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Comparison of different functions for modelling the creep and physical ageing effects in plastics

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Tensile creep data have been obtained from specimens of different age of polypropylene, poly(vinyl chloride) and an epoxy, at 23°C and at low stress. The data are classified as being either short or long term which reflects the duration of the test period with respect to the initial age of the material. In short term tests further ageing of the material during the measurement period can be ignored whereas in long term tests it cannot. Three functions containing both material and age dependent parameters have been used to analyse these data. The results show that all the functions fit the data from both short and long term tests equally well over the period of measurement. However, differences of approximately 8% between the functions are observed if the long term fits are extrapolated by 2 decades to creep times in excess of 3 years. Crown copyright © 1996 Published by Elsevier Science Ltd.

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INTRODUCTION

The creep behaviour of glassy materials is not only dependent on test conditions such as the applied stress or the temperature but also on the physical age of the testpiece. The physical age t_e of the material at the start of a creep test is defined as the storage time at the test temperature between quenching from an elevated temperature ($T > T_g$) and the instant of load application.

The influence of physical ageing on the β process of both amorphous and semicrystalline polymers is to reduce its magnitude (noting that the molecular origins of this process are different for these materials) whilst the mean retardation time and a parameter characterising the width of the retardation time spectrum remain unchanged[1-3]. In contrast, analyses of the α process suggests that the mean retardation time τ increases with increasing age of the material while the magnitude of the process ΔD_α and a parameter m characterizing the width of the retardation time spectrum remain constant[3-5]. Again the molecular origins of the α process are different for amorphous and semicrystalline polymers. The α process in amorphous polymers is associated with molecular activity which leads to the glass–rubber transition whilst in semicrystalline polymers the α process is thought to reflect changes in the conformation of tie molecules which are an integral part of the crystal lamellae[1,6].

A number of empirical functions containing age dependent parameters have been successfully used to describe the effects of physical ageing on creep of both amorphous and semicrystalline polymers. These functions differ in both their generic form and in the procedures used to obtain the parameters required by them. In this paper a systematic comparative study of examples of these functions in terms of their suitability for modelling creep is presented. The materials selected for this study included an example of an amorphous thermoplastic [poly(vinyl chloride), PVC], an amorphous thermoset (epoxy) and a semicrystalline polymer (polypropylene).

BACKGROUND

Analysis of short term data

Some of the parameters required by the empirical functions used to describe creep of polymers can be determined from a series of short term tests where the test duration is limited to a time correspondening to 0.3 t_e. This effectively ensures that the age of the testpiece remains constant during the test. The remaining parameters that are required to fully describe long term creep behaviour can only be obtained from tests of longer duration ($t > 10\,t_e$) where the testpiece further ages during the test.

The functions used tend to fall into two classes; those based on power laws and those containing a kernel of the form $\exp(t/\tau)^m$ where the two adjustable parameters, m and τ define the spread and location of the function along the time axis t. Values for the exponent m can range from 0 to 1 although in practice values of ≈ 0.3 are commonly encountered. The kernel in this form is consistent with the stress relaxation function, $\exp(-t/\tau)^m$ proposed by Kohlrausch[7] which has been extensively used by Struik and others[4,8] to describe the creep of amorphous polymers over limited timescales. The time-dependent compliance $D(t)$ over a limited timescale is then defined as:

