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Creep and physical ageing of polypropylene: a comparison of models

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Tensile creep data obtained from testpieces of polypropylene at various ages and a number of different stresses have been circulated to five laboratories as part of a round-robin exercise. The aim of this exercise was to compare functions that are currently being used to model the effects of physical ageing and stress on the creep behaviour of plastics, with a view to producing an international standard in this area. All of the functions studied were able to successfully model the effects of physical ageing on the creep of plastics over a limited timescale, where the age of the specimen under test remained effectively constant. However, the fits to longer duration tests where further ageing of the testpiece occured during the creep were more discriminating, revealing differences in the ability of some of the models to accurately describe the data. Additional disparities became apparent in modelling long-term data obtained at high stresses which appeared to change the apparent age of the material, causing higher than expected creep rates. Further work is proposed to study the origin of some of the discrepancies before the preparation of a draft standard can be undertaken. Crown copyright © 1997 Published by Elsevier Science Ltd.

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INTRODUCTION

A number of models for describing the effects of physical ageing on the creep behaviour of thermoplastics have been described in the literature during recent years[1–4], some of which are traceable to equations that were either developed to describe stress relaxation in plastics[5] or charge decay in polymer dielectrics[6]. Often there are only subtle differences between these models and at the present time there is little information to guide potential users in their selection and use. To redress this problem the National Physical Laboratory has recently formed a European Technical Committee composed of representatives from industry and academia within Europe†. The role of this comittee has been to assess the potential for standardizing the analysis of creep data obtained from plastics, taking into account the effects of physical ageing. As part of this exercise creep data obtained from polypropylene testpieces of different age and at various stresses (*Table 1*) were circulated to a number of laboratories for analysis (*Table 2*) following their own procedures. The results of this exercise are presented here.

EXPERIMENTAL

The unreinforced polypropylene (Royalite, Propylex) was obtained as a 9 mm thick compression moulded sheet from VT Plastics (UK). Rectangular testpieces of nominal dimensions 10 × 4 × 180 mm were machined from this sheet, annealed at 130°C for 4 h and then slowly cooled over a period of approximately 6 h to room temperature (23°C). This annealing procedure stabilizes the crystallinity of the material with respect to subsequent thermal treatments. The density of the annealed material was determined by hydrostatic weighing in distilled water at 23°C and found to be 907 kg m^{-3}, a value which corresponds to a calculated crystallinity level of 61%[7].

The physical age of a material is characterized by the period of storage, t_e at the test temperature between quenching from an elevated temperature, T, and the instant of load application. This temperature T has to be greater than the temperature T' at which the relaxation process controlling the creep of the material reaches equilibrium. T' for many polymers corresponds to the glass transition temperature. However, for polypropylene, T' relates to a dominant α relaxation process which is responsible for creep and ageing at room temperature. This relaxation process is thought to be associated with changes in the conformation of amorphous tie molecules which couple with motions within the crystal lamellae[4]. An overlapping short-time β process is associated with the glass transition of the bulk amorphous phase[4].

Prior to creep testing, the testpieces were first heated to $T = 80°C$ for a period of 30 min. This was found to satisfactorily erase any previous ageing effects associated with the α-process that occurred during the period of slow cooling after annealing and subsequent storage at room temperature. Repeated heating of testpieces to this temperature was found not to affect the level of crystallinity as indicated by density measurements. After annealing at 80°C the testpieces were quenched into water at 23 ± 1°C and after a period of 3–5 min, removed and dried. They were then mounted in tensile creep rigs which have been described elsewhere[4,8] and stored at the test temperature (23 ± 0.2°C) for various periods of time, t_e.

Test programme

At low stresses, i.e. those that fall within the linear portion of the stress–strain curve the age of the testpiece

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remains effectively constant for a period of time after application of a load. This period of time is typically taken to be $0.3t_e$, and defines a short-term test. A series of such tests can be carried out using a single specimen which remains mounted within the test rig if adequate recovery periods ($\sim 10t_e$) are allowed between successive loadings. This minimizes the variations associated with material variability and sample misalignment.

Long-term creep tests are those where the test period exceeds the short-term time limit and hence further ageing of the testpiece occurs. Wherever possible long-term tests at low stress were conducted using the same testpieces from which short-term data were obtained after heating to 80°C to erase the influence of previous thermal treatments.

The application of high stresses, i.e. in excess of those that fall within the linear portion of the stress–strain curve results in testpieces of a given age creeping at a greater rate than expected. At present opinions differ regarding the molecular basis of this phenomenon, but it has been described by several workers as a process of de-ageing or rejuvenation. A practical consequence of de-ageing is that the short-term creep data obtained by repeatedly subjecting a testpiece at certain elapsed times to a cycle of loading followed by a period of recovery (as described above) will be markedly different from that obtained from single load applications at the same elapsed times. This becomes self-evident if we consider repeatedly applying a stress to a testpiece for a period of time corresponding to $0.3t_e$ at elapsed times of 3, 7, 24 and 72 h. If each application of the load results in de-ageing of the material then the creep data obtained for $t_e = 72$ h will be very different from that measured by applying a stress to the sample which has not been subjected to a stress and allowed to age for a period of 72 h after quenching from an elevated temperature. Thus the advantage of repeatedly testing a specimen which remains mounted in the creep rig is lost.

The repeatability of the creep tests was typically within 2%. A normalization procedure was used to ensure matching of the long-term creep data to that obtained for the same elapsed time in a short-term test.

Table 1 Details of the creep data supplied by the National Physical Laboratory for the round-robin analysis (T = 23°C)

Applied stress (MPa)	Initial age of the testpiece, t_e (h)	Applied stress (MPa)	Initial age of the testpiece, t_e (h)
3	3 (short term)	3	72 (long term)
3	7 (short term)	9	7 (long term)
3	24 (short term)	9	24 (long term)
3	72 (short term)	9	72 (long term)
3	240 (short term)	11.8	24 (long term)
3	7 (long term)	15	24 (long term
3	24 (long term)		

RESULTS AND SURVEY OF ANALYSIS METHODS

Figure 1 shows the influence of physical ageing on the creep behaviour of polypropylene subjected to a tensile stress of 3 MPa over a limited timescale of $0.3t_e$, where t_e refers to the initial age of the material. From this figure it is evident that the creep curves shift to longer times with increasing age, although this can also be interpreted as a progressive decrease in compliance for any given creep time. *Figure 2*(A) shows long-term data obtained at a stress of 3 MPa for the elapsed times indicated. From this figure it is apparent that the rate at which the material creeps decreases with time as further ageing occurs causing the creep curves to converge. The effect of stress on the long-term creep behaviour of testpieces aged for 24 h prior to the application of a load is shown in *Figure 2*(B).

Whilst some of the parameters required by the creep functions can be determined from short-term tests, others can only be derived from long-term measurements. In the following sections we will describe the models used by the various laboratories to analyse both short- and long-term creep data measured at low and high stress.

Analysis of low stress short-term data

Generally the parameters required to model short-term creep data at a given elapsed time represent the compliance at zero time (D_0), a mean retardation time (τ) which positions the curve on the time axis and a parameter (m) which characterizes its width along the time axis. Struik and others (including **Laboratory 4**)[1,9] have extensively used a function containing these parameters which is of the form

$$D(t) = D_0 \exp[(t/\tau)^m] \qquad (1)$$

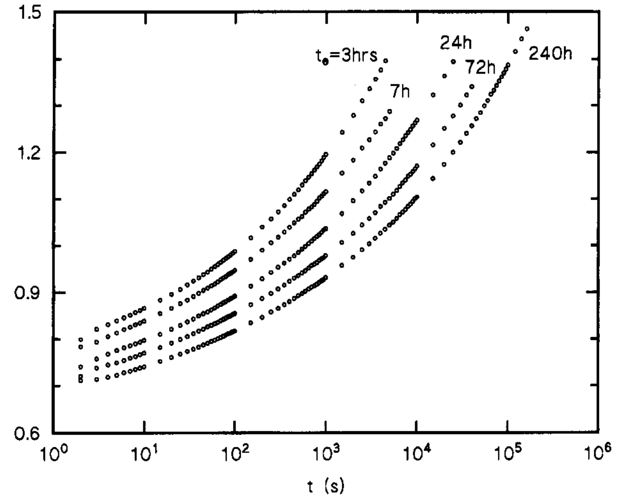

Figure 1 Short-term creep data obtained from a testpiece subjected to a tensile stress of 3 MPa at the elapsed times indicated

