Creep and recovery behaviour of ultra-high molecular weight polyethylene in the region of small uniaxial deformations

L. J. Zapas and J. M. Crissman
Center for Materials Science, National Bureau of Standards, Washington, DC 20234, USA
(Received 26 April 1983)

The creep and recovery behaviour of an ultra-high molecular weight polyethylene (UHMWPE) has been studied in the region of small uniaxial deformations. At deformations as small as 5×10^{-4} the stress–strain behaviour is non-rectilinear and the recovery cannot be described by a theory of fading memory. A new one-dimensional constitutive relation is presented which describes quantitatively the multistep creep and recovery behaviour of this material in the case where the specimens are not mechanically preconditioned. The multistep in strain–stress relaxation behaviour of the UHMWPE has also been investigated for the case in which the second step in strain is approximately half the magnitude of the first step. Calculations of the strain necessary to give the observed stress in a two-step stress-relaxation experiment have been made assuming that the stress-relaxation experiment can be represented by a series of multistep creep experiments where in each step the stress is adjusted so as to maintain a constant deformation. The agreement between the experimental values and the calculated values are very good. The proposed equation, which describes plasto-viscoelastic behaviour, appears to be able to describe quantitatively the creep and recovery behaviour of a wide range of semicrystalline polymers.

Keywords Constitutive equation; creep; mechanical preconditioning; recovery; stress-relaxation; ultra-high molecular weight polyethylene

INTRODUCTION

Well over a hundred years ago it was found[1,2] that creep and recovery data obtained on natural polymeric materials could be reproduced only when the specimens were subjected to prior mechanical conditioning. About forty years ago Leaderman[3], in his classic work on the 'Elastic and Creep Properties of Filamentous Materials and Other High Polymers', reported that the same behaviour was true for synthetic polymers which he had studied. It was observed that the creep and recovery behaviour could be described by the Boltzmann Superposition Principle only when the material was subjected to mechanical preconditioning. The necessity to precondition the material raises questions as to what is measured as material properties, and what the measured properties have in common with the properties of the virgin, or unpreconditioned, polymer.

To understand this behaviour in more detail, the mechanical behaviour of unpreconditioned specimens of an ultra-high molecular weight polyethylene (UHMWPE) having a molecular weight of $\approx 4\times10^6$ has been examined. It has been established that the recovery behaviour of this polymer following creep cannot be described by viscoelasticity. The recovery following a creep experiment, even one in which the maximum strain attained is 10^{-3} or less, does not decay to zero, but tends to plateau to a finite value. This behaviour has led to the formulation of a new one-dimensional constitutive equation which describes plasto-viscoelasticity. In the new derivation, the assumption is that the undistorted state of the material depends upon the prior stress history; i.e., the strain at which the material finds itself may be different than that which the experimeter observes. The material strain can be described by viscoelasticity, whereas that which is observed cannot be.

EXPERIMENTAL

The polymer used in this study was a commercial-grade UHMW linear polyethylene. As received, the raw polymer was in the form of a powder, which, to the knowledge of the authors, contained no additives such as antioxident or stabilizers. It had a manufacturer's specified intrinsic viscosity of ≈ 25 dl g^{-1}, which, based on the manufacturer's method of estimating molecular weight from dilute solution viscometry measurements, corresponds to a molecular weight of $\approx 4\times10^6$.

The specimens were prepared by compression molding under vacuum according to the following procedure. The vacuum mold was initially filled with a predetermined amount of the UHMWPE powder, placed in the press and heated with only light contact pressure applied on the mold. When the platens attained 135°C a pressure of 2.4 MPa was applied on the mold for a short period and then released. The mold chamber was then subjected to vacuum. The mold was heated to 200°C and maintained at this temperature for 10 min. A pressure of 8.25 MPa was applied to the mold and heating was stopped. The press was then cooled at ≈ 1°C min^{-1} to <80°C before the mold was removed from the press. The sheets, which were

0032-3861/84/010057-06$03.00

15 cm dia. and 0.10 cm thick, were stored at room temperature for at least one month prior to use. The density of sheets prepared in this manner was in the range 0.934–0.936 g cm^{-3}. The density was determined at 23°C with a water/ethanol density gradient column.

Single and multistep creep and recovery experiments were carried out on the unpreconditioned specimens using a servo-controlled hydraulic test machine. The specimens were cut with a die to conform with the dumbbell geometry described in ASTM D638, Type IV[4], except that in the present case the length of the narrow portion was approximately 5.0 cm. The strain was determined with an extensometer which was attached to the specimen at the centre of the gauge section. The gauge length of the extensometer was 1.27 cm, approximately one fourth the length of the gauge section of the specimen. For the multistep creep and recovery experiments, the extensometer was zeroed prior to the application of the first step in strain, and then was not adjusted throughout the duration of the experiment.

