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The creep behaviour of ultra-high modulus polypropylene

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The creep and recovery behaviour of highly drawn polypropylene monofilaments has been studied over the temperature range 20 to 50° C. A range of samples was examined to identify the influence of draw ratio and molecular weight. It is concluded that the permanent flow creep arises from the presence of two thermally activated processes, one of which relates to the α-relaxation process and is associated with the crystalline regions of the polymer, and the second with the molecular network.

1. Introduction

The creep and recovery behaviour of ultra-high modulus polyethylenes have been described in a number of previous publications from this laboratory [1–4]. The present paper describes the extension of such studies to ultra-high modulus polypropylenes, where previous publications have been limited to measurements of either the 10 sec isochronal creep modulus or the dynamic mechanical behaviour in extension, both measured at very low strains of 0.1% or lower [5, 6].

Following the precedent of the previous publications on polyethylene, creep and recovery measurements have been undertaken in the temperature range from ambient to 50° C on a series of samples covering the effects of draw ratio and molecular weight. It will be shown that the results for polypropylene are analogous to those for polyethylene. In particular, at high stress levels the low molecular weight samples show a constant creep rate after a comparatively short time. Moreover the stress and temperature dependence of this creep rate can be analysed in terms of a simple thermally activated process. For lower stress levels, and for all stress levels in high molecular weight material, more sophisticated analyses are required, but it will again be shown that the previous studies of polyethylene have provided very useful guidelines.

2. Experimental procedure

2.1. Preparation of samples

Samples were prepared from two commercial grades of polypropylene, Dypro 9375-55, manufactured by Diamond Shamrock Corporation, and Shell GM-6100 (Shell Chemicals Ltd). The weight-average molecular weights of the polymers are given in Table I. In both cases continuous monofilaments 1 to 2 mm diameter were produced by melt spinning. The melt temperatures were 220 and 230° C for the low and high molecular weight polymers, respectively. The spun monofilaments were subsequently drawn by stretching between moving rollers, which passed the monofilament through a heated glycerol bath. The ratio of the angular velocities of the rollers was adjusted to give draw ratios in the range 10 to 17.5 as indicated in Table I.

The temperature of the glycerol bath was maintained at 130° C in all cases. This temperature is higher than the optimum temperature of 110° C established for drawing at low rates in a tensile testing machine, but was found to give better runnability for this continuous process, where the drawing rates reached 10 m min^{-1}.

2.2. Creep measurements

Creep and recovery measurements were made using a tensile dead-loading creep extensometer similar to that originally designed by Morgan and Ward [7], and later developed by Wilding and Ward [1] for the polyethylene creep studies. The apparatus in its final form for the present experiments is shown schematically in Fig. 1. The sample is held vertically between two clamps C1, C2, the upper clamp C1 being firmly fixed to a plate which can be moved up and drawn by a screw thread arrangement. When positioned correctly the plate is locked to the framework F by three locking screws. Under the range of loads used the framework has negligible deformation. The oven O surrounding the sample S is heated by compressed air controlled by a Eurotherm proportional controller. Overall the temperature of the sample can be controlled to ±0.5° C.

The bottom clamp C2 is attached to the core of a linear displacement transducer. The initial setting-up procedure ensures that the transducer core is positioned near the top of the linear region of the transducer. To simplify setting up a standard sample length of 15 cm was adopted which gave a gauge length of approximately 12 cm. Previous work by Wilding and Ward [1] has shown that this length is adequate to avoid any end effects.

A pan is attached to the lower clamp so that the weight W can be applied. This is accomplished by a lifting ring P on a rack and pinion so that the load can be applied and removed with minimum disturbance to the sample.

Creep and recovery data were obtained using two processing methods. In Version 1 (Fig. 1) the data

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TABLE I Sample details

Sample	Grade	$\bar{M}_w$	Draw ratio	Room-temperature 10 sec modulus (GPa)
A	Dypro 9375-55	185 000	10	10.68
B	Dypro 9375-55	185 000	17.5	14.66
C	Shell GM 61	400 000	10	8.26
D	Shell GM 61	400 000	12.5	9.12

were recorded on to punched paper tape. An integral digital voltmeter/timer/punch driver unit (developed at Leeds) recorded the output voltage accurate to 1 mV, on to paper tape either at equal time intervals or equal intervals in $\log_2$(time). This accuracy was approximately equivalent to an extension of ±0.002% for the short transducer used for the stiffest samples, or 0.01% for the larger transducer used for low-draw samples. The complete tape was then fed into a paper tape reader for transfer to the Leeds Amdahl mainframe computer.

In Version 2 (see also Fig. 1), used for later measurements in this research, the paper tape punch was replaced by an Acorn Atom microcomputer, equipped with analogue-to-digital conversion, a real-time clock and a floppy disc drive. In this case the voltage accuracy was equivalent to ±0.03% extension. A program was developed for simultaneously monitoring up to eight creep machines. The program recorded the output and performed initial data processing to produce creep strain against log(time) and log(creep strain rate) against creep strain. In addition to recording data at equal intervals in log(time) the program also took a reading if the strain had altered by more than 0.2% from the last reading. This provided more data in the region of constant strain rate, which was required to test the applicability of the various theoretical models. If required, the data could be transferred from the floppy disc to the mainframe computer.

