Time dependent recovery of oriented polyethylene

S. A. GORDEYEV, I. M. WARD*
IRC in Polymer Science and Technology, The University of Leeds, Leeds, LS2 9JT
E-mail: i.m.ward@leeds.ac.uk

The recovery behaviour after creep of oriented linear polyethylenes has been studied over the temperature range 20–60 °C. A range of samples was examined to identify the influence of draw ratio and molecular weight. It has been shown that in spite of significant differences in recovery strain level, the recovery kinetics are not affected over a wide range of the structural variations and experimental conditions. It is concluded that the time dependent recovery behaviour is consistent with a model where two thermally activated processes are acting in parallel. More exact values for the activation parameters for both processes of the model have been obtained by taking into account the time dependent distribution of the applied stress between these two processes. © *1999 Kluwer Academic Publishers*

1. Introduction

In a number of previous publications from this laboratory [1–3] the plastic flow creep as well as the viscoelastic creep behaviour of oriented polyethylene (PE) have been described in considerable detail. The main conclusion of these investigations is that the total creep behaviour of oriented linear PE, including the initial time dependent behaviour, can be described very satisfactorily by a model in which two thermally activated processes, each in series with an elastic element, are assumed to act in parallel.

The aim of the present paper is to examine the validity of this model for the time dependent recovery behaviour, on the assumption that the kinetics of creep and recovery should be described by the same set of parameters. With significant simplification of this initial model for the case of recovery, the recovery kinetics can be easily modelled analytically and some of the parameters of the total model can be calculated from the fitting of the experimental data. However, analytical equations can only be obtained for both creep and recovery behaviour at low applied stresses. It also has to be emphasised that the simple two-process model should be regarded only as a semi-quantitative model to provide physical insight into the deformation mechanisms. For a precise description of the viscoelastic behaviour, a distribution of relaxation times would be required and the finite value of the loading time should also be taken into account.

2. Experimental

Samples were prepared from two commercial grades of linear polyethylene with different molecular weights, BP 6007 and BP H020 manufactured by BP Chemicals Ltd. Sample information is summarised in Table I. Tape samples A-1 and A-2 were cut from sheets quenched after compression moulding and then drawn to different draw ratios at different temperatures in an Instron tensile test machine fitted with a high temperature oven. Because there was significant scatter in the mechanical behaviour of tapes in the creep experiments the monofilament samples B, C-1 and C-2 were prepared by melt spinning using standard extrusion techniques and then drawn in either one or two stages in a continuous process to fixed draw ratios. All samples were annealed in air at $(115 \pm 5)°C$ for 20 h and then cooled slowly to room temperature in order to stabilise their structure. Further experiments showed that there is no qualitative affect of the sample preparation procedures on the creep and recovery behaviour.

The creep and recovery measurements were made at temperatures of 20, 40 and 60 °C using a standard dead-loading creep apparatus in which the deformation was measured by grip displacement. Details of the apparatus and experiments have been given elsewhere [4]. The recovery data were obtained after various creep times for several levels of applied stress. The duration of the recovery tests was at least 10^5 s ($\sim$30 h) and the sample strain after this test was considered as residual.

3. Results and discussion

Sherby-Dorn plots [5] describing creep strain rate as a function of creep strain are probably the most instructive method of graphical presentation for the tensile creep experiments. The initial monotonically declining part of the plot corresponds to the viscoelastic response of the material, while permanent deformation is clearly associated with the appearance of a plateau (Fig. 1). For analysis of the kinetics of creep and recovery, however, a plot of strain rate versus time is more informative. In

---

Sample	Polymer grade	M_w/1000	M_n/1000	Draw ratio	E_T (GPa)	Comments
A-1	6007	131	19	7	4.8	Drawn at 20 °C
A-2	6007	131	19	12	9.2	Drawn at 75 °C
B	6007	131	19	9	13.7	Drawn at 90 °C
C-1	H020	312	33	9	15.8	Drawn at 90 °C
C-2	H020	312	33	20	38.6	C-1 drawn at 120 °C
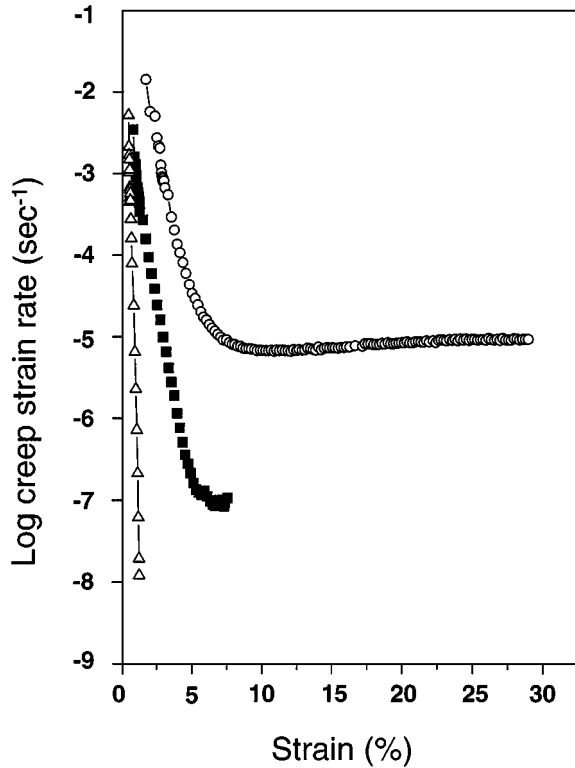
Figure 1 Sherby-Dorn plots for: ($\bigcirc$) sample A-1, $\sigma^{appl} = 100$ MPa; ($\triangle$) sample B, $\sigma^{appl} = 33$ MPa; ($\blacksquare$) sample C-2, $\sigma^{appl} = 200$ MPa.

