Creep recovery of PVC and polypropylene

B E Read and P E Tomlins

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B E Read and P E Tomlins
Division of Materials Metrology
National Physical Laboratory
Teddington
Middlesex
United Kingdom
TW11 0LW

ABSTRACT

Tensile creep and recovery data have been obtained for PVC and polypropylene at 23 °C for different age states, creep durations and stress levels. The recovery behaviour has been analysed by a superposition procedure involving an extension to our model for nonlinear creep and different assumptions regarding possible variations in retardation time during the recovery. Accurate predictions have been made of the recovery following long-term, low-stress creep in polypropylene by allowing for the physical ageing (increase in retardation time) which occurs during the creep. Attempts to predict the recovery after creep at elevated stresses have been partially successful, and suggest further studies of an apparent deaging at the unloading stage and subsequent reactivation of ageing.
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National Physical Laboratory
Teddington, Middlesex, United Kingdom, TW11 0LW

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Approved on behalf of Chief Executive, NPL,
by Dr M K Hossain, Head, Division of Materials Metrology
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1 INTRODUCTION

It is widely accepted that Boltzmann's Superposition Principle can be used to predict the recovery of a polymer specimen after removal of a constant load that is sufficiently small for the material to exhibit linear viscoelastic behaviour\(^1\). Modified superposition procedures have also been applied to analyses of recovery following nonlinear creep at elevated stresses\(^3\)\(^{-}\)\(^4\). However, in the case of glassy and semicrystalline plastics, the proposed modifications have not been very successful. In particular, they have not explained why the residual strain is often initially smaller and subsequently larger than that predicted by linear superposition\(^4\)\(^,\)\(^5\).

The observed discrepancies could partly arise from the failure to account for structural changes associated with physical ageing during the creep and recovery periods and from possible deaging effects during the loading and unloading stages\(^6\)\(^{-}\)\(^{12}\). In fact, physical ageing during creep at a low stress level could produce errors in the predicted recovery using Boltzmann's superposition method. To explore these possibilities, investigations are being undertaken of the recovery behaviour of PVC and polypropylene (PP) following creep for different durations at various stress levels. The data are being analysed on the basis of a superposition procedure incorporating extensions to our model for physical ageing and nonlinear creep\(^12\)\(^{-}\)\(^{15}\). The purpose of this report is to discuss some initial results of these investigations, after summarising the creep and recovery models and the experimental technique.

2 SUMMARY OF NONLINEAR CREEP MODEL

The creep behaviour of a polymer subjected to a constant uniaxial tensile or compressive stress \(\sigma\) is conveniently specified by the compliance function \(D(t)\) defined by

\[
D(t) = \varepsilon(t)/\sigma
\]

where \(\varepsilon(t)\) is the measured time-dependent strain. At low stress levels, and for a given material age, \(\varepsilon(t)\) is proportional to \(\sigma\) at all times \(t\). A single curve of \(D(t)\) versus \(t\) then serves to characterise this linear creep behaviour. However values of \(D(t)\) decrease with increasing physical age of the material and thus depend on the elapsed time \(t_e\) between cooling the specimen from an elevated temperature (at which the structure of the polymer is at equilibrium with respect to the creep process) and the instant of load application\(^7\). At stress levels above about 3 MPa, the onset of nonlinear behaviour is reflected by an increase in \(D(t)\) with \(\sigma\).

For several glassy and semicrystalline plastics, the variation of compliance with time can be represented to a good approximation by the equation\(^12\),\(^14\),\(^15\)

\[
D(t) = D_0 \exp \left( -\int_0^t \frac{du}{t_0(u)} \right)^\gamma
\]

where \(D_0\) is the compliance in the limit of short creep times, \(t_0(u)\) is a mean retardation time for the creep process and \(\gamma\) a constant that characterises the width of the retardation region along the time axis. The integral accounts for variations in \(t_0(u)\) due to physical ageing during the creep for all times \(u\) between 0 and \(t\).

