Temperature and stress influence in the description of time-dependent materials

José R. S. André[(1)] and José J. Cruz Pinto[(2)]

[(1)] Department of Mechanical Engineering, Technology and Management School, Guarda Polytechnic Institute, Portugal, jandre@ipg.pt

[(2)] CICECO/Department of Chemistry, University of Aveiro, Portugal , cpinto@dq.ua.pt

Summary: A new creep compliance equation has been developed and validated, yielding a fully coupled time-temperature-stress formulation, with long-term predictive capability. Stress-induced changes in intrinsic time scale were investigated by non-linear creep tests on an ultra-high molecular weight polyethylene (UHMW-PE), at three temperatures. The creep compliance *vs.* time curves at five different stress levels were determined and shifted along the logarithmic time axis to get an attempted master compliance curve at a given reference stress level, according to the concept of time-stress equivalence. Experimental data for the polyethylene were obtained and analysed to identify the extent to which time-stress superposition relationships may be valid, and it is shown that they are only approximations, limited to narrow ranges of the experimental variables, in contrast with the proposed model that more accurately fits the experimental behaviour.

Introduction

Synthetic polymers play an increasingly important role in the modern world. A structurally efficient design and effective material utilisation usually require a good understanding and modelling of the non-linear deformation behaviour of the materials involved.

During creep at constant stress, strain increases with time. Moreover, the higher the applied stress, the higher the strain rate at any given time. When we define and measure the creep compliance of the UHMW-PE used, $D(t)$, as the ratio of measured time-dependent strain, $\varepsilon(t)$, to the applied constant stress, σ_0, the compliance curves for stresses of 1 and 2 MPa nearly coincide with each other. This implies that below *ca.* 2 MPa, the measured strain is almost exactly proportional to the applied constant stress, and the creep behaviour at stresses below 2 MPa may thus be characterized by a single $D(t)$ curve, indicating that the creep behaviour is linear. However, at stresses higher than 2 MPa, corresponding $D(t)$ values increase with the applied stress, which marks the onset of non-linear creep behaviour. This non-linear effect results from a change of timescale: at higher stress levels, the material will creep faster and the distribution of the relaxation times of the material is shifted to shorter times and is also narrowed by stress, as well as temperature.

Previous models for the interpretation of the creep behaviour of polymers are mainly empirical or semi-empirical [1, 2] and do not directly take into account the physical (molecular) underlying mechanisms, namely the conformational and other transitions responsible for the material's non-linear viscoelastic behaviour.

Theoretical Model and Calculation Procedure

References [3, 4] develop the detailed dynamics of gauche-trans conformational transitions, as the simplest possible paradigm of localized motions at the molecular scale within the material, but a wide range of other possible motions, both of localized or cooperative nature (*e.g.* varying combinations of single local crankshaft motions), yield qualitatively similar but quantitatively different physical response behaviour. The common result of the modelling of such motions is that each of them may be described by a non-linear modified Voigt-Kelvin unit or standard linear solid, showing fully coupled (strictly not separable) temperature and stress dependence, that automatically degenerate into linear viscoelastic behaviour at (and

only at) low stress values. Each characteristic retardation time has been shown to be of the form

$$\tau = \frac{\sigma_0}{c_0' \sinh(\beta \sigma_0)}$$ (1)

with c_0' proportional to $e^{-E_0'/kT}$, E'_0 being a local activation energy and $\beta = v^{\#}/(k_B T)$, where $v^{\#}$ is a corresponding activation volume, k_B is Boltzmann's constant and T the absolute temperature.

A more recently developed cooperative segmental theory of molecular dynamics (CSTMD) quantifies and explicitly predicts the effective relative weights of the various retardation times (which turn out to be a complex but workable combinatorial problem [5, 6]), as an approximate truncated (at some very short time τ_1) log-normal distribution, and this same spectrum shape is here assumed, though treating τ_1 and the average retardation time, τ^*, as adjustable parameters. We nevertheless stress that the complete theory is fully predictive in this respect.