Table 2 Participating laboratories

Laboratory number	Laboratory	Researchers
1	DSM Research, The Netherlands	P. Steeman
2	Deutsches Wollforschungsinstitut, Germany	F.-J. Wortmann
3	Eindhoven University of Technology, The Netherlands	L. Govaert, C. v. Haag and E. Klompen
4	National Physical Laboratory, United Kingdom	P.E. Tomlins and B.E. Read
5	Université Libre du Bruxelles, Belgium	S. Hellinckx and N. Heymans

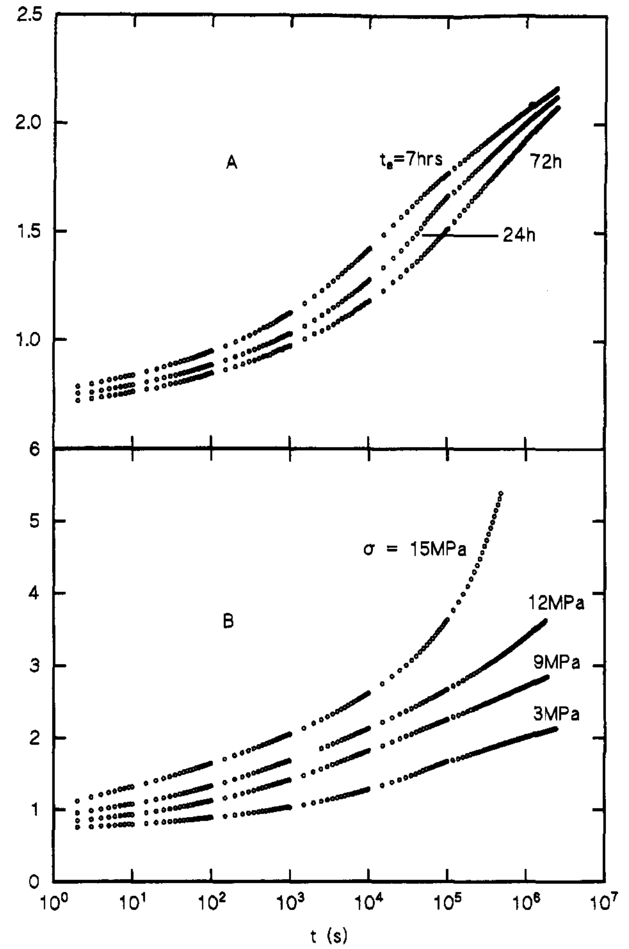

Figure 2 (A) Long-term creep of polypropylene as a function of the initial elapsed times indicated, in response to a tensile stress of 3 MPa. (B) The long-term creep behaviour of polypropylene as a function of stress. The testpieces were aged for a period of 24 h prior to load application

noting that the exponential term of this equation is consistent with the stress relaxation function, $\exp[-(t/\tau)^{m}]$ originally proposed by Kohlrausch[5]. This function assumes a constant compliance contribution from any underlying relaxation process. Although being constant for each test, τ increases with increasing age of the material and can be used to define an ageing rate μ where μ = dlog τ/dlog t_e.

Laboratory 1 modified Struik's function [equation (1)] to include a time-dependent pre-exponential factor to potentially account for any contribution to the creep from the underlying β-process, which slightly tilts the calculated creep curves. Thus equation (1) can be rewritten as

$$D(t) = D_0(t/\tau)^a\exp[(t/\tau)^b] \qquad (2)$$

where a and b are constants. Unlike equation (1), D_0 is the compliance not at zero time but at a time coresponding to that at which the quantity $(t/\tau)^a \exp[(t/\tau)^b] = 1$. Values for the parameters were obtained by using a least-squares optimization routine to fit equation (2) to each short-term data set. A scaling relationship

$$\log\tau = \log\tau_r + \mu\log(t_e/t_{e,r}) \qquad (3)$$

was used to model the effect of physical ageing on short-term creep where the subscript r refers to measurements obtained for a reference elapsed time, $t_{e,r}$. This scaling relationship implies that a master curve can be generated from a series of short-term creep curves using horizontal shifts of the data following equation (2).

Compliances calculated using either equation (1) or equation (2) will tend to infinity at long times. This does not occur with the functions employed by **Laboratories 2** and **4**. **Laboratory 2** graphically constructed a short-term master curve using a combination of horizontal and vertical shifts without reference to any particular creep function. The time axis of this master plot is referred to as a reduced time. From this plot creep curves can be calculated for any elpased time by suitable scaling of the time axis of the master plot according to

$$\log t_{red} = \log t - \mu\log t_e \qquad (4)$$

where μ is Struik's ageing rate obtained from a plot of log of the horizontal shift factor *versus* log t_e. The master plot was described by **Laboratory 2** by the function

$$D(t) = D_0 + \Delta D(1 - \exp[-(t/\tau)^m] \qquad (5)$$

which reaches an upper compliance limit at long times defined by the magnitude of the relaxation process (ΔD).

Laboratory 4 used a similar function to equation (5), except that the power m only applies to the exponential term:

$$D(t) = D_0 + \Delta D(1 - \exp[-(t/\tau)]^m) \qquad (6)$$

This function is referred to as the Williams–Watts equation as it is consistent with a creep recovery function of the form $\exp[-(t/\tau)^{m}]$ which, in turn, is analogous to that proposed by Williams and Watts to describe charge decay in polymer dielectrics.

Laboratory 4 also considered the power law

$$D(t) = D_0 + \Delta D(t/\tau)^m \qquad (7)$$

which is derived from the Williams–Watts function [equation (6)] by expanding it as a series and ignoring all but the first term. ΔD and τ may be combined into a single parameter $K(= \Delta D/\tau^m)$ such that it is consistent with Findley's equation[10]. For both the Williams–Watts and power law functions the effect of ageing is generally described by an elapsed time dependent τ and ΔD is assumed to be constant. **Laboratory 4** has used the relationship[11]

$$\tau = At_e^{\mu} \qquad (8)$$

to model the elapsed time dependence of τ together with equation (1) or equation (6). For some materials, including polypropylene, the limiting compliance at short times D_0 also appears to depend on elapsed time according to

$$D_0 = Wt_e^{-\nu} \qquad (9)$$

where W and ν represent the intercept and slope, respectively, of a plot of log D_0 *versus* log t_e.

Laboratory 5, although principally accounting for ageing in terms of a progressive increase in τ, also allowed the magnitude of the retardation process, ΔD, to depend on elapsed time. They assumed that the creep rate for the α-relaxation was governed by a diffusion process[12,13] and derived a power law for the short-term creep compliance:

$$D(t) = D_{0\beta} + (1 - A_1 t_e^{\phi})D_1 + \frac{A_1 t_e^{\phi} D_a}{\Gamma(1+m)}\left(\frac{t}{\tau}\right)^m \qquad (10)$$

The retardation time, τ was expressed in the form

$$\tau = \tau_0\left(\frac{t_e}{\tau_0}\right)^{\mu} \qquad (11)$$

where τ_0 is a reference retardation time for $t_e = \tau_0$, and we note that equation (11) is equivalent to equation (8) with $A = \tau_0^{1-\mu}$. In equation (10) $D_{0\beta}$ and $(1 - A_1 t_e^{\phi})D_1$ are the unrelaxed compliance and the retardation magnitude, respectively, of the underlying β-process. This process is assigned to motions in the bulk amorphous phase related to a (lower) glass transition and is considered to be fully relaxed. The third term on the right-hand side of equation (10) is the time-dependent compliance contribution from the α-process. The factors $1 - A_1 t_e^{\phi}$ and $A_1 t_e^{\phi}$ are the age-dependent fractions of the amorphous material which participates in the β- and α-process, respectively. Evidence for the dependence of these fractions on age can be found from infra-red spectra[12] and from the age dependence of the β relaxation strength. D_a governs the magnitude of the α-process, m is a distribution parameter and Γ represents a gamma function.