For both PVC and PP it was found\(^15\) that \(D_0\) decreased gradually with increasing \(t_e\) and tended to increase with increasing \(\sigma\). Furthermore, the value of \(\gamma\) was essentially independent of \(t_e\) and \(\sigma\) for PVC, whereas for PP it decreased slightly with increasing \(t_e\). However the variations in \(D_0\) and \(\gamma\) were generally small, and good fits to the creep data
were obtained assuming that these quantities were independent of creep time \( t \).

As exemplified by the data for PVC in Figure 1, the most obvious effect of increasing \( t_w \) is to shift the short-term regions \((t<t_w)\) of the compliance curves to longer times. This corresponds to an increase in the initial retardation time \( t_0(0) \) with increasing \( t_w \). It is also clear (Figure 2) that, for a given \( t_w \) the short-time parts of the compliance curves shift horizontally to shorter times with increasing stress. This effect is opposite to that produced by physical ageing, and is ascribed to a reduction in \( t_0(0) \), although opinions differ\(^{10}\) as to whether this involves a stress-induced deaging (rejuvenation) of the material.

In the long-term regions of creep curves \((t>t_w)\) significant increases in \( t_0 \) occur with increasing creep time owing to further ageing which occurs simultaneously with the creep. This effect is allowed for by the integral in equation (2), and it is assumed that the further ageing has a negligible influence on \( D_0 \) and \( \gamma \). From analyses of long-term data on the basis of equation (2), the relation

\[
t_0(t) = (A t_w^{2\mu} + C t^{2\mu'})^{1/2}
\]

has been shown\(^{14,15}\) to describe the variation of \( t_0(t) \) over a wide range of creep time. Here the parameters \( A(\sigma), \mu(\sigma), C(\sigma) \) and \( \mu'(\sigma) \) usually decrease with increasing stress and \( C \rightarrow A \rightarrow A_0 \) and \( \mu' \rightarrow \mu \rightarrow \mu_0 \) as \( \sigma \rightarrow 0 \). However, our data for PVC could be represented\(^{14}\) to a good approximation by a constant value of \( \mu' = \mu = 0.86 \) over the stress range \((6-24 \text{ MPa})\) investigated.

The variation of retardation time with \( t_w \), stress and creep time is conveniently illustrated in Figure 3 by plots of \( \log t_0 \) versus \( \log (t_w+t) \) for PVC. The linear dependence of \( \log t_0(0) \) on \( \log t_w \) (obtained from analyses of short-term data) is consistent with the first term in the brackets in equation (3), the values of \( \mu \) and \( A \) corresponding to the respective slopes and intercepts (at \( \log t_w=0 \)) of these plots. Also shown is the initial decrease in \( t_0 \) and its subsequent increase with creep time (due to physical ageing) after applying an elevated stress at the specified \( t_w \). Values of \( \mu' \) and \( C \) in equation (3) correspond to the slopes and intercepts, respectively, of the long-time asymptotes to these curves.

The creep behaviour under uniaxial compressive stress has been studied for PVC over the stress range between 6 MPa and 24 MPa and for \( t_w = 24 \text{ h and 240 h}^{12,14} \). Compliance curves again shifted to longer times with increasing age of the specimen and to shorter times with increasing applied stress, although the shift with stress was substantially smaller in compression than in tension. The curves could also be modelled using equations (2) and (3) with \( \gamma, D_0 \) and \( \mu(=\mu') \) values essentially the same as those derived in tension. For a given stress magnitude in the nonlinear range, values of \( A \) and \( C \) were larger than those obtained under tension, reflecting the smaller stress-induced decrease in retardation time \( t_0 \).

3 MODELS FOR CREEP RECOVERY

3.1 LINEAR BEHAVIOUR

We first recall the established method for predicting the residual strain in a specimen following the removal of a small tensile stress in the linear viscoelastic range\(^{3,5}\). As illustrated schematically in Figure 4, the stress is applied at \( t=0 \) and gives rise to the instantaneous and delayed strain. The effects of removing the stress at time \( t' \) are then modelled by assuming that this is equivalent to applying a negative (compressive) stress of equal magnitude to the positive tensile stress, both the positive and negative components being continuously active. The residual strain during recovery, \( \varepsilon_c(t) \), is then calculated by superposing the strains (indicated by the dashed lines in Figure 4) resulting from the respective stress components. For linear behaviour, the negative strain component at time \( t \) equals the creep strain \( \varepsilon_c(t-t') \) at time \( t-t' \) (see Figure 4) and we may write
\[ \varepsilon_r(t) = \varepsilon_c(t) - \varepsilon_c(t-t') \]  

