Physical ageing and short-term creep in amorphous and semicrystalline polymers

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(Received 15 September 1989; accepted 14 November 1989)

Studies have been made of the effect of physical ageing at 23°C on the short-term creep of polycarbonate (PC), poly(butylene terephthalate) (PBT) and high density polyethylene (HDPE) at creep times between 10^{-8} and 10^5 s. The age state of each polymer sample was specified by the elapsed time t_e at 23°C between quenching from a temperature at which the structure is close to equilibrium with respect to the α-retardation process and the start of a creep test. With increasing age, a small decrease was evident in the relaxed compliance $D_{R\beta}$ of the β-retardation process in each polymer and relationships between $D_{R\beta}$ and t_e were derived from quantitative analyses of the data. For the amorphous PC and semicrystalline PBT, this decrease could reflect a slight reduction in the number of groups participating in the localized secondary process. It also appeared for PC and PBT that the average retardation time for the glass–rubber α-process increased with t_e, with negligible change in the shape of the retardation time distribution or the magnitude of the α-retardation. For HDPE, the small decrease in $D_{R\beta}$ with increasing t_e for the glass–rubber β-process is similar to that found for polypropylene and might involve conformational changes of amorphous tie-molecules. The results for HDPE deviate from the predictions of Struik's model of ageing in semicrystalline polymers and suggest that, for the crystal-related α-process, changes in retardation magnitude or shape of the retardation time distribution may occur with increasing age.

(Keywords: creep; physical ageing; amorphous polymers; semicrystalline polymers)

INTRODUCTION

It is widely recognized that the structural changes associated with the physical ageing of polymers can have a marked effect on the creep and related viscoelastic behaviour[1–7]. However, for the various types of retardation process observed in amorphous and semicrystalline materials, opinions often differ about the extent to which these effects involve increases in retardation times, changes in shape of the distributions of retardation times or changes in magnitude of the retardation processes. These uncertainties arise largely from limitations in the experimental timescales, which usually cover only a small part of a single retardation region.

Short-term creep data have now been obtained for several polymers as a function of age state over wide ranges of time (10^{-8}–10^5 s) using a combination of static and dynamic techniques. Both the ageing and the creep measurements were made at room temperature. After a brief survey of relevant data and the methods of analysis, results are presented in this paper for an amorphous polymer, polycarbonate (PC), and for two semicrystalline polymers, poly(butylene terephthalate) (PBT) and high density polyethylene (HDPE). The results are discussed in terms of the influence of ageing on the resolved contributions to the creep from slightly overlapping α- and β-retardation regions. Particular consideration is then given to the validity of the model recently proposed by Struik to account for physical ageing effects in semicrystalline polymers[2].

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BACKGROUND SURVEY

This paper is concerned mainly with the physical ageing and subsequent creep of polymers at a temperature T (particularly room temperature) in the range $T_\alpha > T > T_\beta$. Here T_α and T_β are the temperatures of the α- and β-relaxation regions determined from dynamic mechanical measurements as a function of temperature at a constant frequency around 1 Hz[8,9]. Before the creep experiments, the samples are first heated to a temperature around or above T_α for a period sufficient to erase any previous ageing and yield an equilibrium (or essentially constant) structure with respect to the α-process. After the samples are quenched from this temperature to temperature T, they are stored for different elapsed times t_e before the creep tests are started. In seeking new equilibrium structures, the samples physically age during this period through slow molecular rearrangements associated with the α-process. The elapsed time t_e thus provides a measure of the physical age of a sample. It should be emphasized that this paper relates exclusively to short-term creep behaviour for which creep times t are always $\lesssim 0.2t_e$ so that any further ageing during the creep test is negligible[1,5].

Figure 1 illustrates schematic curves of tensile creep compliance $D(t)$ plotted against $\log t$ at temperature T for two samples of a given polymer with different age states. The ages are characterized by t_e and t_{er}, respectively, where t_{er} is some reference elapsed time. The curves were drawn on the basis of data obtained for various polymers at room temperature over about 13 decades of time[3–5] and they were extrapolated to cover more than 20 decades. Over this extensive time range, two overlapping

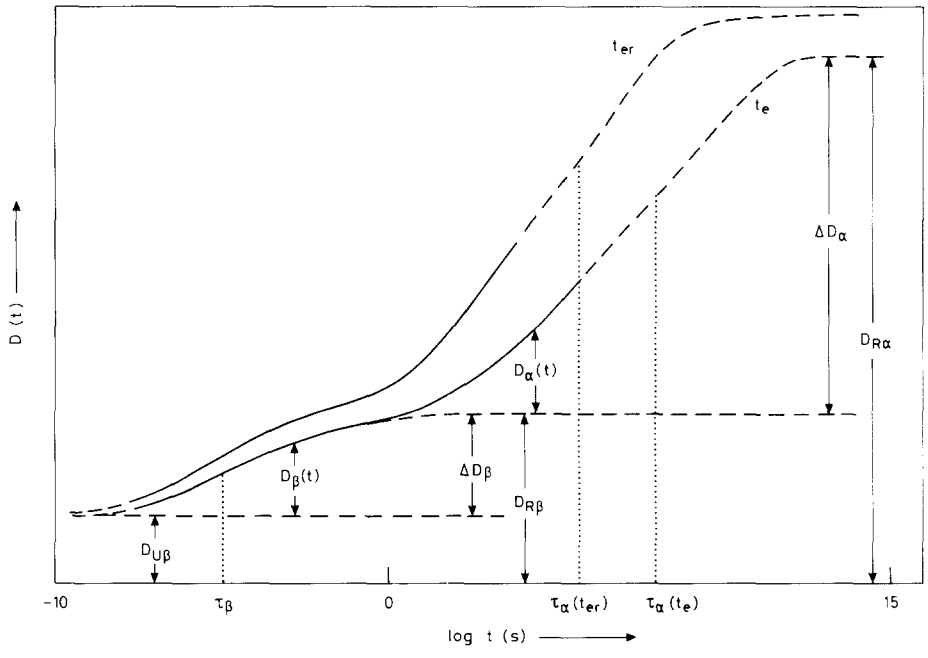


Figure 1 Schematic illustration of parameters used to describe the creep curve measured after an elapsed time t_e over a wide time range encompassing the α- and β-retardation regions. Also indicated are possible changes in creep behaviour with increasing elapsed time from t_{er} to t_e

retardation regions are frequently evident, a long time α-region and a short time β-region, which correspond to the respective relaxations observed at T_α and T_β in low frequency dynamic studies. For a given age t_e the creep compliance may be written[4,5]

$$D(t)=D_{U\beta}+D_\beta(t)+D_\alpha(t) \tag{1}$$

where, as indicated in *Figure 1*, $D_{U\beta}$ is the unrelaxed compliance for the β-retardation. $D_\beta(t)$ and $D_\alpha(t)$ are the compliance contributions from the respective β- and α-processes and may be expressed in the form

$$D_\beta(t)=\Delta D_\beta \psi_\beta(t, \tau_\beta, n) \tag{2}$$

and

$$D_\alpha(t)=\Delta D_\alpha \psi_\alpha(t, \tau_\alpha, m) \tag{3}$$

Here $\Delta D_\beta = D_{R\beta} - D_{U\beta}$ and $\Delta D_\alpha = D_{R\alpha} - D_{R\beta}$, $D_{R\beta}$ and $D_{R\alpha}$ being the relaxed compliances for the β- and α-retardations, respectively (*Figure 1*). The creep functions $\psi_\beta(t, \tau_\beta, n)$ and $\psi_\alpha(t, \tau_\alpha, m)$ each vary between 0 and 1 as t increases from 0 to ∞ and may be written in forms consistent with established empirical expressions such as the Cole–Cole or the Williams–Watts functions[5]. The mean retardation times τ_β and τ_α then correspond to the times at which inflection points occur in the $D(t)$ *versus* $\log t$ curves and n $(0<n\leqslant 1)$ and m $(0<m\leqslant 1)$ are parameters which characterize the widths (shapes) of the respective retardation time distributions and which decrease in value as the distributions broaden[5,7].