Figure 2 Log(creep strain rate) against log(time) plots at room temperature for: ($\bigcirc$) sample A-1, $\sigma^{appl} = 100$ MPa; ($\triangle$) sample B, $\sigma^{appl} = 33$ MPa; ($\blacksquare$) sample C-2, $\sigma^{appl} = 200$ MPa.

Figure 3 Effect of applied stress and loading time on the recovery after creep for sample A-1: (a) $\sigma^{appl} = 60$ MPa, loading time: ($\square$) 30 s, ($\bullet$) 10^4 s, ($\blacktriangle$) 10^5 s; (b) $\sigma^{appl} = 80$ MPa, loading time: ($\blacksquare$) 10^3 s, ($\diamond$) 10^4 s, ($\blacktriangledown$) 10^6 s; (c) $\sigma^{appl} = 100$ MPa, loading time: ($\blacklozenge$) 10^2 s, ($\bigcirc$) 10^3 s, ($\triangle$) 10^4 s; (- - - -) apparent linear fit by $\lg(\dot{\varepsilon}) = -2\lg(\text{time}) - 1.1$.

this presentation, the immediate elastic component of deformation, which is not experimentally measured, is excluded from consideration. In this case (Fig. 2), linear viscoelastic behaviour is described by a straight line on the log (strain rate) versus log (time) plot and the plastic flow component produces the deviation from linearity.

The evidence from experimental observations is that in the range where linear viscoelasticity applies, all the samples show complete recovery on unloading and the time dependence of the recovery strain rate is the same as the creep strain rate. The first aim of the present study was therefore to determine the affect of the presence of any plastic deformation on the recovery behaviour. It was found that the deviation from linear viscoelasticity in the creep experiment could be produced in two ways: first by applying higher stress and secondly by increasing the loading time even at relatively low applied stress. The effect of loading conditions was studied in some detail on the sample A-1 and recovery data at room temperature were obtained after various creep times from 30 to 4×10^5 s for several applied stresses in the range from 40 to 150 MPa. Fig. 3 shows that neither the applied stress value nor the loading time affect the recovery strain rate behaviour. It was also found, rather
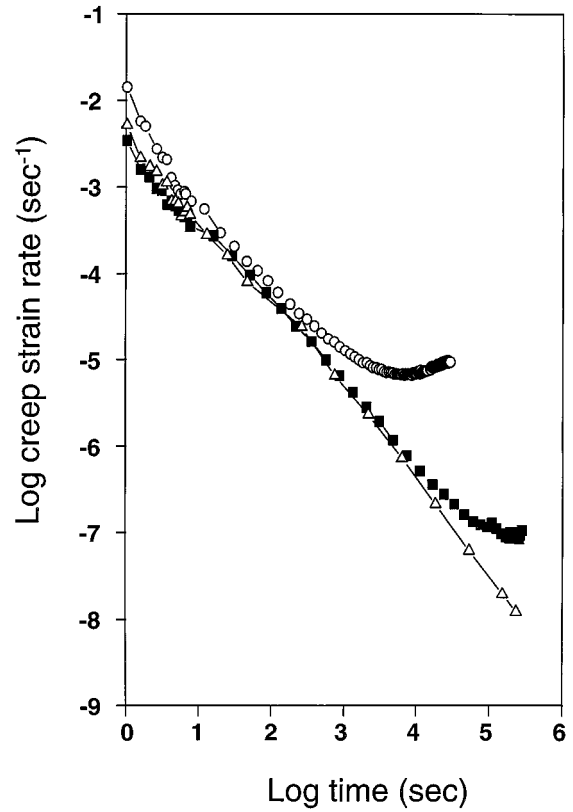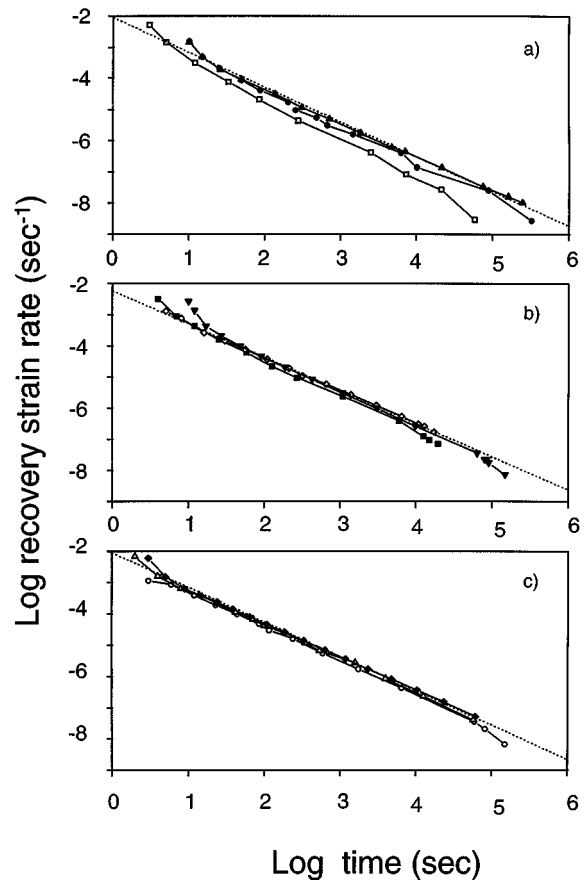
surprisingly, that repeating these tests for the samples B and C at various temperatures produced no significant differences in behaviour. In all cases the recovery data as well as the linear creep strain rates are fitted very well by the straight line $\lg(\dot{\varepsilon}) = c + d \cdot \lg(t)$, where $c = -1.1$, $d = -2.0$. The recovery of sample A-1 at the low applied stress (Fig. 3a) after a very short creep time (30 s) slightly differed quantitatively from the general recovery behaviour of the other samples.