Following procedures established in previous studies, samples were conditioned by loading at the highest stress level to be employed (approximately 0.3 GPa) for 10 sec and then permitting recovery over a period of at least one hour. In general, conditioning tests were carried out at 50° C, the highest temperature of measurement. Some early tests were also carried out where samples were both conditioned and measured at 30° C. Repeating these tests with conditioning at 50° C produced no significant differences in behaviour.

3. Results and discussion

3.1. Low molecular weight samples

Creep and recovery data for the low molecular weight samples tested at 30° C are shown in Figs 2a and b. Results are presented for a similar range of stress levels in each case, and it can be seen there is the anticipated reduction in creep response with increasing draw ratio, associated with increasing molecular orientation. It can also be seen that at low stresses the recovery curve follows the creep curve very closely. As the stress level is increased the initial recovery becomes greater than the initial strain, but the recovery curve at longer times is below the creep curve, indicating the presence of permanent flow. These results are very similar to those obtained for highly drawn polyethylene, and as in that case, it is more instructive to plot the creep strain rate as a function of creep strain, as originally proposed for polymethylmethacrylate by Sherby and Dorn [8]. Sherby–Dorn plots for low and high draw ratio monofilaments are shown in Figs 3a and b, respectively. It can be seen that in all cases the strain rate falls rapidly from an initially high value, and at high stresses a constant strain rate is soon obtained as a function of strain (i.e. time). For the lowest stress in the low draw ratio sample, however, it can be seen that the curve drops very rapidly with no detectable flattening out. At this stress level the strain apparently approaches a limiting value. Similar behaviour was noted in high modulus polyethylene. In practical terms, it is then possible to define a critical stress level below which permanent flow does not occur, and the creep strain is totally recoverable.

For the higher stress levels, it is informative to plot the constant "plateau" creep rate as a function of

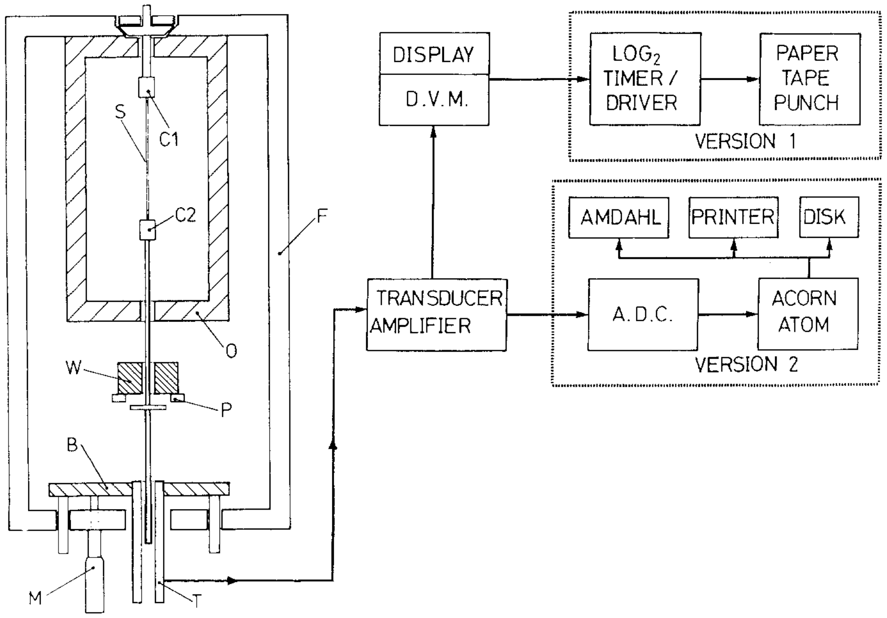

Figure 1 Schematic diagram of creep apparatus and block diagrams of computing arrangements. D.V.M. = digital voltmeter, A.D.C. = analogue–digital converter.

