Influence of physical ageing on the non-linear viscoelasticity of polycarbonate

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The molecular origin of the non-linear viscoelasticity of polycarbonate (PC) has been studied by creep measurements at room temperature for three different states of physical ageing. The non-linearity of the isochronous stress–strain diagrams was analysed according to the Boyd–Jansson model. It was found that although the stresses (up to 27 MPa) caused marked non-linearity, they did not influence the physical ageing stage, as measured with a control load. The linear compliance component of the Boyd–Jansson model, in both longitudinal and transverse directions, was barely influenced by the physical ageing state of the PC, although the non-linear compliance component, in both longitudinal and transverse directions, changed considerably. It is proposed that the origins of the non-linearity of quenched polycarbonate at room temperature are stress activated changes in the α' and β mechanisms. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

The development of the non-linear viscoelasticity of amorphous glassy polymers with increasing strain is gradual[1], and becomes marked at a strain of ~0.5–1%. Boyd *et al.*[2] have derived a stress–strain relationship based on a two-site relaxation model with a stress dependent compliance $\epsilon = \sigma(D_1 + D_2\sigma)$. Accurate measurements have shown[2–4] that the curves of the isochronous stress–strain diagrams can be satisfactorily described by this equation.

From studies of the change in volume[5–7] and segmental orientation measured by infra-red dichroism[8] during tensile deformation, it is known that the transition from approximately linear to markedly non-linear viscoelasticity is accompanied by a pronounced increase in the volume change, and by the onset of large-scale molecular motions and local chain orientation in the stress direction.

Several molecular explanations of the non-linear viscoelasticity have been proposed:

— Stress-induced changes in the deformation mechanisms[8] acting at a certain time/temperature, such as acceleration of the mechanisms, changes in the nature of the mechanisms, activation of new mechanisms, etc.
— Stress saturation of the relaxed (equilibrium) compliance associated with the local group motion (β-relaxation)[2].
— Strain-induced softening processes[9].
— Strain-induced structural rearrangement that reduces the resistance of deformation in much the same manner as does raising the temperature[10].

— A reduction in retardation times for the creep process and a small increase in the relaxed compliance level of the β-process[11].
— A competition between 'structure formation' due to ageing and 'structure destruction' due to deformation[12].
— Crazing and local plastic deformation in fracture[13].

We now present results from a study of the influence of access enthalpy (volume) caused by quenching on the non-linear viscoelastic behaviour. Polycarbonate offers unique possibilities for such a study: (a) it has a broad time–temperature interval between the main and secondary transitions, (b) at room temperature, the secondary (β) mechanism is relaxed and the main transition (α) is not active[14], resulting in low creep rate and only weak viscoelastic non-linearity[4], and (c) an additional transition between the β- and α-mechanisms has been found for PC in the quenched non-equilibrium state[14–18]. Since this transition has been proposed[16] to be a precursor to the α-process and since it disappears on annealing, it has been designated[19] as α'.

EXPERIMENTAL

Due to the large difference in mechanical behaviour generally found for macroscopically identical samples compared to the accuracy needed for the determination of the non-linear viscoelasticity, the isochronous stress–strain diagram is usually based on creep measurements on only one sample.

In this work, the aim was to study the influence of access enthalpy on the non-linear viscoelasticity and to examine whether the stress influenced the state of physical ageing. Therefore, the isochronous stress–

Table 1 Thermal pretreatment conditions used to produce different physical ageing states

Condition	Ageing temperatue (°C)	Ageing time (h)
A	22	1.5
B	22	22
C	120	12
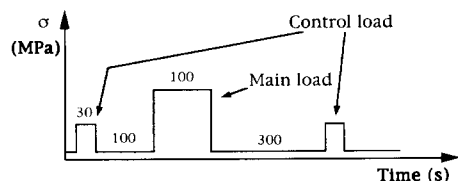
Figure 1 The loading procedure used for PC samples aged at room temperature

strain diagrams had to be based on creep measurements at different states of physical ageing, without any further influence of the ongoing ageing during the measurement. To ensure that the thermodynamic state was the same at all stress levels for one isochron, the sample used for this isochron was reheated to a temperature above the glass transition (T_g), quenched and then aged under controlled conditions before each creep measurement. To avoid any possibility that the ongoing ageing influenced the measurement, the ageing time was at least ten times the measuring time. According to Read *et al.*[20] any further ageing during the creep test is negligible if the elapse time, i.e. the time between the quench and the beginning of the creep test, is at least five times the creep time.