The recovery behaviour of oriented semicrystalline polymers after the removal of an applied load is associated mainly with the recovery of non-crystalline interfibrillar regions, which are essentially a stretched molecular network. The existence of a molecular network in oriented PE has been confirmed by measurements of thermal expansion [6] and shrinkage force [7]. In the simplest theoretical interpretation of the network stress-extension behaviour [8] the internal stress, σ, is related to the network chain density N and the extension ratio λ, by the relationship

$$\sigma \sim NkT(\lambda^2 - \lambda^{-1}) \tag{1}$$

where k is Boltzmann's constant and T the absolute temperature. One would therefore expect changes in the kinetics of recovery if the structure of the network is changed. According to Equation 1, one of the ways to change the properties of the interfibrillar material is to change the molecular orientation in the sample by changing the draw ratio λ. Samples C-1 and C-2 with two very different draw ratios λ were therefore examined in an attempt to determine the effect of orientation on recovery behaviour (Fig. 4). Unexpectedly, over the wide range of draw ratios studied, all the samples showed very similar behaviour in terms of recovery strain rate as a function of time. As in the case of the various creep conditions for the samples A-1, A-2 and C the recovery can be described by a straight line with the same coefficients. Even the isotropic sample A ($\lambda = 1$) demonstrates the same recovery behaviour after low stress creep.

Two other parameters also affecting the stress-extension behaviour of intrafibrillar network are the network chain density, N and the absolute tempera-
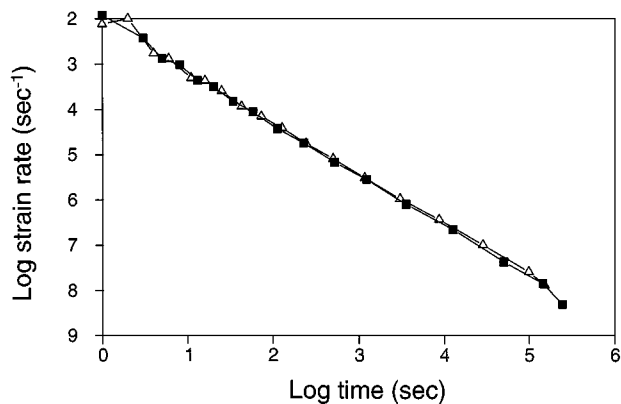
Figure 5 Effect of molecular weight on log(recovery strain rate) against log(time): (■) sample B, $t = 60\,°C$; (△) sample C-1, $t = 60\,°C$.
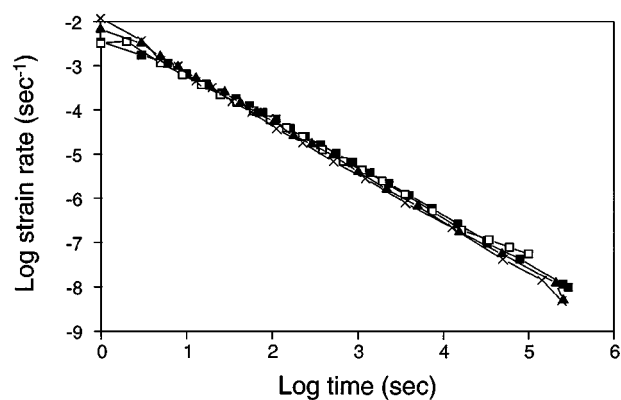
Figure 6 Effect of temperature on log(recovery strain rate) against log(time) for sample A-1: (■) $t = 60\,°C$, creep time 1.5×10^5 s; (□) $t = 40\,°C$, creep time 6×10^4 s; (▲) $t = 40\,°C$; (×) $t = 60\,°C$.

ture of experiment, T. The first parameter relates to the molecular weight of polymer and would be expected to be identified by a comparison of the recovery behaviour of samples B and C after creep under similar conditions. It was therefore surprising that neither molecular weight nor temperature causes any significant change in the recovery kinetics (Figs 5 and 6).