All of the above equations assume a continuous distribution of retardation or relaxation times, characterized by a parameter m about some mean value τ. **Laboratory 3** did not follow this route but calculated the compliance from a summation of contributions from discrete retardation times, τ_i according to

$$D(t) = D_0 + \sum_{i=1}^{n} D_i(1 - \exp[-(t/\tau_i)]) + t/\eta_0 \qquad (12)$$

where η_0 is a viscosity term. A consequence of considering discrete values of τ is that the magnitude term ΔD is also broken down into a number of compliance contributions D_i. Equation (12) was used to model a single creep curve (t_e = 72 h) which was subsequently scaled through changes in the retardation times τ_i by the factor

$$\tau_i(t_e) = f_e \tau_i \qquad (13)$$

in order to model short-term creep curves at other elapsed times. $f_e = (t_e/72)^{\mu}$ where 72 refers to the elapsed time (in hours) of the reference data set and μ is Struik's ageing rate.

Analysis of low stress long-term data

Beyond the short-term limit of $0.3t_e$ the age of the testpiece and hence τ progressively increase with time. This gradual change of τ can be modelled by replacing t/τ in equation (1), equation (6) or equation (7) by

$$\int_0^t \frac{du}{\tau(u)} \qquad (14)$$

where values of the instantaneous retardation time $\tau(u)$ are integrated over the time range $u = 0 \rightarrow t$. If, using equation (8) we now substitute

$$\tau(u) = A(t_e + u)^{\mu} \qquad (15)$$

into equation (14), then the long-term compliance is given by equation (1), equation (5), equation (6) or equation (7) with t/τ replaced by $\lambda/\tau(0)$ where λ is an effective time given by

$$\lambda = \frac{t_e}{1-\mu}\left[\left(1 + \frac{t}{t_e}\right)^{1-\mu} - 1\right] \qquad (16)$$

and $\tau(0) = At_e^{\mu}$ is now written for the retardation time at t = 0. The effective time parameter in this form was used by all laboratories in conjunction with the appropriate short-term creep equations to model long-term data. However, **Laboratory 4** also used a hyperbolic function of the form

$$\tau(u) = (\tau^2 + C^2 u^{2\mu'})^{0.5} \qquad (17)$$

to describe the time-dependent increase of τ. In this equation $\tau = \tau(0)$ is the initial retardation time characteristic of the short-term part of a long-term test [equation (8)] and C and μ' are constants. This function when substituted into equation (14) was used by **Laboratory 4** to model long-term low stress data after replacing t/τ by equation (14) in equation (1), equation (6) or equation (7).

Laboratory 3 found it necessary to extend their master curve obtained by shifts of short-term creep curves measured at low stress to cover a wider timespan in order to reach the compliance levels that are seen in long-term tests. This was achieved by time-stress superposition where the low stress short-term master curve (obtained for σ = 3 MPa and t_e = 24 h) was extended by appropriate shifts of the short-term parts of long-term creep curves measured at high stresses (for t_e = 24 h). The short-term region of the creep curves obtained at the higher stresses was assumed to be $t_e/3$, implying that the shift factor $f_\sigma(\sigma)$ arises from Eyring stress-activated flow rather than a stress-induced deageing (decrease in t_e). Whilst equation (12) is still used to model the extended master curve, variations in compliance due to stress or elapsed time are accomodated by changes in τ_i. This is achieved by extending equation (13) to include a stress factor f_σ, such that it becomes

$$\tau_i(t_e, \sigma) = f_e f_\sigma \tau_i \qquad (18)$$

where τ_i is the ith retardation time computed at 3 MPa for t_e = 24 h, and

$$f_\sigma = \frac{(\sigma/\tau_e)}{\sinh(\sigma/\tau_e)} \qquad (19)$$

where τ_e is a material constant in the Eyring flow model[14].

Laboratory 3 subsequently used their extended short-term master curve to predict long-term creep by replacing time t in equation (12) by the effective time expression of equation (16).

Analysis of high stress long-term data

As previously mentioned the application of high non-linear stresses to testpieces of the same age has a profound effect on the creep response and appears to shift the creep curves to shorter times, as can be seen in *Figure 2*(B). This phenomenon can be interpreted as a 'deageing' effect where a testpiece of a given age creeps at a rate comparable to that of a much younger material, giving rise to the concept of an effective elapsed time $t_{e,\text{eff}}(\sigma)$. The uncertainty in the apparent age of the material complicates the analysis of high stress data since it is difficult to define a short-term region, i.e. $t < 0.3t_{e,\text{eff}}$ unless $t_{e,\text{eff}}$ is known. Furthermore it has not been established whether or not τ is constant over the timescale $0.3t_{e,\text{eff}}$.

Faced with these difficulties **Laboratory 1** assumed that the shape of the short-term region of the high stress long-term creep curves (defining a short-term limit as $t < 0.1t_e$) remained the same as that obtained at low stress and used equation (2) to model the creep data over this timescale, keeping a and b constant. Changes in compliance were accomodated by allowing D_0 to increase and τ to decrease with increasing stress. The decrease in τ was attributed to stress-induced deageing of the polymer, i.e. a change from a known age t_e to an effective age $t_{e,eff}(\sigma) < t_e$.

Predicted long-term compliances at high stress were then determined using equation (2) with $\tau = \tau(\sigma)$ after replacing t with an effective time λ [equation (16)] and with t_e replaced by $t_{e,eff}(\sigma)$ to account for the reactivation of ageing during the creep.

Laboratory 3 used their short-term master curve [equation (12)] based on stress-time superposition in conjunction with equations (16), (18) and (19) to model the effects of elevated stress on long-term creep.

Laboratory 4 utilized the Williams–Watts equation for long-term creep [equations (6), (8), (9) and (17)] coupled with a stress-dependent contribution to the compliance kt^n arising from a presumed viscous flow process that follows or merges with the recoverable creep, i.e.

$$D(t) = D_0 + \Delta D\left(1 - \exp\left[-\left(\int_0^t \frac{du}{\tau(u)}\right)^m\right]\right) + kt^n \quad (20)$$

The presence of the integral in this equation indicates that ageing is still assumed to accompany the creep and $\tau(u)$ is again given by equations (8) and (17) where A, μ, C and μ' may each depend on stress. The inclusion of the viscous flow term follows the approach of Wilding and Ward to modelling the creep of highly oriented polyethylene[15].

COMPARISONS OF MODELS WITH DATA

Low stress short-term data

Figures 3–5 show comparisons of the fits to short-term creep data (σ = 3 MPa) obtained by all of the laboratories involved in the exercise using the parameters given in *Tables 3–7*. It is apparent from these figures that all of the models described above accurately describe the data.

Each of the laboratories were asked as part of the round-robin exercise to predict the short-term creep curve for a specimen aged for 1500 h. From *Figure 6* it is evident that all of the predictions underestimate the creep for this specimen. These discrepancies suggest that the τ values predicted by linear extrapolations of $\log \tau$ *versus* $\log t_e$ data may be larger than the actual τ at long t_e and may reflect some apparent curvature in the $\log \tau - \log t_e$ plots. This could correspond to a decrease in the apparent μ value with increasing t_e, suggesting that equations such as equation (8) require modification. However, the discrepancies seem more likely to have arisen from errors in the estimated predicted creep curves due to the neglect of overlap from the β-process. Such errors would increase with increasing t_e owing to an increase in the relative contribution from this process. If this hypothesis is correct then 'true' estimates of τ could be obtained by modifying the creep functions to take account

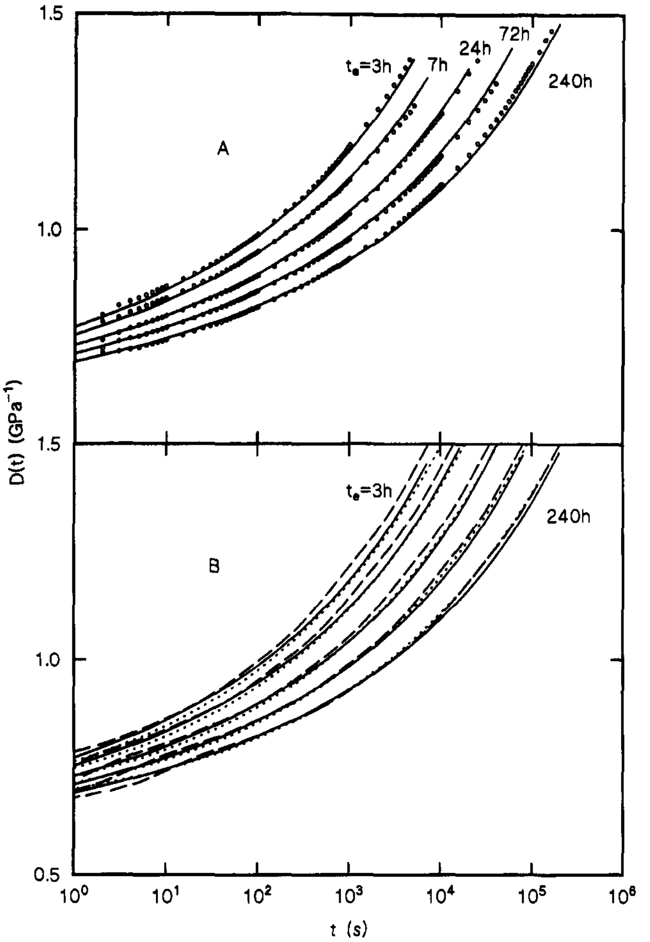

Figure 3 (A) Fits (————) to short-term creep data (σ = 3 MPa) by **Laboratory 1** [equations (2) and (3), see *Table 3*]. (B) Comparison of the short-term fits obtained by **Laboratories 1** (————), **2** [equations (4) and (5), see *Table 4*] (···) and **3** [equations (12) and (13), see *Table 5*] (- - -)