The single-step stress-relaxation measurements were carried out prior to the availability of the test machine. These measurements were made on specimens cut in the form of a 'T' bar. In this geometry the width of the narrow section is constant over the entire length of specimen not contained within the grips, but is wider in the sections contained within the grips. The strain was determined by measuring the distance between fiducial marks with a cathetometer. Two-step strain–stress-relaxation measurements were carried out using the test machine and extensometer. The machine was operated in stroke control. To carry out a two-step experiment in which the second step strain was one half that of the first step, the stroke control voltage was reset at the appropriate time to be one half the initial value. However, because of end effects at the grips, the actual strain in the gauge section of the extensometer was not quite one half the initial strain.

All of the creep and recovery and stress relaxation experiments were carried out at 23 ± 0.5°C.

RESULTS AND DISCUSSION

Creep and recovery

In this experiment the material, at rest up until time $t=0$, is subjected to a constant load for a time t_1, after which the load is removed and the strain is measured as a function of time. Shown in *Figure 1* are creep and recovery data for specimens which were subjected to applied stresses in the range 1–8 MPa. In these experiments the deformation was kept sufficiently small so that the constant load experiments could be considered as constant true stress experiments. At the largest stress ($\sigma_A = 8$ MPa), the maximum strain attained at $t_1 = 10^3$ s was 0.025, whereas at $t=1$ s it was 0.009, so that the applied stress during the creep step was constant within 1.5%. For smaller values of σ_A and t_1 the change in stress during the creep step was <0.5%. However, even at the smallest levels of applied stress, the creep behaviour was non-linear, as shown in *Figure 2* where on log–log coordinates the stress is plotted *versus* strain for various isochrones. The deviations from linearity can be seen by comparing the observed behaviour to the dashed line having unity slope.

Also shown in *Figure 1* are the recovery data for times up to 10^4 s after removal of the applied stress. The dashed lines represent the predicted recovery assuming a

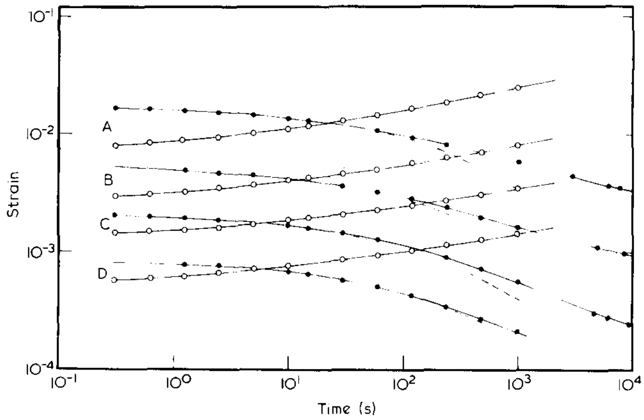

Figure 1 Creep strain (○) and strain during recovery (●) *versus* time (log–log coordinates) from experiments carried out at constant t_1 (10^3 s) but varied applied stress σ_A. ---, Recovery predicted using equation (1b). A, 8; B, 4; C, 2; D, 1 MPa

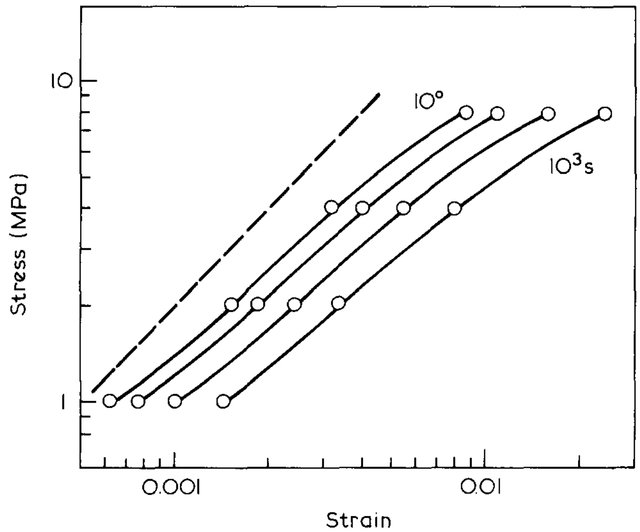

Figure 2 Isochronal stress–strain curves determined from the creep data shown in *Figure 1* (log–log coordinates). The dashed line with unity slope depicts rectilinear behaviour

superposition principle given by an equation of the type:

$$\varepsilon(t) = \int_{-\infty}^{t} H^*(\sigma(\xi), t-\xi)t-\xi)\mathrm{d}\xi + H(\sigma(t), 0) \quad (1a)$$

where $\varepsilon(t)$ is the strain at time t and H^* is the derivative of the function H with respect to the second argument. From equation (1a) the strain during recovery at time t after a creep experiment of duration t_1 is given by:

$$\varepsilon(t) = \varepsilon_c(\sigma, t+t_1) - \varepsilon_c(\sigma, t) \quad (1b)$$

where $\varepsilon_c(\sigma, t)$ corresponds to the strain in a creep experiment at time t, and the applied stress is σ. Although the predictions from equation (1b) are in good agreement with the data early during the recovery, at the larger values of t the deviations become progressively larger.