It appears from these results that the elastic component of the polymer network does not affect the time-dependent recovery behaviour of oriented PE. However, the recovery of the network also depends on a viscous component of deformation, which is associated mostly with chain slip processes, in which the molecules slide past each other parallel to their length. In phenomenological terms the origin of viscous flow is the movement of macromolecule segments relative to each other and can be described by the activation parameters of a thermally activated process. It seems plausible that creep and recovery are to be considered as one continuous process: loading, creep, unloading, recovery. We apply the two-process model (Fig. 7a) to elucidate the apparent insensitivity of the recovery kinetics of oriented PE to sample structure and creep conditions. All the elements of the model are involved in the response of the system at loading and during the creep but the stiffness of the springs defines mainly the initial distribution of the applied stress between the arms of the model. The stress in each arm is then determined by the relative viscosities of the dashpots. If the values
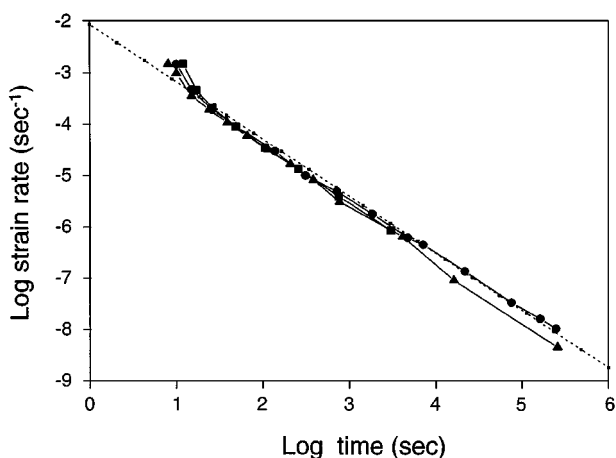
Figure 4 Effect of draw ratio on log(recovery strain rate) against log(time) for sample A:(▲) $\lambda = 1$; (●) $\lambda = 8$; (■) $\lambda = 15$; (- -□- -) apparent linear fit.
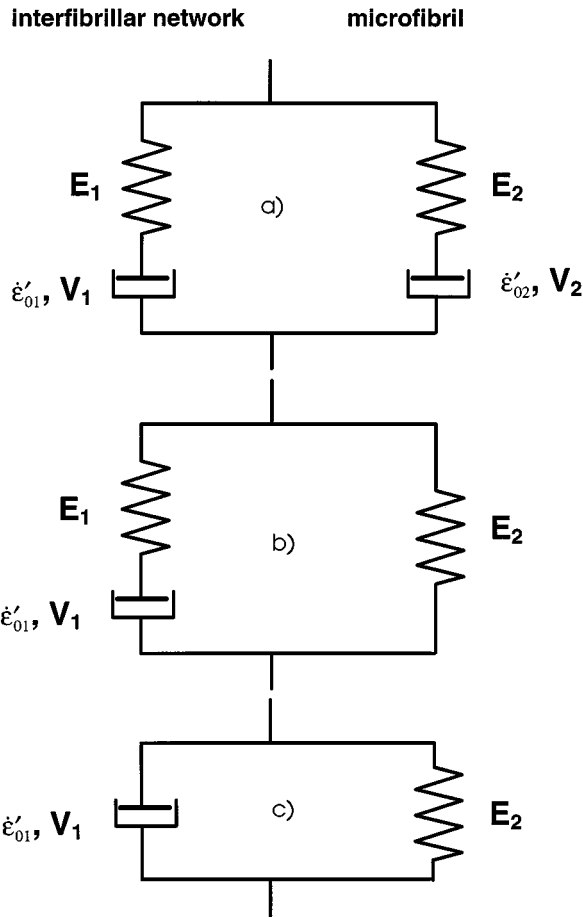
interfibrillar network   **microfibril**

Figure 7 Models of mechanical behaviour: (a) two-process; (b) standard linear solid; (c) model for recovery after creep.

of the two viscosities differ significantly, at low applied stress the stress in one of the arms will be low enough to neglect any dashpot deformation in this arm. In this case the initial model (Fig. 7a) can then be simplified to the model shown in Fig. 7b, well-known as the standard linear solid.