$$D(t) = D_0 \exp(t/\tau)^m \quad (1)$$

where D_0 is the limiting compliance at short times. The

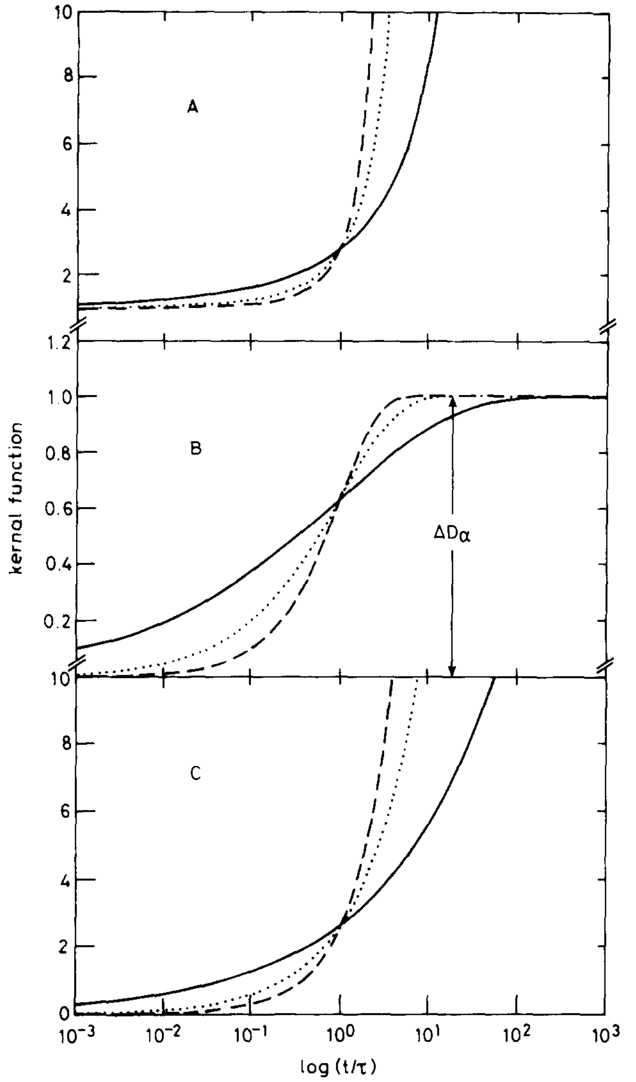

Figure 1 The normalized time dependence of the various short-term function kernels where A = Struik [equation (1)], B = Williams–Watts [(equation (2)] and C = power law [equation (3)]. The three lines shown in each case correspond to different values of the exponent $m = 1$ (– – – –), 0.66 (.....) and 0.33 (———)

time dependent behaviour of this function with different values of the exponent is shown in *Figure 1A* for a case where $D_0 = 1$. From this figure it is apparent that the rate at which the function rises depends on both the value of m and the ratio t/τ becoming very rapid for $t > \tau$.

The kernel described above has also been expressed in a slightly different form as $1 - \exp - (t/\tau)^m$ and incorporated into a function of the form[1].

$$D(t) = D_0 + \Delta D_\alpha(1 - \exp - (t/\tau)^m) \qquad (2)$$

where ΔD_α defines the magnitude of the relaxation process. This function has been successfully used to describe short-term creep in semicrystalline polymers[1] and is consistent with the creep recovery function $\exp -(t/\tau)^m$ which itself is analogous to that proposed by Williams and Watts[9] to describe charge decay in amorphous polymer dielectrics. Although the parameters D_0, τ and m serve the same purpose as those of equation (1) it should be emphasized that in practice they have different values which reflects the different origins of these functions. This is particularly so for the time constant τ which is generally several decades larger in equation (2) than the corresponding value for equation (1). Equation (2) unlike equation (1) has a limiting compliance both at short and very long times which is defined by the magnitude of the relaxation process, ΔD_α as shown in *Figure 1B*. It is apparent from this figure that the function is asymmetrical and has an inflection point defined by τ at a time where the compliance is 63.2% of the long time limiting value.

A power law can be obtained by expanding the Williams–Watts function (equation 2) as a series and ignoring all but the first term which is of the form

$$D(t) = D_0 + \Delta D_\alpha(t/\tau)^m \qquad (3)$$

which is consistent with Findley's[10] equation $D(t) = D_0 + Kt^m$. This can be used as a function which contains either three or four adjustable parameters depending on whether the quantities ΔD_α, τ and m are amalgamated into a single parameter $K = \Delta D_\alpha/\tau^m$. The time dependency of the power law is similar to the Struik function although the rate at which it rises is less rapid as shown in *Figure 1C*.

Analysis of long term data

Equations (1)–(3) are only valid if the effective age of the material under test is constant as is the case for creep times $\leq 0.3\, t_e$. Beyond this short term limit the testpiece becomes progressively older with time producing a gradual decrease in D_0 and increase in τ. The change in magnitude of D_0 during a long term test is often very small and tends to be ignored for the sake of simplicity in functions which describe long term creep. The progressive increase of τ with creep time leads to a decrease in the rate at which the material creeps. This can be described replacing the quantity $\exp(t/\tau)^m$ by an integral $\exp([\int_0^t \mathrm{d}u/\tau(u)]^m)$ where u is a dummy time variable. It has been suggested that $\tau(u)$ is a hyperbolic function of the form[4]:

$$\tau(u) = (\tau^2 + C^2u^{2\mu'})^{0.5} \qquad (4)$$

where τ represents the initial value of $\tau(t)$ and C and μ' are adjustable parameters. Substitution of the long-term kernel into equations (1)–(3) yields:

$$D(t) = D_0 \exp\left[\int_0^t \frac{\mathrm{d}u}{(\tau^2 + C^2u^{2\mu'})^{0.5}}\right]^m \qquad (5)$$

$$D(t) = D_0 + \Delta D_\alpha\left(1 - \exp - \left[\int_0^t \frac{\mathrm{d}u}{(\tau^2 + C^2u^{2\mu'})^{0.5}}\right]\right) \qquad (6)$$

and

$$D(t) = D_0 + \Delta D_\alpha\left(\int_0^t \frac{\mathrm{d}u}{(\tau^2 + C^{2\mu'})^{0.5}}\right)^m \qquad (7)$$

respectively.

