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Analysis of the non-linear creep of high-density polyethylene

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Short- and long-term tensile creep tests of high-density polyethylene (HDPE) have been performed at different stress levels under an ambient temperature of 20°C. The effects of stress and physical ageing on the creep compliance are studied. The short-term creep data show that the distribution of relaxation times of HDPE is shifted even by a very low stress. Acceleration of creep can be realized by applying high stresses, and a momentary master curve of creep compliance can be constructed using the time–stress superposition principle. At low stresses, though the material exhibits strong non-linearity, the ageing rate μ is found to be independent of stress. A unified non-linear creep relation is obtained that incorporates the physical ageing effect and predicts the long-term creep behaviour with good agreement with experiments.

(Keywords: high-density polyethylene; creep; time–stress superposition)

INTRODUCTION

Creep is not only an important phenomenon in its own right within the framework of viscoelasticity but is also of great significance in the design of plastics products, as it reflects the load-bearing capacity of end-products. Structural design engineers are faced with the challenge of creep rupture and other time-dependent failures of polymer structures in engineering. An assessment of durability should be made at the design stage in order to prevent premature failures and to avoid intolerably large deformation.

Various empirical equations have been proposed for describing the creep behaviour of polymers. Among others, the Kohlrausch–Williams–Watts (KWW) relation seems to be relatively versatile and has been widely used to fit the creep data of many polymers[1–4]. If a low-strain (linear) tensile creep is concerned, the creep compliance $D(t)$ can be expressed by the KWW relation as:

$$D(t)=D_0 \exp[(t/t_0)^{\gamma}] \qquad (1)$$

where t_0 is a mean relaxation time dependent on temperature and ageing time, and D_0 and γ are constants. This relation, however, is only valid for creep over limited periods of time at the start of α relaxation[5]. Extrapolating creep data to longer times using equation (1) or other empirical creep laws will inevitably introduce errors into the results.

The so-called time–temperature superposition principle makes it possible to trace out the creep behaviour of polymers over a much longer effective range of time by making measurements at higher temperatures. If the material is thermorheologically simple, the distribution of relaxation times will be shifted when the temperature changes. The creep compliance at two different temperatures T_0 and T_1 can be related by the following equality:

$$D(t, T_0)=D(t/a_T, T_1) \qquad (2)$$

where a_T is the time–temperature shift factor given by the Williams–Landel–Ferry (WLF) equation[6]:

$$\log a_T=\frac{C_1(T-T_g)}{C_2+(T-T_g)} \qquad (3)$$

In equation (3), T_g is the glass transition temperature and C_1 and C_2 are constants. The WLF equation has been justified from consideration of the effect of free volume in polymers[7]. It is accepted that the distribution of relaxation times of a polymer is shifted by a change in temperature through the temperature-induced change in free volume. Most amorphous polymers are found to be thermorheologically simple. Some successful applications of the time–temperature superposition principle have been reported in the book by Tobolsky[8]. Owing to the complex coupling of the crystalline phase and the amorphous phase, the mechanical behaviour of a semicrystalline polymer is more complicated than that of an amorphous polymer. The time–temperature superposition principle is generally not applicable to semicrystalline polymers[9–11].

Under temperatures below the glass transition temperature T_g, a polymer undergoes progressive structural changes in order to reach thermodynamic equilibrium. This is the phenomenon known as physical ageing. Characteristically, physical ageing is accompanied by a reduction of free volume[1]. As a result, the material will become stiffer and stiffer after quenching from a temperature above T_g. Therefore, physical ageing is a phenomenon of great importance for polymers under constant temperature. Equation (1) and the master curve constructed using the time–temperature superposition principle describe only the behaviour of short-term creep.

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Short-term creep means either that the creep time t is short compared with the physical age of the polymer as determined by the elapsed time t_e between quenching from temperature above T_g and the start of the creep test, or that progressive ageing is assumed not to take place during the creep test. To give a reasonable description of creep response over a wide range of times, the physical ageing effect must be included in creep modelling.