The standard linear solid provides a good first order description of creep behaviour in polymers, where the low initial creep compliance is described by the stiff spring E_1 acting in parallel with the soft spring E_2, and as the flow in the dashpot occurs, the final 'relaxed' creep compliance is reached which is determined only by the magnitude of the soft spring E_2. An essential feature of the standard linear solid representation is that the kinetics of creep and recovery are more tractable mathematically [3]. It is also compatable with the two process model of Fig. 7a. Unloading both the two process model and the standard linear solid involves the instantaneous recovery of the stiff spring E_1. The dashpot V_2 in the opposite arm of the model can therefore be removed from consideration of the recovery behaviour. Essentially, only two elements of the initial model, the spring E_2 and the dashpot V_1, are involved in the recovery response which is then described by the model of Fig. 7c.

Thus from the viewpoint of describing recovery, it is immaterial which of the models shown in Fig. 7 is used for the description of creep. Moreover, whether it is the complete recovery after low stress creep, or the partial recovery after permanent flow creep, only the

activation parameters of the dashpot 1 can be calculated from recovery data.

As mentioned above, the first stage is loading with an applied stress σ^{appl}. If the time of loading is short compared with the shortest sample relaxation time it is possible to use the assumption that the initial stress distribution is defined by the spring stiffnesses. We call this the instantaneous loading approximation. This assumption is reasonable for the all experiments to be described. Then, the initial stresses in each arm (i.e. at the moment $t = 0$) are proportional to the applied stress and the modulus of the spring:

$$\sigma_1^{\mathrm{creep}}(0) = \frac{\sigma^{\mathrm{appl}} E_1}{E_1 + E_2}, \quad \sigma_2^{\mathrm{creep}}(0) = \frac{\sigma^{\mathrm{appl}} E_2}{E_1 + E_2}, \quad (2)$$

To describe the response of the material after loading, the time dependence of stress in each of the arms of the model should be known. However, exact (analytical) expressions for instantaneous stresses during creep can be obtained only for the low applied stress range [3]:

$$\sigma_1^{\mathrm{creep}}(t) = \frac{2kT}{V_1} a \tanh\{\exp(\delta_1 - t/\gamma_1)\}$$

$$\sigma_2^{\mathrm{creep}}(t) = \sigma^{\mathrm{appl}} - \frac{2kT}{V_1} a \tanh\{\exp(\delta_1 - t/\gamma_1)\} \quad (3)$$

where

$$\delta_1 = \ln \tanh\left(\frac{V_1 \sigma_1^{\mathrm{creep}}(0)}{2kT}\right), \quad \gamma_1 = \frac{kT}{\dot{\varepsilon}_{01}' E V_1},$$

$$E = \frac{E_1 E_2}{E_1 + E_2}$$

The equation for the time dependent creep strain of the standard linear solid can be obtained as described previously (see Equation 5 in Ref. [3])

$$\varepsilon^{\mathrm{creep}}(t) = \frac{a}{b} + \frac{1}{b} \ln[f(t)] \quad (4)$$

where

$$a = \frac{\sigma^{\mathrm{appl}} V_1}{kT}, \quad b = \frac{E_2 V_1}{kT},$$

$$f(t) = \frac{1 - \exp[-b(At + k)]}{1 + \exp[-b(At + k)]}$$

in which

$$K = -\frac{1}{b} \ln\left[\frac{1 - G}{1 + G}\right], \quad G = \exp\left[\frac{b\sigma^{\mathrm{appl}}}{E_1 + E_2} - a\right],$$

$$A = \left(\frac{E_1}{E_1 + E_2}\right) \dot{\varepsilon}_{01}'$$

and the creep strain rate is

$$\dot{\varepsilon}^{\mathrm{creep}}(t) = \frac{\dot{\sigma}_2^{\mathrm{creep}}(t)}{E_2} = \frac{\dot{\varepsilon}_{01}' E_1}{E_1 + E_2} [\sinh\{\delta_1 - t/\gamma_1\}]^{-1} \quad (5)$$

Following the presentation of the recovery model (Fig. 7c) the value of instantaneous recovered strain

(elastic recovery) is therefore determined by the deformation of spring 1 at the last moment t_c of loading:

$$\varepsilon^{\mathrm{rec}}(0) = \frac{\sigma_1^{\mathrm{creep}}(t_c)}{E_1} = \frac{\sigma^{\mathrm{appl}} - \sigma_2^{\mathrm{creep}}(t_c)}{E_1} \quad (6)$$

The initial stress for the recovery process in arm 2 is then

$$\sigma_2^{\mathrm{rec}}(0) = \sigma_2^{\mathrm{creep}}(t_c) - \varepsilon^{\mathrm{rec}}(0)E_2$$
$$= \sigma^{\mathrm{appl}} - \sigma_1^{\mathrm{creep}}(t_c)\left[1 + \frac{E_2}{E_1}\right] \quad (7)$$

and the time dependence of the recovery stress is:

$$\sigma_2^{\mathrm{rec}}(t) = -\sigma_1^{\mathrm{rec}}(t) = \frac{2kT}{V_1} a \tanh\{\exp(\delta_2 - t/\gamma_2)\} \quad (8)$$

where

$$\delta_2 = \ln \tanh\left(\frac{V_1 \sigma_2^{\mathrm{rec}}(0)}{2kT}\right), \quad \gamma_2 = \frac{kT}{\dot{\varepsilon}_{01}' E_2 V_1}$$

