Comprehensive Modelling of the Experimental Temperature and Stress Response of Time-Dependent Materials

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Summary: The stress- and temperature-dependent non-linear creep behaviour of polymers and other materials is quantitatively modelled as a superposition of a wide range of activated motions at the molecular scale, covering wide but well-defined space and time scales. The resulting time, temperature and stress dependences are coupled (not fully separable) except at low stress values, where linear viscoelastic behaviour is directly obtained, improving on previous (approximate or questionable) time-temperature and time-stress superposition or equivalence relationships. The behaviour has been shown to have a strong cooperative nature, which may be interpreted in terms of varying clusters of identifiable structural elements within the material. Reasonably good descriptions of the experimental creep behaviour of both amorphous and semicrystalline polymers have already been achieved, but this work concentrates on the behaviour of an amorphous polycarbonate (PC), including the physical characterization and modelling of its retardation time spectrum.

Keywords: cooperative effects; creep; macromolecular dynamics; modelling; polycarbonates

Introduction

The comprehensive and accurate modelling of the (thermal, viscoelastic, etc.) behaviour of time-dependent (polymer and other) materials still remains a challenge to materials science. Non-linear creep behaviour of amorphous and semi-crystalline polymers is just one aspect of such challenge, on which this contribution is focused.

Previous and current interpretations and modelling of the creep behaviour of polymers have relied and still rely mostly on empirical or semi-empirical formulations, without directly taking into account the physical (molecular) underlying mechanisms, namely the conformational and other transitions, at the molecular scale, responsible for the materials' non-linear viscoelastic behaviour.[1–6] A feature of most of these descriptions is the separation of the effects of stress and time, in addition to that of temperature, into separate factors making up the strain, $\varepsilon(t,\sigma_0,T)$, or creep compliance, $D(t,\sigma_0,T) = \varepsilon(t,\sigma_0,T)/\sigma_0$, which is only an approximation. The emphasis has been on time-temperature and time-stress superposition or equivalence relationships, for interpolation and extrapolation purposes, which may be valid only within limited operating ranges of time, temperature and stress, at best. The approach adopted in this work will instead aim at a predictive model of the behaviour.

Dynamic Modelling

References 7–10 developed the detailed dynamics of gauche-trans conformational

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transitions, for the particular case of polymers, as the simplest possible example of localized motions at the molecular scale within the material (assuming entirely free non-entangled chains), but a wide range of other possible motions, both of localized or cooperative nature (*e.g.* varying combinations of single local crankshaft motions), may be shown to yield qualitatively similar (but quantitatively different) physical response behaviour in real bulk materials. Each of such motions turn out to be describable by a non-linear modified Voigt-Kelvin unit or non-linear standard solid, showing fully coupled (strictly not separable) temperature and stress (σ_0) effects, that automatically degenerate into linear viscoelastic behaviour at (and only at) low stress values, *e.g.* lower tan 10 MPa for a typical polycarbonate. The basic dynamic equation quantifying the creep strain rate is

$$\begin{aligned}\frac{d(\varepsilon' - \varepsilon'_0)}{dt} &\propto \alpha_{g^-} e^{-E'_0/(k_B T)} e^{\beta\sigma_0} \\ &+ \alpha_{g^+} e^{-E'_0/(k_B T)} e^{\beta\sigma_0} \\ &- 2\beta_t e^{-E''_0/(k_B T)} e^{-\beta\sigma_0}, \qquad (1)\end{aligned}$$

which takes into account the gradual gauche-to-trans and trans-to-gauche conformational transitions, against their specific activation energies, E'_0 (lowest) and E''_0, respectively, and where the coefficients of the exponential products represent the instantaneous relative populations of gauche (±) and trans conformations. The parameter β is the activation volume (volume swept by each segment from the ground state to its activated state) divided by $k_B\ T$, where k_B is Boltzmann's constant. In the above references, these populations have been quantified as linearly decreasing (gauche) or increasing (trans) from an initial Boltzmann canonical equilibrium (at constant temperature) with increasing strain. As the sum total of all conformations must be constant and the above expression must also yield zero strain rate at infinite time when the limiting deformation is reached (neglecting viscous flow), one may obtain (full details in Reference 7)

