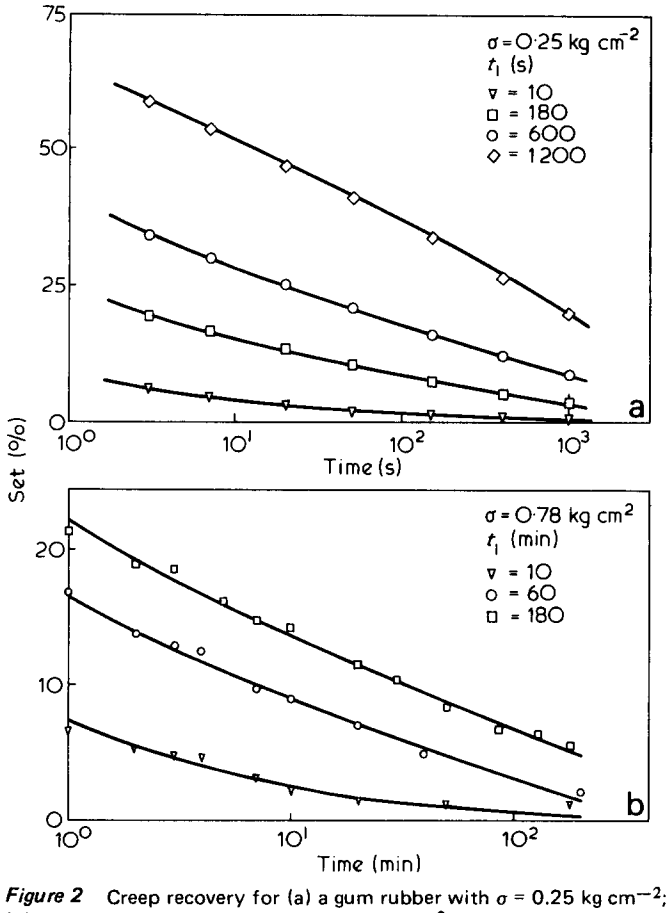

Figure 2 Creep recovery for (a) a gum rubber with σ = 0.25 kg cm^{-2}; (b) a black filled rubber with σ = 0.78 kg cm^{-2}, for different duration of times under applied stress (t_1)

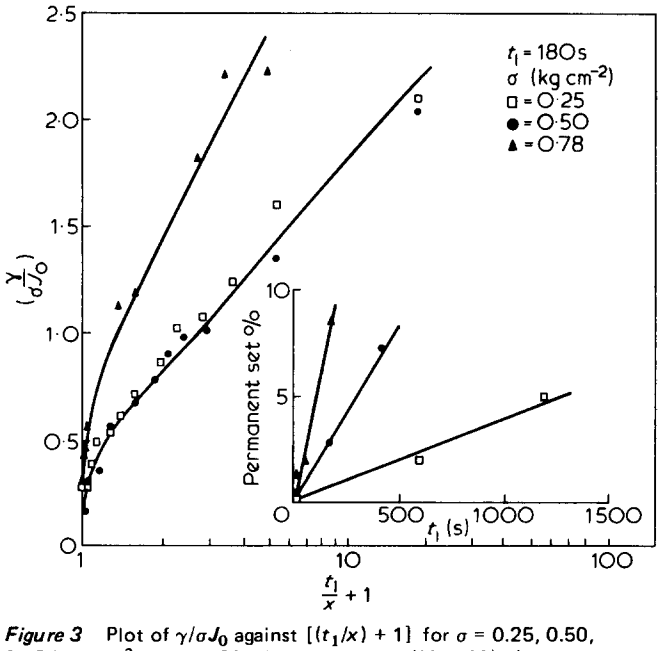

Figure 3 Plot of $\gamma/\sigma J_0$ against $[(t_1/x) + 1]$ for σ = 0.25, 0.50, 0.78 kg cm^{-2} at t_1 = 180 s for gum rubber (V_r = 60); J_0 is the compliance at reference time t_0 (=10 s) appropriate to each load used; the insert indicates the dependence of the permanent set on the time under stress, t_1, for the three stress levels

be applied to the recovery data. *Figure 4* shows the plot of the derived creep compliance, $J(t) - J(10)$ for gum rubber (with Mooney viscosity, V_r = 60) as a function of time (t) for three stresses each applied for a range of times, t_1. For each stress a single master creep curve is derived from the set data by selecting various values of x and t_1, using equation (8). The master creep curve is independent of t_1, and has the same general shape as the experimentally observed creep curves. The curves, however, diverge significantly at both short and long times.