where \( \varepsilon_c(t) \) is the creep strain at time \( t \) when the stress is maintained. Dividing each term in (4) by the applied stress \( \sigma \) during the creep we obtain

\[ D_r(t) = D(t) - D(t-t') \]  

where \( D_r(t) \) will be referred to as the residual compliance. Here \( D(t) \) and \( D(t-t') \) are linear creep functions valid in the limit \( \sigma \rightarrow 0 \) and with \( t' \) and \( t \) small compared with \( t_0 \) so that any variations in retardation parameters due to physical ageing effects are negligible. Assuming that (2) and (3) are valid, equation (5) then becomes

\[ D_r(t) = D_0 \exp \left( \frac{t}{t_0} \right)^\gamma - D_0 \exp \left( \frac{t-t'}{t_0} \right)^\gamma \]  

where \( t_0 = A_0^{-1/\alpha} \) and the values of \( D_0 \) and \( \gamma \) are those observed in the limit \( \sigma \rightarrow 0 \).

3.2 PROPOSED SUPERPOSITION PROCEDURE FOR NONLINEAR BEHAVIOUR

In modelling the recovery behaviour following creep for various durations and at different stresses, we again regard the stress removal as being equivalent to the application of a superposed negative stress. The residual compliance is then written

\[ D_r(t) = D^+(t) - D^-(t) \]  

where \( D^+(t) \) and \( D^-(t) \) are the compliance contributions associated with the positive and negative stress components, respectively, and may be expressed in terms of \( D_0 \), \( \gamma \) and \( t_0 \) each of which could vary with \( t_0 \), stress and time.

Based on the creep investigations of PVC and PP, we will assume that the values of \( D_0 \) and \( \gamma \) may depend on \( t_0 \) and \( \sigma \) but do not vary with time during a creep and recovery test. Our approach thus represents an extension to the linear superposition method that allows particularly for the dependence of \( t_0 \) on stress level and on time during the creep and subsequent recovery. Several cases will be considered, involving different possible forms for the time-dependence of \( t_0 \) during the recovery phase.

3.2.1 Case 1 Pseudo-linear scheme

In this case \( D^+(t) \) and \( D^-(t) \) are identified with \( D(t) \) and \( D(t-t') \) respectively. Therefore \( D_r(t) \) is given by equation (5) but with \( D(t) \) and \( D(t-t') \) now evaluated using equations (2) and (3) for any stress level or timescale range. We thus obtain

\[ D_r(t) = D_0 \exp I_1^\gamma - D_0 \exp I_2^\gamma \]  

\[ I_1 = \int_0^t \frac{du}{(A' t_e^{2\mu} + C' u^{2\mu'})^{1/2}} \]  

3
\[ I_2 = \int_{t'}^{t} \frac{du}{(A^2t_e^{2\mu} + C^2(u-t')^{2\mu'})^{\frac{1}{\nu}}} \]  

(10)

Owing to physical ageing which occurs during the creep, the pseudo-linear scheme cannot be generally valid since it implies according to (9) and (10) (see also Figure 5) that the \( t_0 \) values associated with \( D^*(t) \) and \( D'(t) \), respectively, differ from each other at any time during the recovery. The subsequent schemes each assume that a unique (time-dependent) \( t_0 \) during the recovery period governs the behaviour of both \( D^*(t) \) and \( D'(t) \).