$$\begin{aligned}\frac{d(\varepsilon' - \varepsilon'_0)}{dt} \\ = c_0\ \sinh(\beta\sigma_0)\left[1 - \frac{\varepsilon' - \varepsilon'_0}{\varepsilon' - \varepsilon'_\infty}\right], \qquad (2)\end{aligned}$$

which turns out to be identical to the equation describing the behaviour of a non-linear modified Voigt-Kelvin or standard solid unit with characteristic retardation time

$$\tau = \frac{\sigma_0}{c'_0 \sinh(\beta\sigma_0)}, \qquad (3)$$

with $c'_0 = c_0/(D'_\infty - D'_0)$. As may be seeen, the linear viscoelastic behaviour is automatically accounted for at low stress values, where $\tau = 1/(c'_0\beta)$, irrespective of the stress value.

What has been obtained and described above for a set of gauche and trans conformations, in fact may similarly apply to any set of structural features/motions of given size/amplitude. For example, considering a typical solid polymer, one may describe the material's response as the consequence of any possible combination of n (from 1 up to ∞) single crankshaft motions of a few main chain atoms or functional groups, each with its charateristic retardation time τ_n. In fact, uncorrelated single-segment conformational transitions are not possible.

In a recently developed cooperative segmental theory of materials' dynamics, CSTMD,[11,12] each characteristic retardation time, τ_n, has been physically and mathematically modelled according to an adequately formulated modified version of the transition state theory. Their respective retardation time values, τ_n, were obtained[11,12] as

$$\tau_n = a_0\left[\sinh\left(\frac{a_1}{T}\right)\exp\left(\frac{E'_1}{RT}\right)\right]^n \frac{\sigma_0}{\sinh\left(\frac{n\upsilon_1^{\#}\sigma_0}{RT}\right)}, \qquad (4)$$

where a_0 (in $m^2N^{-1}s$), a_1 (in K), $\upsilon_1^{\#}$ (in m^3/mol) and E'_1 (in J/mol) are physical parameters, the last two being the minimum activation volume and the minimum activation energy, respectively, associated with the motions of the smallest clusters ($n = 1$), *i.e.* of single localized crankshafts.

Actually, the adaptation of the approach to structural motions different from the simple conformational transitions considered above assumed approximately symmetrical potential energy with respect to each activated state, to yield

$$\frac{d\left(\dfrac{\varepsilon'_n - \varepsilon'_{n,0}}{\varepsilon'_{n,\infty} - \varepsilon'_{n,0}}\right)}{dt} = c'_0 \frac{\nu_n^+ - \nu_n^-}{\sigma_0}\left(1 - \frac{\varepsilon'_n - \varepsilon'_{n,0}}{\varepsilon'_{n,\infty} - \varepsilon'_{n,0}}\right) dt, \qquad (5)$$

which is also characteristic of a non-linear modified Voigt-Kelvin or standard solid unit, where $\nu_n^+ - \nu_n^-$ stands for the difference between the numbers of positively and negatively contributing torsional crankshaft n-segment transitions at a definite constant temperature, being given by (cf. Equation 4).

$$\nu'_n = \nu_n^+ - \nu_n^- = \frac{1}{2\pi\tau_n} \qquad (6)$$

The theory[11,12] provides a physical interpretation of the parameters a_0 and a_1, and the above symmetry assumption is expected to have a relatively minor effect. The contributions of References 11 and 12 detailed how to obtain the above transition frequencies and corresponding characteristic times as functions of the above structural parameters. The basis of the theory lies in assuming that local crankshafts and other structural features may randomly associate in clusters of varying size, n, whose activation energies and volumes are multiples of the smallest ones, E'_1 and $\upsilon_1^{\#}$, respectively.

CSTMD also succeeds in explicitly predicting (without further assumptions or parameters) the actual distribution of the above retardation times, τ_n, which turned out to be approximately truncated (at a minimum retardation time τ_1, corresponding to $n = 1$) log-normal (cf. Figure 1, for the calculated discontinuous spectra for a moderately soft material with $E'_1 = 40$ kJ/mol, in the linear regime[11]). In this contribution, however, such distribution has been approximately obtained by directly fitting a continuous log-normal shape to experimental creep data, thus requiring additional parameters.