High-density polyethylene (HDPE) is a semicrystalline polymer with many excellent properties and it is widely used in industry and engineering for structural components such as gas and water pipelines. It has been found[12] that HDPE exhibits a strong non-linear behaviour even at a very low stress level. Linearity of the behaviour of this material seems to exist only at vanishingly small stresses. Equation (1) is no longer valid for describing the momentary (short-term) creep behaviour[10]. Moreover, the time–temperature superposition principle cannot be used for constructing the momentary master curve of creep compliance of HDPE[10,11,13]. It is of great technical relevance to predict the long-term creep behaviour of HDPE with data from short-time tests. To achieve this goal, the short-term creep influenced by the applied stress and the effect of physical ageing in the non-linear region need to be characterized.

The purpose of this paper is to analyse the non-linear creep behaviour of HDPE, and especially to investigate the effects of applied stress and physical ageing on the creep compliance. A unified creep relation will be developed to predict the long-term creep deformation.

EXPERIMENTAL

The compression-moulded HDPE plate (tradename Multilene D 500) with a size of 2000 x 1000 x 50 mm^3 was kindly supplied by Eriks Kunststoffen, The Netherlands. The density of the material is 0.95 g cm^{-3}. The blank from which specimens were machined was cut from the middle of the plate in order to reduce the difference in the degree of crystallinity along the thickness direction. All tests employed round dog-bone specimens with a gauge length of 80 mm and a diameter of 8 mm.

The specimens were heat-treated in an oven at a temperature of 90°C for 18 h in order to eliminate the residual stress and/or strain during processing and machining. For the short- and long-term creep tests the specimens were quenched from 90°C to, and then stored at, the environmental temperature of 20°C for an elapsed ageing time t_e of 4 h before testing. The ageing times of the specimens for tests of the physical ageing effect are 1, 2, 4, 8 and 16 h respectively.

All tests were performed at the ambient temperature of 20 ± 1°C. The short-term creep tests for a time of 1000 s were carried out on an Instron 4505 with a load cell of 1 kN. The stress level at which the creep tests were conducted ranged from 2 to 16 MPa. The tests for examining the ageing effects were performed at three stress levels, 2, 4 and 6 MPa. The long-term creep tests were carried out on a dead-weight creep set-up. In all tests the strain was measured by an Instron extensometer with a full range of 2.5 mm and a gauge length of 25 mm. The experimental data of strain *versus* time were recorded simultaneously by a personal computer.

RESULTS AND DISCUSSION

The short-term creep behaviour

The experimental data of creep for a time of 1000 s are shown in *Figure 1*, where the creep compliance is defined as the strain-to-stress ratio. The tensile load divided by the initial cross-sectional area of the specimen is defined as the stress under which the creep tests were conducted. The strain here is referred to as nominal or engineering strain. Since the creep time is considerably shorter compared with the physical age t_e of the specimens ($t_e = 4$ h), the progressive ageing during creep can be ignored and the experimental data are momentary or short-term results.

Figure 1 shows that the creep compliance is stress-dependent at all stress levels and that the up-swing of the compliance curve increases with the stress level. This indicates that HDPE exhibits a strong non-linear behaviour with the stress dependence and time dependence of creep compliance coupled. For most amorphous polymers there exists a linear viscoelastic region and a transition from linear to non-linear viscoelasticity[14]. However, no linearity for HDPE is observed from *Figure 1*. The linearity of this material seems to exist only at vanishingly small stresses. This could be due to the composite structural features of semicrystalline polymers. According to Struik[10], in a semicrystalline polymer crystals reduce the segmental mobility of amorphous regions close to them. An amorphous region remote from crystals remains undisturbed and hence is more mobile. For HDPE at room temperature, an amorphous region remote from the crystals has passed its T_g and is in the rubbery state, while an amorphous region close to the crystals is still in the glassy state because of the disturbance of the crystals. It could then be argued that at low stresses the crystals only contribute to the elastic deformation[10], and the amorphous region close to the crystals behaves like a bulk glassy amorphous polymer below its T_g and exhibits linear behaviour, while the more mobile amorphous region remote from the crystals exhibits a non-linear behaviour since the free volume can be increased through stress-induced