As the instantaneous recovery at unloading is greater than the instantaneous deformation at loading, the derived creep curve is greater than that observed at short times. A similar phenomenon has been observed by Fuller[8] for the shear deformation of an annular specimen of gum rubber and, by Mindel and Brown[9] in their investigation of the creep behaviour of polycarbonate at high stresses in tension and compression. They attributed the phenomenon in polycarbonate to the inherent asymmetry in the barrier for thermal activation, proposing that even at zero stress and strain the activation energy for a unit of flow to go from the unstrained to the strained state is greater than for the flow process in the reverse direction. The present phenomenon in gum rubber is apparently due to the existence of permanent set in the recovery curve caused by the flow during creep. Further discussion on this will be followed later.

At long times, the experimental creep curve becomes higher than that of the derived curve (*Figure 4*). That is, at

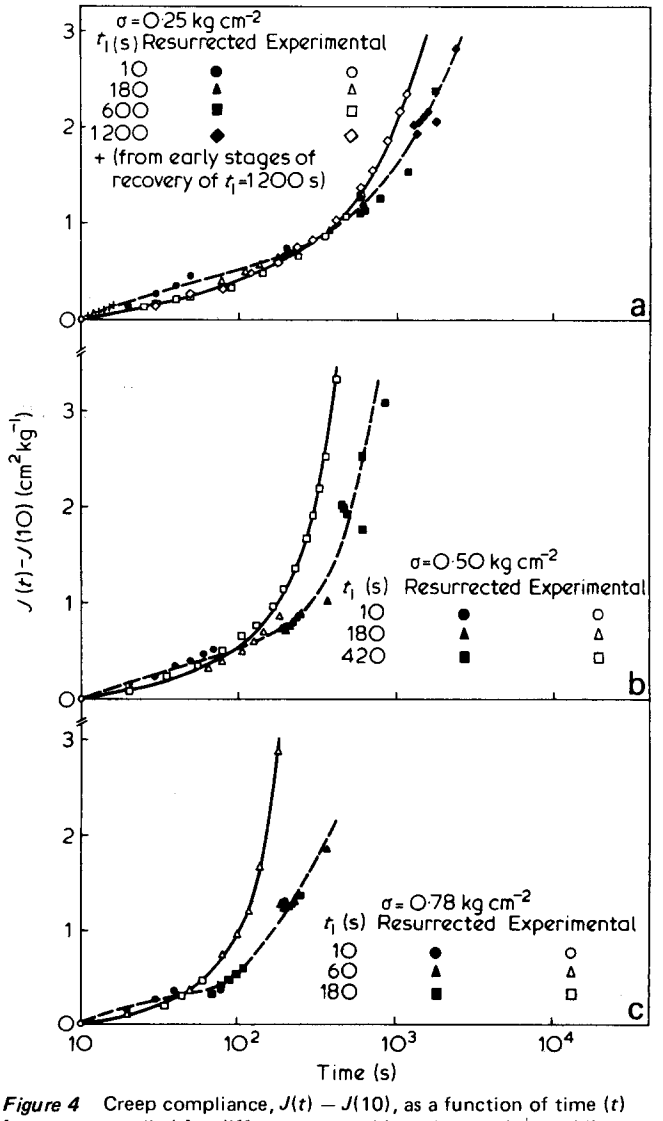

Figure 4 Creep compliance, $J(t) - J(10)$, as a function of time (t) for stresses applied for different t_1 s: solid symbols and dotted lines indicate the resurrected creep obtained from the recovery data; and the solid curves and open symbols show the experimental creep data, for gum rubber (V_r = 60)