It may be observed in Figure 1 that the theory predicts an increase in the level of cooperativity when the temperature is

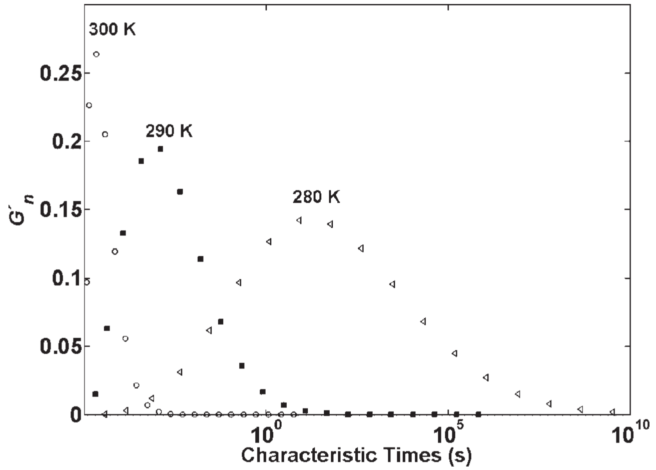

Figure 1.
Cooperative retardation time distribution, $G'_n[\tau_n(T)]$, under a forced excitation within the linear regime (very low stress), below the predicted dynamic crossover transition temperature (315.66 K, in the example of Reference 11), and its variation with cluster size ($n \leq 20$, increasing stepwise from left to right) and temperature.

lowered, as measured by the increase in the average and maximum contributing cluster sizes. Another relevant feature of CSTMD is that a dynamic crossover transition temperature, T_c, is explicitly predicted above the ordinary dynamic mechanical analysis and differential scanning calorimetry glass transition range, which is a significant and entirely new theoretical result.[13]

While the directly CSTMD-predicted (temperature and stress-dependent) retardation time spectra may be directly calculated[11] as

$$G'_n(T,\sigma_0) = \frac{n}{2e(n-1)!}\frac{\tau_n(T,\sigma_0)}{\tau_{avg}(T,\sigma_0)}$$

$$\text{with} \quad \tau_{avg}(T,\sigma_0) = \sum_{n=1}^{\infty}\frac{n}{2e(n-1)!}\tau_n(T,\sigma_0) \tag{7}$$

(by applying relatively simple combinatorial arguments on the random clustering of individual structural segments), from which the creep compliance may be obtained as

$$\frac{D(t,T,\sigma_0)-D_0}{D_\infty - D_0} = \sum_{n=1}^{\infty} G'_n(T)\left[1-\exp\left(-\frac{t}{\tau_n(T,\sigma_0)}\right)\right], \tag{8}$$

in this contribution we adopted the approach of describing the spectra, $L'(\tau)$, as continuous and strictly log-normal, *i.e.*

$$L'(\tau) = \frac{L(\tau)}{\int\limits_{\ln\tau_1}^{+\infty} L(\tau)d\ln\tau}, \quad \text{with} \quad L(\tau) = (D_0 - D_\infty)\frac{b}{\sqrt{\pi}}\exp\left[-b^2\left(\ln\frac{\tau}{\tau^*}\right)^2\right], \tag{9}$$

where b is inversely proportional to the standard deviation of $\ln\ \tau$, *i.e.*$b = b_0/\ln(\tau^*/\tau_1)$, with a constant b_0, and τ^* is an average retardation time, *i.e.* τ_n for the average n, n^* (subsequently, and perhaps wrongly, treated as real number). This of course requires the optimization of additional parameters against the experimental data. The resulting *approximate* time, temperature and stress-dependent creep compliance becomes[7,8]

$$D(t) = D_0 + (D_\infty - D_0) \times \frac{erf(b_0) + erf\left[b\ln\left(\frac{t}{\tau^*}\right)\right]}{1+erf(b_0)}, \tag{10}$$

if we consider the classical Alfrey's approximation, whereby for $\tau < t \rightarrow (1-e^{-t/\tau}) \approx 1$ and $\tau \geq t \rightarrow (1-e^{-t/\tau}) \approx 0$. The temperature and stress dependence lie of course within b and τ^* (cf. Equation 4). D_0 and D_∞ are the instantaneous and infinite time compliances that characterise the material.

Experimental Part

A series of short-term tensile creep experiments were conducted with an amorphous (polycarbonate - PC) at different stress levels (10, 16, 20, 25 and 32 MPa) and three temperatures (30, 40 and 50 °C), making a total of 575 experimental strain or compliance values. The creep compliance data were compared with the above approximate predictions.