Figure 2A shows a comparison between the long-term kernel [equation (5) with $D_0 = 1$] and the short-term kernel [equation (1)] and also illustrates the effects of changing μ' on the behaviour of the function, whilst *Figure 2B* shows the effect of changes in C. It is apparent from these figures that the function is very sensitive to the value of μ' chosen and that changing μ' can to some extent compensate for changes in C.

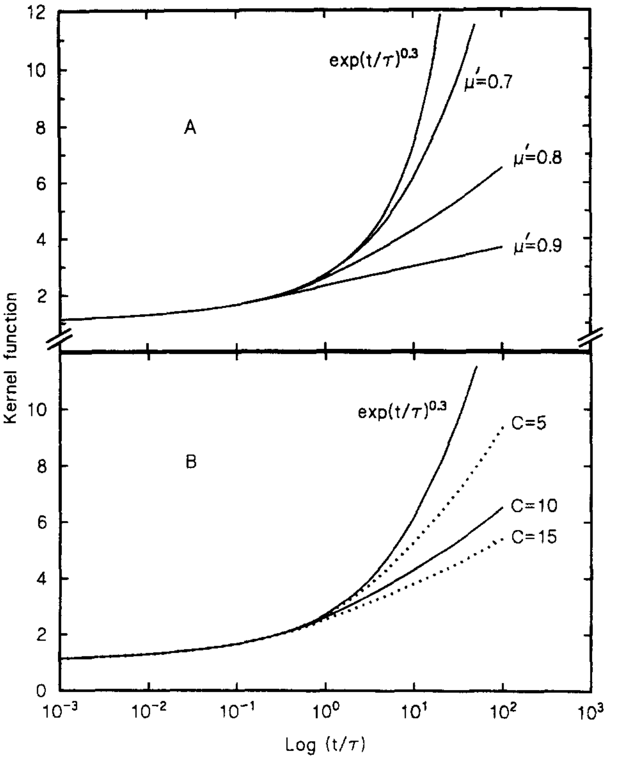

Figure 2 (A) The effect of changes in μ' on the time dependence of the long-term kernel $\exp[\int_0^t \frac{du}{(\tau^2+c^2u^{2\mu'})^{0.5}}]^m$ and a comparison with the short-term kernel $\exp(t/\tau)^{0.3}$. (B) The influence of C on the time dependence of the long-term kernel

EXPERIMENTAL

The polypropylene (Royalite, Propylex) was obtained from VT Plastics (UK) in the form of a 9m thick compression moulded sheet. Specimens machined from this sheet were annealed at 130°C or 4h and allowed to cool slowly overnight to 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 was found to be $907\,\mathrm{kg\,m^{-3}}$. The crystallinity of the material calculated according to this density was found to be 61%[11].

The PVC (ICI, Darvic) was purchased as a 6mm thick transparent sheet from Amari Plastics (UK). The measured density of this material prior to any thermal treatments was found to be $1387\,\mathrm{kg\,m^{-3}}$ at 23°C.

A two-part cold cure epoxy (TE251) was obtained from Evode (UK) and cast into sheets approximately 200 × 14 × 4mm. Curing, although essentially complete within 24h of mixing the two components together, continues to occur, albeit at a reduced rate for several months at room temperature[12]. However, the material can be stabilized by post-curing at 100°C for 30min followed by slow cooling to room temperature.

Prior to creep testing, the specimens were heated to an elevated temperature for a period of 30min in order to erase any previous ageing effects. Values of these temperatures are given in *Table 1*. The specimens were then quenched into water at 23°C and after a period of approximately 5min they were removed and dried. The testpieces were then mounted in creep rigs, which have been described elsewhere[1,13] and stored at the test temperature for various lengths of time defined by $t_{e'}$ where t_e refers to the elapsed time between quenching from the elevated temperature and the application of a load.