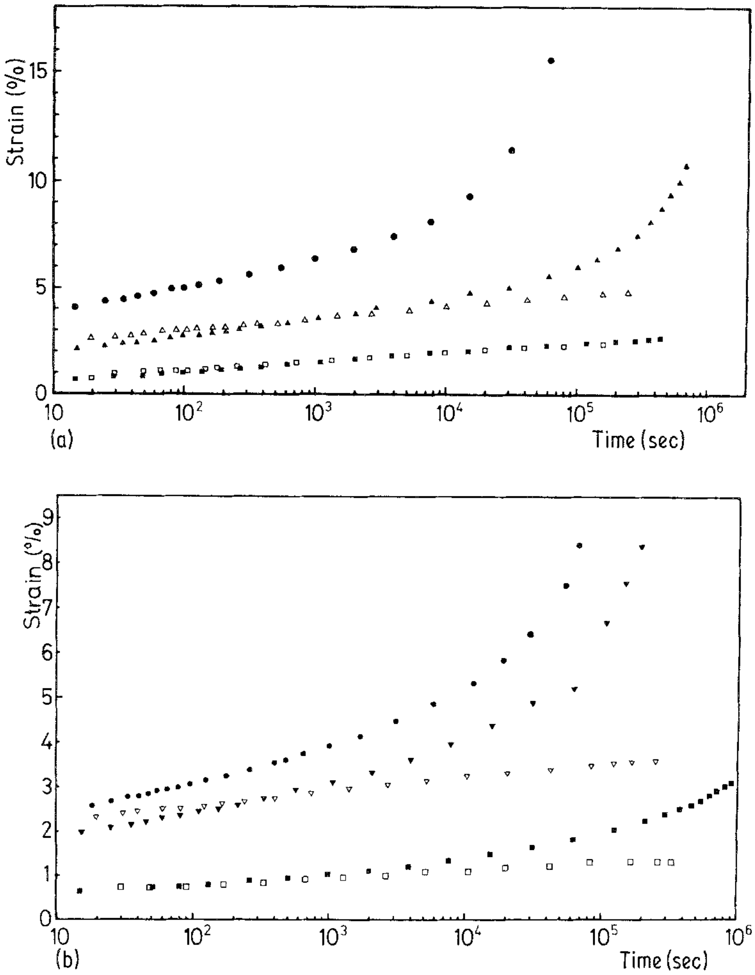

Figure 2 (a) Strain against time plots for Sample A at 30° C, at stress levels of (■) 0.064 GPa, (▲) 0.125 GPa, (●) 0.225 GPa. Solid symbols are creep, hollow symbols recovery. (b) Stress against time plots for Sample B at 30° C, at stress levels of (■) 0.084 GPa, (▼) 0.25 GPa, (●) 0.3 GPa. Solid symbols are creep, hollow symbols recovery.

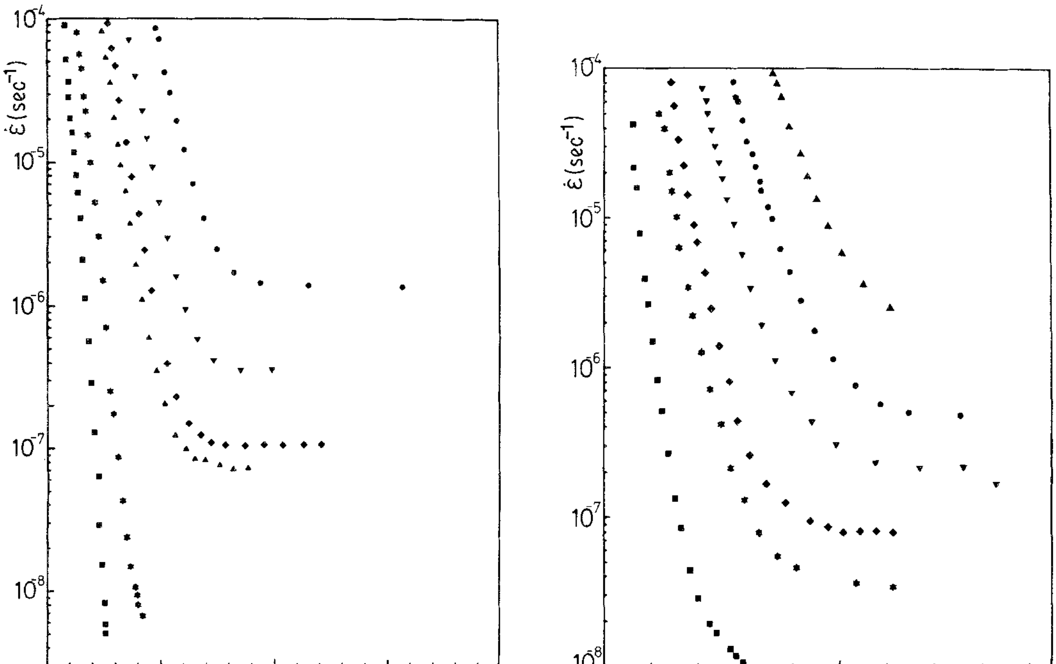

Figure 3 (a) Sherby–Dorn plots for Sample A at 30° C. Stress levels in GPa: (●) 0.225, (▼) 0.175, (◆) 0.15, (▲) 0.125, (★) 0.08, (■) 0.06. (b) Sherby–Dorn plots for Sample B at 30° C. Stress levels in GPa: (▲) 0.35, (●) 0.3, (▼) 0.25, (◆) 0.2, (★) 0.13, (■) 0.054.