In *Figure 3* are shown the results of a series of experiments in which the applied stress was constant (8 MPa) and the duration of the creep step was varied. It is observed that the strain during recovery tends to plateau to a finite value, at least when t_1 is small. This behaviour also occurs for experiments carried out at much smaller

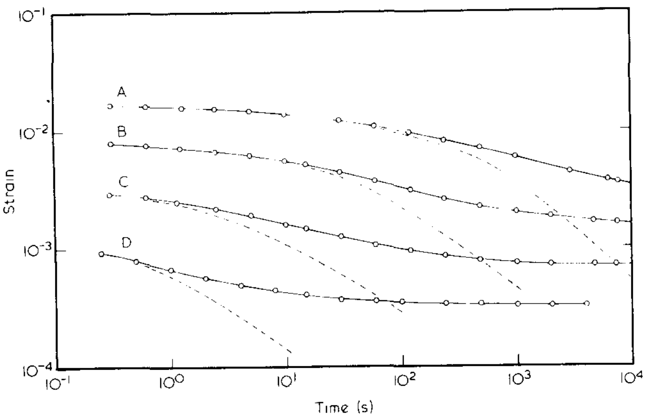

Figure 3 Strain during recovery *versus* time (log–log coordinates) from experiments carried out at constant applied stress (8 MPa) but varied t_1. ---, recovery predicted using equation (1b). t_1: A, 10^3; B, 10^2; C, 10; D, 1 s

applied stresses where the maximum creep strain was of the order of $\leqslant 0.001$. It is evident that the UHMWPE shows a plastic-like behaviour. This behaviour and the behaviour described later cannot be described by the existing non-linear viscoelastic theories of simple materials.

For this reasons the following one-dimensional constitutive equation is introduced. For very small deformations:

$$\varepsilon(t)=\int_0^t J^*(\sigma(\xi),\, t-\xi)\mathrm{d}\xi + J(\sigma(t),\, 0) + \phi\left(\int_0^t \hat{g}(\sigma(\xi))\mathrm{d}\xi\right) \quad (2)$$

where $\varepsilon(t)$ is the observed strain at time t, $\sigma(\xi)$ is the applied stress at time ξ, $\phi(\cdot)$ is a functional which depends on the stress history, and $J(\sigma, t)$ is in the manner of a non-rectilinear compliance multiplied by $\sigma(\xi)$. $J^*(\cdot,\cdot)$ denotes the derivative of $J(\cdot,\cdot)$ with respect to the second argument and $J(0, t)=J^*(0, t)=\hat{g}(0)=0$.

For an experiment in which there is a single-step in stress, the following set of conditions apply:

$$\sigma(\xi)=0 \quad \text{for} \quad \xi<0, \quad \text{and}$$

$$\sigma(\xi)=\sigma \quad \text{for} \quad 0\leqslant\xi\leqslant t \quad (3)$$

Equation (2) then gives:

$$\varepsilon(t)=J(\sigma, t)+\phi(\hat{g}(\sigma)t) \quad (4)$$

For a history involving recovery preceded by creep, where the stress history is given by:

$$\sigma(\xi)=0 \text{ for } \xi<0,$$

$$\sigma(\xi)=\sigma \text{ for } 0\leqslant\xi<t_1, \text{ and}$$

$$\sigma(\xi)=0 \text{ for } t_1\leqslant\xi\leqslant t \quad (t)$$

the strain at time t will be:

$$\varepsilon(t)=J(\sigma, t)-J(\sigma, t-t_1)+\phi(\hat{g}(\sigma)t_1) \quad (6a)$$

If the time of recovery is designated by $\hat{t}$, then substitution of $t=\hat{t}+t_1$ into equation (6a) gives:

$$\varepsilon_{\mathrm{R}}(t_1;\, \hat{t})=J(\sigma, \hat{t}+t_1)-J(\sigma, \hat{t})+\phi(\hat{g}(\sigma)t_1)$$

where $\varepsilon_{\mathrm{R}}(t_1;\hat{t})$ is the strain during recovery at a time t after a creep step of duration t_1. By substitution of $J(\sigma, t)$ and $J(\sigma, t+t_1)$ from equation (4) into equation (6b), the following relation is obtained:

$$\varepsilon_{\mathrm{R}}(t_1;\, t)=\varepsilon_{\mathrm{c}}(t+t_1)-\varepsilon_{\mathrm{c}}(t)-\phi(\hat{g}(\sigma)(t+t_1)) + \phi(\hat{g}(\sigma)t)+\phi(\hat{g}(\sigma)t_1) \quad (7)$$

where $\varepsilon_{\mathrm{c}}(t)$ is the strain during creep at a time t. If:

$$\varepsilon_{\mathrm{r}}(t_1;t)-\varepsilon_{\mathrm{c}}(t+t_1)+\varepsilon_{\mathrm{c}}(t)=\Delta\varepsilon_{\mathrm{RC}}(t_1;\, t) \quad (8)$$

then for the case in which $t=t_1$:

$$\Delta\varepsilon_{\mathrm{RC}}(t_1;\, t_1)=2\phi(\hat{g}(\sigma)t_1)-\phi(\hat{g}(\sigma)2t_1) \quad (9)$$