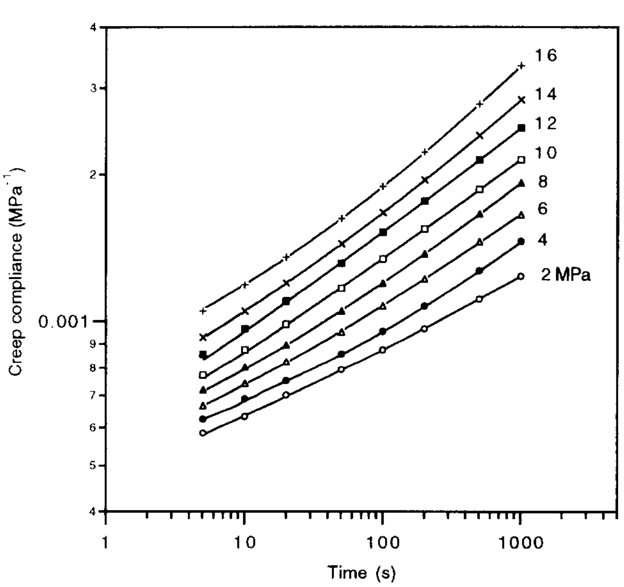

Figure 1 Experimental data of short-term creep ($t_e = 4$ h)

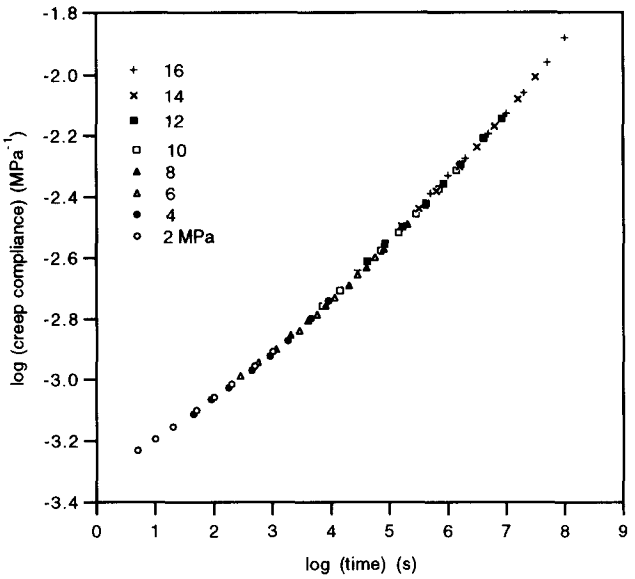

Figure 2 Superposed master curve of creep compliance at 2 MPa

dilatation, as in the situation of a bulk amorphous polymer above its T_g.

The strong non-linearity exhibited by HDPE raises the question as to the way in which the stress dependence and time dependence of the creep compliance are related. The observation from *Figure 1* that the up-swing curvature of the creep compliance increases with the applied stress motivates us to apply the time–stress superposition to construct a master curve of the creep compliance. It is found that if the creep compliance is plotted *versus* time in a double-logarithmic coordinate system, as is shown in *Figure 1*, a consistent master curve can be constructed by applying horizontal and vertical shifts of creep compliance curves into a reference curve. *Figure 2* shows the master curve of creep compliance at 2 MPa. Hence the relation between the creep compliance D at two stress levels can be expressed as:

$$D(t, \sigma_1) = gD(t/a_\sigma, \sigma_2) \tag{4}$$

where $\log g$ and $\log a_\sigma$ are vertical and horizontal shift factors respectively. These are shown in *Figure 3*. From equation (4) it can be seen that time and stress are coupled in the creep compliance through the time–stress shift factor a_σ. It is interesting to notice that this time–stress shift factor can be related to the applied stress by the following expression:

$$\log a_\sigma = \frac{C_1(\sigma - \sigma_0)}{C_2 + (\sigma - \sigma_0)} \tag{5}$$

which is similar to the WLF equation[6] (see equation (3)). In equation (5), C_1 and C_2 are constants and σ_0 is a reference stress. If σ_0 is chosen as 2 MPa, $C_1 = -15.016$ and $C_2 = 28.406$.

It has been realized that the effect of increasing pressure on the mechanical properties of polymers is similar to the effect of decreasing temperature[15–17]. On the basis of the free-volume theory, Ferry and Stratton[18] derived the pressure analogue of the WLF equation in the form:

$$\log a_p = \frac{(B/2.303 f_0)(p - p_0)}{f_0/\kappa_f - (p - p_0)} \tag{6}$$

where a_p is the time–pressure shift factor when pressure changes from the p_0 to p, B is a constant, f_0 is the fractional free volume at the reference pressure p_0, and κ_f is the isothermal compressibility of the free volume. In our uniaxial tensile creep tests under stress σ, the hydrostatic pressure contribution p is $-\frac{1}{3}\sigma$. If σ and σ_0 are replaced by $-3p$ and $-3p_0$ respectively, equation (5) is seen to be consistent with equation (6). Therefore, a tensile stress can change the distribution of relaxation times of HDPE through stress dilatation or stress-induced change in free volume. This feature leads to the stress–time superposition.