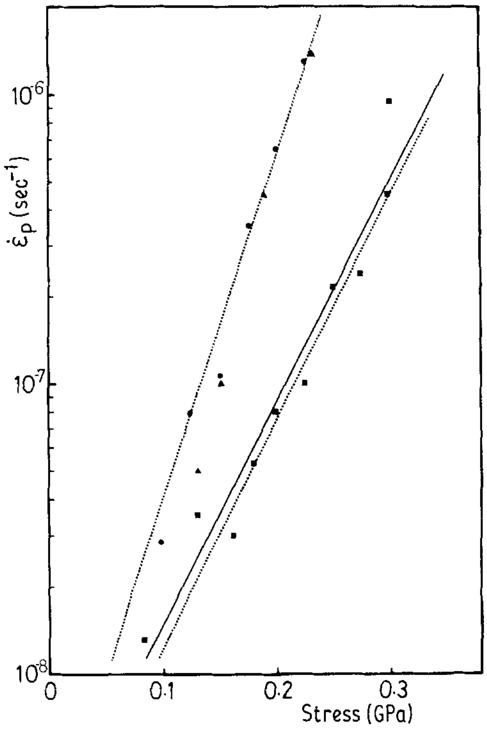

Figure 4 Plateau creep rate $\dot{\varepsilon}_p$ against stress for Sample A conditioned at (●) 30° C, (▲) 50° C; (■) Sample B at 30° C.

applied stress. As shown in Fig. 4, these plots for creep of polypropylene at 30° C show excellent linearity. This is consistent with the representation of the high-stress creep behaviour as a thermally activated Eyring-type process.

The plateau creep rate $\dot{\varepsilon}_p$ at a stress σ is then given by

$$\dot{\varepsilon}_p = \dot{\varepsilon}_0 \exp\left(-\frac{\Delta H}{kT}\right)\sinh\left(\frac{\sigma v}{kT}\right) \qquad (1)$$

where ΔH, v are the activation energy and activation volume, respectively, $\dot{\varepsilon}_0$ is the pre-exponential factor, k and T are Boltzmann's constant and absolute temperature, respectively. For high stress σ this reduces to

$$\dot{\varepsilon}_p = \dot{\varepsilon}_0 \exp\left(-\frac{\Delta H - \sigma v}{kT}\right) \qquad (2)$$

i.e. $\sigma = (\Delta H/v) + (kT/v)\ln(\dot{\varepsilon}_p/\dot{\varepsilon}_0)$ which is consistent with the results shown in Fig. 4, where it is shown that retaining the sinh form does not produce an improved fit.

Creep data for both 30 and 50° C are shown in Figs 5a and b for the low and high draw ratio samples, respectively. It can be seen that the 50° C results cannot be fitted to a single Eyring process (Fig. 6a). These results are similar to those observed in high modulus polyethylene where it was proposed that the behaviour can be represented by the two-process model shown in Fig. 6b. When the plateau creep rate is reached, the behaviour can then be described by the superposition of the two thermally activated processes, acting in parallel so that the stresses are additive. It was found that the data for polyethylene could be very well fitted by assuming that one process (Process 1) with a comparatively large activation volume, predominates at low strain rates and that a second process (Process 2) with a smaller activation volume comes into operation at high strain rates so that the two processes are then acting together. It is also assumed that Process 1 is satisfactorily described by the exponential form of Equation 2, so that the analytical form is given by

$$\frac{\sigma}{T} = \frac{k}{v_1}\left[\ln \dot{\varepsilon}_p - \ln\left(\frac{\dot{\varepsilon}_0}{2}\right)_1 + \frac{\Delta H_1}{kT}\right] + \frac{k}{v_2}\sinh^{-1}\left[\left(\frac{\dot{\varepsilon}_p}{\dot{\varepsilon}_0}\right)_2 \exp\frac{\Delta H_2}{kT}\right] \qquad (3)$$