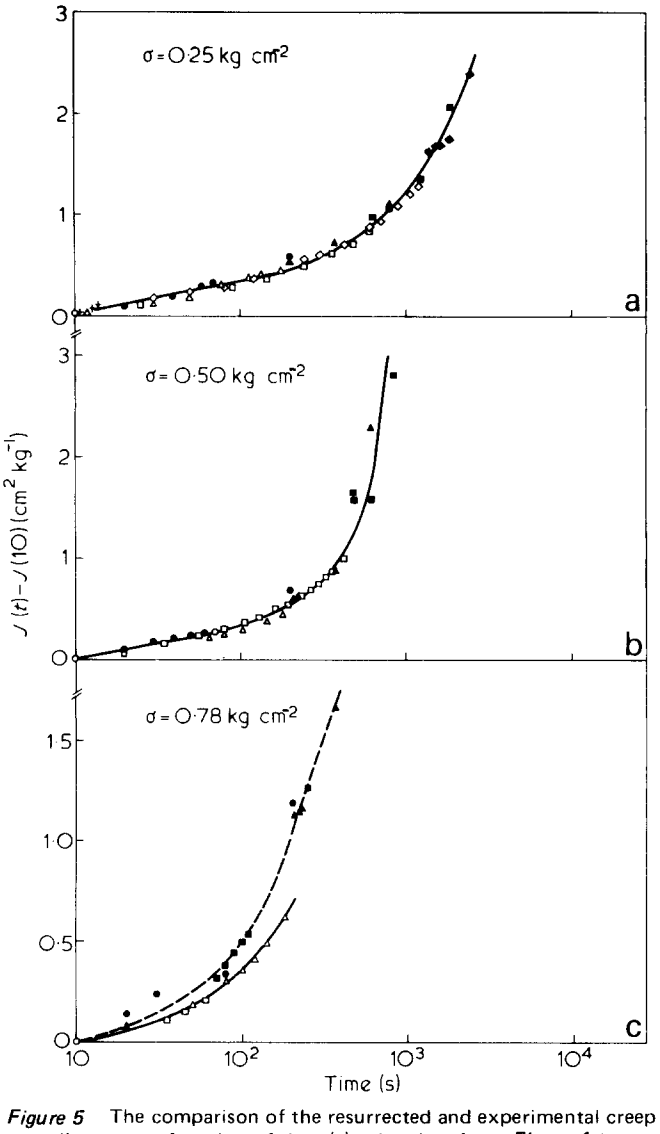

Figure 5 The comparison of the resurrected and experimental creep compliances as a function of time (t) using data from ***Figure 4*** but with the recoverable parts of the experimental data (open symbols: all symbols correspond to ***Figure 4***) corrected for the dimensional changes during deformation using equation (12), and the resurrected compliances (solid symbols) calculated from the recoverable parts of the recovery curves (i.e. corrected for the flow effect)

large t the rate of recovery is slower than the corresponding creep rate. This deviation of the derived curve from that of the experimental curve could in part be due to the fact that a constant tensile load was applied so that the stress increased as the cross-sectional area of the specimen decreased. This effect, which becomes increasingly important at large strains, was not allowed for in the calculation of the creep data as shown in *Figure 4*. Another factor leading to the failure of the superposition principle can be due to the flow processes which are particularly significant at high stresses and long times. This flow behaviour is known to be nonlinear and thus would lead to complications. This flow process would lead to the occurrence of permanent set.

For a more realistic comparison between the experimental and derived creep curves, the above two effects must be taken into consideration. It is difficult to carry out a rigorous correction for the change in specimen cross-sectional area, and hence the true stress, with time. However, an approximate estimate of the creep compliance under constant true stress can be found by assuming constant volume during deformation and defining:

$$J(t)=\frac{\gamma(t)}{\left(F\frac{\lambda}{A_0}\right)} \tag{12}$$

where $\gamma(t)$ is the strain at time t, A_0 is the undeformed cross-sectional area, and λ is the extension ratio at time t.

The non-linear characteristic of the flow behaviour and the consequent permanent set would, as mentioned above, lead to discrepancies with the predictions of the superposition principle. This problem can, to some extent, be circumvented by subtracting the experimentally observed set from the creep and recovery, and treating the remainder by the superposition principle. The permanent set is proportional to time, and is a non-linear function of the stress, as indicated in the insert of *Figure 3*. This time dependent permanent set is subtracted from the observed creep curve and the constant (maximum) value appropriate to the time under load, t_1, is subtracted from the recovery data.