3.2.2 Cases 2 and 3. Continuing increase in \( t_0 \) after unloading

In Case 2 it is assumed that \( t_0(t) \) continues to increase after unloading (due to the continuing ageing) at the same rate that would apply if the load had been maintained. This behaviour is schematically illustrated in Figure 6 and the residual compliance is given by

\[ D_r(t) = D_0 \exp(I_1' + I_2') - D_0 \exp I_2' \]  

(11)

\[ I_1' = \int_{0}^{t'} \frac{du}{(A^2t_e^{2\mu} + C^2u^{2\mu'})^{\frac{1}{\nu}}} \]  

(12)

\[ I_2 = \int_{t'}^{t} \frac{du}{(A^2t_e^{2\mu} + C^2u^{2\mu'})^{\frac{1}{\nu}}} \]  

(13)

Case 3 assumes that, after unloading, the rate of increase of \( t_0(t) \) with time increases to that observed during creep in the limit of zero stress (see Figure 6). The residual compliance is then represented by equations (11) and (12) with \( I_2 \) now given by

\[ I_2 = \int_{t'}^{t} \frac{du}{(t_0')^2 + A_0^2(u-t')^{2\mu'}^{\frac{1}{\nu}}} \]  

(14)

where \( t_0' \) is the value of \( t_0 \) at time \( t' \). Thus

\[ t_0' = (A^2t_e^{2\mu} + C^2u^{2\mu'})^{\frac{1}{\nu}} \]  

(15)

3.2.3 Cases 4 and 5. Transient decrease in \( t_0 \) due to unloading

The rapid initial recovery frequently observed for glassy and semicrystalline polymers in the nonlinear stress range could result from an abrupt decrease in retardation time during the load removal. In this context, Struijk suggested that the mechanical energy dissipated during loading and unloading could generate free volume and thus partially de-age the material. More recently, Santore et al. observed peaks in volume during both the twisting
and untwisting of an epoxy glass specimen for shear strains above 0.01. Although these effects were not considered by the authors to reflect a rejuvenation of the polymer structure, they support the suggestion that a transient decrease in \( t_0 \) could be produced by the load removal.

In Cases 4 and 5 (see Figure 7) the reduction in \( t_0 \) due to unloading at \( t' \) is taken to equal the shift in \( t_0 \) (relative to that for \( \sigma=0 \)) produced by a uniaxial compressive stress having the same magnitude \( \sigma \) as the applied stress during the creep. This is consistent with the superposition procedure and enables the decrease in \( t_0 \) to be calculated from compressive creep data. Following its abrupt decrease, \( t_0 \) is subsequently assumed to increase as a result of further ageing. In Case 4, the rate of the increase is identified with the rate that would apply if the load had been maintained. The residual compliance is then given by equations (11) and (12) with

\[
I_2 = \int_{t'}^{t} \frac{du}{u' (A_r t_0'^2 + C^2 (u-t')^{2\mu_r})^{\frac{\mu_c}{2}}}
\]

where \( t_0' \) is given by equation (15). The quantity \( A_r t_0' \) specifies the minimum retardation time immediately following the load removal where

\[
A_r = \frac{A_c (t_e + t')^{\mu_c}}{A_0 (t_e + t')^{\mu_0}}
\]

and \( A_c \) and \( \mu_c \) are the values of \( A \) and \( \mu \) obtained from a uniaxial compression test at the appropriate stress \( \sigma \).

For Case 5, the rate of increase of \( t_0 \) during the recovery, following its initial decrease, is assumed to equal the rate observed during creep in the limit of zero stress. The residual compliance is given by equations (11) and (12) with

\[
I_2 = \int_{t'}^{t} \frac{du}{u' (A_r t_0'^2 + A_0^2 (u-t')^{2\mu_0})^{\frac{\mu_c}{2}}}
\]

and \( t_0' \) and \( A_r \) given by (15) and (17).

4 EXPERIMENTAL

4.1 MATERIALS

The PVC (transparent ICI Darvic) and PP (Royalite Propylene homopolymer) were obtained in the form of sheets of respective thickness 6 mm and 9 mm. For the creep and recovery tests, specimens with typical dimensions 180 x 10 x 4 mm were machined from the sheets. The PP specimens were first annealed at 130 °C for 4 hours and then cooled slowly to room temperature to stabilise their crystallinity with respect to subsequent thermal treatments.