The effects of physical ageing on creep properties may be considered in terms of possible variations with t_e in the mean retardation times τ_β and τ_α, distribution parameters n and m, and limiting compliances $D_{U\beta}$, $D_{R\beta}$ and $D_{R\alpha}$ (or retardation magnitudes ΔD_β and ΔD_α). *Figure 1* illustrates, for example, a possible increase in τ_α with an increase in elapsed time from t_{er} to t_e and also indicates possible changes in the retardation magnitudes and the breadth of the α-region. Estimates of the various parameters, and their dependence on t_e, can be obtained by fitting appropriate creep functions and limiting compliances to short-term creep data with the aid of dynamic mechanical data and by analysing long-term creep results $(t>0.2t_e)$ on the basis of proposed visco-elastic models[5]. Although such modelling can sometimes be ambiguous, it is capable of yielding insight into the effects of ageing and of assessing the validity of procedures based on the superposability of creep curves of different t_e.

In comparing the results of various analyses it is convenient to distinguish between the behaviour of amorphous and semicrystalline materials, noting that the α and β labels may imply different relaxation mechanisms for different categories of polymer[8,9].

Amorphous polymers

In amorphous polymers the α-process is ascribed to long-range segmental rearrangements associated with the glass–rubber relaxation[8] and T_α is identified with the glass transition temperature T_g. The β-relaxation is a secondary process involving localized main-chain or side-group motions in the glassy material[8]. According to Struik, physical ageing occurs only at temperatures between T_g and T_β and produces a decrease in mobility of the α-process[1]. This interpretation is based on observations that $D(t)$ *versus* $\log t$ curves for different t_e, covering the short-time tail of the α-region, can be superposed by horizontal shifts with occasional small vertical shifts. These superpositions indicate[10] that the shape m and magnitude ΔD_α of the α-process are little affected by ageing and that the horizontal component $\log a$ of the displacement between the curves for elapsed times t_e and t_{er} may be equated to $\log \tau_\alpha(t_e) - \log \tau_\alpha(t_{er})$ (see *Figure 1*). Observations that $\log a$ is often proportional to $\log t_e$ further imply that

$$\frac{d \log a}{d \log t_e} = \frac{d \log \tau_\alpha}{d \log t_e} = \mu \tag{4}$$

so that

$$\tau_\alpha = At_e^\mu \quad (5)$$

where A and μ are constants and the ageing rate μ has values close to unity over wide ranges of t_e at temperatures in the ageing range[1,5].

From the similarity in temperature dependences of dynamic moduli and damping factors for samples cooled at different rates, Struik has also concluded[11] that secondary relaxations of amorphous polymers are unaffected by ageing, and hence that the parameters τ_β, n, $D_{U\beta}$ and $D_{R\beta}$ are each independent of t_e.

Creep data obtained for poly(methyl methacrylate) (PMMA) at 23°C over the time range 10^{-8}–10^5 s were analysed on the basis of equation (1) using a Cole–Cole function to model and extrapolate the β-creep contribution[4]. The $D(t)$ *versus* $\log t$ curves were thereby resolved into the overlapping contributions $D_\beta(t)$ and $D_\alpha(t)$. With increasing t_e, the β-retardation parameters were essentially unchanged and the $D_\alpha(t)$ *versus* $\log t$ curves shifted to longer times with no apparent change of shape (m constant). These results are consistent with Struik's suggestions.

However, the results of some creep and relaxation studies of amorphous polymers do not fully support the above observations. For example, Plazek *et al.*[12] found that torsional creep curves for polystyrene at 90 and 95°C shifted to longer times and also broadened with increasing t_e. These effects were ascribed, on the basis of a microscopic relaxation model, to an increased coupling of the relaxing molecules to their surroundings as characterized by an increase in the value of a coupling parameter equivalent to $1-m$. Small decreases in magnitude of the β-relaxations have also been observed for PMMA and PC from dynamic mechanical[13] and dielectric[14] studies, following ageing at temperatures between T_α and T_β. Although slight decreases in ΔD_β and $D_{R\beta}$ may thus occur with increasing t_e, these studies confirmed that τ_β is unaffected by the ageing.

Semicrystalline polymers with a glass–rubber α-process

For some semicrystalline polymers the α-process is also assigned to the glass–rubber relaxation in the amorphous phase ($T_\alpha = T_g$) and the β-process involves localized secondary molecular motions[8,9]. Such polymers typically have a low-to-moderate degree of crystallinity and include poly(ethylene terephthalate) (PET) and aliphatic polyamides. After ageing at temperatures between T_α and T_β the creep behaviour of these materials is affected in a way similar to that found for amorphous polymers. For example, creep curves for PET at different t_e can be superposed by predominantly horizontal shifts[1], suggesting that the principal effect of ageing involves an increase in τ_α with t_e. Changes in the β-retardation parameters with age state are expected to be small, as is apparent[11] from dynamic mechanical data for quenched PET.

Semicrystalline polymers with a crystal related α-process

Several semicrystalline polymers exhibit a mechanical α-process which requires the presence of crystals and has been ascribed to the motions of amorphous segments which couple with the translation of chains along the c crystal axes[15]. These polymers usually have a high degree of crystallinity and include HDPE, isotactic polypropylene (PP) and polyoxymethylene. The β-process in these materials is assigned to the glass–rubber relaxation of the bulk amorphous phase[15] so that $T_\beta = T_g$.

Creep studies of PP have been reported[2,5,10] after ageing at temperatures between T_α (100°C) and T_β (0°C). Creep data at 23°C over the time range 10^{-8}–10^5 s were modelled on the basis of equations (1)–(3), yielding $D_\beta(t)$, $D_\alpha(t)$ and the associated retardation parameters[5]. Although $D_{U\beta}$, τ_β and n were essentially unaffected by the ageing, a substantial decrease in $D_{R\beta}$ with increasing t_e could be described by

$$D_{R\beta} - D_{U\beta} = \Delta D_\beta = Bt_e^{-k} \quad (6)$$

where B and k are constants. The resolved $D_\alpha(t)$ *versus* $\log t$ curves at different t_e were not accurately superposable by horizontal shifts owing to a slight apparent broadening of the α-retardation (decrease in m) with increasing t_e and some possible decrease in ΔD_α. Unique shift factors $\log a$ could not, therefore, be obtained but the modelling suggested that τ_α increased with t_e according to equation (5) with $\mu = 0.77$. It was proposed that the molecular rearrangements responsible for the room-temperature ageing were of the type involved in the α-process and produced an increased extension of amorphous tie-molecules. This process was considered to increase the activation energy and hence τ_α for the α-process and simultaneously to reduce $D_{R\beta}$.

Struik's model for semicrystalline polymers

A model has been proposed by Struik to account for ageing effects in semicrystalline polymers over wide temperature ranges[2]. The model is based on the concept that the mobility of amorphous segments is reduced near the crystals, so that the glass transition temperature of the amorphous material increases with decreasing distance from the crystal surface. The resulting distribution of T_g is then modelled in terms of lower and upper glass transition temperatures T_g^L and T_g^U, respectively. Here T_g^L is the normal T_g of the more mobile unconstrained amorphous regions and corresponds either to T_β or T_α depending on whether or not the polymer exhibits a crystal-related α-process. T_g^U is the glass transition temperature of the less mobile constrained amorphous regions and for semicrystalline polymers with a glass–rubber α-process is located above T_α in the high temperature tail of the glass–rubber relaxation (which is broadened by the restraining effect of crystals on amorphous phase motions). For polymers with a crystal-related α-process, Struik associates T_g^U with T_α, assuming that crystalline-phase motions are not involved in the α-process but that the crystals act as fillers and reduce the mobility of neighbouring amorphous segments.