In view of equation (4), the expression for creep strain $\varepsilon_c(t)$ can be formulated as:

$$\varepsilon_c(t) = \sigma g \bar{D}(t/a_\sigma) \tag{7}$$

where $\bar{D}(t)$ is the compliance of the superposed master curve, and can be represented by the Prony series as:

$$\bar{D}(t) = D_0 + \sum_{i=1}^{N} D_i\left[1 - \exp\left(-\frac{t}{\tau_i}\right)\right] \tag{8}$$

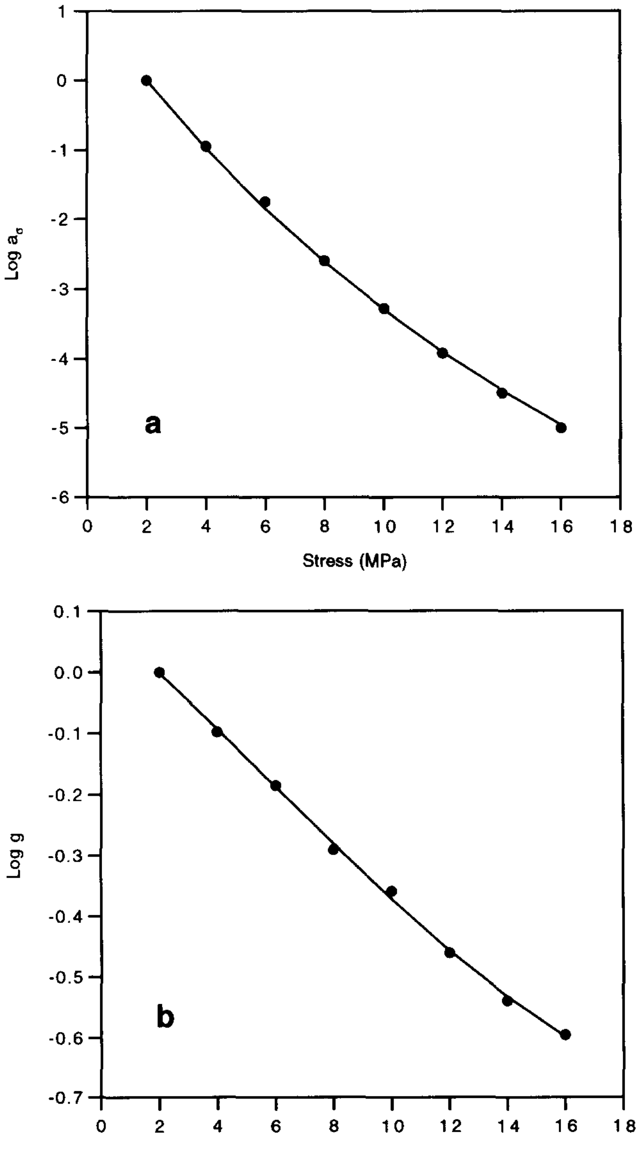

Figure 3 Horizontal shift factor (a) and vertical shift factor (b)

Table 1 Coefficients in the Prony series

i	D_i (MPa^{-1})	τ_i (s)
0	5.1011×10^{-4}	∞
1	1.6145×10^{-4}	10
2	2.4831×10^{-4}	10^2
3	3.7378×10^{-4}	10^3
4	6.5334×10^{-4}	10^4
5	1.0489×10^{-3}	10^5
6	1.8541×10^{-3}	10^6
7	2.9959×10^{-3}	10^7
8	6.0332×10^{-3}	10^8
9	1.5205×10^{-2}	10^9

where the characteristic retardation time τ_i is chosen as 10^i. It is found that taking 10 terms in the Prony series suffices to obtain a good fit of equation (8) to the data in *Figure 2*. D_0 and D_i are thus determined and listed in *Table 1*.