If it is assumed that in its simplest form $\phi(\hat{g}(\sigma)t_1)$ can be represented by:

$$\phi(\hat{g}(\sigma)t_1)=g(\sigma)t_1^{\alpha} \quad (10)$$

where $g(\sigma)=(\hat{g}(\sigma))^{\alpha}$, then from equation (9) it follows that:

$$\Delta\varepsilon_{\mathrm{RC}}(t_1;\, t_1)=g(\sigma)t_1^{\alpha}(2-2^{\alpha}) \quad (11a)$$

For constant σ a plot of $\log\Delta\varepsilon_{\mathrm{RC}}(t_1;t_1)$ *versus* $\log t_1$ should then yield a straight line with slope α. Such a plot is shown in *Figure 4* from which it was found that a straight line of slope 1/3 resulted. Equation (11a) can then be rewritten as:

$$\Delta\varepsilon_{\mathrm{RC}}(t_1;\, t_1)=0.74g(\sigma)t_1^{1/3} \quad (11b)$$

It was also found that the creep curves can be represented reasonably well by the following relation:

$$\varepsilon_{\mathrm{c}}(t)=f_1(\sigma)+f_2(\sigma)t^{1/3} \quad (12)$$

If both the functions ϕ and J have the same exponential dependence on time, as is the case in the present work, it can easily be shown that recovery data, obtained from creep experiments having different durations t_1 (at constant σ), can be superposed onto a master curve with predetermined shift factors. For example, in the present work the recovery at time t after a creep for time t_1 is given by:

$$\varepsilon_{\mathrm{R}}(t_1;\, t)=\theta(\sigma)[(t+t_1)^{1/3}-t^{1/3}]+g(\sigma)t_1^{1/3} \quad (13)$$

where $\theta(\sigma)=f_2(\sigma)-g(\sigma)$. Then the recovery $\varepsilon_{\mathrm{R}}(t;\, t_i)$, where $t_i=\alpha_i t_1$, is

$$\varepsilon_{\mathrm{R}}(\hat{t};\, t_1)=\theta(\sigma)[(\hat{t}+\alpha_i t_i)^{1/3}-\hat{t}^{1/3}]+g(\sigma)\alpha_i^{1/3}t_1^{1/3} \quad (13a)$$

For values of $\hat{t}=\alpha_i t$:

$$\varepsilon_{\mathrm{R}}(t_1;\, t)=\alpha_i^{-1/3}\varepsilon_{\mathrm{R}}(\alpha_i t_i;\, \alpha_i \hat{t})$$

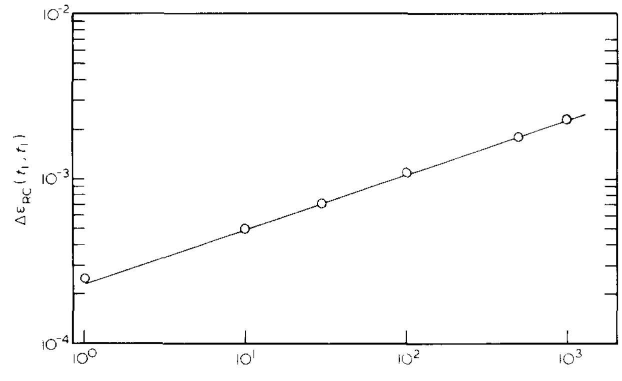

Figure 4 Values of $\Delta\varepsilon_{\mathrm{RC}}$ $(t_1;\, t_1)$ versus t_1 on log–log coordinates