Materials

The polycarbonate (PC) examined in this work was the same as that used in our earlier studies of the non-linear viscoelasticity[4]. It is a commercially available Macrolon 1143 (from Bayer) with a weight-average molecular weight (M_w) of 35000–37000 and a glass transition temperature (T_g) of 148°C, according to the manufacture. The polycarbonate was received in the form of extruded rods with a diameter of 6 mm. Rods were chosen due to the fact that they give a more clearly defined stress–strain distribution under tensile load.

Heat treatment

In order to remove any previous ageing and to reduce possible thermal residual stresses, etc., all the sample rods were annealed at 160°C for 30 min and then quenched in a water bath. To keep the rods straight during this heat treatment, they were held vertically in a copper tube, which gave homogeneous cooling around the sample when it was removed from the oven and quenched.

The thermal pretreatment used to produce the different physical ageing states after the quenching are shown in *Table 1*. The shortest ageing time was chosen to be more than ten times the total creep measuring time in order to ensure that changes due to the ongoing physical ageing was small enough not to influence the measurement. The ageing temperature of 120°C was chosen in accordance with the work of Struik[21] and Golden *et al.*[22].

This temperature is high enough to allow the enthalpy relaxation to reach an approximate equilibrium within a reasonable time.

Tensile creep apparatus

In the tensile creep apparatus the stress was applied in the axial direction of the sample and the resultant longitudinal and transverse strains were measured simultaneously. More detailed descriptions of the tensile creep apparatus, the longitudinal extensiometer and the device used to measure the transverse strain are given elsewhere[4].

The temperature was maintained constant within $< 0.2°C$ during the creep measurements. For a thermal expansion coefficient of $10^{-4}\,°C^{-1}$ this means that the maximum thermal strain as less than 2×10^{-5}. The humidity in the air was about 30% RH during the measurements and did not vary by more than ±5% RH during the creep measurements of one isochron. Because of the low rate of water absorption of polycarbonate[23], the small difference in humidity did not influence the measurements.

The reproducibility of the tensile strains is 2×10^{-5} when a small baseline load is maintained throughout the measurement. Together with the thermal strain, this results in a maximum error in the difference in control strain of 4×10^{-5}.

Tensile creep measurements

The loading procedure used for the samples is shown in *Figure 1*. A small load of 0.8 MPa was maintained throughout the measurement to eliminate the inevitable effects of play, friction and alignment of sample holders and loading system, etc., during the loading and unloading. This small load gave a strain in the longitudinal direction of $\sim 3 \times 10^{-4}$, termed the baseline strain, and was considered not to influence the measurements. A control load was used to check whether the main load influenced the ageing state or damaged the sample. The control load of 7 MPa was applied for 30 s, both before and after the main loads, which were applied for 100 s. The recovery period was only three times the loading time, in order to keep the total measuring time short. This is usually regarded as being too short a period and might mean that the strain and not fully recovered before the next loading. However, in this case it was found that the recovery of the first control load had levelled out so much that the maximum recovery during the next loading time was less than 1×10^{-5}. The small variation in baseline strain, caused by the not fully recovered main strain and the extremely low creep caused by the baseline strain, was compensated for by using general methods based on the assumption that the material behaves in a linear viscoelastic manner and that the change in the physical ageing state during the measurement was negligible. Due to the weak non-linearity of polycarbonate at low stresses, the possible error falls within the accuracy of the measurement.