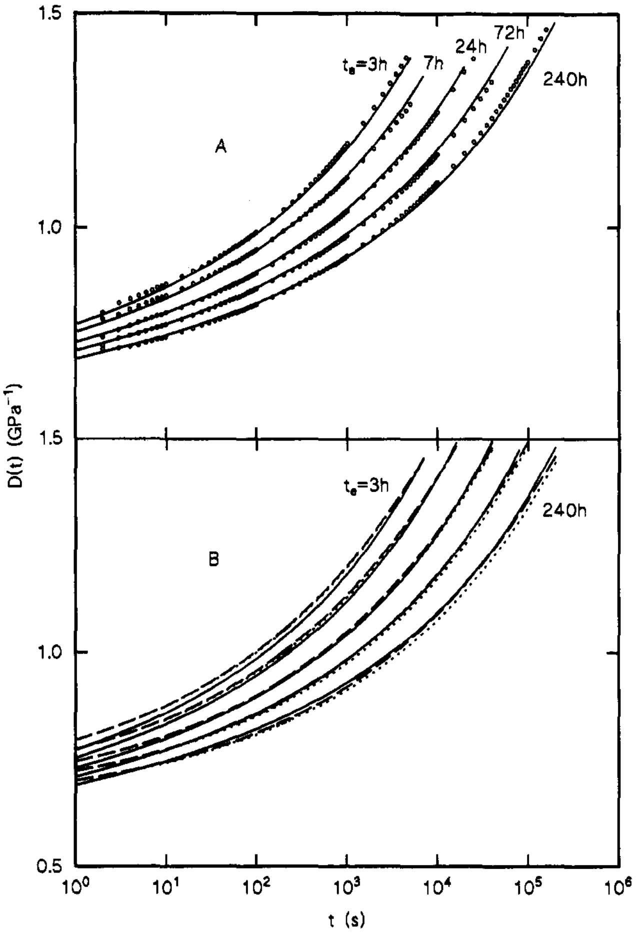

Figure 4 (A) Fits (————) to short-term creep data (σ = 3 MPa) by **Laboratory 1** [equations (2) and (3), see *Table 3*]. (B) Comparison of the short-term fits obtained by **Laboratories 1** (————) and **4** using equations (8) and (9) together with equation (6) (- - -) and equation (7) (···) (see *Table 6*)

of the underlying β-process, e.g. by assuming an inclined baseline[16].

Low stress long-term data

Figures 7–10 show a comparison of fits to the long-term data where differences between the functions begin to emerge, particularly when extrapolated to times in excess of those for which data are available.

Using the effective time expression [equation (16)], **Laboratories 2** and **5** together with equations (5) and (10), respectively, obtained good fits to the long-term data as shown in *Figures 7 and 8*. It should also be noted that extrapolating **Laboratory 5**'s predictions by one decade of time results in the theoretical curves crossing over each other. This crossover which, although difficult to see in *Figure 7*, arises from a dependence of the α-retardation magnitude on t_e^Φ noting that crossover is generally not observed in models which assume this magnitude to be independent of age.

The fit to long-term data obtained by **Laboratory 1** initially tends to slightly underpredict the measured compliances and to overpredict them at longer times as can be seen in *Figure 7*. This may be due to uncertainties associated with the data (as discussed below) rather than shortfalls in the model used. However, it should be noted that the effective time expression [equation (16)] when used in conjunction with equations (2) and (3) can result in small overpredictions of the creep at longer times. This can be attributed to the behaviour of the exponential term in equation (2) which tends to rapidly rise at longer creep times, despite the moderating effect of replacing t by λ.

Laboratories 3 and **4** both used the effective time expression [equation (16)] in conjunction with equations (12) and (6), respectively. Both laboratories underestimated the measured creep compliances at long creep times as shown in *Figures 9 and 10*, despite the predictions accurately describing the data at short times.

Whilst there is no obvious explanation as to why some models which utilize the effective time concept appear to successfully describe the long-term creep data whilst others

Table 3 Values of the parameters used by **Laboratory 1** [equations (2), (3) and (16)]

Parameter	Value
D_0	0.772 GPa^{-1}
a	0.1578
b	0.0146
μ	0.73
Log τ_{ref}	4.602
$t_{e,r}$	1 h

Table 4 Values of the parameters used by **Laboratory 2** [equations (4), (5) and (16)]

Parameter	Value
D_0	0.663 GPa^{-1}
ΔD	1.81 GPa^{-1}
m	0.22
μ	0.68

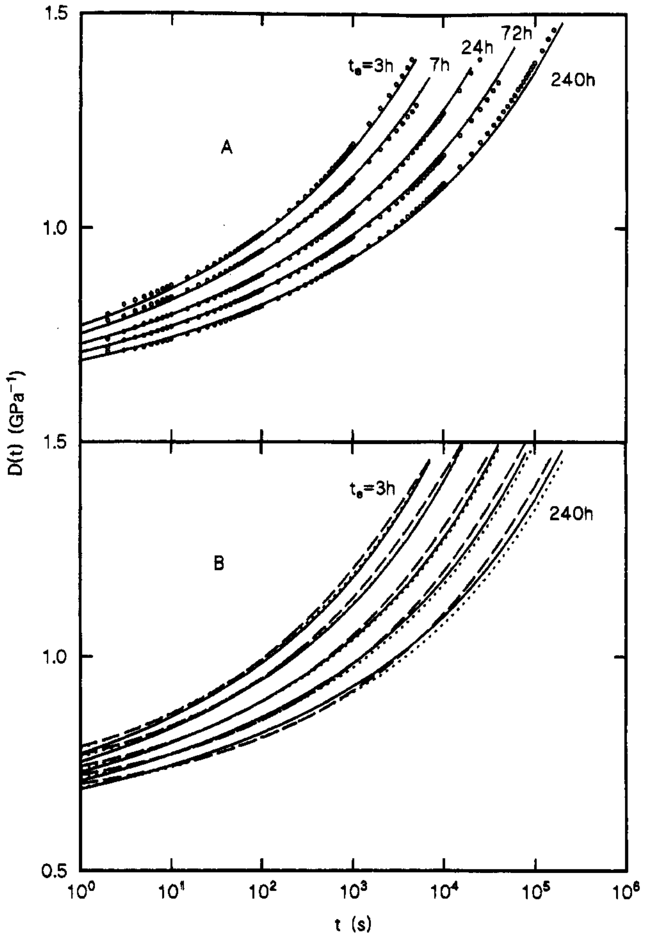

Figure 5 (A) Fits (————) to short-term creep data (σ = 3 MPa) by **Laboratory 1** [equations (2) and (3)]. (B) Comparison of the short-term fits obtained by **Laboratories 1** (————), **4** [equations (1), (8) and (9), see *Table 6*] (···) and **5** [equations (10) and (11), see *Table 7*] (- - -)

Table 5 Values of the parameters used by **Laboratory 3** [equations (12), (16), (18) and (19)]

Parameter	Value (MPa)	Parameter	Value
D_0	6.6993×10^{-4}	η_0	4.7787×10^{11} (MPa s)
D_1	9.7826×10^{-5}	τ_1	3.8636 (s)
D_2	6.5062×10^{-5}	τ_2	39.887 (s)
D_3	1.1688×10^{-4}	τ_3	411.795 (s)
D_4	1.9837×10^{-4}	τ_4	4251.33 (s)
D_5	3.3139×10^{-4}	τ_5	4.389×10^4 (s)
D_6	4.0320×10^{-4}	τ_6	4.531×10^5 (s)
D_7	4.2002×10^{-4}	τ_7	4.678×10^6 (s)
D_8	8.4387×10^{-4}	τ_8	4.829×10^7 (s)