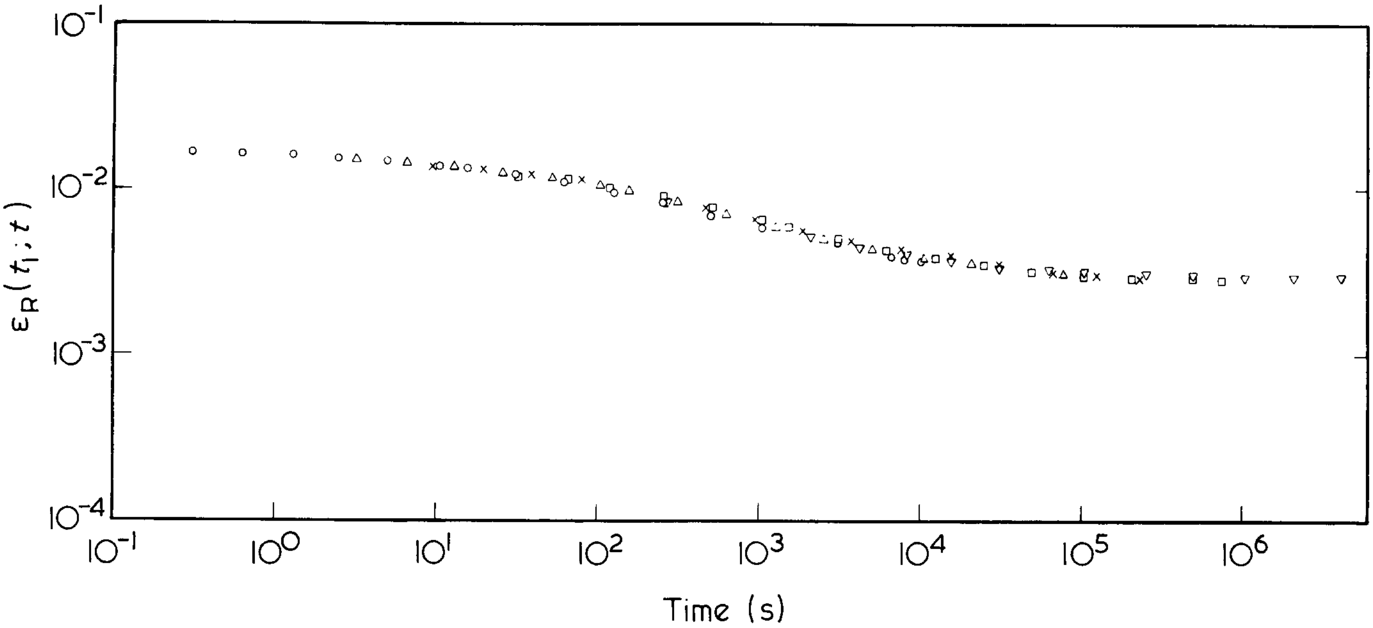

Figure 5 Superposition of the recovery data shown in *Figure 3* onto a master curve for the case where $t_1=10^3$ s

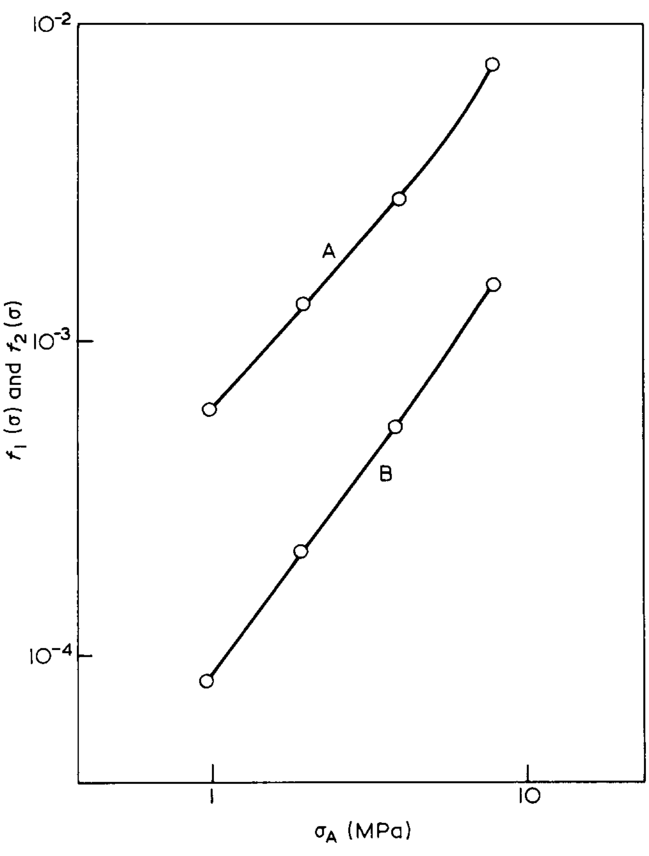

Figure 6 The functions A, f_1 and B, $f_2(\sigma)$ *versus* σ (log–log co-ordinates) determined from the creep data shown in *Figure 1*

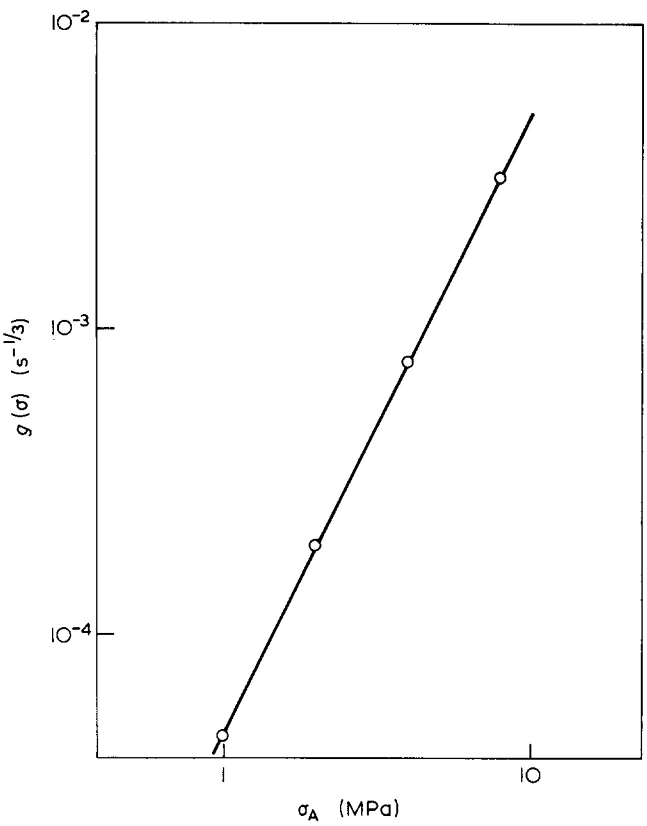

Figure 7 The function $g(\sigma)$ *versus* σ (log–log co-ordinates) determined from the recovery data shown in *Figure 1* and equation (11b)

