

Validation of a non-linear molecular model of polymer creep

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Introduction

Previous models for the interpretation of the creep behaviour of polymers are of course valuable, but mainly empirical or semi-empirical, and do not directly take into account the physical (molecular) underlying mechanisms, namely the detailed conformational and other transitions responsible for the material's non-linear viscoelastic behaviour [1-10].

Any realistic and accurate model should predict and quantify the peculiar and coupled time-temperature-stress behaviour, and this is shown to be possible by adequate kinetic formulation of the frequencies (or retardation times) of the whole range of structural contributors to the material's compliance. One should mention here the old but seminal work by Eyring *et al.* [11,12], which at least had the merit to suggest how one could physically and mathematically link the oldest, Voigt-Kelvin and other, phenomenological models to the actual non-linear physical behaviour at the molecular scale.

Outline of a macromolecular dynamic model of creep

It is not difficult to understand and visualize the dynamic (compliance and/or relaxation) behaviour of any viscoelastic material as resulting from a range of motions/transitions at the molecular scale – whole molecule (or atom)/void interchanges in non-macromolecular materials, and gauche/trans conformational transitions or other motions (e.g. crankshaft) in macromolecular ones. Actually, in polymers, single-segment gauche/trans transitions are not possible without the simultaneous participation of a small set of neighbouring segments, which is exactly what happens in crankshaft motions, but the gauche/trans transitions could be taken as a simple and good paradigm for the microscopic modelling of macromolecular materials' responses to a wide range of physical excitations, of which creep is the example studied here.

In separate contributions to Macro 2004 [13,14], the strategy of quantitatively modelling the cooperative, non-Arrhenius, non-linear response behaviour of macromolecules is addressed in greater detail. In the case of creep, the objective has been the modelling of the creep compliance function to include the effects of time, stress and temperature, duly taking into account that a relatively wide range of structural contributors to the overall material's response are normally involved. In polymers, such contributors turn out to be clusters of $n \geq 1$ macromolecular "segments", the "segments" being the shortest chain elements capable of independently contributing to the actual physical response being considered (chain uncoiling and disentanglement, in creep), like those involved in crankshaft or other motions, rather than the actual individual chain segments capable of conformational changes in isolated macromolecules. Calculations detailed in the above contributions to Macro 2004 suggest that the greatest contributors to the final overall behaviour turn out to be clusters of 2 to 5 "segments". For example, in a polypropylene, a typical "segment" would include at least four main chain carbon atoms and their associated methyls and hydrogens.

It was shown [14,15] that the creep compliance function of each of the above elementary contributors, may be formulated as a function of time, t , mechanical stress, σ_0 , and temperature, T , as a generalized, non-linear, modified Voigt-Kelvin unit, *i.e.*

$$D'(t) = D'_0 + (D'_\infty - D'_0) \left\{ 1 - e^{-\left[c'_0 t \sinh(\beta \sigma_0) / \sigma_0 \right]} \right\}, \quad (1)$$

$$\text{with } c'_0 \propto e^{-E'_0/kT} / (D'_\infty - D'_0), \quad (1a)$$

where β is an activation volume divided by $k_B T$, k_B being Boltzmann's constant and T the absolute temperature. It may be observed that Equation 1 includes the linear, stress-independent, viscoelastic

behaviour at low stress values, where $\sinh(\beta \sigma_0)$ converges to $\beta \sigma_0$. The corresponding (linear or non-linear) characteristic retardation time is

$$\tau = \frac{\sigma_0}{c'_0 \sinh(\beta \sigma_0)} \quad (2)$$

Given the wide variety of contributing structural elements that are involved in the entire range of cooperative motions (with activation energies, E'_0 , and entropies proportional to the various cluster sizes), the logical step to take is to consider an adequate distribution of cluster sizes and corresponding retardation times. A long time ago, Feltham [16] had already shown that a log-normal distribution would be a physically reasonable approximation to the retardation spectra of a wide range of viscoelastic materials. As a matter of fact, however, the analysis of the present and other experimental data [15], showed that there is a minimum retardation time, corresponding to the smallest contributing clusters ($n = 1$) in the least constrained local environment within the structure. So, the overall (real) creep compliance may be formulated [14,15] as