Table 6 Values of the parameters used by **Laboratory 4** for fitting creep data measured at low stress (3 MPa)

Parameter	equations (1), (8), (9) and (17)	equations (6), (8), (9) and (17)	equations (7)–(9) and (17)
m	0.13	0.21	0.20
W (GPa^{-1})	0.627	0.734	0.728
ν	0.0066	0.0110	0.0107
ΔD (GPa^{-1})	—	5.3	5.3
A (s$^{(1-\mu)}$)	20.70	56485	96268
μ	0.711	0.710	0.738
C (s$^{(1-\mu)}$)	16.0	20000	47000
μ'	0.74	0.74	0.76

Table 7 Values of the parameters used by **Laboratory 5** [equations (10), (11) and (16)]

Parameter	Value
$D_0 + D_1$	0.93 GPa^{-1}
ϕ	0.024
$A_1'D_1$	0.2 GPa^{-1} s$^{-0.024}$
$A_1'D_1/\tau_0^{\gamma(1-\mu)}$	0.44 GPa^{-1} s$^{-0.068}$
m	0.22
μ	0.8

do not, there are a number of factors which may influence the quality of the fit. It has been noted that the creep compliances measured in the 3 MPa short-term test sequence (for t_e = 7, 24 and 72 h) are slightly greater than those determined for the short-term parts of the corresponding long-term tests, as shown in *Figure 10*. This mismatch may contribute to an underestimate of long-term compliances using parameters derived from short-term data. Modelling the short-term regions of the long-term creep

Table 8 Values of the parameters used by **Laboratory 4** for fitting long-term data at elevated stresses [equations (6), (8), (9), (17) and (20)]

Parameter	Stress (MPa)			
	2.96	8.97	11.8	14.8
m	0.21	0.20	0.20	0.20
D_0 (GPa^{-1})	0.648	0.59	0.62	0.63
ΔD (GPa^{-1})	5.3	5.3	5.3	5.3
A (s$^{(1-\mu)}$)	56485	14900	8326	2356
μ	0.71	0.54	0.47	0.40
C (s$^{(1-\mu)}$)	20000	33000	38205	29929
μ'	0.74	0.54	0.47	0.40
K (GPa^{-1} s^{-n})	—	—	1.26×10^{-4}	4.27×10^{-4}
n	—	—	0.586	0.649

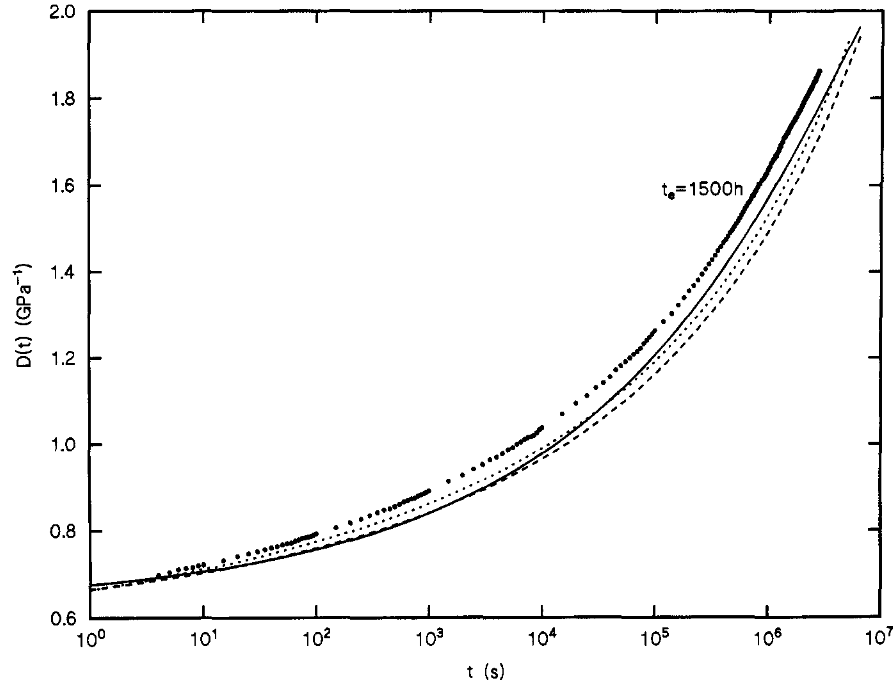

Figure 6 A comparison of predicted short-term creep curves for a testpiece aged for 1500 h and measured data (●). (· · ·) **Laboratory 1** [equations (2) and (3), see *Table 3*], (- - -) **Laboratory 4** [equations (1), (8) and (9), see *Table 6*], and (———) **Laboratory 5** [equations (10) and (11), see *Table 7*]

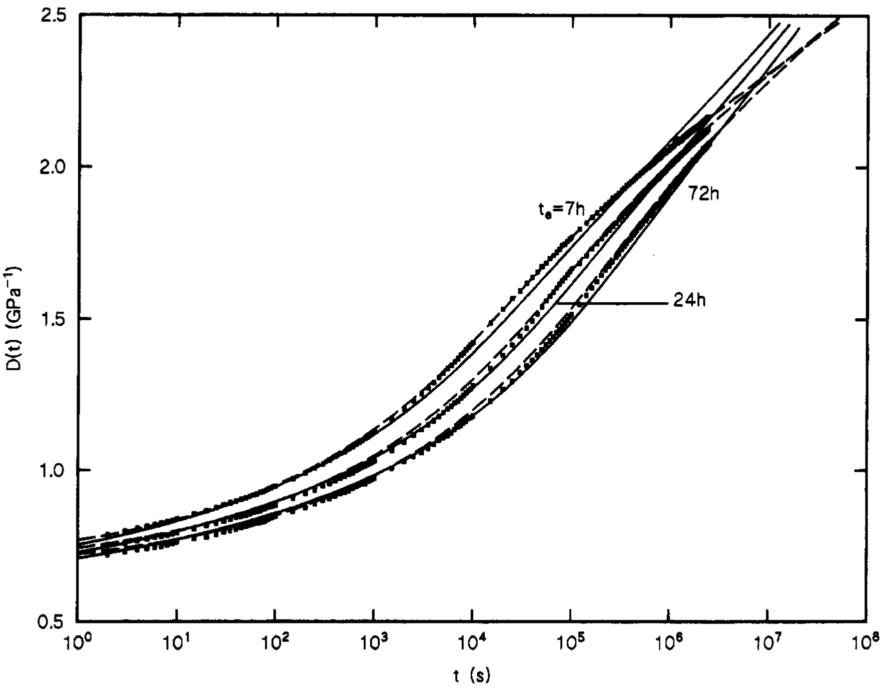

Figure 7 A comparison of the fits to long-term data ($\sigma = 3$ MPa) obtained by **Laboratories 1** [equations (2), (3) and (16), see *Table 3*] (————), and **5** [equations (10), (11) and (16), see *Table 7*] (- - -)