It is next assumed that the total creep compliance is given by

$$D(t) = D_1(t) + D_2(t) \quad (7)$$

where $D_1(t)$ is the compliance contribution from the most mobile regions and $D_2(t)$ the contribution from the less mobile regions. The influence of ageing on secondary processes was not discussed and was presumably assumed to be negligible, as for amorphous polymers.

On the basis of the above model, Struik described the effects of ageing on $D(t)$ in terms of horizontal shifts of the $D_1(t)$ *versus* $\log t$ and $D_2(t)$ *versus* $\log t$ curves to longer times with increasing t_e. Each of the component curves was assumed to be unchanged in shape and magnitude, and the shift rates μ_1 $(= d(\log a_1)/d(\log t_e))$

and μ_2 $(=\mathrm{d}(\log a_2)/\mathrm{d}(\log t_e))$ were assumed to have a dependence on temperature relative to T_g^L and T_g^U, respectively, similar to that found for amorphous polymers. Four characteristic regions of temperature were considered as follows.

Region 1 $(T<T_g^L)$. In this temperature range both amorphous regions are below their respective T_g, from which it is argued that $D_1(t)$ and $D_2(t)$ will be characterized by similar retardation times and ageing rates. It is predicted that the $D(t)$ *versus* $\log t$ curve for elapsed time t_e can be superposed onto the curve for the reference elapsed time $t_{er}>t_e$ by a horizontal shift to longer times by an amount approximately equal to that for each component curve $(\mu\approx\mu_1\approx\mu_2\approx 1)$. This behaviour is illustrated in *Figure 2a* and is consistent with the results for PET mentioned above.

Region 2 $(T\approx T_g^L)$. At temperatures close to T_g^L the creep behaviour is dominated by $D_1(t)$, which enters the central part of its glass–rubber retardation region. The $D_2(t)$ component is relatively small but the shift rate $\mu_2>\mu_1$. On this basis it is predicted[16] that the $D(t)$ *versus* $\log t$ curve for t_e should superpose onto the curve for $t_{er}>t_e$ by a horizontal shift to longer times determined by μ_1, together with a downward vertical shift proportional to $\mu_2-\mu_1$. Results for several polymers, including PP at room temperature, were considered by Struik to be consistent with this prediction. However we have suggested[5] that the downward shifts for PP originate from a decrease in $D_{R\beta}$ with t_e and, because the $D_\beta(t)$ or $D_1(t)$ component is approaching its rubbery plateau at creep times above 1 s, that the room temperature ageing of PP should be considered in relation to Struik's region 3.

Region 3 $(T_g^L<T<T_g^U)$. In this range the $D_1(t)$ component is approaching its rubbery plateau and is no longer sensitive to ageing $(\mu_1=0)$. Struik proposed[16] that this pseudo plateau is not, in fact, flat but that $D_1(t)$ continues to increase slowly according to

$$D_1(t)=A_1+C_1\log t \tag{8}$$

where A_1 and C_1 are constants. Ageing in this region is controlled by horizontal shifts of the $D_2(t)$ component (*Figure 2b*) and the $D(t)$ *versus* $\log t$ curve for t_e should superpose onto the curve for $t_{er}>t_e$ by a horizontal shift to longer times by an amount $\Delta\log a=\mu_2\log(t_{er}/t_e)$ together with an upward vertical shift Δb given by

$$\Delta b=C_1\mu_2\log(t_{er}/t_e)=C_1\Delta\log a \tag{9}$$

In support of this prediction Struik has reported[2] results for several polymers including HDPE in the temperature range from about 0 to 60°C and PP at temperatures above 50°C.

Region 4 $(T\geqslant T_g^U)$. In this region ageing effects are predicted to disappear because the entire amorphous phase is now a mobile rubber. However, downward vertical shifts of the creep curves with increasing t_e were observed for low density polyethylene[2] and PP[17]. These shifts suggest decreases in α-retardation magnitudes and were attributed to crystallization processes.

EXPERIMENTAL

Materials

Information on the materials used in this study is given in *Table 1*. The PC and PBT were supplied by Bayer (UK) as injection moulded plaques having approximate dimensions 150 × 100 × 5 mm. In machining specimens, care was taken not to use material from near the sides

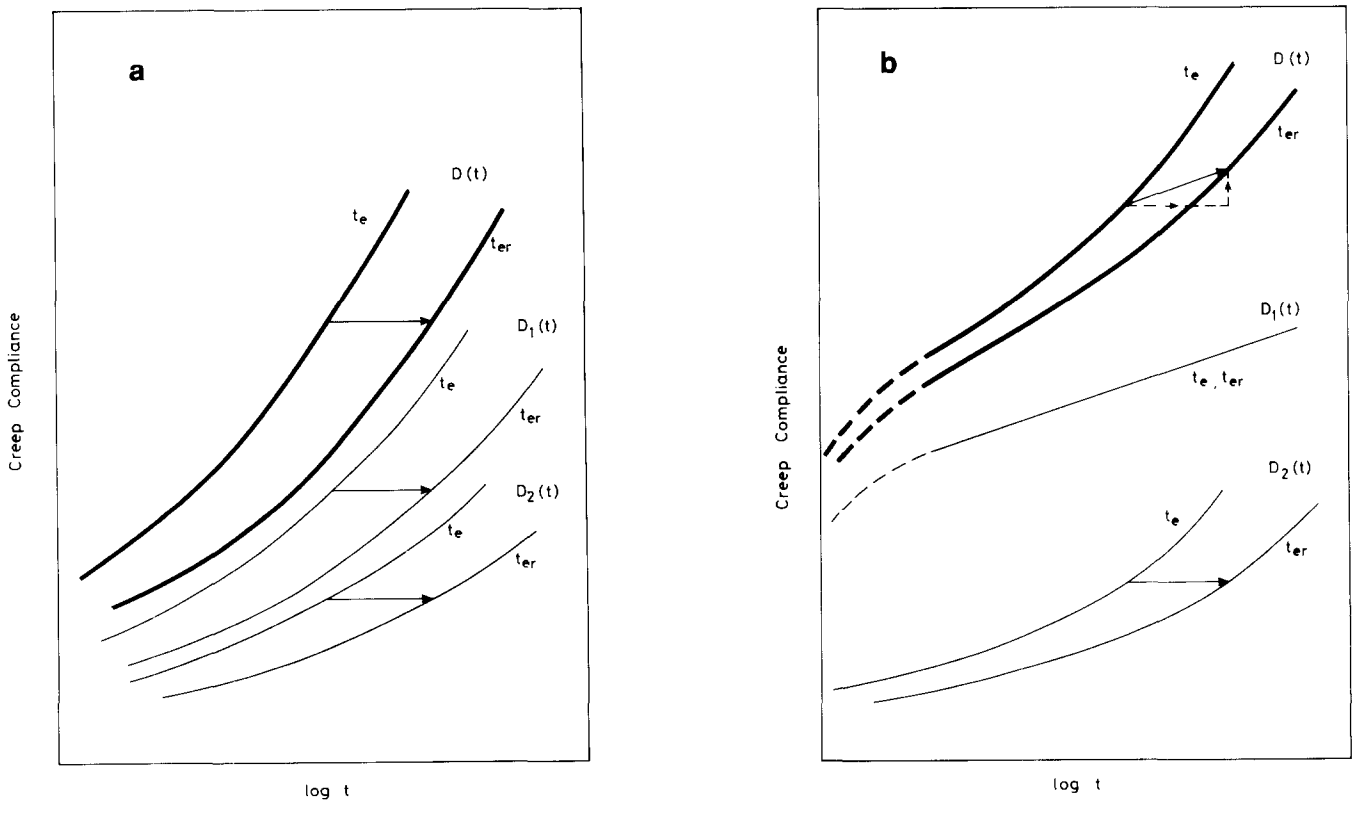


Figure 2 Illustration of the shifts, according to Struik's model for semicrystalline polymers, required to superpose creep curves and their components for an elapsed time t_e onto the curves for the reference elapsed time $t_{er}>t_e$: (a) region 1; (b) region 3