Table 1 Testpiece dimensions, the applied creep stresses and the annealing temperature used to erase all previous ageing effects

Material	Temperature (°C)	Creep stress (MPa)	Typical testpiece dimensions (mm)
Polypropylene (PP)	80	3.0	10 × 4 × 180
Poly(vinyl chloride) (PVC)	85	5.0	12 × 6 × 180
Epoxy	80	4.4	10 × 4 × 180

Typical testpiece dimensions and the stresses employed for all three materials are given in *Table 1*. Comparatively low stresses were used to avoid de-ageing the material[8] which allowed us to measure short-term creep sequentially on single samples which remained within the rigs during the periods of recovery. This procedure minimizes any differences in creep behaviour due to alignment errors or material variability. Long-term creep tests were made using the same sample, wherever possible, as that used to obtain the short-term data. The repeatability of these creep tests was typically within 2%.

RESULTS AND DISCUSSION

Short term data

Figures 3A, *4A* and *5A* show the effect of elapsed time on the short term creep of the three materials studied at constant stress and temperature. In all cases the creep compliance $D(t)$ at a given creep time t decreases with increasing age of the testpiece. In previous work we have analysed such data in terms of equations (1) and (2) obtaining the parameters required by graphical methods. However these parameters can also be obtained in a less labour intensive way by using non-linear least-squares optimization algorithms (the iterative procedure used for solving for several constraints simultaneously employs the Levenberg–Marquardt algorithm which forms part of the mathematical software package Mathcad. Mathcad V.5.0 Plus is supplied by Mathsoft Inc., Cambridge, MA, USA). For example, in order to fit the Struik function [equation (1)] to each of the short term creep curves shown in these figures, values of the three adjustable parameters, D_0, m and τ required by the function can be obtained by using a least-squares optimization procedure. Any dependence of these parameters on the initial age of the material can be determined by plotting the values obtained for each parameter against the initial age of the testpiece. If one or more of the parameters are considered to be constants, i.e. m or D_0 then values for the remaining parameters can be refined by refitting the function to each of the short term creep curves.

For each of the materials the parameter characterizing the shape of the function i.e. m was found to be independent of elapsed time. As is apparent from *Table 2*, values for the Struik function m [equation (1)] were lower than those for the shape parameter of both the Williams–Watts and power law functions [equations (2) and (3), respectively]. Values of m obtained for both

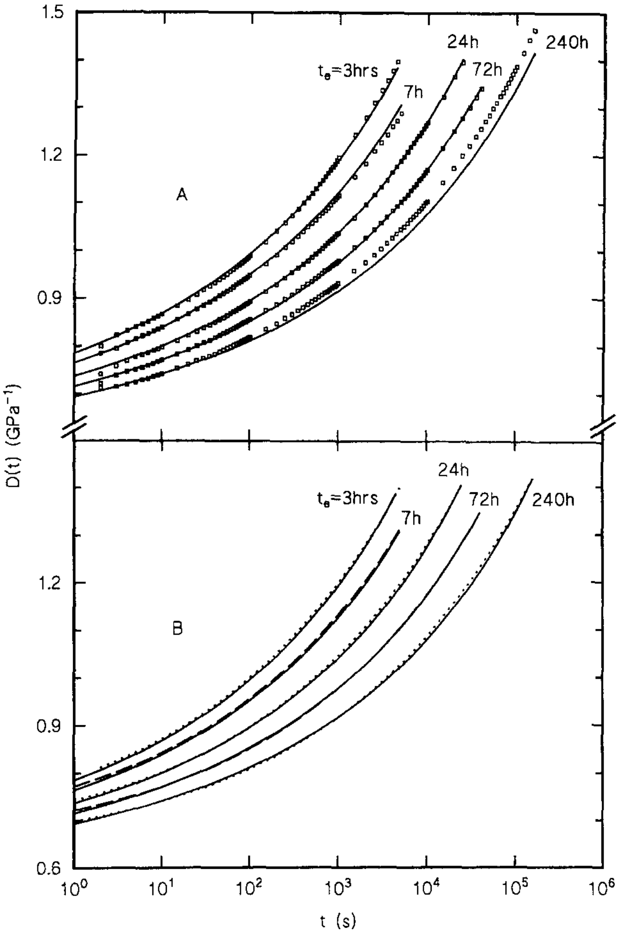

Figure 3 (A) Fits of the Struik function [equation (1)] to polypropylene short-term creep data for $m = 0.13$. D_0 and τ were calculated using equations (8) and (9) with the parameters given in *Table 2*. (B) A comparison of the Struik (———), Williams–Watts [equation (2)] (.....) and power law [equation (3)] (– – – – –). Values for the parameters required by these functions were obtained using equations (8) and (9) in conjunction with *Table 2*