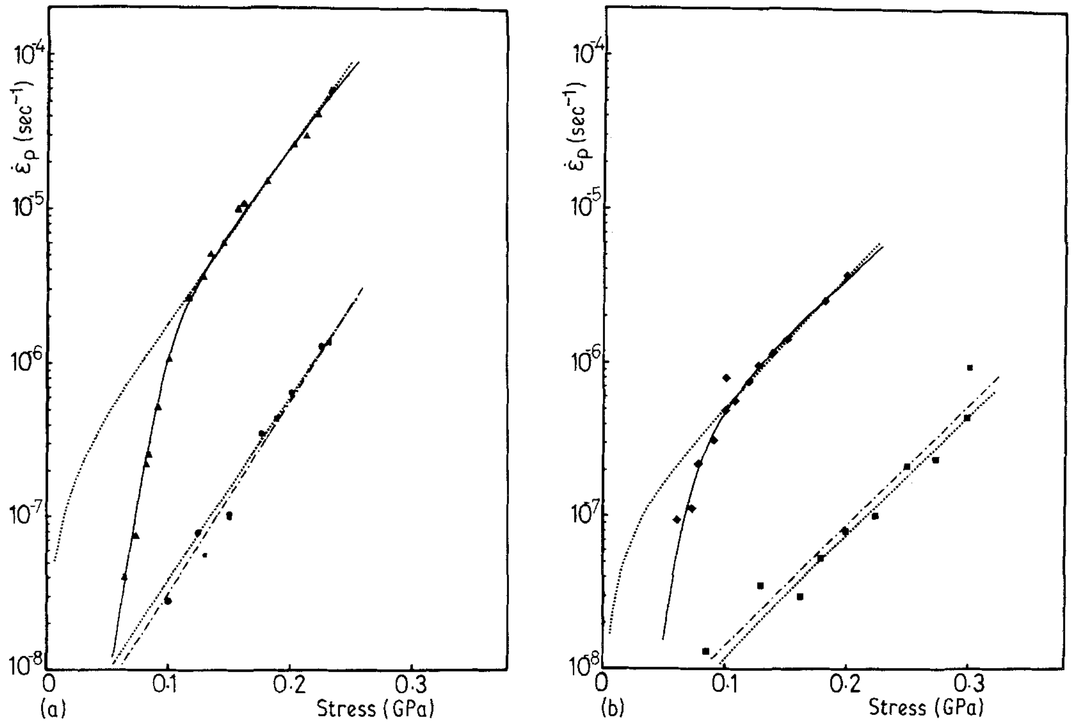

Figure 5 Plateau creep rate against stress for (a) Sample A at (●, ■) 30°C and (▲) 50°C; (b) Sample B at (■) 30°C and (◆) 50°C. (——) Fit to two-process model, (···) sinh fit, (– – –) straight-line fit.

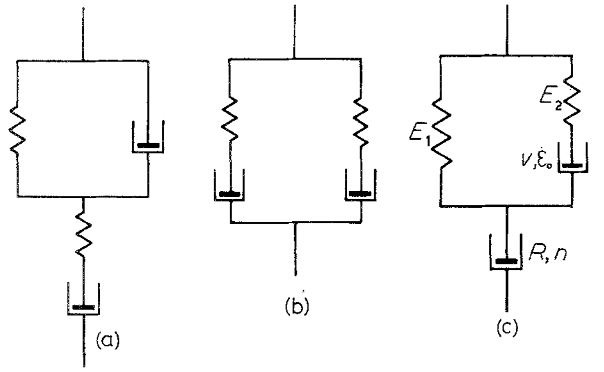

Figure 6 Mechanical models.

Writing $\dot{\varepsilon}_n' = (\dot{\varepsilon}_0)_n \exp(-\Delta H_n/kT)$ gives

$$\frac{\sigma}{T} = \frac{k}{v_1}\left(\ln \dot{\varepsilon}_p - \ln \frac{\dot{\varepsilon}_1'}{2}\right) + \frac{k}{v_2}\sinh^{-1}\frac{\dot{\varepsilon}_p}{\dot{\varepsilon}_2'} \qquad (4)$$

The fitted curves to Equation 4 are also shown in Figs 5a and b using a computer program in which all four variables were varied freely to find a best fit using a least-squares fit criterion. It can be seen that an excellent fit has been obtained, which coincides at high stress levels with the previous fits in terms of a single activated process.

The values of the fitting parameters obtained from the fitting procedures described above are shown in Table II. The relationships between the activation parameters are quite similar to those seen in highly drawn polyethylenes. Values of v_2 in the range 0.074 to 0.126 nm^3 are consistent with a localized chain-slip process, involving a similar number of unit cells as the equivalent process in highly drawn polyethylenes. The values for v_1 are larger and have been associated in polyethylene with the molecular network. The effect of increasing draw ratio is to reduce the value of v_2 markedly and probably the pre-exponential factor decreases also. It is interesting to speculate that increasing draw ratio increases the perfection of the structure so that the activated event becomes more localized (i.e. v_2 falls) and also reduces the number of available sites, thus reducing $\dot{\varepsilon}_2'$. Any decrease in $\dot{\varepsilon}_1'$ with increasing draw ratio reflects the increasing difficulty of finding available deformation processes as the molecular network becomes stretched to its limit. Also $\dot{\varepsilon}_2'$ increases by about two orders of magnitude with increase in temperature from 30 to 50° C, concomitant with the onset of the α-relaxation process.

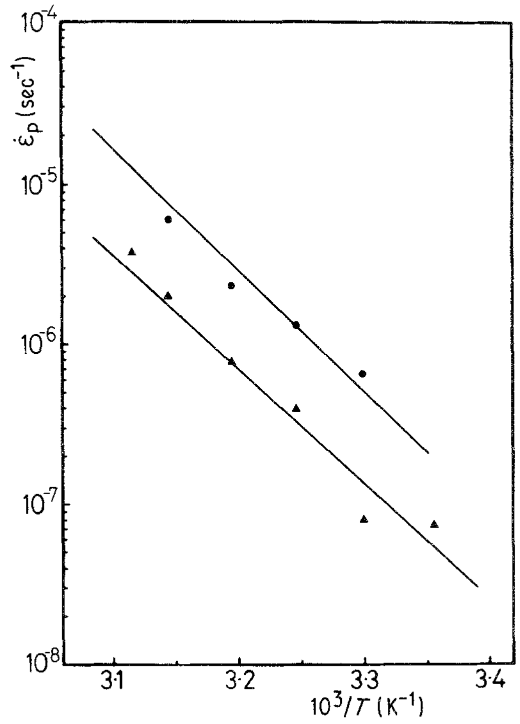

Figure 7 Log $\dot{\varepsilon}_p$ against $1/T$ for (●) Sample A and (▲) Sample B at a nominal stress of 0.2 GPa.