Table 1 Characteristics of the materials investigated

Material	Supplier and trade name	Density at 23°C ($kg\,m^{-3}$)	T_m (°C)	T_α (°C)	T_β (°C)	T_0 (°C)
PC	Bayer (UK) Makrolon 2800	1174		149	−90	150
PBT	Bayer (UK) Pocan B1505	1320	222	60	−81	80
HDPE	BP Chemicals Rigidex HD 5502 EA	957	130	62	−20	63

of the plaques, thus minimizing the effects of orientation and internal stress. The HDPE was obtained from BP Chemicals Ltd in the form of compression moulded sheets of thickness 8–10 mm. After machining specimens from these sheets, their crystallinity was stabilized with respect to subsequent thermal treatment by annealing at 90°C for 6 h and slowly cooling (0.2°C min^{-1}) to room temperature.

The densities in *Table 1* were measured by hydrostatic weighing in distilled water at 23°C. Melting temperatures T_m were determined by differential scanning calorimetry. T_α and T_β are the temperatures of maximum loss factor $\tan\delta$ for the respective α- and β-relaxation regions at a frequency of 1 Hz. These were obtained from dynamic flexural tests on machined strips using a dynamic mechanical thermal analyser (Polymer Laboratories Ltd)[18]. Note that, for PC and PBT, T_α may be identified with T_g, and T_β with the secondary relaxation temperature, whereas for HDPE T_α and T_β are associated with the crystal related α-relaxation and with T_g, respectively.

The dimensions of samples used in the creep tests were typically $150 \times 12 \times 5$ mm; those used in the related dynamic tests at 23°C were approximately $150 \times 10 \times 3$ mm. Before these tests, previous ageing effects were first erased by heating the samples for 30 min at a temperature T_0 (*Table 1*) close to T_α. The samples were then quenched in water at room temperature and stored at 23°C for various periods of elapsed time t_e ranging from 3 to 500 h before testing. The durations of the creep tests were kept short ($\approx 0.2t_e$) to avoid significant further ageing of the samples during the test period.

Measurement of creep compliance

The apparatus used to obtain tensile creep data at 23°C for $t \geqslant 1$ s has been described previously[5,19]. Compliance values determined by this method for different samples of the same age generally agreed to within 2%.

Values of creep compliance at short times between 10^{-8} and 10 s were derived from measurements of the dynamic storage compliance $D'(\omega)$ at frequencies $f(=\omega/2\pi)$ between 0.01 Hz and 5 MHz at 23°C. The techniques used have been described in previous publications[18,20] and comprised a tensile non-resonance method (0.01–100 Hz), an audiofrequency flexural resonance technique (100 Hz–5 kHz) and an ultrasonic method (0.5–5 MHz). As discussed previously[5], creep compliances were obtained from the dynamic data using the approximation

$$D(t) = D'(\kappa/t) \tag{10}$$

where, as indicated, $D'(\kappa/t)$ is the storage compliance measured at an angular frequency κ/t with the constant $\kappa = 0.63$. Values of $D(t)$ determined by this method are considered accurate to within 1%.

DATA ANALYSIS

Figure 3 shows creep curves covering wide ranges of time at different elapsed times for PC, PBT and HDPE. These diagrams illustrate the good agreement between data obtained by the various techniques. For each polymer the long time part of the β-retardation region and onset of the α-region are also evident. The degree of overlap between the α- and β-regions is generally less than that found previously for PMMA[4] and PP[5], relatively extended plateaus being observed in the overlap regions. This increased resolution of α- and β-processes largely reflects the fact that extensive parts of the β-regions occur at times which are too short to be accessible by the available techniques at room temperature. Parameters characterizing $D_\beta(t)$ for PC, PBT and HDPE could not, therefore, be obtained by modelling the short-time data with an empirical Cole–Cole function, as was done[4,5] for both PMMA and PP. However, the decreasing compliance levels with increasing t_e in the plateau region and long time parts of the β-regions suggest that $D_{R\beta}$ decreases with age for each of the three polymers investigated.

The t_e dependence of $D_{R\beta}$ has been studied using compliance data obtained as a function of elapsed time from the fundamental audiofrequency resonance frequencies ω_f. From the results in *Figure 3* it is considered that the measured compliances $D_f(t_e)$ at the creep time $t = 0.63/\omega_f \approx 5 \times 10^{-4}$ s have negligible contributions from the α-mechanisms. It is then assumed that decreases in $D_f(t_e)$ with t_e are associated entirely with decreases in $D_{R\beta}$. *Figure 4* shows plots of $D_f(t_e)$ against $\log t_e$ which are approximately linear for each polymer and may be described by

$$D_f(t_e) = X_1 - X_2 \log t_e \tag{11}$$

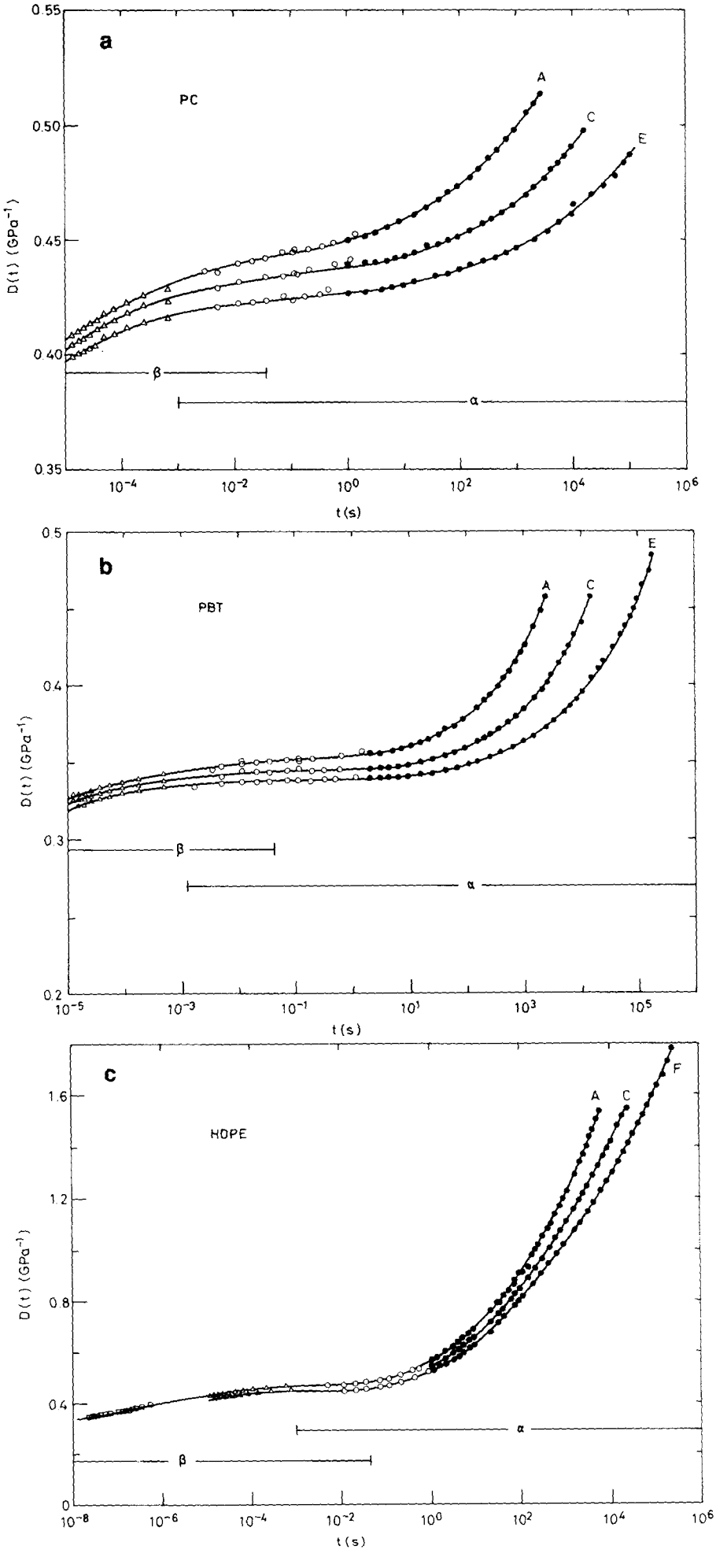
where X_1 and X_2 are constants. Identifying $D_f(t_e)$ with $D_{U\beta} + D_\beta(t)$ it follows from equation (2) that