Starting from an experiment for which the recovery is $\varepsilon_R(t_1,t)$, any other recovery data $\varepsilon_R(\hat{t};t_1)$ can be superposed by first dividing by $\alpha_i^{1/3}$ (the ratio of t_i/t_1), and then shifting along the time axis by α_i. This procedure was carried out for the data shown in *Figure 3*, and the results are presented in *Figure 5*, where t_1 was taken to be 10^3 s. From *Figure 5* it is evident that the material will stop recovering after a time $> \approx 10^6$ s, or a time three orders of magnitude greater than the step time t_1.

The functions $f_1(\sigma)$, $f_2(\sigma)$ and $g(\sigma)$ can be determined from the data shown in *Figure 1* where the time t_1 was constant, but the magnitude of the applied stress was varied from 1 to 8 MPa. The functions $f_1(\sigma)$ and $f_2(\sigma)$ are shown in *Figure 6*. Values for the function $g(\sigma)$ were determined using equation (11b) and these are shown in *Figure 7*. Using the appropriate values of these functions all of the recovery data were reproducible to within at least two per cent. Examples of the calculated values of the recovery are shown in *Figure 8*, where the solid lines

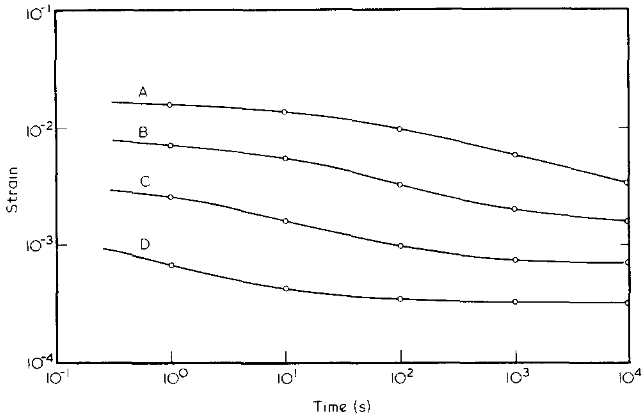

Figure 8 Comparison of the recovery data shown in *Figure 3* (——) and the values of recovery (○) predicted using equation (2). Stress, 8 MPa; t_1: A, 10^3; B, 10^2; C, 10; D, 1 s

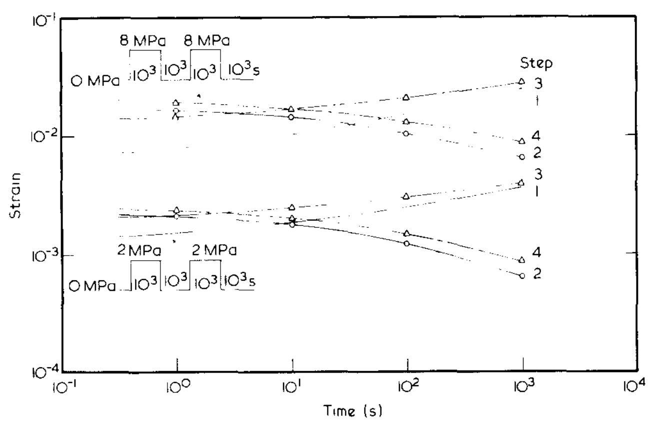

Figure 9 Multistep creep and recovery data for the stress histories indicated. The creep data are represented by the curves labelled 1 and 3, and the recovery data by the curves labelled 2 and 4. △ and ○, predicted values of the creep and recovery calculated using equation (2)

represent the actual data and the open circles the calculated values. It can be seen that there is excellent agreement between the two sets of results.

Multistep in stress creep and recovery

Here, more complicated stress histories involving multistep creep and recovery are considered. In one set of experiments the material, having been at rest up until time $t=0$, was subjected to the multistep stress histories indicated in *Figures 9* and *10*. For these experiments the extensometer was not reset to zero throughout the course of the experiment. The observed responses for the creep and recovery steps are shown in *Figures 9* and *10* as a set of curves labelled 1–4. The time at the onset of each step is taken to be the time $t=0$. The points (circles and triangles) are the values of the strain calculated using equation (2). The agreement is very good. At early times the creep strain during the third step (second creep step) is significantly larger than during the first step, although at very long times the two curves appear to be approaching one another asymptotically. For the recovery it is found that the strain during the fourth step (second recovery step) remains larger than that for the second step and as time increases the ratio of the two becomes larger. From similar experiments, where the recovery period was extended to much longer times, the agreement between the observed response and the calculated values was equally good.