The activation energy ΔH has been calculated from the variation of plateau strain rate with temperature. These plots are shown in Fig. 7 and give values for ΔH of 37.7 ± 7.5 and 34.8 ± 6.6 kcal mol^{-1} for the draw ratio 10 and 17.5 samples, respectively (1 kcal = 4.1868 kJ). This is within the expected range for the activation energy of the α-process in polypropylene, which is usually attributed to a crystalline relaxation process. This result is therefore consistent with the view that Process 2 is associated with a slip process in the crystalline regions, and is similar to that obtained in polyethylene.

3.2. High molecular weight samples

Creep and recovery curves for the two high molecular weight samples at both 30 and 50° C initially appeared to be similar to those for the low molecular weight samples shown in Figs 2a and b. When the corresponding Sherby–Dorn plots are constructed, however, it appears that there is a major difference in that there is no plateau creep but the plots tend to downward-sloping lines (Fig. 8). Similar behaviour was observed

TABLE II Fitted values for the parameters of the different models for low molecular weight monofilaments at different draw ratios and temperatures

Model	Draw ratio	Temperature (° C)	v_1 (nm^3)	$\dot{\varepsilon}_1'$	v_2 (nm^3)	$\dot{\varepsilon}_2'$
Straight line	10	30			0.125	1.5×10^{-9}
sinh fit	10	30			0.114	5.2×10^{-9}
sinh fit	10	50			0.116	2.7×10^{-7}
Two process	10	50	0.509	4.9×10^{-11}	0.126	5.7×10^{-6}
Straight line	17.5	30			0.074	2.5×10^{-9}
sinh fit	17.5	30			0.075	4.1×10^{-9}
sinh fit	17.5	50			0.088	1.4×10^{-7}
Two process	17.5	50	0.628	3.6×10^{-11}	0.080	9.4×10^{-7}

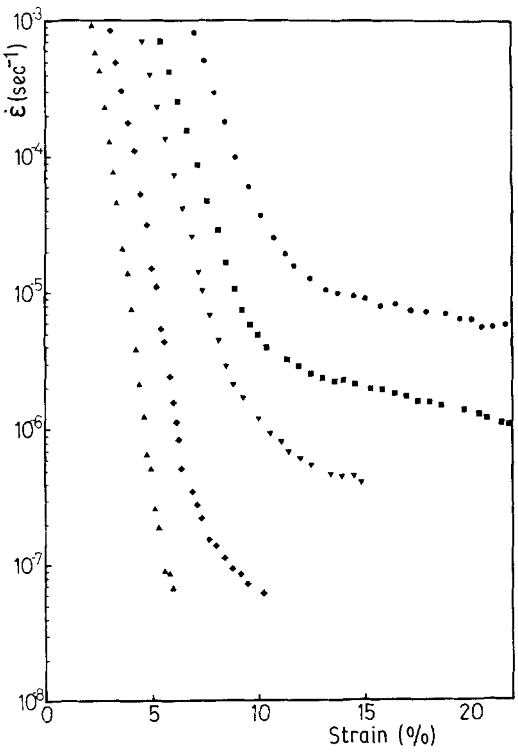

Figure 8 Sherby–Dorn plots for Sample C at 50° C. Stress levels in GPa: (▲) 0.1, (◆) 0.12, (▼) 0.16, (■) 0.2, (●) 0.26.

by Wilding and Ward [4] for high molecular weight polyethylene fibres of low draw ratio. It was shown that this behaviour could be very well described by the model shown in Fig. 6c. This represents a standard linear solid incorporating an Eyring-type dashpot in series with a non-Newtonian dashpot. The total creep $\varepsilon(t)$ at time t for an applied stress σ_0 is given by

$$\varepsilon(t) = \frac{a}{b} + \frac{1}{b}\ln[f(t)] + Rt^n \qquad (5)$$

where

$$a = \frac{\sigma_0 v}{kT}, \qquad b = \frac{E_1 v}{kT},$$

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

in which

$$K = \frac{1}{b}\ln\frac{1 - G}{1 + G}, \qquad G = \exp\left(\frac{b\sigma_0}{E_1 + E_2} - a\right)$$

and

$$A = \left(\frac{E_2}{E_1 + E_2}\right)\dot{\varepsilon}_0'$$

The symbols E_1, E_2 refer to the spring constants in Fig. 6b, the symbols v, $\dot{\varepsilon}_0'$ to the constants of the thermally activated Eyring dashpot, and R, n to the constants of the non-Newtonian series dashpot.

In the first instance the applicability of Equation 5 was tested by fitting the results for the low molecular weight materials. The six parameters (E_1, E_2, v, $\dot{\varepsilon}_0'$, R, n) were allowed to vary freely, and the best fit curve obtained to minimize a chi-squared test on the data. The computer program then used the fitted values to calculate Sherby–Dorn and creep strain in log(time) plots. In most cases a good fit could be obtained, and in all instances where a distinct plateau was observed, the value of n obtained was found to be unity, within experimental error. The value of R then corresponds directly with the plateau creep-rate $\dot{\varepsilon}_p$. Results for the low molecular weight draw ratio 17.5 sample measured at 30° C are shown in Figs 9 and 10, which are strain against log(time) and equivalent Sherby–Dorn plots, respectively.