$$D(t) = D_{0,e} + (D_\infty - D_{0,e}) \frac{\int_{\ln \tau_1}^{+\infty} \left(1 - e^{-\frac{t}{\tau}} \right) e^{-\left[-b^2 \left(\frac{\tau}{\tau_1} \right)^2 \right]} d \ln \tau}{\int_{\ln \tau_1}^{+\infty} e^{-\left[-b^2 \left(\frac{\tau}{\tau_1} \right)^2 \right]} d \ln \tau} \quad (3)$$

which, under the usual and useful approximation that $(1 - e^{-t/\tau})$ is ~ 0 for $\tau > t$ and ~ 1 for $\tau \leq t$, simplifies to

$$D(t) = D_0 + (D_\infty - D_0) \frac{\text{erf} \left[b \ln \left(\frac{\tau^*}{\tau_1} \right) \right] + \text{erf} \left[b \ln \left(\frac{t}{\tau^*} \right) \right]}{\text{erf} \left[b \ln \left(\frac{\tau^*}{\tau_1} \right) \right] + 1} \quad (4)$$

where τ^* is the average retardation time, formulated similarly to Equation 2 with β substituted by a β^* and c'_0 by a $c'_{0,*}$, τ_1 is the minimum retardation time, also similarly formulated with β substituted by a β_1 (smallest of the β values) and c'_0 by a $c'_{0,1}$, and b is proportional to the reciprocal of the standard deviation of the $\ln \tau$ values, *i.e.* $b = b_0 / \ln(\tau^*/\tau_1)$, b_0 being a constant parameter, expectedly between 1.5 and 3. In the above two equations, D_0 and D_∞ are the instantaneous and infinite time creep compliances.

Creep experiments

The creep measurements were carried out with a Zwick Z100 Universal Tensile Testing Machine, equipped with a 2.5 kN load cell and using a Macro extensometer with a deformation measurement range of 100 mm. The strain/force *vs.* time experimental data were automatically recorded, stored and treated on a personal computer. The test specimens were previously conditioned at 23 °C, and the creep tests were conducted at each selected temperature (30, 40 and 50 °C) in a thermostatic chamber, under applied stresses of 10, 16, 20, 25 and 32 MPa, for a polymethylmethacrylate (PMMA), and 2, 4, 6, 8 and 10 MPa, for a polypropylene (PP).

Presentation and discussion of the experimental results

The small average relative deviations between the predictions of this analytical, non-simulative, molecular dynamics model and the experimental creep compliances - 1.15% for PMMA (Figure 1) and 1.32% for PP (cf. Poster), at 40 °C, and other small values at other temperatures and with other materials [15] – quantify their very good agreement.

The plots of Figures 2 and 3 document the validity of Equations 2 and 4, with $b_0 \sim 3$ and 1.5 for PMMA and PP, respectively. The ratio between the slopes of τ^* and τ_1 is ~ 2 to 4 for PMMA and 5 to 6 for PP (cf. Poster), which measure the corresponding ratio of the activation volumes, and therefore the relative size of the corresponding segment clusters that contribute to creep.

The increase of stress (Figures 3 and 4) and/or temperature (cf. Poster) yields increases of b , *i.e.* a decrease in the width of the

material's retardation spectrum. This is the main reason why the applicability of a strict stress-time equivalence or superposition may be seriously questioned, even though a time-temperature equivalent at constant stress still appears to hold [15]. This feature of the behaviour is not surprising, in view of the inseparability of stress and time in Equation 4.

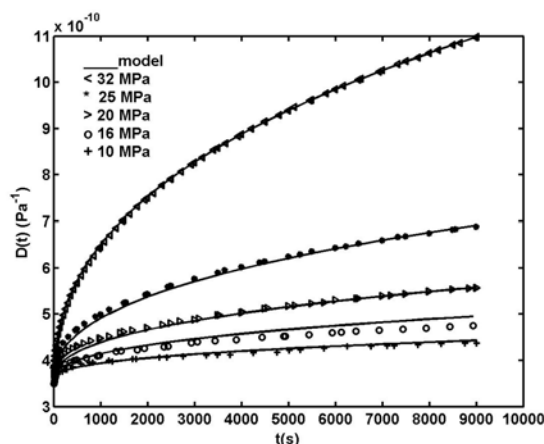


Figure 1. Model fitting (Equation 4) of the creep compliance of PMMA at 40 °C, for the stress values indicated.