The recovery strain of dashpot 1 as well as spring 2, corresponding to this stress is

$$\varepsilon_2^{\mathrm{rec}}(t) = \frac{\sigma_2^{\mathrm{rec}}(t)}{E_2} = \frac{2kT}{V_1 E_2} a \tanh\{\exp(\delta_2 - t/\gamma_2)\} \quad (9)$$

Finally the relationship for the recovery strain rate as a function of time can be obtained simply by differentiating the expression (9) for $\sigma_2^{\mathrm{rec}}(t)$:

$$\dot{\varepsilon}^{\mathrm{rec}}(t) = \frac{\dot{\sigma}_2^{\mathrm{rec}}(t)}{E_2} = \dot{\varepsilon}_{01}'[\sinh(\delta_2 - t/\gamma_2)]^{-1} \quad (10)$$

It was shown previously [1] that the main feature of the recovery behaviour is that after creep below some critical value of applied stress, complete recovery is observed. In particular, the model in Fig. 7c predicts complete recovery with a retardation time:

$$\tau = \frac{\eta_1}{E_2}$$

The experimentally determined recovery kinetics show that the system described by the model 5c has the same retardation time for various combinations of parameters $E_1, E_2, \dot{\varepsilon}_{01}', V_1$ which reflect the differences in structure. One can see easily from Fig. 8 and Equation 8 that the
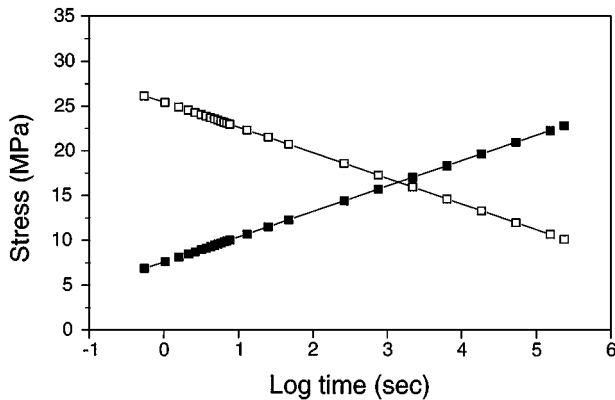
stress in dashpot 1 during recovery is very low and then in the low stress approximation (i.e. if $\sigma V/kT \ll 1$)

$$\sinh\left(\frac{\sigma V}{kT}\right) \approx \frac{\sigma V}{kT} \quad (11)$$

Hence the viscosity of interfibrillar network is given by

$$\eta_1 = \frac{\sigma}{\dot{\varepsilon}} \approx \frac{kT}{\dot{\varepsilon}_{01}' V_1} \quad (12)$$

The recovery time is then

$$\tau = \frac{\eta_1}{E_2} = \frac{kT}{\dot{\varepsilon}_{01}' V_1 E_2} \quad (13)$$

which is exactly the coefficient γ_2 describing the time dependence of the recovery strain rate in Equations 9 and 10.

Thus there are four equations to fit the low stress experiments (i.e. for the case of complete recovery) for the creep strain (4), creep strain rate (5), recovery strain (9) and recovery strain rate (10) vs. time. The fit has been performed using a non-linear curve fit with the simplex search method [9] and the parameters E_1, E_2, $\dot{\varepsilon}_{01}'$, V_1 were obtained as a result of the best fit under the constraint $E_1 + E_2 = E_T$, where E_T is the sample modulus calculated as the slope of an initial part of stress-strain curve. The initial estimates of the activation parameters have been taken from fitting the plateau creep strain rate as a function of applied stress. Some examples of the fit are presented in Figs 9 and 10
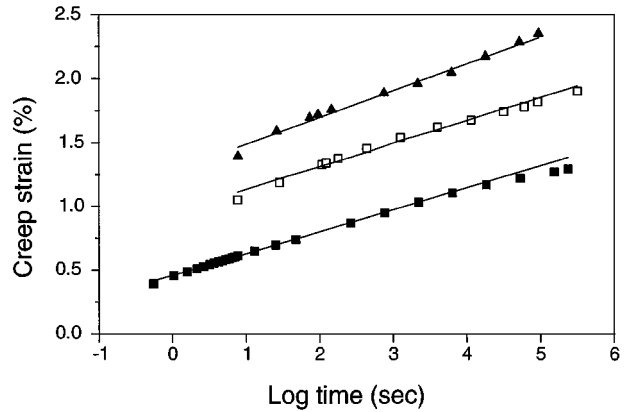
Figure 9 Fitting of creep strain against log(time) for sample B at various temperatures: (■) $t = 20\,^{\circ}\mathrm{C}$; (□) $t = 40\,^{\circ}\mathrm{C}$; (▲) $t = 60\,^{\circ}\mathrm{C}$.