The successful superposition of a master curve of creep compliance indicates that creep tests of HDPE can be accelerated by raising the stress. The time–stress superposition principle can be related to the Schapery thermodynamic theory[19], and has been applied successfully to fibre-reinforced plastics[20,21]. This superposition principle is valid for HDPE at any stress level, since the linearity of this material exists only at vanishingly low stresses, and stress-induced dilatation arises even from a very low stress. For some amorphous polymers such as poly(methyl methacrylate) (PMMA), however, the time–stress superposition principle is found to be applicable at high stresses[22,23], or at moderately high stresses beyond the linear limit only after the β peak is subtracted from the response[24].

Physical ageing effect

Physical ageing in glassy amorphous polymers has been extensively studied. It is accepted that, owing to the ageing effect, the distribution of relaxation times is shifted towards longer times[1]. The temperature range of physical ageing starts from the highest secondary transition temperature and terminates at the glass transition temperature. Physical ageing in semicrystalline polymers is more complicated than in amorphous polymers. Struik[1,10] treated this difficult problem by assuming that crystals reduce the segmental mobility of the amorphous region close to them and, as a result, extend the glass transition temperature to the high-temperature side. The glass transition temperature for a semicrystalline polymer has a wide range from the lower limit T_g^L to the upper limit T_g^U. Below T_g^L the physical ageing mechanism is exactly the same as that in an amorphous polymer. Between T_g^L and T_g^U, the ageing effect is solely due to the amorphous region close to crystals. Above T_g^U, the entire amorphous region enters the rubbery regime, and there is no ageing effect any more. Furthermore, Struik demonstrated that physical ageing influences semicrystalline polymers also by moving the distribution of relaxation times as a whole to the high-temperature side. This idea, however, has been questioned by Chai and McCrum[25], who discovered that for some semicrystalline polymers, e.g. polypropylene, the relaxation spectrum can change shape during physical ageing. The work of Read *et al.*[26] suggested that physical ageing produces an increase in retardation times and broadening of the α relaxation of polypropylene.

In order to examine the physical ageing effect on the creep behaviour of HDPE, a series of creep tests with different elapsed physical ageing times t_e were performed at three stress levels, 2, 4 and 6 MPa. In these tests the creep time $t \leqslant 0.1t_e$, so that the short-term behaviour was assured.

Figures 4–6 display the creep compliance of different elapsed ageing time t_e at 2, 4 and 6 MPa respectively. Time–ageing superposition is tried to form a master curve. It is found that, through a combination of horizontal and vertical shifts, all the creep compliance curves with different ageing time can be brought onto a master curve. This indicates that, at least at room temperature, physical ageing shifts the spectrum of

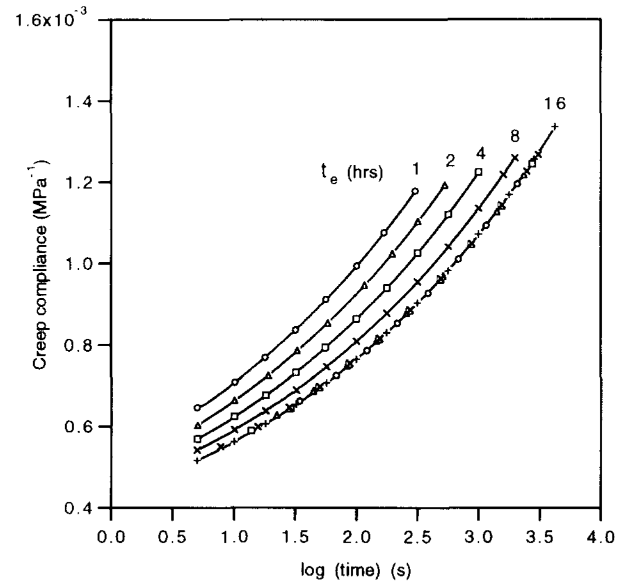

Figure 4 Creep compliance at 2 MPa for various elapsed time t_e after quenching from 90°C to 20°C