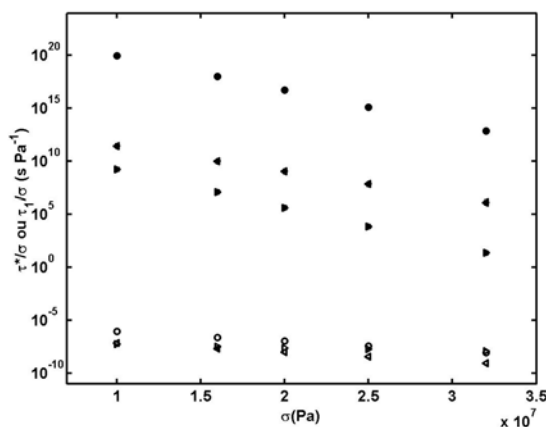


Figure 2. PMMA minimum (empty symbols – o, <, >, at 30, 40 and 50 °C, respectively) and average retardation times (filled symbols) as functions of the applied stress.

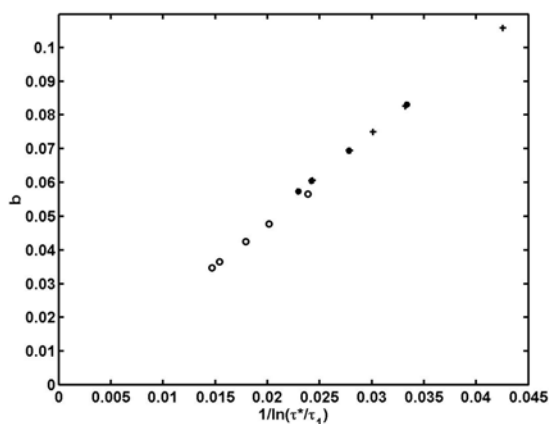


Figure 3. Variation of the parameter b with the minimum and average retardation times, for PMMA at 30 (o), 40 (*) and 50 °C (+).

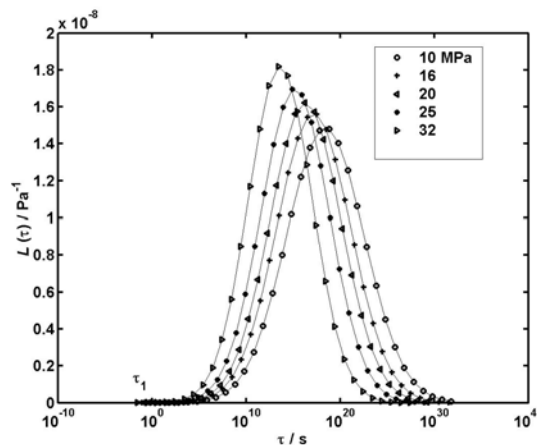


Figure 4. Retardation time spectra of PMMA, at 40 °C, for the stress values indicated.

Finally, it should be stressed that the model and the corresponding parameter calculation algorithm are successful in predicting the same instantaneous, D_0 , and infinite time, D_∞ , compliances, for all stress values (and all test specimens of the same material), and that they agree with the expected typical values ($\sim 10^{-9}$ and 10^{-6} Pa $^{-1}$, for amorphous, and $\sim 10^{-9}$ and $10^{-8-10-7}$ Pa $^{-1}$, for semi-crystalline polymers, respectively – cf. Poster and [15]). The prediction of the correct D_∞ is particularly significant, in view of the fact that the creep experiments lasted not longer than $9 \cdot 10^3$ seconds, barely enough to initiate a truly significant rise in compliance (cf. Poster). Equation (4) predicts a smooth sigmoid compliance change from D_0 to D_∞ .

Conclusions

The non-linear viscoelastic behaviour of polymers, namely creep, may be meaningfully and accurately modelled at the (macro)molecular scale, to account for its characteristic, temperature-dependent, cooperative nature and intrinsic inseparability of the effects of time and stress.

The model correctly portrays the essentials of the true macromolecular dynamics, without the need for complex and time-consuming computer simulations.

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