$$D_{R\beta} = D_f(t_e)/\Phi_\beta(t) \tag{12}$$

where

$$\Phi_\beta(t) = \psi_\beta(t)\left[1 + \frac{D_{U\beta}}{D_{R\beta}}\frac{1-\psi_\beta(t)}{\psi_\beta(t)}\right] \tag{13}$$

Figure 3 Creep curves determined over long time scales for (a) PC, (b) PBT and (c) HDPE. For each polymer, the curves refer to samples with the following selected age states, t_e (h): A, 3; C, 24; E, 216; F, 576. The techniques used to obtain the data were: ●, tensile creep; ○, tensile non-resonance; △, audiofrequency flexural resonance; □, ultrasonic wave propagation. α and β indicate the time ranges over which the α- and β-retardation mechanisms are active


a
PC
A
C
E
D(t) (GPa⁻¹)
0.55
0.50
0.45
0.40
0.35
β
α
10⁻⁴
10⁻²
10⁰
10²
10⁴
10⁶
t (s)
b
PBT
A
C
E
D(t) (GPa⁻¹)
0.5
0.4
0.3
0.2
β
α
10⁻⁵
10⁻³
10⁻¹
10¹
10³
10⁵
t (s)
c
HDPE
A
C
F
D(t) (GPa⁻¹)
1.6
1.2
0.8
0.4
0
α
β
10⁻⁸
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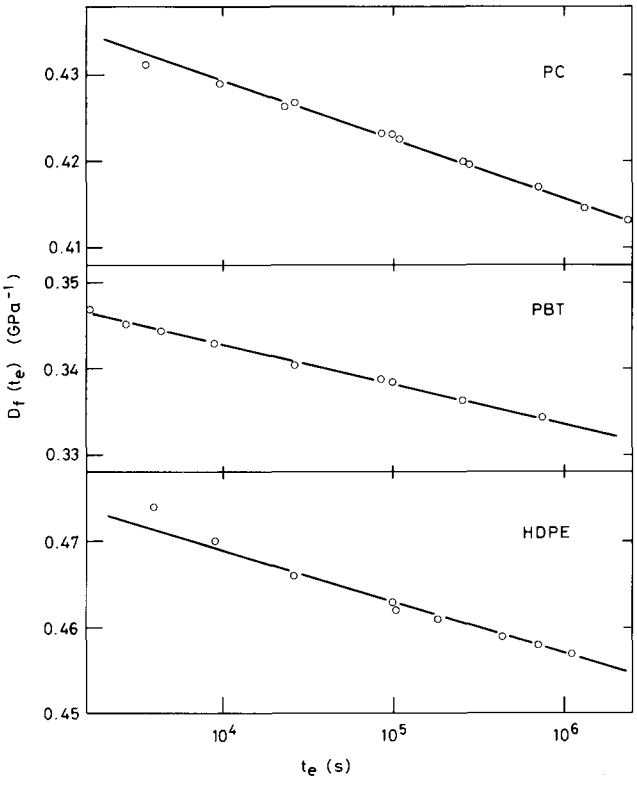

Figure 4 Elapsed time dependence of the creep compliance $D_f(t_e)$ determined from fundamental audiofrequency resonance measurements corresponding to an essentially constant creep time $t \approx 5 \times 10^{-4}$ s for PC, PBT and HDPE

and it is assumed that τ_β, n and hence $\psi_\beta(t)$ are essentially independent of t_e. At $t_e \approx 5 \times 10^{-4}$ s it is evident from *Figure 3* that $\psi_\beta(t) \approx 1$ so that the second term in square brackets in equation (13) is small compared with unity. It follows that $\Phi_\beta(t)$ has a value close to unity and a negligible t_e dependence. Equations (11) and (12) then yield

$$D_{R\beta} = Y_1 - Y_2 \log t_e \tag{14}$$

where $Y_1[=X_1/\Phi_\beta(t)]$ and $Y_2[=X_2/\Phi_\beta(t)]$ are constants which can be obtained from X_1 and X_2, respectively, if $\Phi_\beta(t)$ is known. Values of $\Phi_\beta(t) = D_f(t_e)/D_{R\beta}$ were estimated from the 216 h elapsed time data, taking for $D_{R\beta}$ the compliance values in the plateau regions at times around 10^{-2} s. This yielded the Y_1 and Y_2 values listed in *Table 2*.

It should be emphasized that the decreases in $D_f(t_e)$ with t_e were only about 1.3–1.6% per decade and that, for each polymer, plots of $\log D_f(t_e)$ against $\log t_e$ were also approximately linear. As discussed elsewhere[21], this observation, together with equation (12), suggests that $D_{R\beta}$ may be expressed in the alternative form

$$D_{R\beta} = [V/\Phi_\beta(t)]t_e^{-\nu} = Wt_e^{-\nu} \tag{15}$$

where constants V and W are approximately equal numerically to X_1 and Y_1, respectively, in (11) and (14) and values for the slopes $\nu = -\mathrm{d}(\log D_{R\beta})/\mathrm{d}(\log t_e)$ are also included in *Table 2*. Note that equation (15) is similar in form to equation (6), which characterizes the elapsed time dependence of the retardation magnitude ΔD_β in PP rather than $D_{R\beta}$.

Figure 5 illustrates the $D_{R\beta}$ levels determined from equation (14) or (15) using the parameters given in *Table 2*. It is not clear whether the calculated decreases in $D_{R\beta}$ with increasing t_e involve decreases in $D_{U\beta}$ or ΔD_β or both. However, it was observed from the audiofrequency data on each polymer that the rate of compliance decrease $-\mathrm{d}D(t)/\mathrm{d}(\log t_e)$ was smaller for the higher resonance modes ($t \leqslant 10^{-5}$ s) than for the fundamental resonance at $t \approx 5 \times 10^{-4}$ s. This evidence reflects a tendency for the creep curves at different t_e to converge with decreasing t at very short times and indicates that decreases in $D_{R\beta}$ arise predominantly from reductions in ΔD_β.