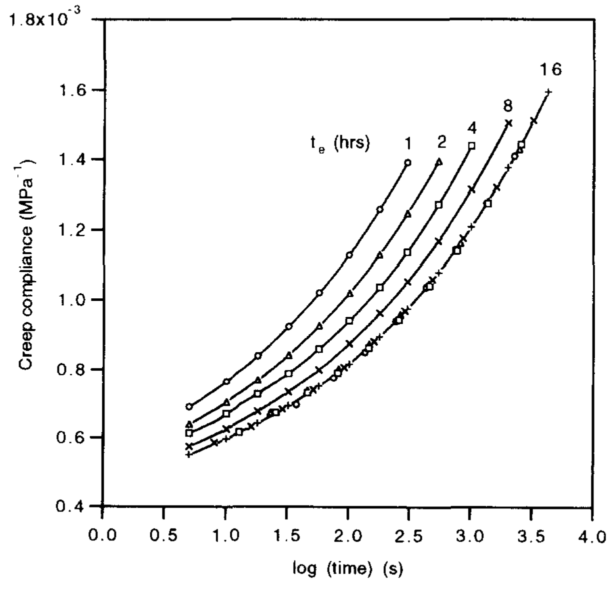

Figure 5 Creep compliance at 4 MPa for various elapsed time t_e after quenching from 90°C to 20°C

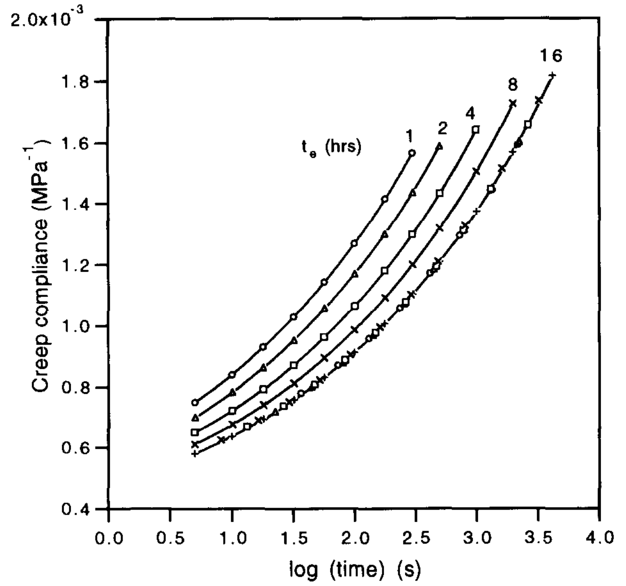

Figure 6 Creep compliance at 6 MPa for various elapsed time t_e after quenching from 90°C to 20°C

relaxation times to longer times, which is consistent with Struik's results in ref. 10. According to Struik's model[1,10], the horizontal shift may be thought to be from the amorphous region close to the crystals with its T_g above the environmental temperature, while the vertical shift is due to the amorphous region far from the crystals, which has passed its glass transition temperature and is insensitive to physical ageing.

The horizontal shift factor a_e is of special interest, as it can be used to calculate the ageing rate μ, a quantity necessary for incorporating the physical ageing effect in the long-term creep expression. The ageing rate μ is defined as:

$$\mu = \frac{\mathrm{d}\log a_e}{\mathrm{d}\ \log t_e} \tag{9}$$

If $\log a_e$ is plotted against $\log t_e$, the slope gives the value of μ, as shown in *Figure 7*.

It is known that a high stress can partially erase the previous ageing and thus rejuvenates a polymer specimen. In the linear region of an amorphous polymer, the rejuvenation effect due to a stress is negligible and the ageing rate μ is independent of the applied stress. The rejuvenation effect becomes significant after onset of non-linearity in an amorphous polymer, with the ageing rate decreasing with the applied stress. The stress dependence of ageing rate of various amorphous polymers has been summarized in ref. 1. From *Figure 7* it is seen that μ for HDPE is nearly constant and approximately equal to 0.69 for the three stress levels concerned, although the material exhibits strong non-linear behaviour, as shown in *Figure 1*. As discussed above, at low stress levels, the non-linearity arises from the more mobile amorphous region remote from the crystals, which is in the rubbery state and insensitive to physical ageing. The less mobile amorphous region close to the crystals, which is responsible for the ageing effect, however, exhibits linear or weak non-linear behaviour. The applied stress is not high enough to erase the previous ageing of this part of the amorphous region. Therefore, the rejuvenation of HDPE by stresses is not so pronounced as that of amorphous polymers in the region of non-linear viscoelasticity.