Prior to the creep tests, the PVC and PP specimens were heated for 30 minutes at 85 °C and 80 °C respectively, to erase previous ageing effects. They were then quenched in water at 23 °C and maintained at this temperature for various times \( t_e \) (usually 24 h) before applying the load. Creep durations \( t' \) around 1 h or 8 h were usually employed but, for PP, a low-stress creep and recovery test was carried out with \( t' = 481 \) h to study the effects of physical ageing during the creep on the subsequent recovery.
4.2 MEASUREMENT OF COMPLIANCES

Compliances $D(t)$ and $D_r(t)$ were determined from measurements of the time-dependent strains $\varepsilon(t)$ and $\varepsilon_r(t)$, respectively, during the application of a constant tensile stress $\sigma$ and after its subsequent removal. The specimen was held vertically between a lower fixed clamp and an upper clamp through which loads were applied via a pivoted lever arm having a 5:1 ratio advantage. Extensions were measured using two calibrated extensometers of 50 mm gauge length located on opposite faces of the specimen. Each extensometer comprised an inductive displacement transducer contacting the specimen via two knife edges, one attached to the body of the transducer and the other to its core. The voltage output from each extensometer was amplified by a bridge-amplifier circuit and sampled at specified time intervals by a data logger. The first readings were recorded at 1s after both the application and removal of the load. At the completion of the respective creep and recovery tests, the data were dumped to a PC for subsequent analysis.

All creep and recovery measurements were made at a temperature of $23.0 \pm 0.2 \, ^\circ\text{C}$ by locating the specimens in temperature-controlled chambers within a temperature-controlled room. For specimens of a given age, the measured compliances could usually be reproduced to within 2%.

5 RESULTS AND DISCUSSION

In this section, experimental and theoretical creep and recovery curves for PVC and PP will be compared for different stress levels, age states and creep durations. Note that the recovery data will be represented by plots of $D_r(t)$ versus log $(t-t')$ rather than log $t$. By effectively expanding the timescale at short recovery times this allows the validity of the analytical recovery functions to be more easily assessed in this region. Values for the parameters employed in deriving the theoretical curves are given in the Figure captions. These parameters were obtained using computer methods to optimise the fits of equations (2) and (3) to the creep curves for the respective polymers.

5.1 ANALYSIS OF LOW-STRESS DATA

Figure 8 shows creep and recovery curves for PVC at a low stress of 5 MPa. Over the entire range of recovery time investigated, it is seen that the residual compliance curve can be accurately modelled by means of equations (8)-(10). This result is expected from the low stress level and the fact that $t' << t_e$ and $t \leq t_e$. Under these conditions the age of the material is essentially constant and equations (8)-(10) reduce approximately to the linear function (6). As illustrated in Figure 9, equations (8)-(10) also yield a fairly accurate prediction of the recovery curve for PP following creep under a stress of 3 MPa and for a duration $(t' = 1 \, \text{h})$ that is again much shorter than $t_e$ (24 h).

The effects of increasing the creep duration at low stress are exemplified in Figure 10 which shows creep and recovery curves for PP with $\sigma = 3 \, \text{MPa}$, $t_e = 24 \, \text{h}$ and $t' = 481 \, \text{h}$. The pseudo-linear scheme (Case 1) now underestimates substantially the observed $D_r(t)$ values, the discrepancy initially increasing with $t-t'$ but tending to decrease at very long recovery times. This result is ascribed to physical ageing (increase in $t_0$) which occurs during the creep, as a result of which the assumptions $D'(t) = D(t)$ and $D'(t) = D(t-t')$ yield a relative underestimate of the retardation times associated with $D'(t)$ and a consequent overestimate of the magnitude of $D'(t)$ relative to $D'(t)$. Consistent with this interpretation is the good agreement seen in Figure 10 between the observed recovery and that predicted by Cases 2-5 respectively. In making this comparison it was assumed that, at a stress of 3 MPa, $A = A_0 = A_0$ and $\mu = \mu' = \mu_0$ so that Cases 2, 3, 4 and 5 each yield essentially the same predicted $D_r(t)$ curve. The possible ageing effect due to unloading (Cases 4 and 5) then vanishes and each scheme accounts for physical ageing during the creep and recovery by assigning the same time-dependent $t_0$ to $D'(t)$ and $D'(t)$.
5.2 EFFECTS OF INCREASING STRESS