Predicted vs. Experimental Results

Figure 2 shows a set of predicted and experimental creep compliance results for a polycarbonate at 40 °C, for the quoted five different stress levels (increasing from bottom to top) near and above the linear viscoelastic limit. The agreement is very satisfactory, within average relative errors of 0.2 to 1.8 %, and is also reproduced for the same stress levels at 30 °C and 50 °C. Figure 3 shows the results obtained at 50 °C. At not too short times, the agreement is even better for all temperatures and stresses. Table 1 presents the values of the model parameters calculated by directly fitting the approximate theoretical

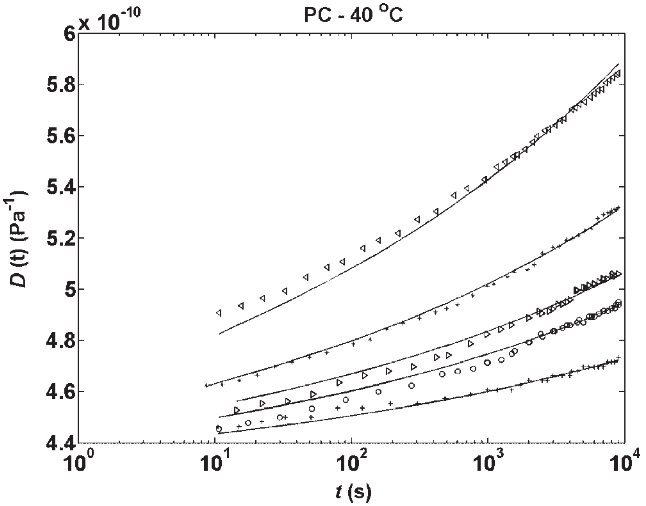

Figure 2.
Experimental and model-predicted creep compliances of PC at 40 °C.

compliances to the experimental ones, where $A_1 + B_1T = \upsilon_1^{\#}$. They apply to all data, *i.e.* to all 15 creep curves and 15 different test specimens.

The model successfully predicts the main features of the behaviour, namely its non-linearity (degenerating into full linearity at very small stresses), such that a stress-time equivalence or superposition results as not strictly valid, except as a rough approximation, as also recently demonstrated [7,8,14]. The fact that the correct magnitudes have been predicted for D_0 (0.439 10^{-9} Pa^{-1}) and D_∞ (3.98 10^{-6} Pa^{-1}), the latter being completely beyond the time scale of the experiments ($<10^4$ s), is of the utmost significance, illustrating the predictive power of the model. The predicted creep compliances for all (includingt extremely long) times, up to D_∞, are shown in Figure 4, for the same material under 20 and 32 MPa, at 40 °C.

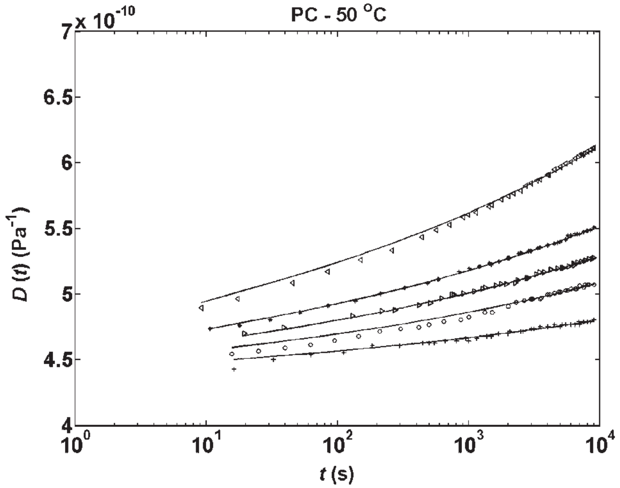

Figure 3.
Experimental and model-predicted creep compliances of PC at 50 °C.

Table 1.
Model Parameters.