Unified creep expression for predicting the long-term creep behaviour

In the above discussions about the short-term creep tests, the physical age of each specimen is assumed to be frozen, since the creep time is considerably shorter than the elapsed time t_e. The master curve of creep compliance constructed using the time–stress superposition principle is also a momentary one. No progressive physical ageing is taken into account in that stage. The physical ageing has been seen to influence HDPE in such a way that it shifts the relaxation times to longer times. For a long-term creep test, not only the elapsed time t_e before the test but also the progressive ageing during creep will affect the behaviour of polymers. The progressive ageing must be incorporated in the creep relation derived above in order to predict the long-term creep deformation of HDPE.

The progressive ageing effect during creep can be accounted for by introducing an ageing reduced time (effective time)[1,11], which is defined as:

$$\psi_e = \int_0^t \frac{\mathrm{d}\tau}{a_e} \tag{10}$$

In view of (9), a_e can be expressed as

$$\frac{1}{a_e} = \left(\frac{t_e}{t+t_e}\right)^{\mu} \tag{11}$$

Substituting equation (11) into equation (10), we obtain the ageing reduced time:

$$\psi_e = \frac{t_e}{1-\mu}\left[\left(1+\frac{t}{t_e}\right)^{1-\mu} - 1\right] \tag{12}$$

Replacing the time t with the ageing reduced time ψ_e in equation (7) leads to:

$$\varepsilon_c(t) = g\sigma\bar{D}(\psi_e/a_\sigma) \tag{13}$$

Substituting equations (8) and (12) into equation (13), we finally obtain the unified creep relation for HDPE in

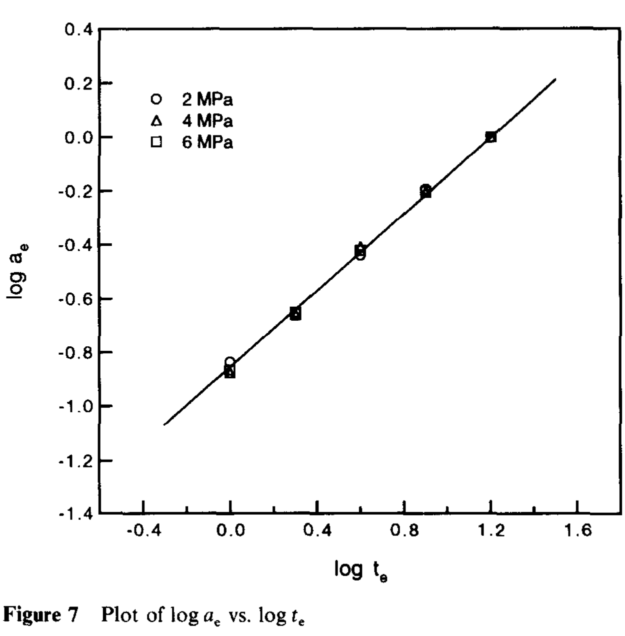

Figure 7 Plot of $\log a_e$ vs. $\log t_e$

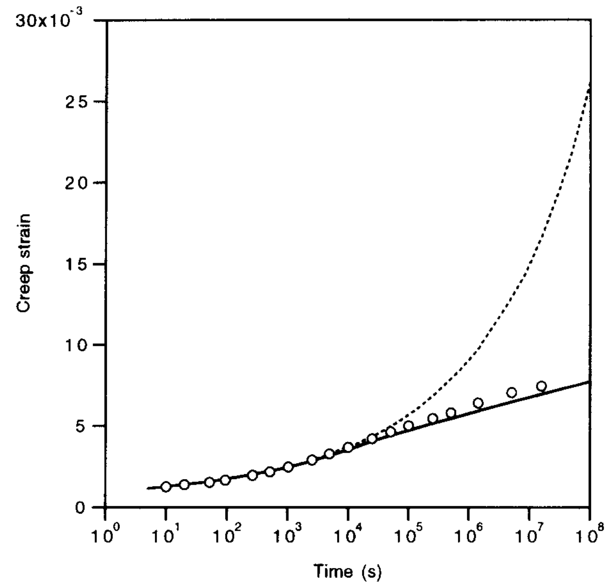

Figure 8 Momentary creep calculated using equation (7) (---), prediction from equation (14) (——) and the experimental data of long-term creep at 2 MPa (○); $t_e = 4$ h, $\mu = 0.69$