Figure 8 Distribution of applied stress in arms of the standard linear solid at creep: (□) arm 1, (■) arm 2.
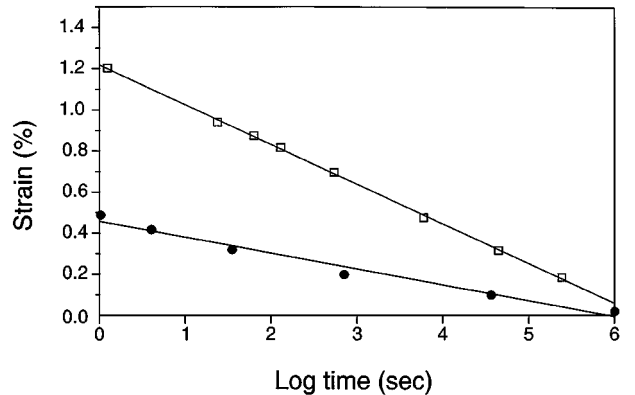
Figure 10 Fitting of recovery strain against log(time) at room temperature for: (●) sample C-2, $\sigma^{\mathrm{appl}} = 100$ MPa; (□) sample C-1, $\sigma^{\mathrm{appl}} = 33$ MPa.

TABLE II Fitted parameters to the recovery and the recoverable creep model

Sample	T (°C)	σ^{appl} (MPa)	$\dot{\varepsilon}'_{01}$ (s^{-1})	V_1 (nm^3)	E_1 (GPa)	E_2 (GPa)	$\tau = \eta_1/E_2$ (s)
A-1	20	30	8.0×10^{-12}	1.6	4.0	0.8	3.94×10^8
A-2	20	30	7.0×10^{-12}	1.2	8.0	1.2	4.01×10^8
B	20	33	2.1×10^{-12}	3.25	12.0	1.65	3.59×10^8
B	40	32	2.2×10^{-12}	4.4	10.0	1.25	3.57×10^8
B	60	33	2.7×10^{-12}	4.8	7.0	1.05	3.38×10^8
C-1	20	33	3.0×10^{-12}	3.0	14.5	1.3	3.46×10^8
C-2	20	100	1.2×10^{-12}	1.1	30.0	8.6	3.56×10^8

and the values of the fitting parameters obtained from the fitting described above are shown in Table II.

Values for the activation parameters of the two-process model for the materials studied here have been reported previously [1, 2]. Those values were based on the equilibrium creep rates in the low stress range. The values for the activation volume of the interfibrillar network, V_1 presented here (Table II) are much higher than in previous papers ($V_1 \sim 0.5$ nm^3). The first point to note is that the earlier estimates of V_1 were made on the assumption that the stress in arm 1 is equal to the total applied stress. In the present study the time dependent distribution of applied stress between the arms of the model is taken into account and as can be seen from Fig. 8, at long creep times, arm 1 holds only about one-third of the applied stress. The previously reported values of V_1 [1, 2] were therefore too low because the stress values used in the equation for the Eyring dashpot strain rate were overestimated. It has to be concluded, therefore, that the values of V_1 obtained here are more correct. In a previous paper [3] an attempt was made to describe the time-dependence of the creep and stress relaxation behaviour of highly oriented PE. A different model was adopted and different values for V_1 were obtained. These were smaller than the values obtained in the present study and in the other previous papers [1, 2] and were associated with a crystal process, in contradiction to the conclusions here.

Although the analysis of the recovery kinetics does not allow calculation of the activation parameters for the other thermally activated process described by $\dot{\varepsilon}'_{02}$ and V_2, if the values of $\dot{\varepsilon}'_{01}$ and V_1 have been obtained, the stress in arm 1 can be calculated for the equilibrium creep. Then the parameters of the second process can be calculated on the basis of the experimental data for the equilibrium creep rate as a function of the stress in arm 2. Again, as for the case of V_1, this approach gives more exact values for V_2 because the stress distribution is taken into account. For example, for the sample A-1 the values of the pre-exponential factor $\dot{\varepsilon}'_{02}$ and the activation volume V_2 obtained following this more exact approach are 3×10^{-7} s^{-1} and 0.16 nm^3, respectively, compared with 3×10^{-7} s^{-1} and 0.10 nm^3 from calculations on the basis of the dependence of the plateau creep strain rate on applied stress.

Next to be noted is the different relationship between the values of the elastic parameters E_1 and E_2 between the present and previous calculations. Although it was stated in paper [3] that the springs have the same

significance as in the two-process model, the relative values of E_1 and E_2 obtained there are in contradiction to the present results. First, if it is assumed that $E_1 < E_2$ there is not even qualitative similarity to the present experimental data when the fitting procedure is performed. Only if $E_1 > E_2$ do the Equations 5 and 10 produce a straight line for both the creep and recovery kinetics on the log(strain rate) versus log(time) plot. Comparison of the stress relaxation and recovery kinetics for these samples also suggests that $E_1 > E_2$. In terms of the standard linear solid model, recovery from creep occurs due to the energy stored in spring 2 whereas in stress relaxation the same dashpot is driven mostly by spring 1. Experimental results to be reported separately [10] for the stress relaxation strain rate show that stress relaxation in oriented PE occurs several times faster than recovery. Hence, spring 1 must be stiffer than spring 2, in good agreement with the present results.