By subtracting the $D_{R\beta}$ values from the total measured compliances $D(t)$, contributions $D_\alpha(t)$ from the α-processes were obtained for times down to those corresponding to the estimated completion of the β-processes. For PC and PBT, the resulting plots of $D_\alpha(t)$ against $\log t$ for different elapsed times could be superposed within experimental error by horizontal shifts as shown in *Figure 6*. The magnitudes of these shifts yielded, according to equation (4), $\mu = 1.0$ for PC and $\mu = 0.74$ for PBT. However, the $D_\alpha(t)$ *versus* $\log t$ curves for HDPE at different t_e (*Figure 6*) clearly diverge with increasing t and cannot therefore be superposed by horizontal shifts.

DISCUSSION

For the amorphous PC and semicrystalline PBT the α-region is assigned to the glass–rubber retardation and the β-region to a secondary retardation process. With regard to the secondary processes, the small decreases in $D_{R\beta}$ with increasing t_e could arise from small decreases in the concentration of groups participating in the localized motions which would produce reductions in ΔD_β. This result does not support Struik's observations[11] but is consistent with the results of other workers[13,14].

The horizontal superposition of $D_\alpha(t)$ *versus* $\log t$ curves for PC and PBT at different t_e suggests that ageing produces an increase in τ_α and that the shape of the retardation spectrum and magnitude of the α-retardation are little affected. This result is supported by a recent analysis[21] of short-term and long-term creep curves for PBT which could be modelled by using $\mu = 0.76$ and values of m (≈ 0.36) and ΔD_α (1.5 GPa^{-1}) which were essentially independent of t_e. However, small variations in m and ΔD_α, which would be masked by the superposition procedure, cannot be discounted. The horizontal superposition also agrees with Struik's data analysis for both amorphous[1] and semicrystalline[2] polymers aged at temperatures below T_g. Furthermore, it shows that the behaviour over this temperature range is not influenced by the presence of the crystalline phase in PBT.

In HDPE the β-region is associated with the glass–rubber relaxation process in the amorphous phase[15] and the decrease in $D_{R\beta}$ with increasing t_e might be due to conformational changes of amorphous tie-molecules, as proposed[5] for PP. The observed divergence of the $D_\alpha(t)$ *versus* $\log t$ curves with increasing t for the crystal related α-process could involve either a broadening of the

Table 2 Calculated values of parameters specifying the dependence of $D_{R\beta}$ on t_e

Material	Y_1 (GPa^{-1})	Y_2 (GPa^{-1})	W (GPa^{-1} s$^\nu$)	ν
PC	0.461	0.0068	0.461	0.0069
PBT	0.364	0.0047	0.364	0.0060
HDPE	0.493	0.0058	0.493	0.0055

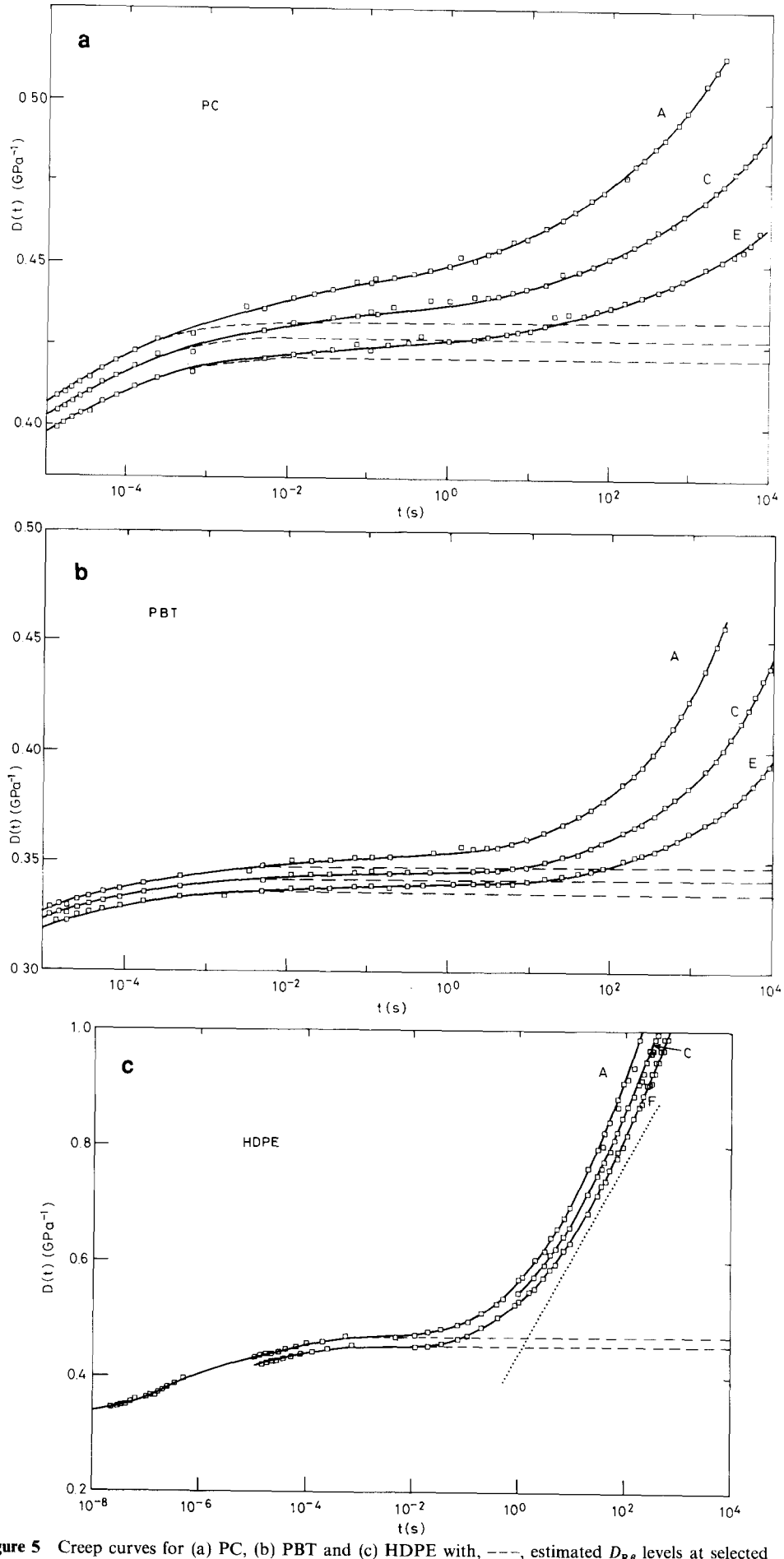

Figure 5 Creep curves for (a) PC, (b) PBT and (c) HDPE with, ---, estimated $D_{R\beta}$ levels at selected age states. A, C, E, and F refer to the t_e values given in *Figure 3*. For HDPE, ··· indicates the constant long-time slope for the β-creep contribution predicted by Struik's model for semicrystalline polymers in temperature region 3