A second set of experiments was carried out in which the stress histories were similar to those described previously except that the extensometer in each case was reset to zero just prior to the application of the third step (at the end of the first recovery step). These results are presented in *Figure 11*. In this case the creep at the early times is now the same for both the first and third steps, but at longer times the strain during the second creep step (third step in stress) is slightly less than that of the first step. This behaviour provides an indication that mechanical preconditioning is occurring in the material. Also, it can be seen from *Figure 11* that the recovery during the fourth step occurs much more rapidly than during the second step. In fact the recovery is even more rapid than that predicted by equation (1b).

Using equation (3) the behaviour for various stress histories has been calculated and it is evident that mechanical preconditioning may lead to a behaviour which can be described by the simple superimposition principle given by equation (1b). However, this may not be true for all types of mechanical preconditioning. In subsequent work the results of mechanical preconditioning for this as well as other materials will be considered.

Single and two-step in strain–stress relaxation

The multistep in strain–stress relaxation behaviour of UHMWPE can be described using the theory of Bernstein, Kearsley, and Zapas[5] (BKZ theory) provided that

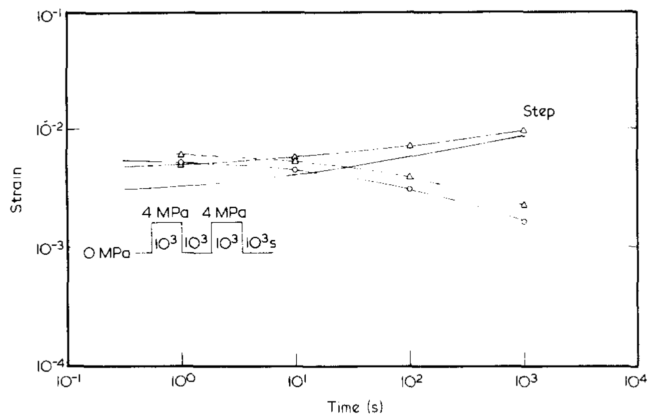

Figure 10 Multistep creep and recovery data for the stress history indicated. The labelling is the same as in *Figure 9*

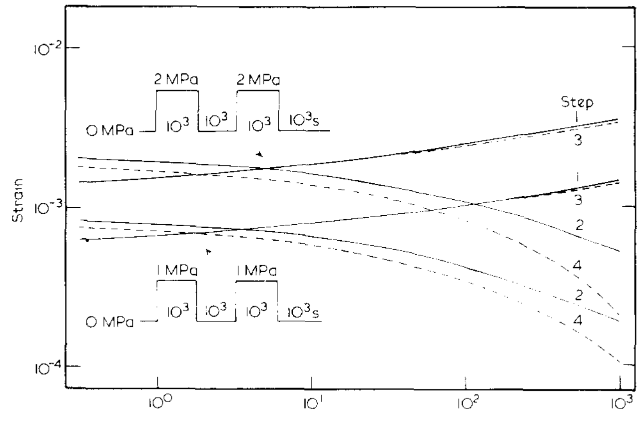

Figure 11 Multistep creep and recovery data for experiments carried out in which the extensometer was re-zeroed just prior to the application of the third step. The labelling is the same as in *Figure 9*

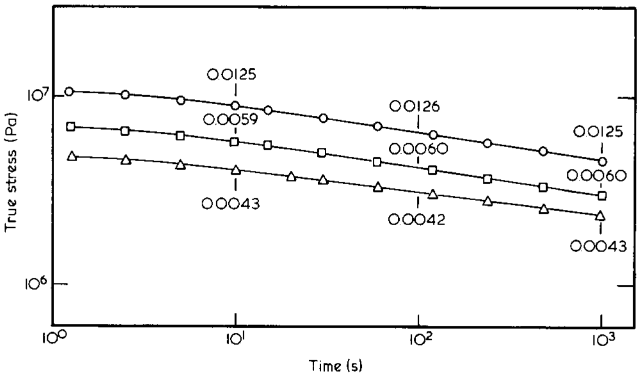

Figure 12 Single step in strain stress-relaxation data obtained at strains of 0.0125 (○), 0.0060 (□), and 0.0043 (△). The numbers are the calculated values of strain

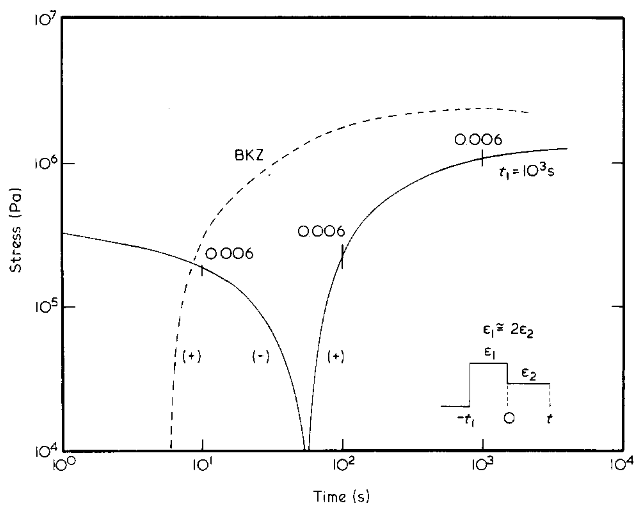

Figure 13 Results of a two-step in strain–stress-relaxation experiment in which $\varepsilon_1 \cong 2_{\varepsilon_2}$ and $t_1 = 10^3$ s