The resulting non-linear creep compliance, with the usual and useful approximation that $\left(1 - e^{-t/\tau}\right)$ is ~ 0 for retardation times such that $\tau > t$ and ~ 1 for $\tau \leq t$, and neglecting the effect of the initial transient in ordinary tensile creep experiments (fast stress ramp from 0 to some very short time t_0) [3, 7], simplifies to

$$D(t) = D_0 + (D_\infty - D_0) \frac{erf(b_0) + erf\left[b \ln\left(\frac{t}{\tau^*}\right)\right]}{1 + erf(b_0)} \quad ,$$ (2)

where τ^* is the average retardation time, formulated similarly to Equation 1, with an average activation volume yielding β^* (average activation volume divided by $k_B T$) and an average activation energy, E^*, b_0 is a constant parameter expectedly between 1.5 and 3 [3, 4] and $b = b_0 / \ln(\tau^*/\tau_1)$, where τ_1 is the minimum retardation time - also similarly formulated with β^* substituted by a β_1 (smallest of the β values) and E^* by a minimum local activation energy, E'_{01}; b is simply proportional to the reciprocal of the standard deviation of the $\ln \tau$ values. In the above two equations, D_0 and D_∞ are the instantaneous and infinite time creep compliances, for which the model and calculation algorithm successfully yield the correct magnitude (from creep data within a limited time range), depending on the type of polymer.

Experimental

A series of short-term creep tests were conducted at different stress levels (1, 2, 4, 6 and 8 MPa) and three temperatures (30, 40 and 50 ºC). This particular work focused on a semi-crystalline polymer – an UHMW-PE - as 150 mm x 10 mm x 4 mm test specimens, cut and adequately machined from sheets.

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 collected, stored and treated on a personal computer. The test specimens were previously conditioned at 23ºC, and the creep tests were conducted at each selected temperature (30, 40 and 50ºC) in a thermostatic chamber, under each of the above applied stresses.

Time-Temperature-Stress Superposition or Equivalence Principle

According to the time-temperature-stress superposition (or equivalence) principle (TTSS), the time-dependent mechanical properties of viscoelastic materials at different temperatures and

stress levels may be shifted along the time scale, to construct a master curve at given reference temperature and stress.

From Figure 1, it may be concluded that, when the stress increases at constant temperature, the curves are not simply affected by horizontal shifts, as the creep strain rate also significantly increases. Actually, although to a lesser extent, the same behaviour may be detected when the temperature increases.
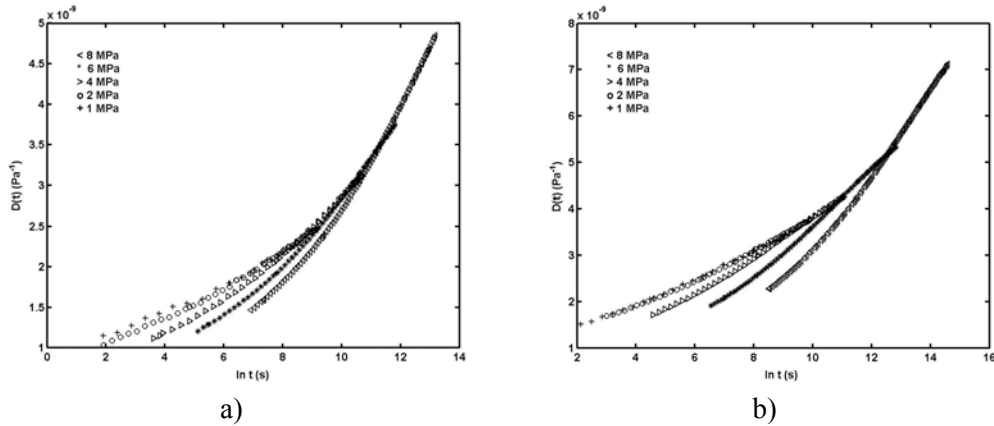

a)   b)

Figure 1. Time-stress superposition test: creep compliance master curves for UHMW-PE at 1 MPa: a) 30 ^{o}C and b) 40 ^{o}C.

This behaviour may be explained by the decrease in the width of the retardation spectra, $L(\tau)$, when stress or temperature increase [7]. Thus, as changes in shape of the retardation spectra seem to be experimentally confirmed for this and other polymer materials [3, 4], and in view of the resulting low quality of the attempted master curves of Figure 1, one is forced to conclude that a time-stress superposition (TSS) should not be applicable. Thus, the possibility of accelerating creep by increasing the applied stress, in order to predict long time behaviour from short time tests, seems compromised or reduced to a somewhat crude approximation.

The increase of stress and/or temperature yield increases of b, i.e. a decrease in the width of the material's retardation time spectrum [3, 4, 8, 9]. An increase in temperature also shortens all individual retardation times, with most significant effects on the longest ones (precisely those that most critically determine the long-term creep behaviour, particularly at low stress), due to their highest associated activation energies.