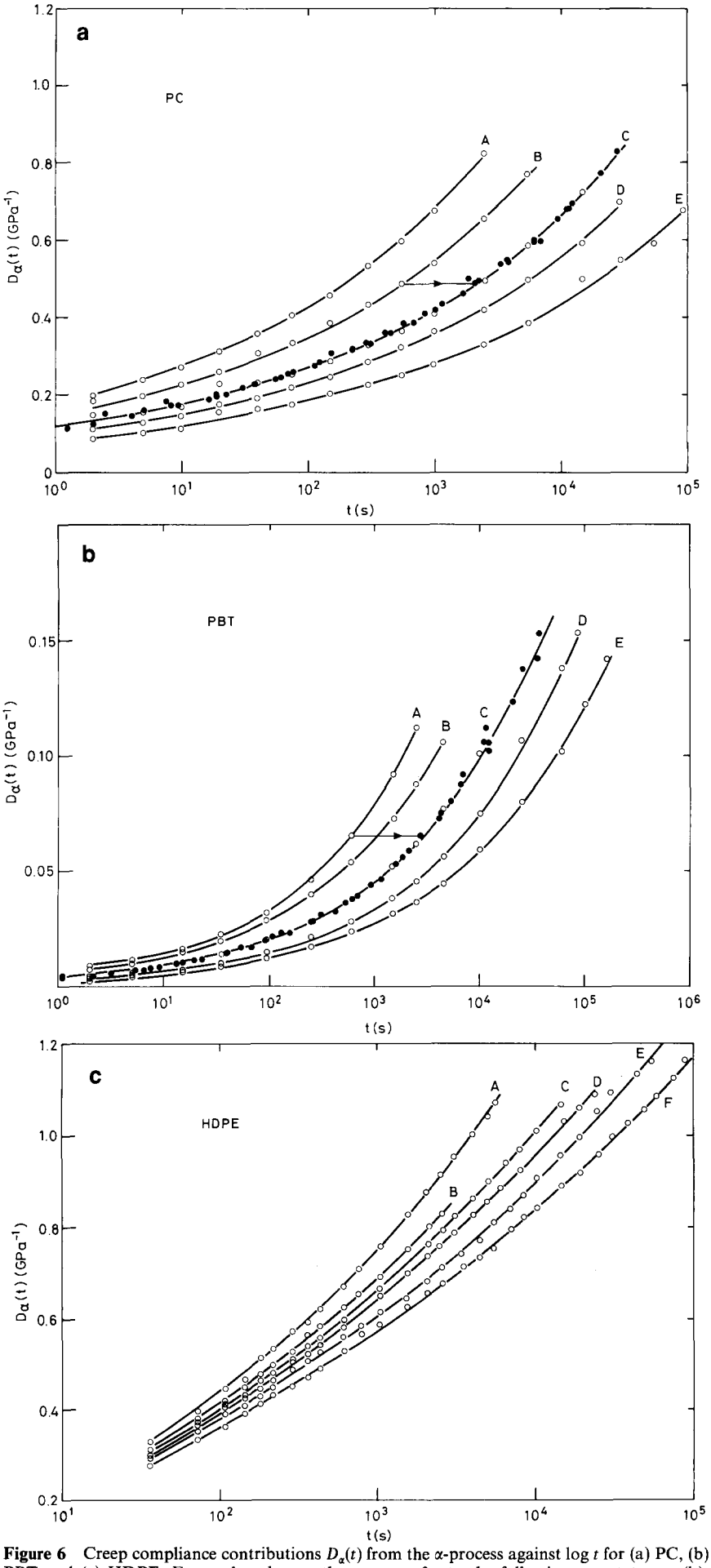

Figure 6 Creep compliance contributions $D_\alpha(t)$ from the α-process against log t for (a) PC, (b) PBT and (c) HDPE. For each polymer, the curves refer to the following age states, t_e (h): A, 3; B, 7.5; C, 24; D, 72; E, 216; F, 576. For PC and PBT, the arrows indicate that curves for different t_e could be superposed by essentially horizontal shifts

α-region or a decrease in ΔD_α or both. A preliminary attempt to model the creep behaviour of HDPE in the α-region indicates that m may be decreasing with increasing t_e, corresponding to a broadening of the retardation spectrum. Possible origins of an apparent broadening are being considered, including the existence of overlapping α and α′ crystal related processes[8] which may differ from each other with respect to the t_e dependence of retardation times. Quantitative analyses of both short-term and long-term data should serve to distinguish between various possible ageing effects in the α-region.

Validity of Struik's model for semicrystalline polymers

With regard to Struik's classification of ageing in semicrystalline polymers[2], our studies of PBT are relevant to temperature region 1 ($T < T_g^L \approx T_\alpha$). In this region it is predicted (*Figure 2a*) that the $D(t)$ *versus* $\log t$ curves at different t_e should be superposable by predominantly horizontal shifts. Within experimental error, this prediction is supported by the creep data for PBT in *Figure 7*. The horizontal components of the shifts in this diagram yield a μ value (*Table 3*) equal to that obtained from the superposition of $D_\alpha(t)$ *versus* $\log t$ curves in *Figure 6*. The very small downward vertical components of the shifts (negative Δb) are attributed to decreases in $D_{R\beta}$ for the secondary process, as evidenced by the approximate equality of the values of $db/d(\log t_e)$ (*Table 3*) and $dD_{R\beta}/d(\log t_e) = -Y_2$ (*Table 2*). The similarity noted above between the results for PBT and PC is consistent with the suggestion that the effects of ageing in this region are similar to those for amorphous polymers[2].

The data obtained for HDPE should be discussed in relation to Struik's temperature region 3 ($T_\beta \approx T_g^L < T < T_g^U \approx T_\alpha$) if T_α is associated with an upper glass transition temperature. Results shown in *Figure 8* appear to support the prediction for this region (*Figure 2b*) that a $D(t)$ *versus* $\log t$ curve at t_e should be superposable onto the curve at $t_{er} > t_e$ by a horizontal shift together with an upward vertical shift Δb. The t_e dependence of the shift factors obtained from this diagram are included in *Table 3* and we note that results similar to those in *Figure 8* were reported by Struik for HDPE over a similar time range[2]. However, if our data over a wider range of time are considered, then it is seen (*Figure 9*) that the superposition fails in the short time region.

According to equation (9) it is also predicted for region 3 that

$$db/d(\log a) = C_1$$

where C_1 is the long-time slope of the $D_1(t)$ *versus* $\log t$ curve (*Figure 2b*) for the mobile amorphous regions. From the data in *Table 3* we obtain $db/d(\log a) = (1/\mu)\, db/d(\log t_e) = 0.165\,\mathrm{GPa}^{-1}$. *Figure 5* shows for HDPE that this predicted value for the slope C_1 is much larger than the slope in the plateau region or the estimated long-time slope of the β-region, which is close to zero for $t > 10^{-2}$ s. Because the β-region is assigned to the glass–rubber retardation for the mobile amorphous material, the difference between these slopes further exemplifies the discrepancies between our data for HDPE and Struik's predictions for region 3. These discrepancies cast doubt on the proposed significance of the large upward vertical shifts of the creep curves necessary to achieve superposition through subsequent horizontal shifts. It follows that the observations of constancy of shape and magnitude of the α-retardation (or Struik's upper glass–rubber region) implied by these super-

Table 3 Elapsed time dependence of the horizontal and vertical shift factors obtained from the apparent superposition of creep curves over limited time ranges