The values of the parameters obtained from the fitting procedures for the results, such as those shown in Figs 9 and 10, are given in Table III. It can be seen

TABLE III Fitted values for the time-dependent creep model parameters for selected low molecular weight results

Draw ratio	Temperature (° C)	Stress level (GPa)	E_1 (GPa)	E_2 (GPa)	v (nm^3)	$\dot{\varepsilon}_0'$	$\dot{\varepsilon}_p'$ (sec^{-n})	n
10	30	0.124	2.09	5.31	0.536	1.92×10^{-8}	7.02×10^{-8}	1.000
10	30	0.200	2.62	8.67	0.379	4.59×10^{-8}	6.6×10^{-7}	1.000
10	50	0.084	1.45	4.07	0.872	5.49×10^{-8}	2.36×10^{-7}	1.000
10	50	0.100	1.57	15.6	0.846	2.99×10^{-9}	9.99×10^{-7}	1.000
17.5	30	0.162	5.33	8.1	0.300	8.67×10^{-8}	4.5×10^{-8}	1.000
17.5	30	0.299	5.3	7.91	0.209	1.24×10^{-7}	4.27×10^{-7}	0.998
17.5	50	0.091	2.96	8.49	0.641	1.68×10^{-8}	2.96×10^{-7}	1.000
17.5	50	0.139	2.76	8.44	0.498	8.44×10^{-9}	1.13×10^{-6}	1.000

TABLE IV Fitted values for the time-dependent creep model parameters for selected high molecular weight results

Draw ratio	Temperature (° C)	Stress level (GPa)	E_1 (GPa)	E_2 (GPa)	v (nm^3)	$\dot{\varepsilon}_0'$	R (sec^{-n})	n
10	30	0.15	2.34	19.4	0.443	3.36×10^{-7}	5.2×10^{-5}	0.511
10	50	0.119	1.4	21.0	0.720	4.17×10^{-8}	8.99×10^{-5}	0.500
10	50	0.221	1.9	13.2	0.412	8.32×10^{-8}	6.85×10^{-4}	0.509
12.5	30	0.161	2.34	5.07	0.401	1.05×10^{-7}	8.3×10^{-6}	0.492
12.5	30	0.235	3.25	7.26	0.297	2.84×10^{-7}	3.52×10^{-5}	0.497
12.5	50	0.161	2.11	3.98	0.410	1.99×10^{-6}	6.81×10^{-5}	0.499
12.5	50	0.241	2.55	3.97	0.280	7.47×10^{-6}	2.7×10^{-4}	0.500
12.5	50	0.270	1.84	14.0	0.313	7.86×10^{-8}	3.87×10^{-6}	0.900

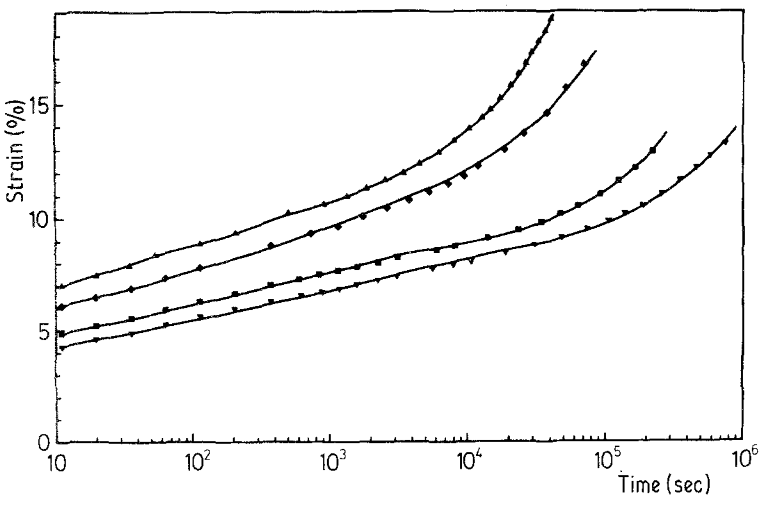

Figure 9 Creep against log(time) for Sample B at 30° C. Solid lines are the time-dependent model freely fitted to the data. Stress levels in GPa: (●) 0.3, (▼) 0.25, (■) 0.2, (▲) 0.16.

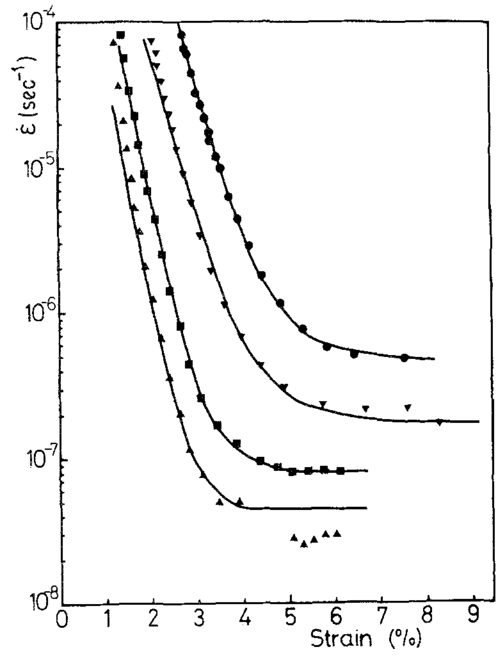

Figure 10 Sherby–Dorn plots for Sample B at 30° C. Solid lines are the time-dependent model freely fitted to the experimental data. Stress levels in GPa: (●) 0.3, (▼) 0.25, (■) 0.2, (▲) 0.16.

that the values of E_1 and E_2 are, to a first approximation, independent of stress. In general terms, E_1 and E_2 represent the stiffness associated with the network and the crystalline stiffening elements in the structure, respectively.