In Figure 11(a) creep and recovery data are presented for PVC with \( t_e = 24 \) h, \( t' = 8 \) h and a stress level of 14.8 MPa. The pseudo-linear scheme now underestimates the \( D_r(t) \) values only at the longer recovery times. This effect is similar to that observed at low stress and long \( t' \) (see Figure 10) and is ascribed to physical ageing during the creep. Although the \( t'/t_e \) ratio is relatively small, the fractional increase in \( t_0 \) during the creep is enhanced by the high stress, so that the magnitude of \( D^*(t) \) is again overestimated relative to that of \( D^r(t) \). At short recovery times this effect may be offset by some deaging at the unloading stage (see below). The close agreement between the observed \( D_r(t) \) values and those predicted by the pseudo-linear scheme may then partly arise from these compensating effects and partly from the plateau in the creep curve for PVC at short times, as a result of which variations in \( t_0 \) will have little influence on \( D_r(t) \). Figure 11(b) shows that the predicted recovery curves for Cases 2, 3, 4 and 5, respectively, each lie close to the experimental curve at both short and long times. For each case, the long-time discrepancy found with the pseudo-linear scheme is substantially reduced, reflecting the use of the same \( t_0 \) value to govern the behaviour of both \( D^*(t) \) and \( D^r(t) \) and an increase in \( t_0 \) with time due to a reactivation of ageing during the recovery phase.

Figure 12(a) presents data obtained for PVC at the higher stress of 24 MPa with \( t_e \) and \( t' \) having essentially the same values as employed for the tests at 14.8 MPa. The Case 1, pseudo-linear, predictions again underestimate \( D_r(t) \) at long recovery times, the difference between measured and calculated values being larger than that at the lower stress. A significant overestimate of residual compliance is now observed at short recovery times and similar short-time discrepancies are clearly evident with the Case 2 and 3 predictions in Figure 12(b). These effects are ascribed to some deaging (decrease in \( t_0 \)) at the unloading stage that is not accounted for in the Case 1-3 calculations. The discrepancies are reduced somewhat with the Case 4 and 5 predictions (Figure 12(b)), each of which includes an estimate of deaging due to unloading. In fact the Case 4 prediction gives the closest fit to the experimental recovery curve in both the short and long-term limits, and similar results have been obtained at \( \sigma = 24 \) MPa for a PVC specimen of increased age (\( t_e = 72 \) h).

The effects of increasing stress on the recovery behaviour of PP are similar to those observed for PVC. Figure 13(a) shows creep and recovery curves obtained for PP at a stress of 9 MPa and values of \( t_e \) (24 h) and \( t'(8 \) h) the same as those employed for PVC. The pseudo-linear, Case 1, predictions again overestimate and underestimate the residual compliance at short and long times, respectively. The relative magnitude of these two discrepancies is larger for PP than for PVC and increases when the value of \( t'/t_e \) is decreased at constant \( \sigma \) (compare Figures 13(a) and 14(a)).

Figures 13(b) and 14(b) again illustrate that the Case 1 discrepancies are substantially reduced when allowance is made for deaging due to unloading and for physical ageing during the creep and recovery. In the absence of compressive creep data on PP, note that estimated values of \( A_e \) and \( \mu_c \) were used in the Case 4 and 5 predictions. The estimates assumed that decreases in log \( t_0 \) due to deaging by a uniaxial compressive stress are one half that produced by a tensile stress of the same magnitude. In the short- and long-time limits, the Case 4 predictions again provide the closest agreement to the experimental \( D_r(t) \) values. However, there is scope for improving the overall fits to the recovery curves. This seems to require functions that allow some increase in the deaging due to unloading and a more rapid subsequent increase in \( t_0 \). Future work will be aimed at establishing such functions, and extending these investigations to the time-dependent deformations during intermittent loading.
6 CONCLUSIONS

(1) The pseudo-linear superposition procedure underestimates the residual compliances of thermoplastics during their recovery following long-term creep at low stresses. An accurate prediction of the recovery is obtained by a superposition analysis that allows for the physical ageing of the material during the creep.