Material	μ	$\frac{db}{d(\log t_e)}$ (GPa^{-1})
PBT	0.74	−0.0046
HDPE	0.70	0.115

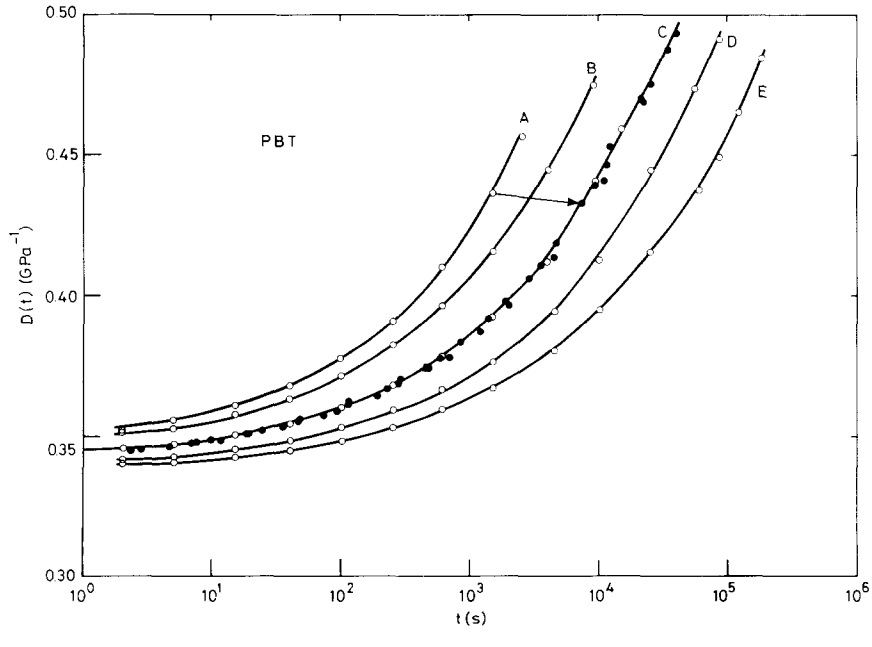

Figure 7 Creep data for PBT samples with different age states. A–E correspond to the t_e values given in *Figure 6*. The arrow indicates that the curves can be superposed by horizontal shifts to longer times together with small downward vertical shifts

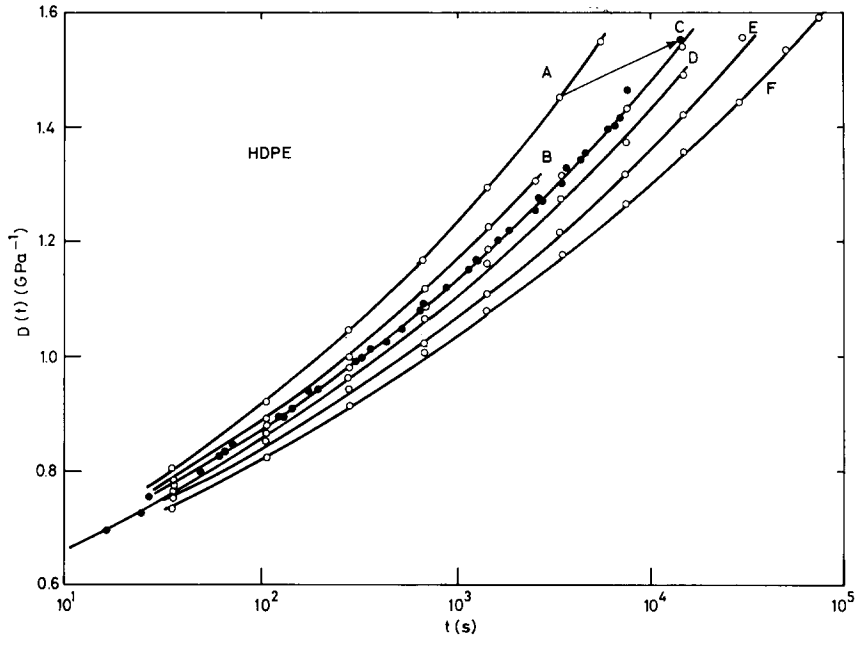

Figure 8 Creep curves for HDPE samples of different age states. A–F refer to the t_e values given in *Figure 6*. The arrow indicates that in the time range 10^2–10^4 s the curves can be approximately superposed by upward vertical shifts together with horizontal shifts to longer times

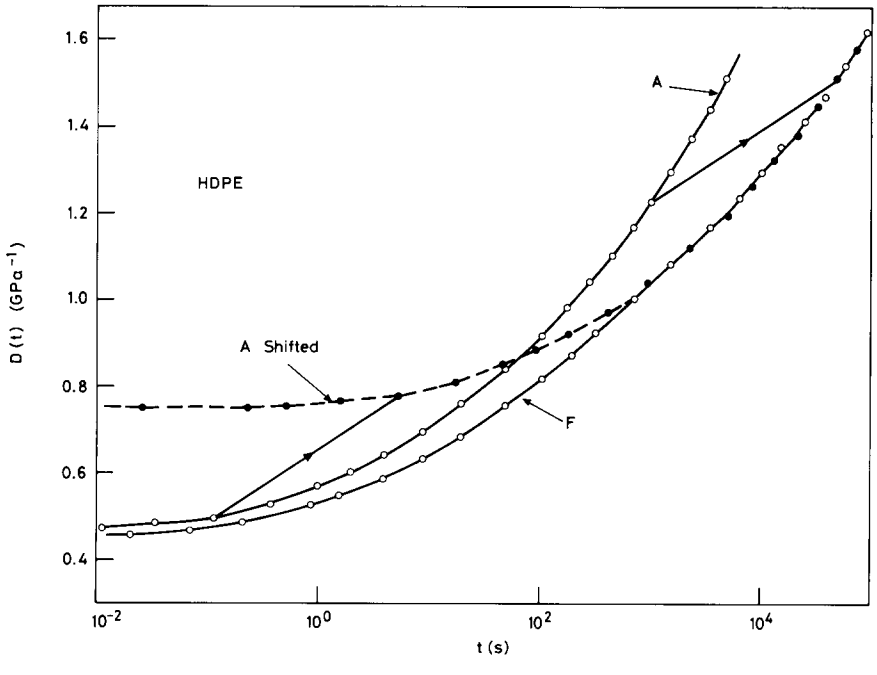

Figure 9 Creep data for HDPE samples with $t_e = 3$ h (curve A) and $t_e = 576$ h (curve F) over an extended time range 10^{-2}–10^5 s. The superposition of curve A onto curve F, by shifting in the direction of the arrows, can be achieved only for times $> 10^3$ s

positions is also of questionable validity. As noted above, both the magnitude and the shape of the α-retardation could vary with the age state of HDPE.

CONCLUSIONS

An analysis of creep data covering up to 13 decades of time at 23°C has provided information on the influence of physical ageing on the α- and β-retardation processes in amorphous and semicrystalline polymers. For the materials investigated, $T_\alpha > 23°C > T_\beta$, where T_α and T_β are the temperatures of maximum loss factor around 1 Hz. The age state of each polymer was characterized by the elapsed time t_e at 23°C between quenching from a temperature around T_α and the start of the creep experiment.

For the amorphous PC and semicrystalline PBT, ageing appears to yield a small decrease in relaxed compliance $D_{R\beta}$ for the secondary β-retardation process. This may involve slight decreases in retardation magnitude ΔD_β and hence in the number of groups participating in the localized secondary process. The α-retardation region

for both PC and PBT is associated with the glass–rubber relaxation, and curves of the α-compliance contribution $D_\alpha(t)$ against $\log t$ shift to longer times with increasing t_e. The apparent superposition of such curves at different t_e by horizontal shifts agrees with Struik's observations and suggests that ageing produces an increase in mean retardation time τ_α, while the magnitude ΔD_α and shape of the retardation–time distribution are essentially unaffected.

For HDPE, ageing produces a small decrease in $D_{R\beta}$ for the glass–rubber β-retardation process. This decrease is similar to, but smaller than, that observed for polypropylene and could involve conformational changes of amorphous tie-molecules. Curves of $D_\alpha(t)$ against $\log t$ cannot be superposed by horizontal shifts. This indicates that the shape or magnitude of the α-retardation may be changing with increasing t_e. The results for HDPE are inconsistent with Struik's model for the ageing of semicrystalline polymers in his temperature region 3.

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