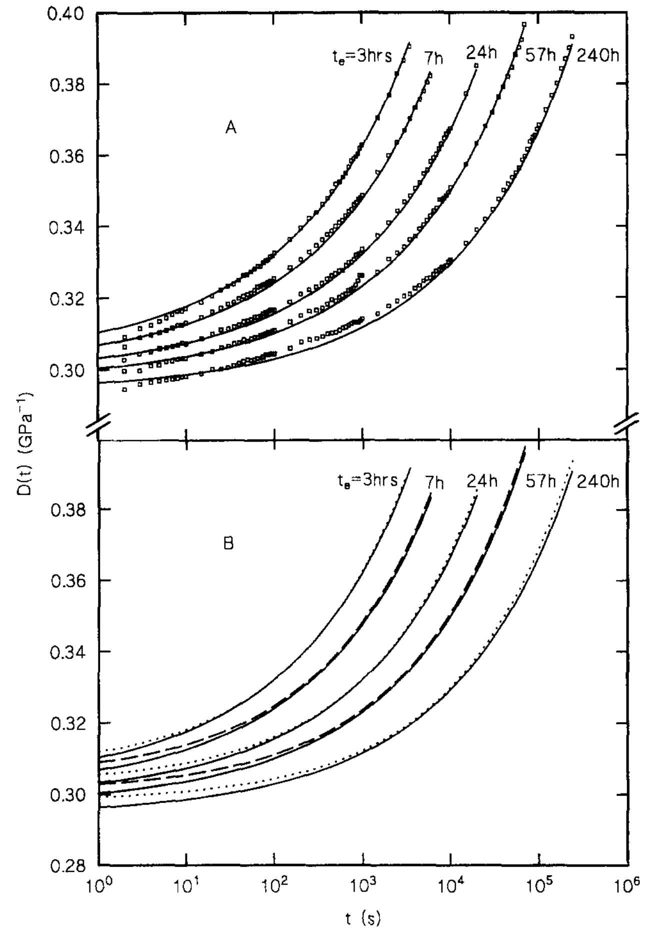

Figure 4 Fits of the Struik function [equation (1)] to PVC short-term creep data for $m = 0.29$, and D_0 and τ were calculated using equations (8) and (9) with the parameters given in *Table 2*. (B) A comparison of the Struik (———), Williams–Watts [equation (2)] (.....) and power law [equation (3)] (– – ––). Values for the parameters required by these functions were obtained using equations (8) and (9) in conjunction with *Table 2*

Table 2 Summary

		Parameters derived from data obtained for creep times $\leq 0.3\,t_e$					Parameters derived from data obtained for creep times $> 0.3t_e$		
Material	Function	m	A (s$^{1-\mu}$)	μ	w (GPa^{-1} s$^{\nu}$)	ν	C (s$^{1-\mu}$)	μ'	Assumed value for ΔD_α (GPa^{-1})
PVC	Struik	0.29	104.3	0.883	0.320	0.0060	440	0.74	—
(215°C)	Williams–Watts	0.35	22 264	0.890	0.327	0.0068	72 820	0.75	3.0
	Power law	0.34	29 642	0.895	0.326	0.0066	145 000	0.72	3.0
Epoxy	Struik	0.20	10.63	0.905	0.395	—	—	—	—
(23°C)	Williams–Watts	0.27	22 993	0.908	0.407	—	—	—	5.0
	Power law	0.26	44 238	0.896	0.407	—	—	—	5.0
PP	Struik	0.13	19.70	0.711	0.627	0.0066	21.0	0.72	—
(23°C)	Williams-Watts	0.21	56 485	0.710	0.734	0.0110	20 000	0.74	5.3
	Power law	0.20	96 268	0.738	0.728	0.0107	47 000	0.76	5.3

of these latter functions are equal within the tolerance of experimental error which is considered to be ±0.01.

Values for the parameter ΔD_α required by both the Williams–Watts and power law functions were estimated as being $\approx 10D_0$ except for polypropylene, where the value chosen was based on previous work[1]. It should be noted that these functions are rather insensitive to the value of this parameter providing that the measured compliances are significantly less than the compliance level of ΔD_α.

The increase of τ with elapsed time can be described by a function of the form[8]