Applying the corrections due to the change in cross-section and to the permanent set, the revised experimental creep and derived creep compliances are shown in *Figure 5*. The agreement is excellent at low stresses (*Figures 5a* and *5b*) but at highest stress used ($\sigma=0.78$ kg cm^{-2}) the derived creep compliance is still somewhat too high. The corrections which have been applied go some way towards removing the discrepancies with the predictions of the superposition principle. However, the fact that the results at the high stress still show a discrepancy, albeit reduced, suggest that the simple corrections are not large enough. This may be due to the non-linearity in the stress–strain curve at $\sigma \geqslant 0.78$ kg cm^{-2} as indicated by the results in *Figure 3*.

The effectiveness of the two correction factors undoubtedly depends upon the stress level. At low stresses ($\leqslant 0.50$ kg cm^{-1}) where they are most effective (*Figures 5a*, *5b*), their relative contributions change with the time of creep t. This can be seen from *Figure 4* where the discrepancy at short time is due primarily to permanent set in the recovery curve (and thus in the derived creep curve) as a result of flow under stress during creep; the interpretation of the data at these times is not much influenced by changes in cross-sectional area due to flow. However, at longer times ($t \geqslant 300$ s for $\sigma=0.25$ kg cm^{-2}, *Figure 4a*) this latter effect is substantial. For the recovery curve, $J(t-t_1)$, one constant value of permanent set, corresponding to t_1, is subtracted from the data at all times. This constitutes a maximum correction for $J(t-t_1)$ at $(t-t_1) \ll t$ and hence has a more pronounced effect (reduction in magnitude) on the early part ($t \ll t_1$) of the derived creep curve: the relative reduction in magnitude of the derived creep curve is thus greater at shorter times ($t \ll t_1$). However, the correction for the effect due to changes in cross-sectional areas, using equation (12), on the experimental creep data is more effective at long times where the flow regime is the predominant feature.

A change in the Mooney viscosity (V_r) in the gum rubber from 60 to 40 does not introduce any significant variation in the shape of the derived creep curve except that the onset of the steady flow regime for $V_r=40$ occurs earlier than for $V_r=60$.

The introduction of carbon black has a great influence on the rheological properties of the rubber. *Figures 6* and *7* show the reduction in magnitude in both the creep and recovery compliances by the addition of carbon black into

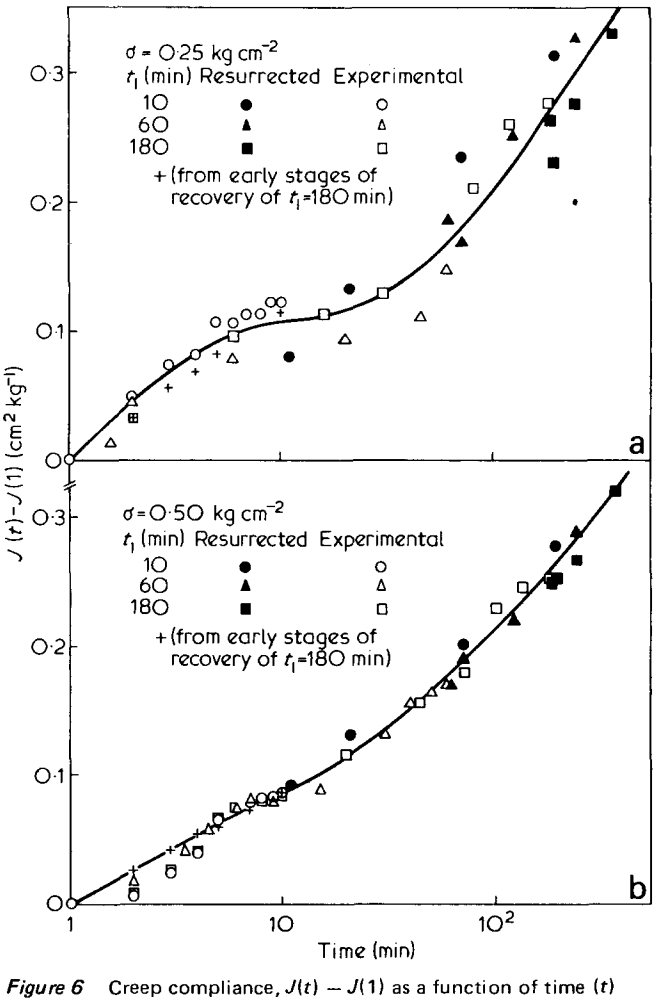

Figure 6 Creep compliance, $J(t) - J(1)$ as a function of time (t) for two applied stresses and for different t_1s for black-filled rubber: solid symbols are the resurrected creep from the recovery data and the open symbols show the experimental creep data