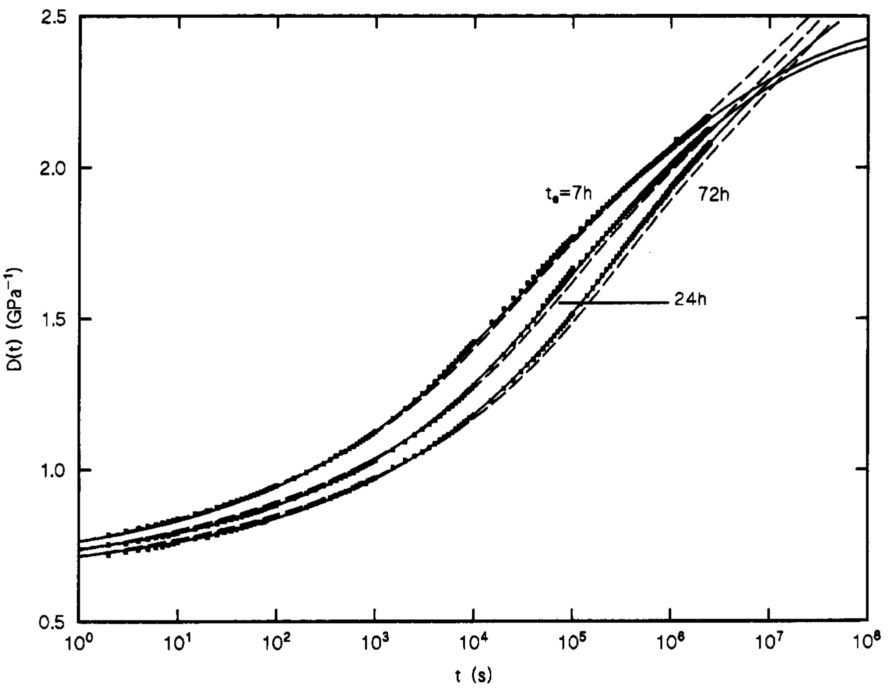

Figure 8 A comparison of the fits to long-term data ($\sigma = 3$ MPa) obtained by **Laboratories 2** [equations (4), (5) and (16), see *Table 4*] (————) and **4** [equations (1), (8), (9) and (17), see *Table 6*] (- - -)

curves overcomes this practical problem, but introduces greater uncertainty in the t_e dependence of the derived parameters. The most successful fits to the long-term data were obtained by modelling each long-term data set, where uncertainties in the elapsed time dependence of the parameters are eliminated. **Laboratory 1** reported an improved fit to the long-term creep curves when all the parameters required by equations (2), (3) and (16) were derived from these data.

The predictions based on equations (6) and (7) with equation (17) replacing equation (15) (**Laboratory 4**) are almost identical over the timescale of the tests, as shown in *Figure 11*, and in good agreement with the long-term data. Extrapolation of the predictions to longer times does result in small differences appearing between curves predicted by the two functions for a given elapsed time. This may be due to the use of slightly inappropriate values for the parameters rather than inaccuracies in the models themselves.

In a previous study on the creep of PVC as a function of stress using equation (17) it was shown that C values were initially less than A values for stress levels

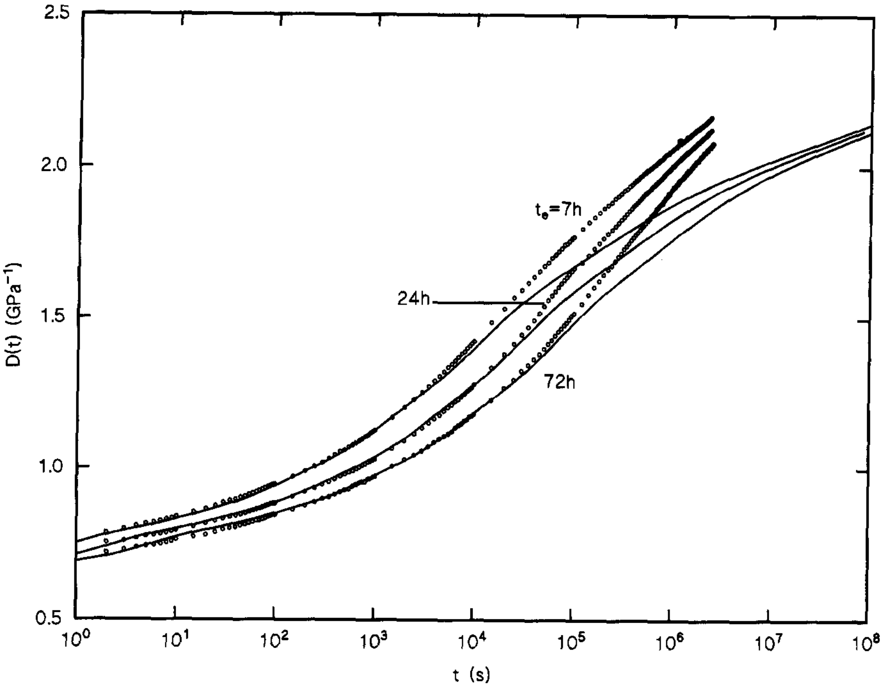

Figure 9 A comparison of the fits (———————) to long-term data ($\sigma = 3$ MPa) obtained by **Laboratory 3** [equations (12), (16), (18) and (19), see *Table 5*]

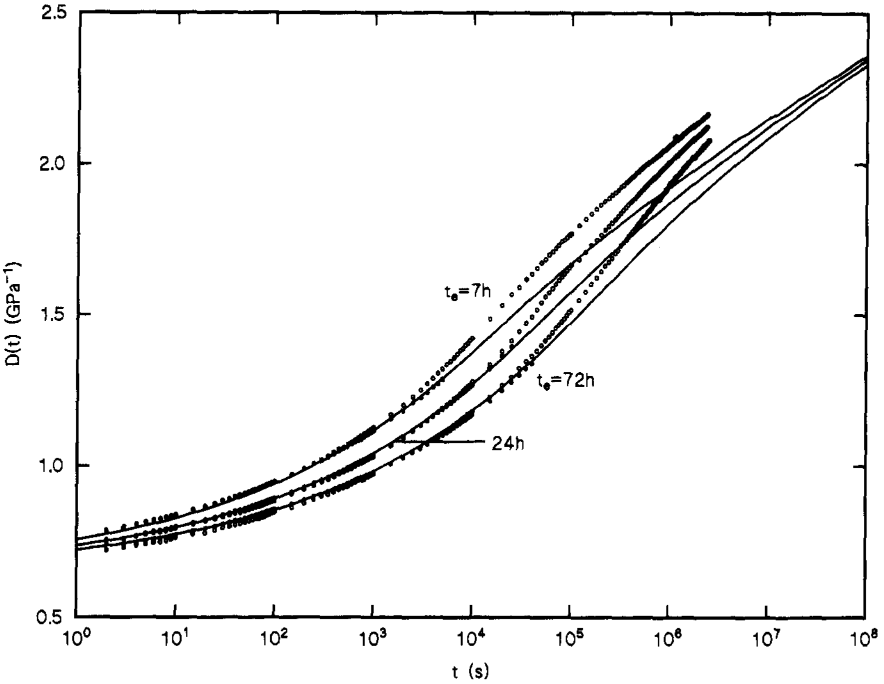

Figure 10 A comparison of predictions obtained using the Williams–Watts function (equation 6) after substitution of an effective time (equation 16) (———————) for time with long-term data ($\sigma = 3$ MPa) obtained by **Laboratory 4** (*Table 5*). Note the small mismatch between short-term data (●) and long-term measurements (○)

corresponding to the onset of non-linearity. This result is also apparent for polypropylene (*Table 6*) and suggests that even at 3 MPa the creep response of this material is non-linear, at least at long times where the measured strain exceeds 0.3%. This finding is supported by **Laboratory 3** who found evidence of non-linearity in Eyring plots of log shift factor *versus* equivalent stress. If this hypothesis is correct then it provides a possible explanation as to why some of the laboratories have underestimated the long-term compliances for a stress of 3 MPa using equation (16).

High stress long-term data

Figure 12 compares the fits obtained by **Laboratories 1** and **3** to the data obtained at a stress of 9 MPa. Whilst **Laboratory 1** obtained a good agreement between the calculated creep curves and the experimental data, those findings obtained by **Laboratory 3** underestimated the

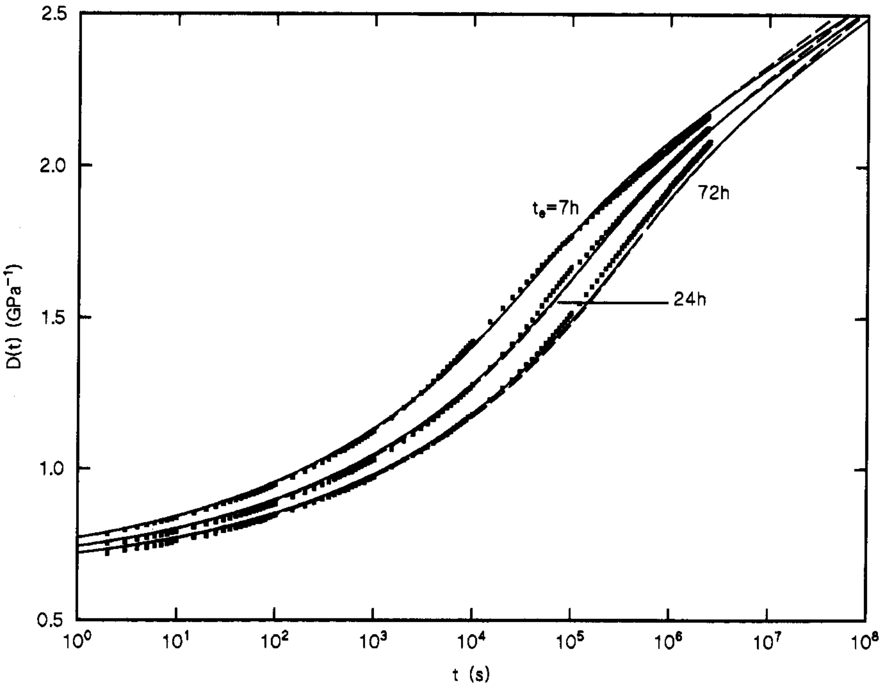

Figure 11 A comparison of the fits to long-term data ($\sigma = 3$ MPa) obtained by **Laboratory 4** using the Williams–Watts [equation (6)] (———) and power law functions [equation (7)] (- - -) with equations (8), (9) and (17), see *Table 6*