each subsequent step in strain is larger than the previous one. However, in a two-step experiment in which the second step is approximately one half the magnitude of the first step, the values predicted by the BKZ theory vary significantly from the experimental values. To establish whether the present one-dimensional theory can describe this behaviour, it is necessary to invert a non-linear equation. To overcome this difficulty calculations of the values of strain necessary to give the observed stress have been made. In this scheme, it is assumed that a stress-relaxation experiment can be represented by a series of multistep creep experiments where in each step the stress is adjusted so as to maintain constant deformation. As a first step it was established that the proposed equation gave consistent results with single-step, stress-relaxation data, as shown in *Figure 12*. The circles, squares, and triangles correspond to single step stress-relaxation data obtained at strains (ε) of 0.0125, 0.0060 and 0.0043 respectively. The numbers shown represent the calculated values of strain at times of 10^1, 10^2, and 10^3 s. There is very good agreement between the actual strains and the calculated values of strain.

Figures 13 and *14* show results of similar calculations carried out for two-step in strain–stress-relaxation experiments in which the second step was approximately half the value of the first step. In *Figure 13* the two curves labelled (+) and (−) represent the values of the stress observed during a two-step experiment in which $\varepsilon_1 = 0.0125$, $\varepsilon_2 = 0.0060$, and the duration of the first step

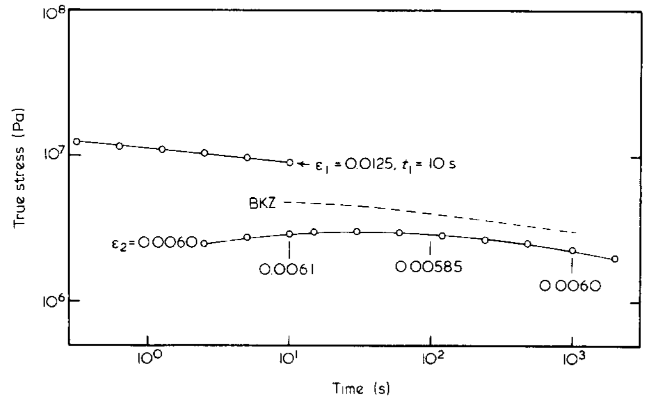

Figure 14 Results of a two-step in strain–stress-relaxation experiment in which $\varepsilon_1 \cong 2_{\varepsilon_2}$ and $t_1 = 10$ s

was 10^3 s. The first step data are shown by the circles in *Figure 12*. In a two-step experiment, where $\varepsilon_2 = \frac{1}{2}\varepsilon$, the observed stresses can be negative at early times when the step time t_1 is relatively long. Upon application of the second step in strain the specimen initially may be in compression. The symbols (−) signifies that at times up to ≈ 60 s the values of the observed stress are negative. The numbers shown correspond to the calculated values of the strain. Also shown for comparison (dashed line) is the second-step stress predicted by the BKZ theory.

Figure 14 shows the results of a second experiment in which the first- and second-step strains were again $\varepsilon_1 = 0.0125$ and $\varepsilon_2 = 0.0060$, but the duration of the first step was only 10 s. In the latter experiment the stress during the second step was not observed to attain a negative value. In both experiments it can be seen that there is good agreement between the actual values of the step strain and the calculated values.

CONCLUSIONS

A new one-dimensional constitutive equation is presented which describes quantitatively the creep and recovery behaviour in uniaxial extension of an ultra-high molecular weight polyethylene in the region of small deformations. The proposed equation, which describes plasto-viscoelastic behaviour, applies equally well to specimens of UHMWPE subjected to creep and recovery in uniaxial compression. Using the proposed relation it can be shown that, under certain conditions of mechanical preconditioning, it may be possible to obtain specimens of the UHMWPE for which the creep and recovery data can be described by a simple superposition rule. It has been established also that difficulties encountered in applying the BKZ theory to multi-step stress-relaxation experiments have been overcome. It appears that the new description will be capable of describing the behaviour, at small deformations, of a wide variety of other semi-crystalline polymers.

REFERENCES

1 Weber, W. *Pogg. Ann. Physik* 1835, **4**(2), 247
2 Weber, W. *Pogg. Ann. Physik* 1841, **24**(2), 1
3 Leaderman, H. 'Elastic and Creep Properties of Filamentous Materials and Other High Polymers' The Textile Foundation, Washington, D.C., 1943
4 'ASTM 1978 Annual Book of ASTM Standards', Parts 35 and 36, Soc. Testing and Materials, 1916 Race Street, Philadelphia, PA. 19103
5 Bernstein, B., Kearsley, E. A. and Zapas, L. J. *Trans. Soc. Rheol.* 1963, **7**, 391