The two remaining parameters describe the behaviour of the Eyring dashpot in the model, and have no obvious physical significance. It is noted that v falls steadily with increasing stress level.

In the case of the high molecular weight samples, free fits to the experimental data were performed, as for the low molecular weight samples, but with an initial given value of n set at or near 0.5. This implies that the steady-state creep is strain-hardening at a rate which is inversely proportional to the strain. This procedure was found to give a good fit to the data for most of the results at low stress levels, with values of n very close to 0.5. Typical results are shown in Figs 11 and 12, and the fitting parameters obtained are summarized in Table IV. At higher stress levels the value of n rose to nearly unity, suggesting that the behaviour is approaching that of plateau creep. This behaviour is illustrated in Fig. 12 for the highest stress

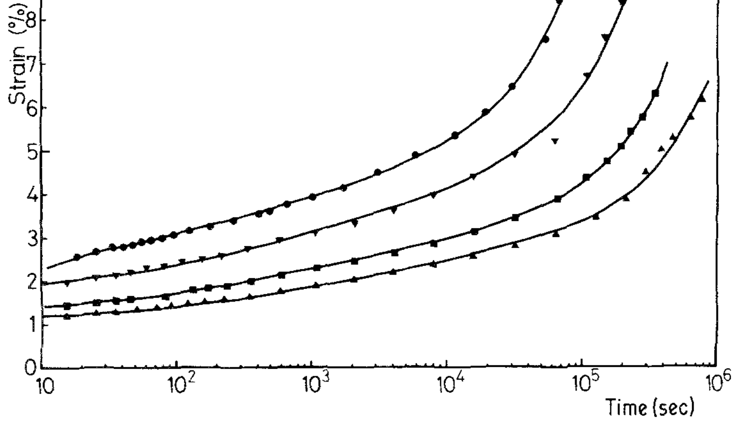

Figure 11 Creep against log(time) for Sample D at 50° C. Solid lines are the time-dependent model fitted to the data. Stress levels in GPa: (●) 0.27, (▼) 0.24, (■) 0.18, (▲) 0.16.

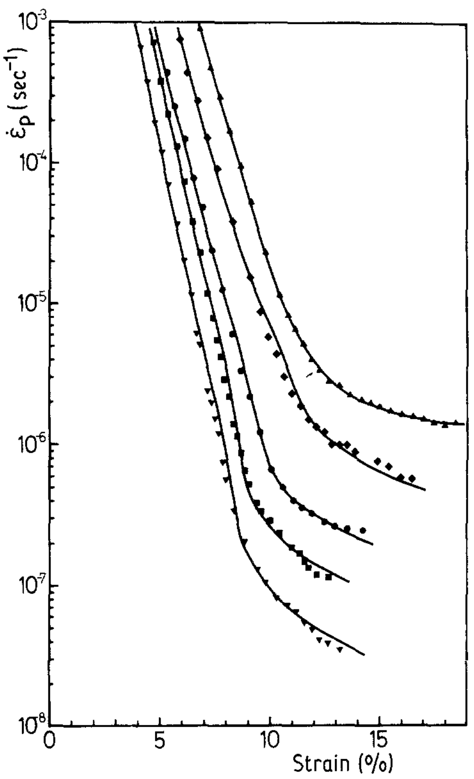

Figure 12 Sherby–Dorn plots for Sample D at 50° C. Solid lines are the time-dependent model fitted to the data. Stress levels in GPa: (▲) 0.27, (◆) 0.24, (●) 0.20, (■) 0.18, (▼) 0.16.

level. It is tentatively concluded that the high molecular weight samples would reach plateau creep behaviour at high stress levels, but brittle failure intervenes before this is achieved.

4. Conclusions

The creep and recovery behaviour of high modulus polypropylene shows many similarities to that of high modulus polyethylene. As for polyethylene, it has been found useful to determine the creep rate as a function of time, and examine the validity of simple mechanical models.

For low molecular weight samples the creep rates reached a constant "plateau" value at high stress levels. At room temperature the stress dependence of these plateau creep rates was consistent with their representation in terms of a single thermally activated process. At 50° C the behaviour could be accurately represented by a two-process model where there is a low activation volume process in parallel with a large activation volume process. The activation energy of the low activation volume process is similar to that for the α-relaxation process, and the activation volume ($\sim 0.1\,\text{nm}^3$) is consistent with a localized crystal-slip process. Following the previous work on polyethylene, the larger activation value process is tentatively associated with the molecular network.

The high molecular weight samples do not in general appear to reach a constant creep rate. Following previous experience with polyethylene, a modified model was introduced, which permits the representation of a necessary degree of strain-hardening.

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