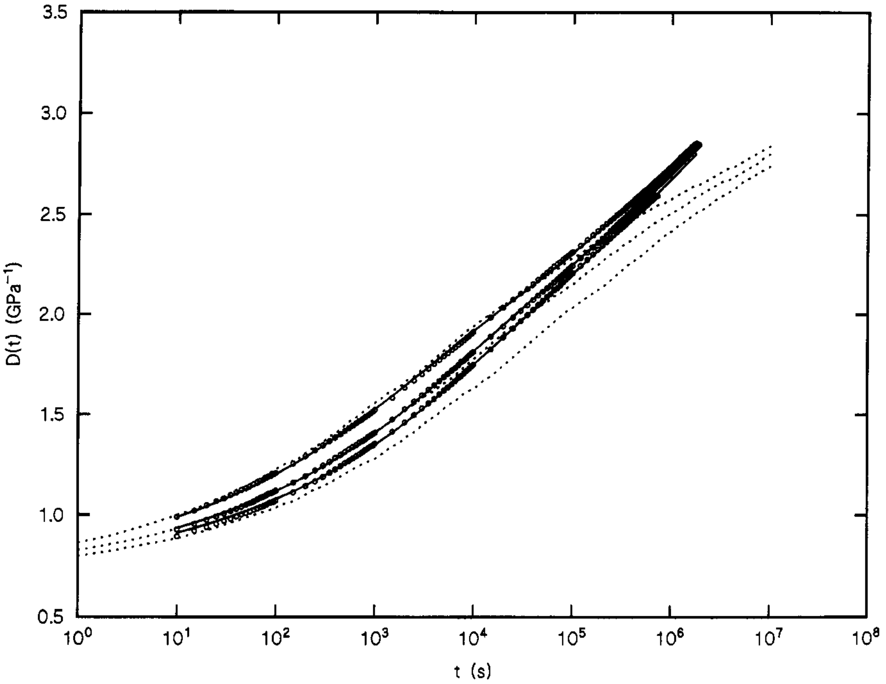

Figure 12 A comparison of the fits to long-term high stress data ($\sigma = 9$ MPa) obtained by **Laboratories 1** (———) [equations (2), (3) and (16), see *Table 3*] and **3** (· · ·) [equations (12), (16), (18) and (19), see *Table 5*]

compliances at the longer creep times. These underestimates of compliance may be attributable to the difficulty in estimating the short-term time limit from the high stress data which may be significantly less than the $t_e/3$ assumed due to the deaging effect of the applied stress.

Figure 13 shows a good agreement between the experimental curves for $\sigma = 9$ MPa and the theoretical curves based on equations (6) and (17) without the viscous flow term (**Laboratory 4**) for creep times of up to 10^6 s. Beyond this time the predictions begin to underestimate the measured compliances which may imply the onset of a long-term process such as viscous flow.

In *Figure 14* creep curves calculated for stresses of 11.8 and 15 MPa by **Laboratory 3** are compared with measured compliances. From this figure it is apparent that the generalized Voigt model is not particularly successful at describing creep in response to an applied stress of 15 MPa. This may be due to an additional contribution to the compliance by a viscous flow term which was considered by **Laboratory 4** and included in equation (20). The effect of

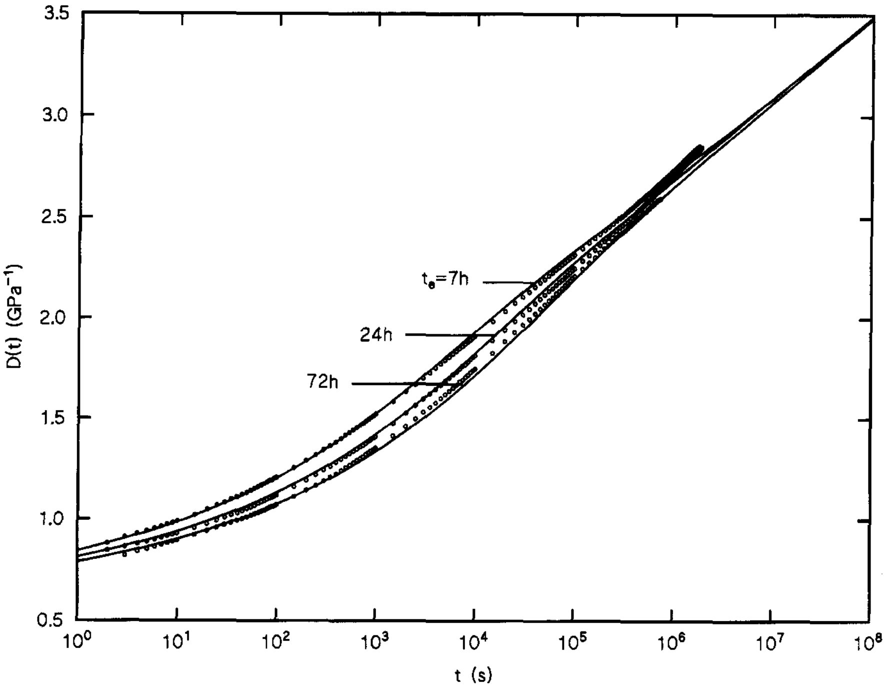

Figure 13 Fits to long-term high stress data ($\sigma = 9$ MPa) obtained by **Laboratory 4** [equations (6), (8), (9) and (17), see *Table 6*] assuming no contribution to the calculated compliances from a viscous flow process. Ignoring this additional term may be responsible for the mismatch between theory and measured data at longer times

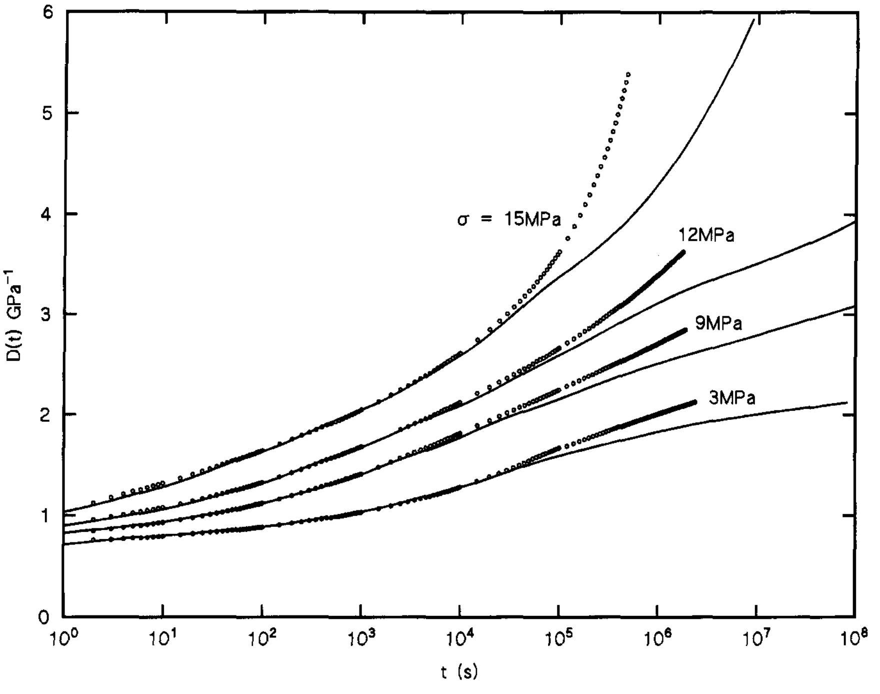

Figure 14 Calculated compliance curves (————) based on equations (12), (16), (18) and (19) (*Table 5*) by **Laboratory 3** are compared with measured data obtained at the stresses shown for testpieces with an initial t_e = 24 h

including this additional term in the calculations is shown in *Figure 15*. *Figure 16* shows the relative contributions from the proposed viscous flow mechanism and retardation of the α-process which caters for progressive ageing of the testpiece during the measurement period. *Figure 16* also shows that the extrapolated short-term calculation [equation (6)] severely underestimates the compliances at long creep times. This is contrary to that normally observed for low stress data where the calculated short-term creep normally predicts much higher compliances than those experimentally determined. These findings tend to support the suggestion of an additional compliance contribution, which becomes increasingly important as the applied stress increases.