Because process 2 is mainly associated with the crystalline phase, one would expect that the modulus of the spring in arm 2 should be higher than the modulus of spring 1, i.e. the interfibrillar network. However, as mentioned above, all attempts to fit the data using other combinations of parameters ($E_1 < E_2$ or $E_1 \approx E_2$) have been unsuccessful. It is concluded therefore that for the oriented material, arm 2 in the two process model should be associated with a microfibril, which is the basic element of the structure of oriented semicrystalline polymers. Following previous interpretations, the activation volume V_2 is consistent with a crystalline deformation mechanism such as the propagation of defects through the crystallites while the modulus E_2 is consistent with the elasticity of the intrafibrillar non-crystalline regions. As for the comparatively low value of the microfibril modulus E_1, it has been shown by Zaitsev *et al.* [11] that the initial modulus of the microfibril in oriented PE is much lower than the crystal modulus.

Following Equation 13, the time dependent recovery of oriented PE is mainly determined by the properties of two distinct non-crystalline regions. The higher the elasticity of the intrafibrillar material and the lower the viscosity of the interfibrillar network, the faster the material recovers. It appears, however, that over the wide range of structures and experimental conditions studied here, it is very unlikely that these properties change separately. As seen from Table II the value of the retardation time is the same for all samples and all conditions. Although discussion of the structural aspects of the network deformation is unlikely to be very productive in terms of this phenomenological approach, nevertheless, some simple conclusions can be proposed. First, it is be seen that in oriented PE, the interfibrillar non-crystalline material is always much more stretched than the intrafibrillar regions and the total Young's modulus of material is determined mostly by value of E_1. As mentioned above, the value of E_2 (as for any polymer network) is proportional to absolute temperature and the density of the interfibrillar network. It is evident from our temperature measurements that the viscosity η_1 has the same dependence on temperature as E_2. Also, because the retardation time, i.e. the ratio of η_1 to E_2 is the same for samples B and C, the molecular weights of

which differ significantly, it appears that the viscosity η_1 and the modulus E_2 depend in a complementary fashion on molecular weight of the polymer as well as with the temperature of experiment. It is to be concluded, therefore, that the only way to change the kinetics of recovery is to change separately the structures of the interfibrillar and intrafibrillar non-crystalline regions.

4. Conclusions

In this paper particular emphasis has been given to understanding the time dependent recovery behaviour of oriented PE. To examine the validity of simple mechanical models it has been found instructive to describe the recovery kinetics in terms of the time dependence of strain rate. It has been shown that in spite of significant differences in recovery strain level, over a wide range of the structural variations and experimental conditions the recovery kinetics are not affected.

Analytical relationships for the time dependence of strain and strain rate of creep at low applied stresses as well as for recovery have been developed in terms of the two process model. The values of the activation parameters for the low stress process as well as the elastic constants of the model have been obtained by accurate fitting of the time dependent creep and recovery data. It has also been shown that more exact estimates of the activation parameters of the high stress process can be obtained by a combination of time dependent and equilibrium creep data. Quantitative relationships between the parameters obtained show that the second arm of the model is associated with the microfibril rather than with the crystalline regions only. The time dependent recovery behaviour is therefore determined by the relationship between the elasticity of the intrafibrillar non-crystalline regions and the viscous properties of the interfibrillar network. The present results suggest that these properties change in such a way that even for significant transformations of structure such as those caused by hot drawing the recovery kinetics of oriented PE samples which have been carefully annealed to stabilise their structure, is very similar.

References
1. M. A. WILDING and I. M. WARD, *Polymer* **22** (1981) 870.
2. I. M. WARD and M. A. WILDING, *J. Polym. Sci., Polym. Phys. Ed.* **22** (1984) 561.
3. M. A. WILDING and I. M. WARD, *J. Mater. Sci.* **19** (1984) 629.
4. J. DUXBURY and I. M. WARD, *ibid.* **22** (1987) 1215.
5. O. D. SHERBY and J. E. DORN, *J. Mech. Phys. Solids* **6** (1956) 145.
6. G. A. J. ORCHARD, G. R. DAVIES and I. M. WARD, *Polymer* **25** (1984) 1203.
7. G. CAPACCIO and I. M. WARD, *Colloid and Polym. Sci.* **260** (1982) 46.
8. L. R. G. TRELOAR, "The Physics of Rubber Elasticity," 3rd ed. (Clarendon Press, Oxford, 1975) p. 271.
9. J. E. DENNIS, JR. and D. J. WOODS, in "New computing Environments: Micro-computers in Large Scale Computing," edited by A. Wouk (SIAM, 1987) pp. 116–122.
10. S. A. GORDEYEV and I. M. WARD, to be published.
11. M. G. ZAITSEV, S. A. STREMYAKOV and S. A. GORDEYEV, *Int. J. Polym. Mater.* **22** (1993) 25.