D_0/Pa^{-1}	D_∞/Pa^{-1}	b_0	a_0/s	a_1/K	E_1'/(kJmol^{-1})	A_1/(m^{3}mol^{-1})	B_1/(m^{3}mol^{-1}K^{-1})
$.439\ 10^{-9}$	$3.98\ 10^{-6}$	3.20	$1.73\ 10^{-34}$	$2.29\ 10^{-3}$	199.4	$8.24\ 10^{-4}$	$5.34\ 10^{-7}$

Those creep compliance values (Figure 4), as well as those for three other polymers, do not lend support to simple time-stress superposition relationships.[7,8]

Figure 5 illustrates the retardation spectra calculated by fitting the latter simplified version of the model to the experimental creep results of PC at 40 °C (cf. Equation 9). Their general shape is similar to those of Figure 1. The spectra for 16 and 20 MPa (the two closest stresses) are nearly superposed, which may be the result of experimental errors and of the possible imprecision incurred by treating n^* as a real number, in addition to using Alfrey's approximation in Equation 10. It may again be observed that, although only the shortest retardation times are within the time scale of the experiment, the model is able to account for the very small influence of all other (including extremely long) retardation times.

Before closing, two comments on the parameter values of Table 1 should be made. From $a_1 = h\nu_1^{\#}/(2k_B)$,[11] where h is Planck's constant, one may obtain $\nu_1^{\#}$ $\sim$9.54 10^7 Hz for the frequency of transition/jump of the activated to the final states (the so-called crossover frequency), which is within the expected range for a relatively rigid material.[13] Finally, for simplicity, Equation 4 does not make explicit that CSTMD predicts that the parameters a_1 and E_1' are not independent, namely $a_1 = F(E_1', T_c)$ where F is known[11,12] and T_c is the crossover temperature (always difficult to measure), whose experimental PC value could not be found in the literature. However, for many other materials, it is often verified that $T_c \sim 1.2\ T_g$.[13] This will eliminate one parameter, while ensuring greater theoretical consistency and accuracy. So, may be the a_1 and/or E_1'value(s) will need future correction.

Conclusions and Perspectives

This simplified version of the CSTMD theory successfully formulates and predicts non-linear polymer creep behaviour, with the calculations yielding physically

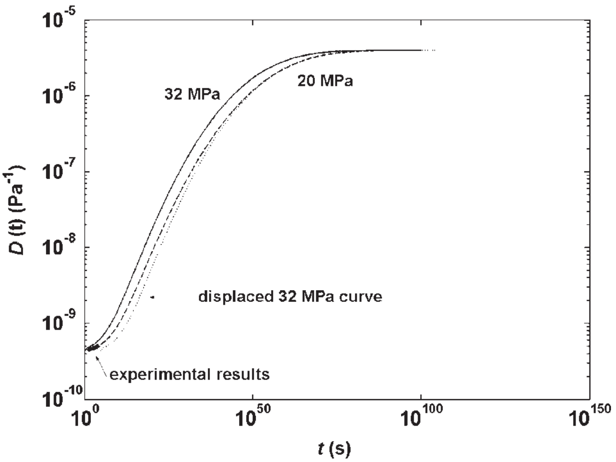

Figure 4.
Example of stress-time non-superposition in PC at 40 °C.

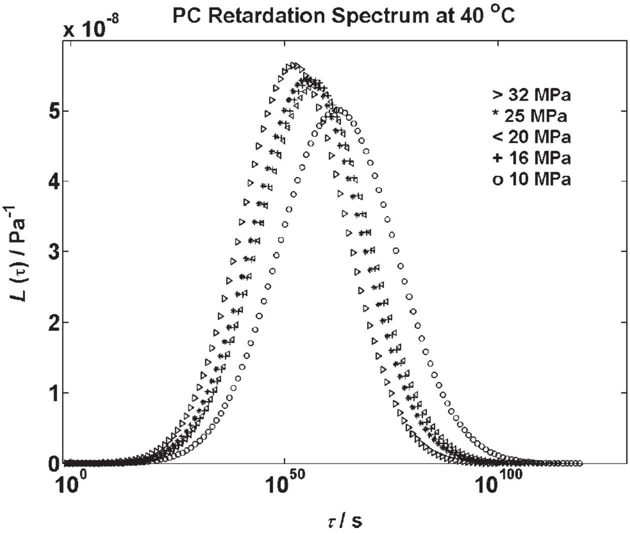

Figure 5.
Retardation time spectra of PC, at 10, 16, 20, 25 and 32 MPa, and 40 °C.

meaningful parameter values that characterize the dynamics of the material's structure. The full theory will enable the direct calculation of the complete retardation time distribution and the corresponding time-, temperature- and stress-dependent creep compliances with a further reduced number of parameters. In this case, Alfrey's approximation will not need to be made, thus additionally improving the accuracy of the calculations. These will also quantify the variation of the cooperativity level with temperature and (possibly) stress.

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