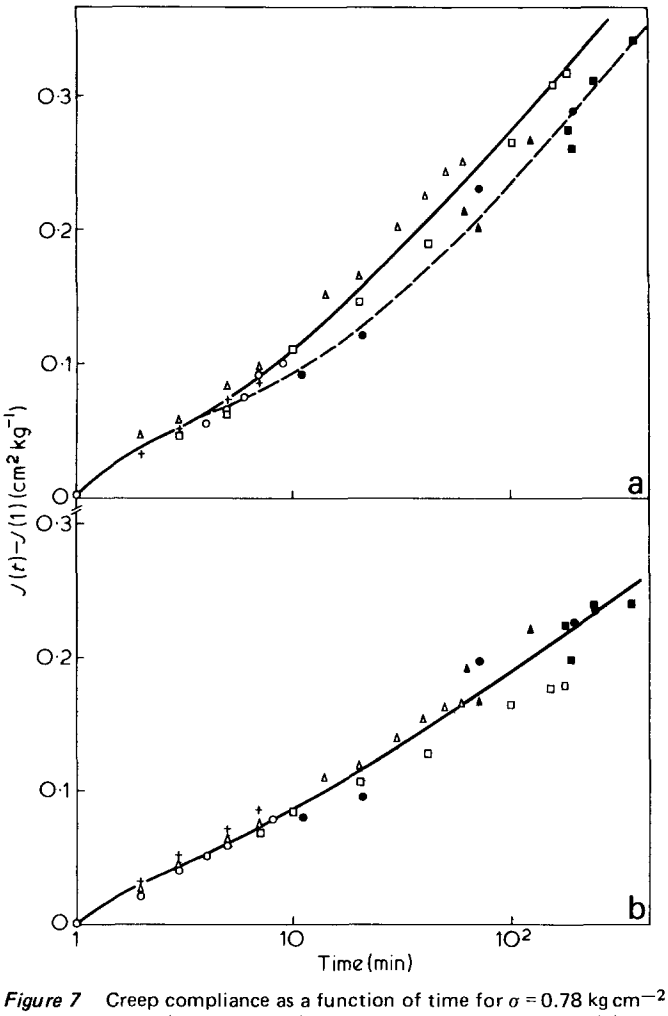

Figure 7 Creep compliance as a function of time for $\sigma = 0.78$ kg cm^{-2} and different t_1s (as in *Figure 6*) for carbon-black filled rubber: (a) as in *Figure 6* uncorrected for the non-linear effects of flow and dimensional changes during tensile deformation; (b) both the resurrected and experimental data have been corrected for the above non-linear effects similar to those in *Figure 5*

the gum rubber. The carbon black has stiffened the rubber, and reduced the tendency to flow, giving a creep compliance closer to that observed for vulcanized rubbers.

It is difficult to prepare a completely homogeneous unvulcanized filled rubber sheet. As different test-pieces are used in the experiment, the variation among specimens causes some scatter in the results especially at low stresses and short creep times. The agreement between the experimental and derived creep curves as in *Figure 6* for $\sigma = 0.25$ and 0.50 kg cm^{-2} are good even without taking account for the non-linearity effects due to flow and the time dependent variation of the specimen cross-section during creep. But when the applied stress increases to $\sigma = 0.78$ kg cm^{-2}, there is a significant discrepancy between the experimental and resurrected creep curves though the general shape is the same, as shown in *Figure 7a*. This discrepancy can be removed by the corrections proposed above. The reason why the results from the black-filled rubber give better agreement, is, no doubt, because these materials show less permanent flow under the stresses used here.

CONCLUSION

In conclusion, therefore, it appears that the Boltzmann superposition principle can provide a useful starting point for the analysis of flow and recovery data from unvulcanized rubbers. It is, however, important to correct for the non-Newtonian flow, which leads to the permanent set, and which cannot be accommodated by the superposition principle. The non-linear effect due to cross-sectional area changes on deformation is only approximately taken into account by the simple approach used. In view of the limitations of these corrections, the agreement between theoretical predictions and experiment is remarkably good.

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