(2) Following creep at elevated stresses, the residual compliances are initially smaller and subsequently larger than those predicted by the pseudo-linear scheme. These effects can be largely accounted for by a superposition scheme that incorporates the effects of physical ageing during the creep and recovery, and assumes that a deaging occurs at the unloading stage. To improve the accuracy of the predictions, further work is required to ascertain the magnitude of the deaging and subsequent rate at which the ageing is reactivated during the recovery.

7 REFERENCES


ACKNOWLEDGEMENTS

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FIGURE CAPTIONS

Fig. 1 Tensile creep compliance curves at 21.5 °C for PVC at a stress of 5 MPa and different age states $t_e$. Theoretical curves (———) were obtained by fitting equations (2) and (3) to the data.

Fig. 2 Tensile creep curves for PVC at 23 °C, $t_e = 240$ h and different stress levels $\sigma$. The theoretical curves (———) were derived using equations (2) and (3).

Fig. 3 Dependence of retardation time $t_0$ on age $t_e$ and creep time $t$ for PVC at 23 °C. (o) and (●), plots of log $t_0$ v. log $t_e$ obtained from analyses of short-term creep data at 5 MPa and 24 MPa respectively. (---), dependence of extrapolated zero-stress log $t_0$ values on log $t_e$. (———), variation of log $t_0$ with log ($t_e + t$) in long-term creep tests during and after the application of a 24 MPa stress at $t_e = 24$ h and $t_e = 240$ h respectively. (—→), locus of the long-time asymptote to the (———) curves.

Fig. 4 Illustration of the superposition method for calculating the residual strain $\varepsilon_r(t)$ during the recovery of a specimen after removal of a stress $\sigma$ in the linear viscoelastic range.

Fig. 5 Dependence of the retardation time $t_0$ on time for PVC according to the pseudo-linear scheme. (———), calculated variation of $t_0$ before, during and after the application of a 24 MPa stress at $t_e = 24$ h. (———) and (———), variations of the $t_0$'s associated with $D^*(t)$ and $D^t(t)$, respectively, after the load removal.

Fig. 6 Time-dependence of $t_0$ for PVC according to Cases 2 and 3 respectively. (———), calculated variation of $t_0$ before, during and after the application of a 24 MPa stress at $t_e = 24$ h. (—→), proposed variation of $t_0$ after the load removal according to Case 2 and Case 3 as indicated.

Fig. 7 Time-dependence of $t_0$ for PVC according to Cases 4 and 5 respectively. (———), calculated variation of $t_0$ before, during and after the application of a 24 MPa stress at $t_e = 24$ h. (—→), proposed variation of $t_0$ after the load removal according to Case 4 and Case 5 as indicated.

Fig. 8 Creep and recovery curves for PVC for a stress of 5 MPa, age $t_e = 24$ h and creep duration $t' = 1$ h. (●), creep compliance $D(t)$ versus log $t$; (o), residual compliance $D_r(t)$ versus log ($t+t'$). (———), theoretical curves based on equations (2) and (3) for $D(t)$ and equations (8)-(10) (Case 1) for $D_r(t)$. Parameters as follows: $D_0 = 0.308$ GPa$^{-1}$, $\gamma = 0.30$, $A = 76$ s$^{1-\mu}$, $C = 58$ s$^{1-\mu}$, $\mu = \mu' = 0.86$.

Fig. 9 Creep and recovery curves for PP for a stress of 3 MPa, age $t_e = 24$ h and creep duration $t' = 3687$s. Point symbols and equations used for theoretical curves as in Fig. 8. Parameters as follows: $D_0 = 0.638$ GPa$^{-1}$, $\gamma = 0.16$, $A = C = 10.39$s$^{1-\mu}$, $\mu = \mu' = 0.77$. 
Fig. 10  Creep and recovery curves for PP for a stress of 3 MPa, age \( t_e = 24 \) h and creep duration \( t' = 481 \) h. Point symbols as in Fig. 8. (----), theoretical curves based on equations (2) and (3) for \( D(t) \), equations (8)-(10) for \( D_{c}(t) \) (Case 1) and equations (11)-(13) for \( D_{C}(t) \) (Cases 2-5). Parameters as follows: \( D_{0} = 0.58 \) GPa\(^{-1} \), \( \gamma = 0.13 \), \( A = C = A_{c} = A_{0} = 10.39 \) s\(^{-1}\mu \), \( \mu = \mu' = \mu_{c} = \mu_{0} = 0.77 \).