Due to the very slow ageing process after ageing at 120°C, the length of the measuring time is not a problem with respect to the ageing time. The same sample was therefore, used without reheating, as long as no differences were observed in the control measurements. The loading procedure for the samples aged at 120°C is shown in *Figure 2*. In this case, the loading time for the
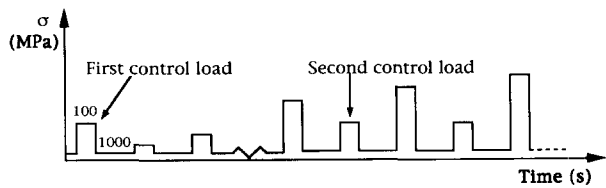
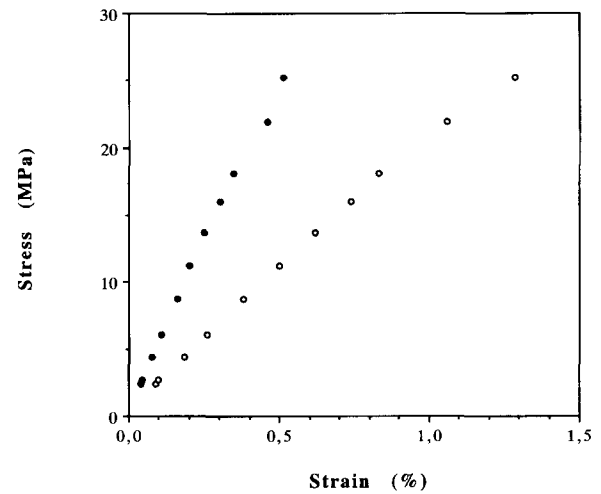**Figure 2** The loading procedure used for PC samples aged at 120°C

Figure 4 Isochronous stress–strain diagram at 100 s after a physical ageing time of 1.5 h at room temperature: (O) longitudinal; (●) transverse
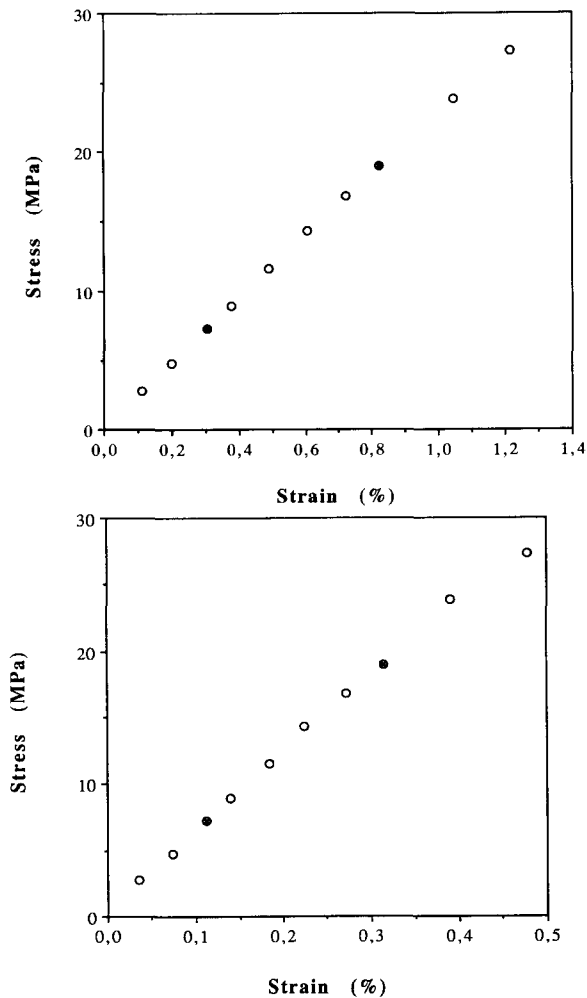
Figure 3 Isochronous (100 s) stress–strain diagram for PC aged at 120°C for 18 h (O) measured in the longitudinal direction; this figure also includes data (x) obtained from reference measurements made with only the control load and a load producing ~ 0.8% strain. The results shows that the loading procedure before the 0.8% strain does not influence the creep. (b) Isochronous (100 s) stress–strain diagram for PC aged at 120°C for 18 h (O) measured in the transverse direction; this figure also includes data (x) obtained from reference measurements

control load was also 100 s the same as for the main loads, and the recovery time was 1000 s. The control load was applied at the beginning of the measurements, as before, but then not again until after the main load produced a strain of 0.005, since it was known that low stresses do not influence the physical ageing state of the polymer[21].