$$\tau = At_e^\mu \tag{8}$$

where μ is the rate of ageing determined from a plot of

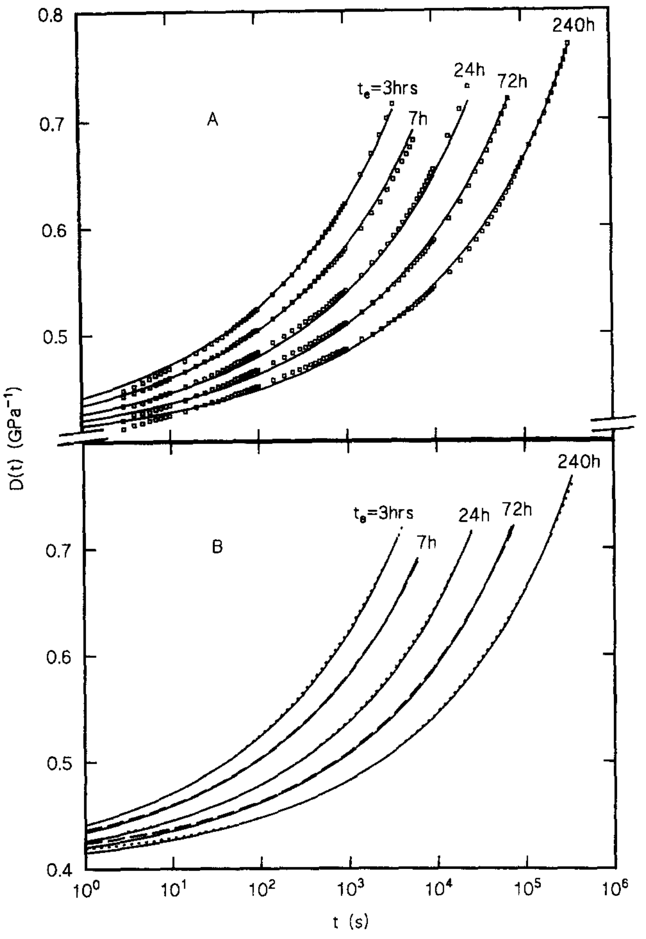

Figure 5 (A) Fits of the Struik function [equation (1)] to epoxy short-term creep data where $m = 0.20$. D_0 and τ were calculated using equations (8) and (9) with the parameters given in *Table 2*. (B) A comparison of the Struik (———), Williams–Watts [equation (2)] (.....) and power law [equation (3)] (– – – –). Values for the parameters required by these functions were obtained using equations (8) and (9) in conjunction with *Table 2*

log τ vs log t_e as shown for example, in *Figure 6*, for polypropylene. Whilst the ageing rate μ is quantitatively similar for all three functions, the value of A obtained for the Struik function [equation (1)], is much smaller than that obtained for the Williams–Watts and power law functions [equations (2) and (3), respectively] as shown in *Table 2*. This reflects the difference in the magnitude of the respective τ values.

D_0 was found to be independent of elapsed time for the epoxy and to progressively decrease with increasing elapsed time for both PVC and polypropylene, as observed by other authors[1,4,8,15]. The elapsed time dependence of D_0 can be described by

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

Values for W and ν were obtained from the intercept and slope, respectively, of a plot of log D_0 vs log t_e as shown in *Figure 7* for polypropylene and tabulated in *Table 2*. Values for the intercept W are equivalent within experimental error for both the power law and Williams–Watts functions for both PVC and polypropylene which are greater than those obtained using the Struik function.

Figures 3A, *4A* and *5A* show fits to the short term creep data using the Struik function with values of D_0 and τ obtained from equations (8) and (9) using the parameters given in *Table 2*. These fits are compared with those obtained using the Williams–Watts and power law relationships in *Figures 3B*, *4B* and *5B* where the values of D_0 and τ used are again based on equations (8) and (9) using the parameters given in *Table 2*. From these figures it is evident that all three functions describe the data equally well, although it is worthy of note that there is a small difference between both the Williams–Watts and the power law and the Struik function at very short times in PVC.

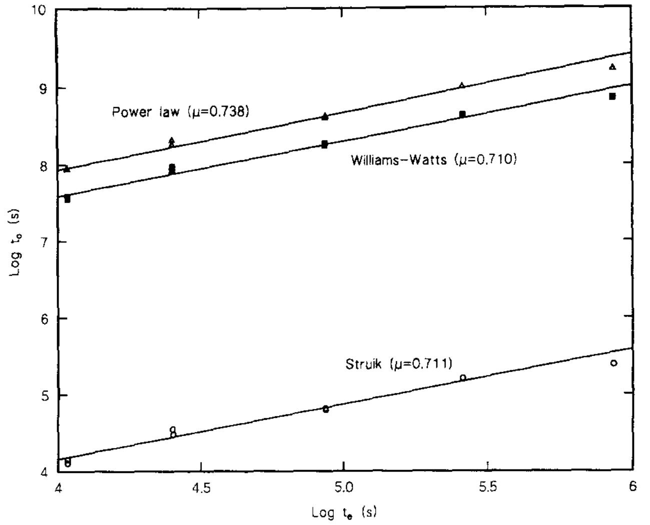

Figure 6 The elapsed time dependence of τ for polypropylene has a slope corresponding to the ageing rate μ and an intercept A [equation (8)]