Fig. 11  
(a), Creep and recovery curves for PVC for a stress of 14.8 MPa, age \( t_e = 24 \) h and creep duration \( t' = 7.25 \) h. Point symbols and equations as in Fig. 8. (b), Comparison of experimental recovery data with theoretical curves calculated from equations (11)-(13) (Case 2), equations (11), (12), (14) and (15) (Case 3), equations (11), (12), (16) and (17) (Case 4), and equations (11), (12) and (18) (Case 5). Parameters as follows: \( D_{0} = 0.315 \) GPa\(^{-1} \), \( \gamma = 0.32 \), \( A = 24 \) s\(^{-1}\mu \), \( A_{c} = 68.1 \) s\(^{-1}\mu \), \( A_{0} = 87 \) s\(^{-1}\mu \), \( C = 42 \) s\(^{-1}\mu \), \( \mu = \mu' = \mu_{c} = \mu_{0} = 0.86 \).

Fig. 12  
(a), Creep and recovery curves for PVC for a stress of 24 MPa, age \( t_e = 24 \) h and creep duration \( t' = 8 \) h. Point symbols and equations as in Fig. 8. (b), Comparison of experimental recovery data with theoretical curves calculated as in Fig. 11(b). Parameters as follows: \( D_{0} = 0.326 \) GPa\(^{-1} \), \( \gamma = 0.32 \), \( A = 4 \) s\(^{-1}\mu \), \( A_{c} = 28 \) s\(^{-1}\mu \), \( A_{0} = 87 \) s\(^{-1}\mu \), \( C = 22 \) s\(^{-1}\mu \), \( \mu = \mu' = \mu_{c} = \mu_{0} = 0.86 \).

Fig. 13  
(a), Creep and recovery curves for PP for a stress of 9 MPa, age \( t_e = 24 \) h and creep duration \( t' = 8 \) h. Point symbols and equations as in Fig. 8. (b), Comparison of experimental recovery data with theoretical curves calculated as in Fig. 11(b). Parameters as follows: \( D_{0} = 0.54 \) GPa\(^{-1} \), \( \gamma = 0.124 \), \( A = 3.4 \) s\(^{-1}\mu \), \( A_{c} = 5.94 \) s\(^{-1}\mu \), \( A_{0} = 10.39 \) s\(^{-1}\mu \), \( C = 10.5 \) s\(^{-1}\mu \), \( \mu = 0.517, \mu' = 0.605, \mu_{c} = 0.644, \mu_{0} = 0.77 \).

Fig. 14  
(a), Creep and recovery curves for PP for a stress of 9 MPa, age \( t_e = 24 \) h and creep duration \( t' = 1 \) h. Point symbols and equations as in Fig. 8. (b), Comparison of experimental recovery data with theoretical curves calculated as in Fig. 11(b). Parameters as in Fig. 13.
PVC 21.5°C  5MPa

$D(t)$ (GPa$^{-1}$)

$t_e=3$ h  24 h  72 h

$t$ (s)

Fig 1
Fig 2

PVC 23°C, $t_0 = 240$ h

$\sigma = 24$ MPa

$18$ MPa

$12$ MPa

$6$ MPa

$10^{-7}$ $10^{-6}$ $10^{-5}$ $10^{-4}$ $10^{-3}$ $10^{-2}$ $10^{-1}$ $10^0$ $10^1$ $10^2$ $10^3$

$0.9$ $0.8$ $0.7$ $0.6$ $0.5$ $0.4$ $0.3$
Fig 9

PP 3MPa

t_e = 24h

t' = 3687s
PVC 24MPa

$\tau_e = 24h$

$\tau' = 8h$

$D(t)$

$D'(t)$

GPa $^{-1}$

$10^0$

$10^1$

$10^2$

$10^3$

$10^4$

$10^5$

$10^6$

Fig 12a