Quality of the Model Fits to the Experimental Data

The very small relative deviations (2.2 % and 0.8 %, at 30 and 40°C, respectively) between

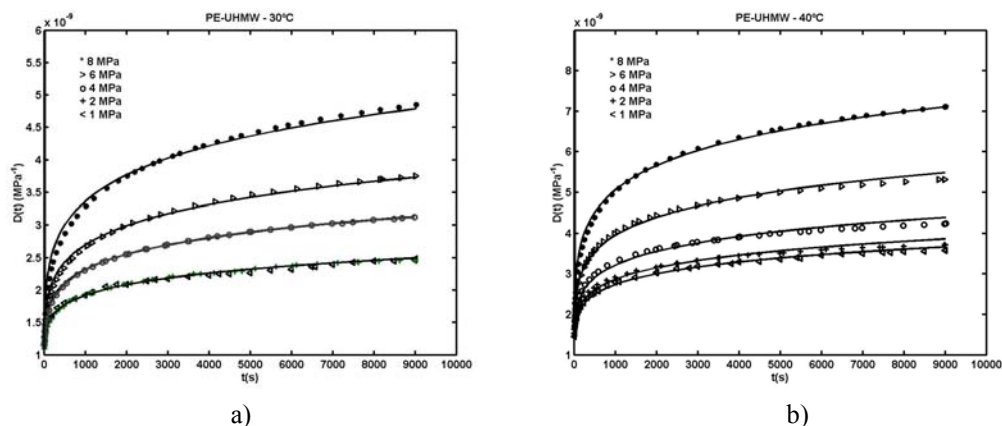a)   b)

Figure 2. Model fitting (Equation 2) of the creep compliance of PE-UHMW at 30 ºC and b) 40 ºC.

the experimental creep compliances and the model predictions (Equation 2) quantify the excellent agreement illustrated in Figures 2a) and 2b).

Figure 3 illustrates the model's long-term predictive power (for 4 and 8 MPa, at 40 °C), together with the non-superposition of the curves at those two stress values, itself the result of the previously discussed changes in spectral width.
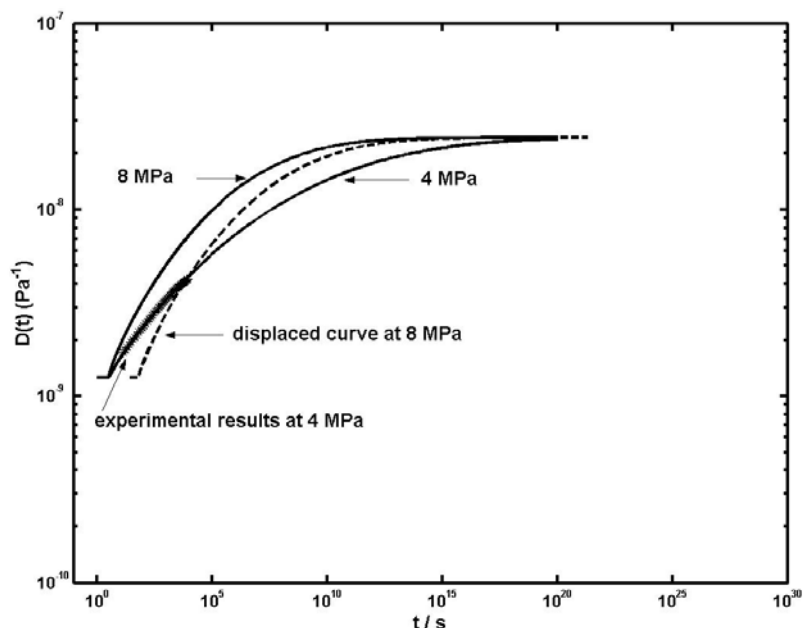

Figure 3. UHMW-PE model predicted creep curves at 40 °C, and 4 and 8 MPa, and the latter shifted to longer times.

Conclusions

The non-linear viscoelastic behaviour of polymers, namely creep, may be meaningfully and accurately modeled at the (macro)molecular scale, to account for its characteristic, temperature-dependent, cooperative nature and intrinsic inseparability of the effects of time, temperature and stress. Using the developed creep compliance equation, it was possible to predict long-term deformations from short-term tests (9000 seconds).

Acknowledgements

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