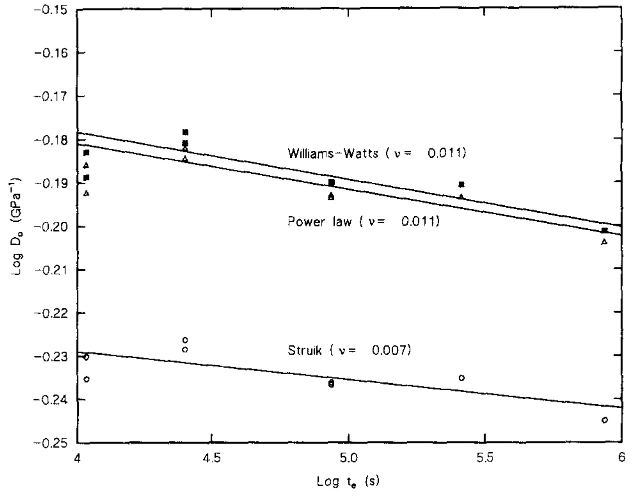

Figure 7 The dependence of D_0 for polypropylene on elapsed time yields an intercept w and a slope ν [equation (9)]

Long term data

Figures 8A and *9A* show the results of comparatively long duration creep tests using testpieces of three different initial ages for PVC and polypropylene. These data can be modelled using equations (5)–(7).

Estimates of the long-term parameters C and μ' were obtained using a non-linear least squares optimization algorithm[15] to fit each of the equations (5)–(7) to each of the long term creep curves noting that the integrals of these equations need to be solved numerically [definite integrals were numerically determined using the

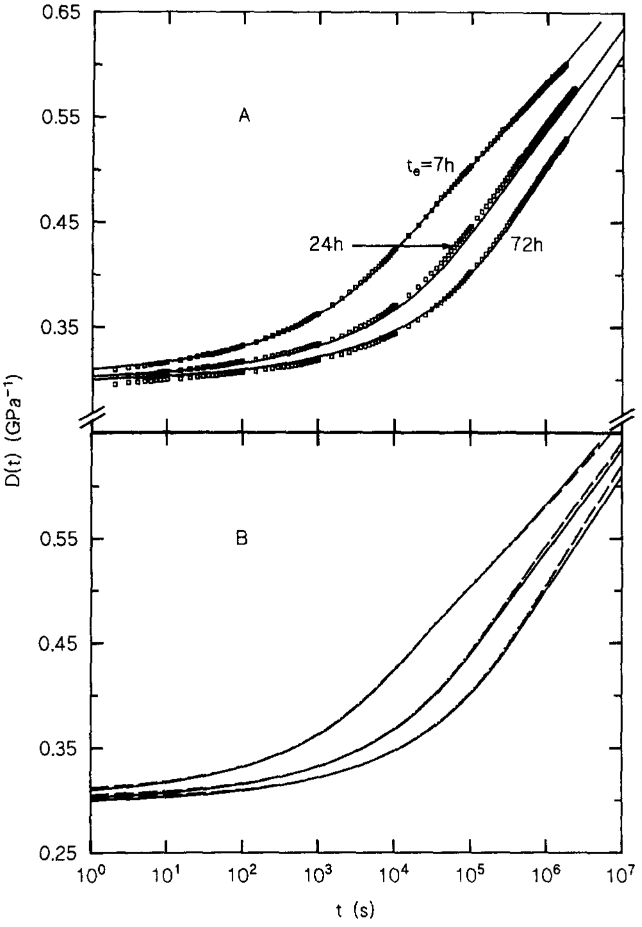

Figure 8 (A) Fits to long-term PVC creep data obtained from testpieces with initial ages of 7, 24 and 72 h, respectively, are based on equation (5), the Struik function. D_0 and τ were calculated using appropriate parameters from *Table 2* with equations (8) and (9). Values for C and μ' (given in *Table 2*) which were found to be independent of elapsed time were optimized for the 7 and 24 h data. (B) A comparison of long-term fits based on equations (5) (———), (6) (– – – –) and (7) (. . . . .). Values for the parameters required by these functions were obtained as described in (A)