In the case of the samples aged at 120°C, a reference measurement was made to check the successive increase in load did not affect the material in a way that was not indicated by the control strain. This measurement was

made on the same sample after reheating to 160°C and quenching, followed by ageing. On this occasion the only loads were the control load and the load producing a strain of 0.008.

Determination of the non-linearity of the isochronous stress–strain curve

The non-linearity of the longitudinal and transverse isochronous stress–strain diagrams was determined according to the Boyd–Jansson mode[2] and the following relationship:

$$\epsilon = \sigma D(\sigma) = \sigma(D_1 + D_2\sigma) \qquad (1)$$

where D_1 is the linear compliance component and D_2 the non-linear compliance component. The compliance components in the transverse direction, resulting from the longitudinal stress, are indicated by the suffix t (as used in earlier reports[4]).

The second-order equation was fitted to the data by a least-squares method, using the MATLAB program from The Math Works Inc.

RESULTS

Samples aged at 120°C for 18 h

In the case of the samples aged at 120°C, the difference between the control strains was less than 3×10^{-5} up to a strain of 0.012. The influence of the main stresses was therefore negligible, and it was possible to use only one sample to create the total isochronous stress–strain curve. All strains were reversible within the accuracy of the measurements.

Two 100 s isochronous stress–strain curves in the longitudinal and transverse directions are shown in *Figure 3*, together with the results of the reference measurements. The compliance components for these curves are as follows: $D_1 = 0.376$ GPa^{-1}, $D_2 = 2.3$ GPa^{-2}, $D_{t1} = 0.132$ GPa^{-1}, $D_{t2} = 1.4$ GPa^{-2}. It is also seen in *Figure 3* that the reference measurements, made with only the control load and load producing a strain of ~ 0.008, agree perfectly. This confirms the conclusion that the loading procedure, at least up to a strain of 0.008, does not influence the ageing state.

Table 2 The linear and non-linear compliance components of PC shown for different isochronous times and thermal pretreatment conditions

| | Longitudinal | | | | | | Transverse | | | | | |
| | $D_1 \times 10^6$ MPa^{-1} | | | $D_2 \times 10^6$ MPa^{-2} | | | $D_{t1} \times 10^6$ MPa^{-1} | | | $D_{t2} \times 10^6$ MPa^{-2} | | |
Thermal pretreatment	10 s	30 s	100 s	10 s	30 s	100 s	10 s	30 s	100 s	10 s	30 s	100 s
A	363.0	367.0	365.0	4.20	4.50	5.30	143	145	147	1.9	2.0	2.3
B	367.0	366.0	366.0	3.90	4.40	4.90	–	–	–	–	–	–
C	406.0	409.2	412.2	1.25	1.26	1.29	169	168	169	0.3	0.3	0.4
C	371.0	374.0	376.0	2.30	2.30	2.30	132	121	132	1.4	1.4	1.4

Samples aged at 22°C for 1.5 and 22 h

In the case of the samples aged at 22°C, the difference between the control strains was less than $\pm 3 \times 10^{-5}$ up to a strain of 0.012, for both ageing times. Thus, also in this case, the influence of the main stress was negligible and within the limit of the accuracy. From the creep measurement made with the lowest main stress (0.001) it was also established that the ongoing ageing did not influence the measurements.