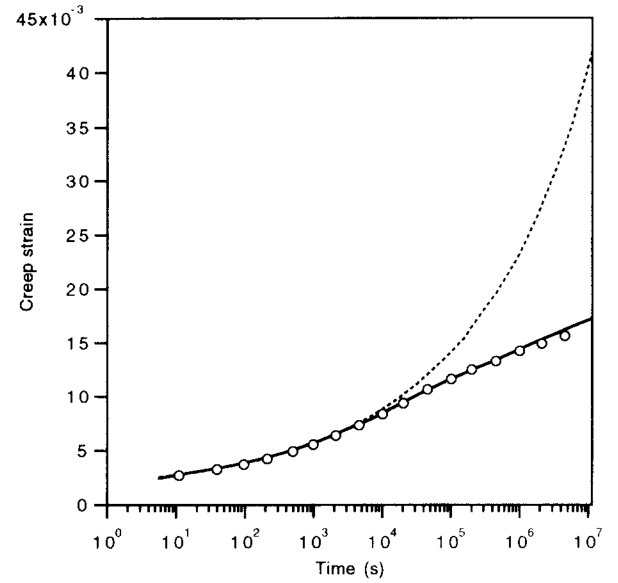

Figure 9 Momentary creep calculated using equation (7) (---), prediction from equation (14) (——) and the experimental data of long-term creep at 4 MPa (○); $t_e = 4$ h, $\mu = 0.69$

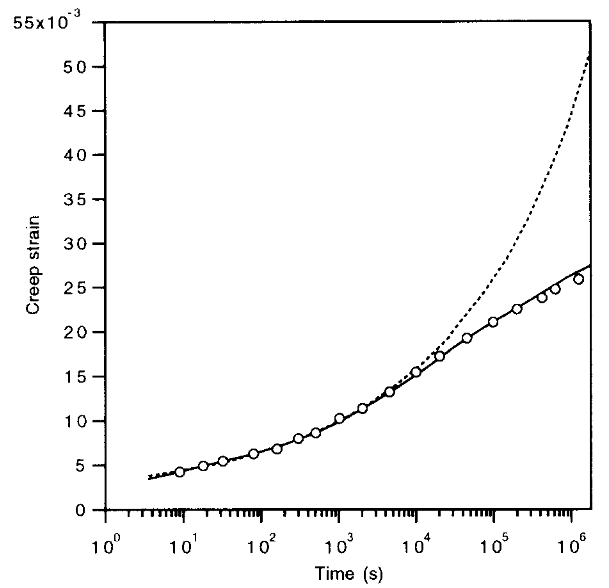

Figure 10 Momentary creep calculated using equation (7) (---), prediction from equation (14) (——) and the experimental data of long-term creep at 6 MPa (○); $t_e = 4$ h, $\mu = 0.69$

the following form:

$$\varepsilon_c(t)=\sigma g\left\{D_0+\sum_{i=1}^{10} D_i\left[1-\exp\left(-\frac{t_e[(1+t/t_e)^{1-\mu}-1]}{(1-\mu)\tau_i a_\sigma}\right)\right]\right\} \tag{14}$$

With equation (14) it is possible to predict the long-term creep deformation of HDPE. *Figures 8–10* show the momentary creep calculated using equation (7), the prediction from equation (14) and experimental data of creep at 2, 4 and 6 MPa respectively. It is seen that the actual long-term creep curve deviates from the momentary creep curve at about 10^4 s and becomes flattened at long times due to the physical ageing effect. The prediction is seen to agree very well with the experimental data, with the discrepancy less than 7.5% up to 10^6 or 10^7 s.

CONCLUSIONS

HDPE exhibits strong non-linear behaviour. The distribution of relaxation times is shifted towards shorter times by a stress through stress dilatation or stress-induced change in free volume. Creep can be accelerated by raising stress and a master curve of creep compliance can be constructed by the time–stress superposition principle.

At room temperature, physical ageing shifts the distribution of relaxation times of HDPE to longer times. The time–elapsed time superposition suggested by Struik[10] for semicrystalline polymers is still applicable. The ageing rate is independent of the low applied stress, and the rejuvenation effect due to stress is negligible, although the material is already in the strong non-linear regime at a very low stress.

A unified creep relation incorporating the physical ageing effect is derived, which is capable of predicting the long-term creep deformation of HDPE. The prediction compares favourably with the experimental data.

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