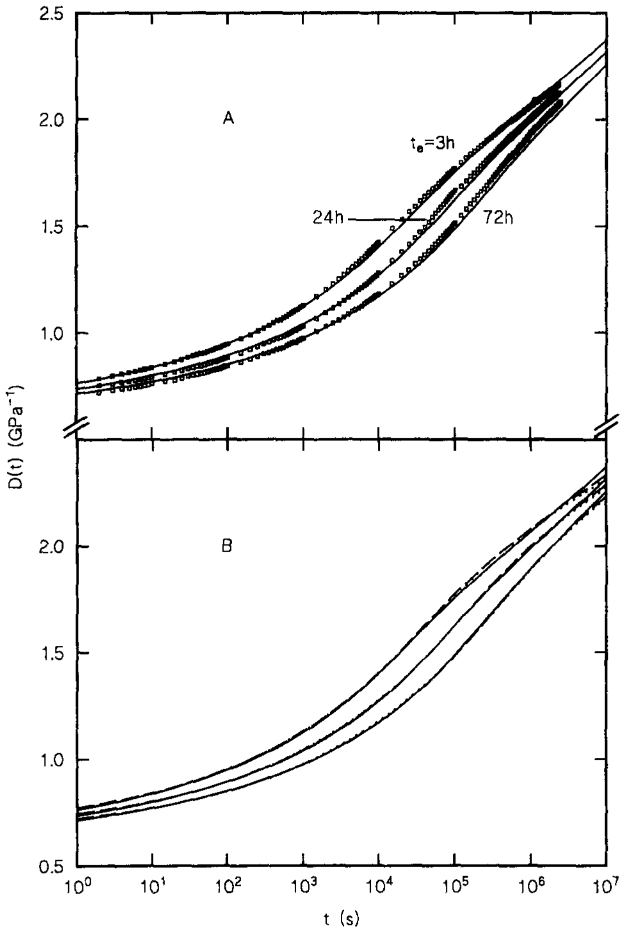

Figure 9 (A) Fits to long-term polypropylene data from testpieces with initial ages of 3, 24 and 72 h, respectively, based on equation (5) as described in the caption to *Figure 8A*. (B) A comparison of long-term fits based on equations (5) (———), (6) (– – – –) and (7) (. . . . .). Values for the parameters required by these functions were obtained as described in the caption to *Figure 8A*

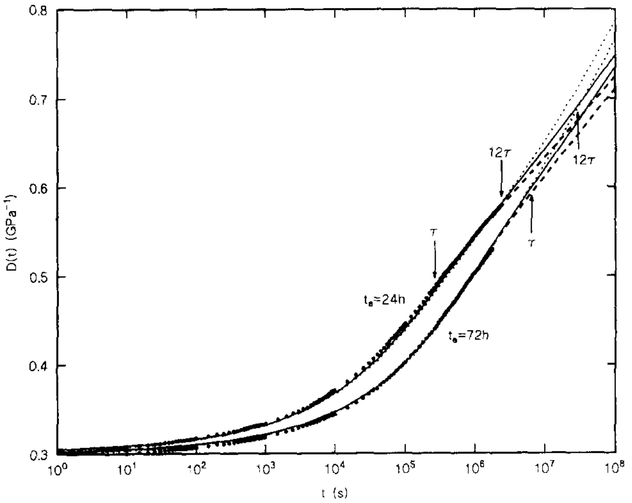

Figure 10 A comparison of extrapolated long-term fits to PVC data at elapsed times of 24 and 72 h based on equations (5)–(7). The τ values indicated are those for the Struik function [equation (5)]

Romberg algorithm contained within the mathematical software package Mathcad (see above details)]. The results showed that both C and μ' were independent of elapsed time. These initial estimates of C and μ' were further optimized for each material by simultaneously fitting each of the equations (5)–(7) to all three long term creep curves. The resultant values are given in *Table 2*. *Figures 8A* and *9A* show long term fits of the Struik function [equation (5)] to both PVC and polypropylene based on the parameters given in *Table 2*. *Figures 8B* and *9B* show a comparison of the Struik fits with those of the Williams–Watts and power law functions [equations (6) and (7), respectively]. The agreement between these functions is very good.

Comparison of long term extrapolations

Figure 10 shows a comparison of extrapolated data based on fits to the long-term experimentally obtained data for PVC using equations (5)–(7). It is evident from this figure that there are no obvious differences between the functions over the time span of the creep tests. However by extrapolating the fits to longer times differences of about ≈ 8% between the functions do become apparent at times around 10^8 s. Similar differences between the extrapolated fits were also observed for polypropylene. Note that the extrapolated compliances predicted by the Struik function are larger than those predicted by both the Williams–Watts function or the power law. This could reflect inaccuracies in equation (1) which is considered to be valid only for times t up to about $12\tau^6$. However, the question of which of these predictions is the most appropriate for describing long-term creep data can only be resolved by modelling creep data obtained over much longer periods of time. It should be noted that the *predicted* compliances extrapolated over two decades to times in excess of 3 years agree to within 10%, irrespective of the model chosen based on creep data obtained from tests lasting approximately 3 weeks.

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