Two 100 s isochronous stress–strain curves in the longitudinal and transverse directions for an ageing time of 1.5 h are shown in *Figure 4*. The curves are evidently non-linear in both the longitudinal and transverse directions. The compliance components were calculated to be as follows: $D_1 = 0.365$ GPa^{-1}, $D_2 = 5.3$ GPa^{-2}; $D_{t2} = 2.3$ GPa^{-2}.

Only a small decrease in non-linearity could be detected when the ageing time was increased to 22 h.

The influence of measuring time and ageing time on the non-linearity

The compliance components determined for different annealing and measuring times are summarized in *Table 2*. In an earlier study, concerning the influence of orientation on the non-linear viscoelastic properties of polycarbonate[4], we found the following values of the linear compliance components for unoriented samples aged at 120°C for 24 h: $D_1 = 0.40 \pm 3\%$ GPa^{-1}, $D_{t1} = 0.15 \pm 5\%$ GPa^{-1}, $D_2 = 1.6 \pm 13\%$ GPa^{-2} and $D_{t2} = 0.8 \pm 11\%$ GPa^{-2}. These results are based on several isochronous stress–strain diagrams for different samples. Comparing these earlier results with this present data, it is found that the two samples subjected to pretreatment C probably display extreme values, and that $\pm 3\%$ and $\pm 5\%$ are good estimations of the deviation in the linear compliance component in the longitudinal and transverse directions, respectively, for these kinds of measurements. The accuracy of the measurements if not therefore good enough to enable any conclusions to be drawn about variations in the longitudinal, D_1, and transverse, D_{t1}, linear compliance components with variations in the ageing time or in the measuring time, in the present interval. In contrast, both the longitudinal and transverse non-linear compliance components (D_2 and D_{t2}, respectively) showed a pronounced dependence on both ageing and measuring time, with the exception of the samples aged at 120°C which showed no time-dependence for these relatively short creep times.

The values of D_2 (100 s) and D_{t2} (100 s) were ~ 130–310% and 64–475% larger, respectively, for the samples aged at 22°C for 1.5 h than those obtained for the
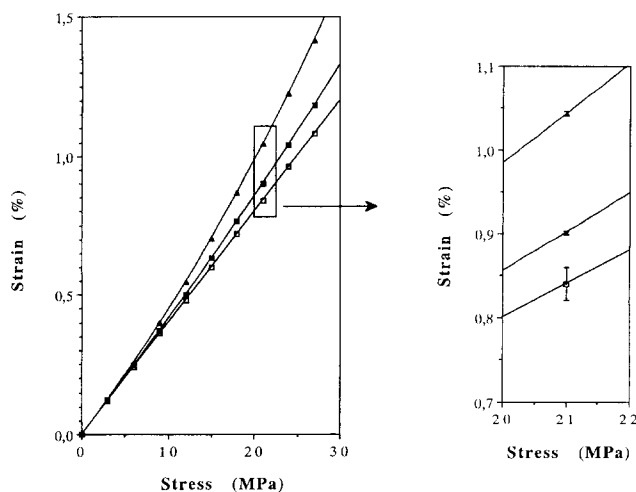

Figure 5 Strains at 21 MPa for the physical ageing states A and C, together with the linear part of the strain; error bars correspond to the scatter in the control strain

samples aged at 120°C for 18 h. The values of D_2 (100 s) and D_{t2} (100 s) were ~ 15–18% larger than the values of D_2 (30 s) and D_{t2} (30 s) obtained for the samples aged at 22°C for 1.5 h.

DISCUSSION

The proposed mechanisms for the molecular origin of the non-linear viscoelasticity include processes causing both reversible and non-reversible deformation. In this study, the deformation has been reversible within the accuracy of the measurements and the ongoing physical ageing did not influence the measurements. In *Figure 5*, the strains at 21 MPa are shown for different thermal heat treatments, together with the linear part of the strain corresponding to $\alpha \times D_1$. The error bars correspond to the scattering in the control strain. It is obvious that the effect of the non-linearity is considerably larger than the difference in control strain and that the difference in non-linearity between the two extremes in the physical ageing state is much larger than the scatter.