SUGGESTIONS FOR FURTHER WORK

The results of this round-robin analysis show that the potential exists for standardizing the analysis of creep data to include the influence of physical ageing. However, some

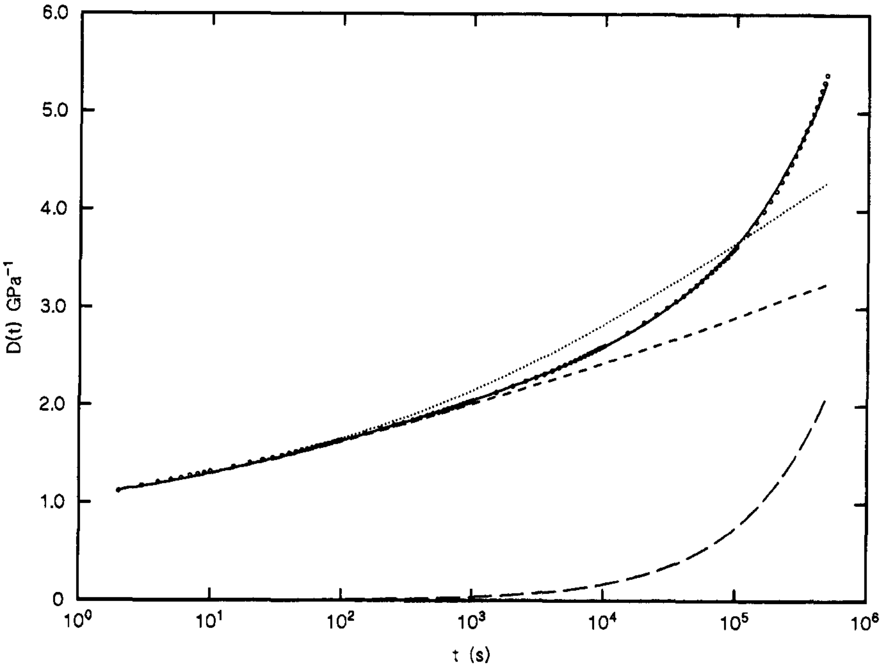

Figure 15 Fits (————) to long-term data (O) (initial $t_e = 24$ h) at the stresses indicated obtained by **Laboratory 4** assuming further ageing of the material with time and a viscous flow contribution to the compliance [equations (17) and (20), see *Table 8*]. The alternative fit to the data obtained at 9 MPa (- - -) is based only on further ageing of the testpiece under load [equations (6), (8), (9) and (17)] and does not consider a compliance contribution from viscous flow

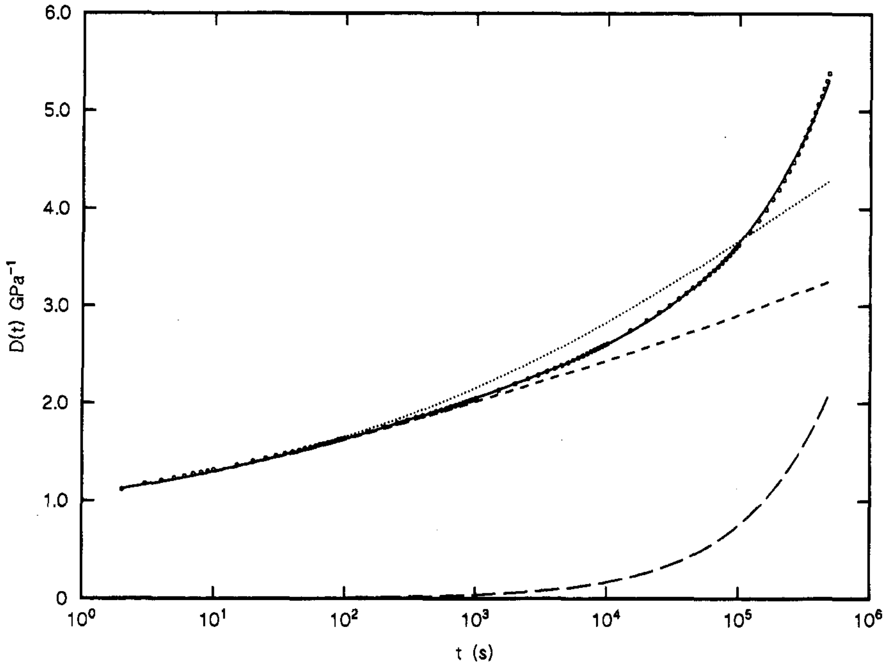

Figure 16 A comparison of an extrapolated short-term creep curve (· · ·) based on equations (6), (8) and (9) (*Table 6*) (**Laboratory 4**) with long-term creep data obtained for a testpiece of $t_e = 24$ h and at a stress of 24 MPa. (- - -) represents the expected long-term creep curve [equations (6), (8), (9) and (17), see *Table 8*] and (– – –) is the calculated contribution to the measured compliances from a viscous flow process described by kt^n. (————) is the combination of viscous flow and long-term creep calculated from equations (15) and (20), see *Table 8*

areas of the modelling require further consideration before the preparation of a draft standard can be undertaken. Any attempt at standardization should only consider the creep behaviour over a restricted range of applied stresses comparable to those found in practice as the use of materials at highly non-linear strains is obviously not recommended. Typically this practical limit is defined by the stress or time required to double the compliance, thus the need to develop models capable of describing four- to five-fold increases in compliance is of a low priority.

For the grade of polypropylene studied in this round-robin there are two main areas of work relating to the modelling of low stress creep which require further research. These should address the following questions:

- Why does the extrapolation of the short-term function to long elapsed times not appear to work for any of the proposed models? Is it due to the effects of overlap of the β-process on the derived τ values, or to an inaccuracy in the function which describes the elapsed time dependence of τ (i.e. an apparent decrease of μ with increasing t_e).
- Are the underestimates of the low stress compliance at long times due to limitations of some of the proposed creep models, inaccuracies in the effective time expression [equation (16)] or the measured strains being just within the non-linear range of the stress–strain curve?

Some laboratories participating in this exercise predicted long-term creep behaviour using models containing parameters that they derived from short-term creep data, whereas others used models which have some parameters that can only be derived from long-term creep data. This difference between the models can result in a mismatch of the measured and calculated compliances at long times. This may be a reflection of the small experimental differences between the short- and long-term data (as previously mentioned) in that the parameters derived from a set of short-term creep curves may be inappropriate for a different set of long-term creep curves. This topic requires further study before standards can be developed; in particular there is a need to establish the influence of measurement reproducibility on the accuracy of model predictions.

CONCLUSIONS

All of the seven functions described in this paper are equally successful in modelling the effects of physical ageing on the short-term creep behaviour of polypropylene obtained from testpieces aged for between 3 and 240 h at the comparatively low stress of 3 MPa. Extrapolating these functions to predict the creep curve of a testpiece aged for 1500 h resulted in an underestimate of compliances. Further work is required to establish if this reflects a limitation of the functions used to describe the elapsed time dependence of τ, or whether the derived values of τ are too small for long t_e as a consequence of the overlap effects of the β-process.

Differences between the models become more apparent when predictions are compared with longer duration tests where the testpiece continues to age during the measurement period. Such differences may be due to inaccuracies in the basic creep functions, the expressions for τ or λ used to describe further ageing of the material during creep, or the onset of non-linearity.

Modelling creep at elevated stresses introduces more assumptions regarding the stress and time dependence of the required parameters, which has resulted in some degree of mismatch between the theoretical curves and those experimentally determined. This may imply the existence of another process which contributes to the compliance at long times and which becomes active at elevated stresses.

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