It is possible to draw the conclusion that under the present conditions, the different physical ageing states cause no measurable changes in the linear compliance component for polycarbonate, whereas the effects on the non-linear compliance component are considerable, and that it is possible for the non-linearity to occur without changing the physical ageing state. Thus, physical ageing is not the direct origin of the non-linearity although it influences it, and the softening associated with the non-linearity may appear to be a 'de-ageing' of the material.

However, this softening vanishes when the stress is removed, at least for stresses up to 25 MPa for polycarbonate. This is in accordance with measurements on the secondary transitions during and after application of a tensile load. It was indicated that both the β and α' peaks increase and broaden during the loading[24], while after the removal[25] of the load the high-temperature side of the β-loss peak only changed slightly and was independent of the degree of the tensile deformation, whereas the effect on the α' transition was larger.

Dynamic mechanical studies on the influence of physical ageing on the secondary transitions of PC have shown that the intensity and the position of the β-loss peak on the temperature axis are not affected by the thermal history[18,21,26]. However, a small change in the high temperature side of the peak has been found, with this depending on the heat-treatment temperature. It appears that annealing above 80°C increases the high-temperature side[18,26,27], whereas ageing at lower temperatures results in a decrease[18,25,27]. In the case of the intermediate α'-mechanism it is obvious that the previous history has a strong influence on it[14,16,18,19,21,25,27]. Read et al.[20] have reported a small decrease of the relaxed β-compliance, $D_{R\beta}$, with ageing. Unfortunately, they did not specify the creep stress of their measurements which makes it impossible to directly compare their results with ours.

According both to our own results on the very low non-linearity of PC in the annealed state and the negligible influence of the ageing state on the linear compliance component, and to earlier results on the influence of ageing on the secondary transitions, we propose that the non-linear compliance component is associated with stress-activated changes in the α'- and β-mechanisms.

It is worth noting that it is possible that the linear compliance component in our measurements would have been slightly lowered if an ageing at room temperature had been performed in addition to the annealing.

The proposed origin of the non-linearity of polycarbonate is also in accordance with our earlier measurements[4] on polycarbonate oriented above T_g and aged at 120°C for 24 h. It was shown that orientation decreased both the linear and non-linear compliance components of the polycarbonate. This indicates that both the β- and the α'-mechanisms are decreased with increased orientation above T_g. In the case of the α'-process, it is known that cold-working increases the process due to the high stresses involved, but for orientation above T_g it is most plausible that this process causes no α' process except for the thermal stresses induced by the quenching. Because of the long ageing time at elevated temperatures for the oriented samples, the thermal stresses were strongly reduced. Therefore, it is clear that the α'-mechanism is negligible for these samples, and the non-linearity may be due to stress activation of the β-mechanism, and perhaps, after long times, also the α-mechanism.

This latter point is also confirmed by the study of Ito and Hatakeyama[28] who found that both the α- and β-relaxations of polycarbonate change with drawing at 170°C. The T_g, the frequency of the maximum in dielectric loss (f_{max}) and the dielectric relaxation strength of the β-mechanism attained a maximum at

draw ratios in the range of 1.6 to 2.0. From infra-red dichroism studies and density measurements it was suggested that intramolecular regularity did not increase at draw ratios beyond 2.0.

CONCLUSIONS

The non-linear viscoelastic behaviour of polycarbonate, quenched from 160°C to room temperature and then aged at different ageing times and temperatures, has been analysed according to the Boyd–Jansson two-site model. It was found that:

— The linear compliance component in both the longitudinal and transverse directions barely changes with either physical ageing state or measuring time over the interval studied.
— The non-linear compliance component varies with physical ageing state and measuring time.
— The state of physical ageing influences the non-linear viscoelasticity but it is not the origin of it.
— A reasonable explanation for the non-linear behaviour of quenched PC at 22°C is the influence of stress-activated changes in the α'- and β-mechanisms.

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