

PREDICTION OF LONG TERM CREEP BEHAVIOUR OF PMMA FROM SHORT TIME TESTS

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Introduction

In contrast with most previously published works, which are semi-empirical, interpolative and (limitedly) extrapolative [1, 2], the model developed here enables the prediction of the non-linear creep compliance of a given amorphous or semi-crystalline polymer [3, 4], providing the values of the physical parameters have been experimentally determined, for a reasonably wide range of temperature and applied stress values.

Macromolecular dynamic model of creep

It was show [5, 6] that the creep compliance function may be formulated as a function of time, t , mechanical stress, σ_0 , and temperature, T , as

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

where where τ^* is an average retardation time, formulated as

$$\tau^* = \frac{\sigma_0}{c_0^* \sinh(\beta^* \sigma_0)} \quad (2)$$

where β^* is an average activation volume divided by $k_B T$, k_B being Boltzmann's constant and T the absolute temperature, $c_0^* \propto e^{-E_0^*/kT}$, 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.

Experimental

Material

The test specimens of poly(methylmethacrylate) 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.

Creep Tests

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.

Presentation and discussion of the experimental results

Figure 1a) shows the model fitting (Eq. 1) of the creep compliance of PMMA at 30°C. The increase of stress (Fig. 1b)) and/or temperature yields increases of b , *i.e.* a decrease in the width of the material's retardation spectrum.

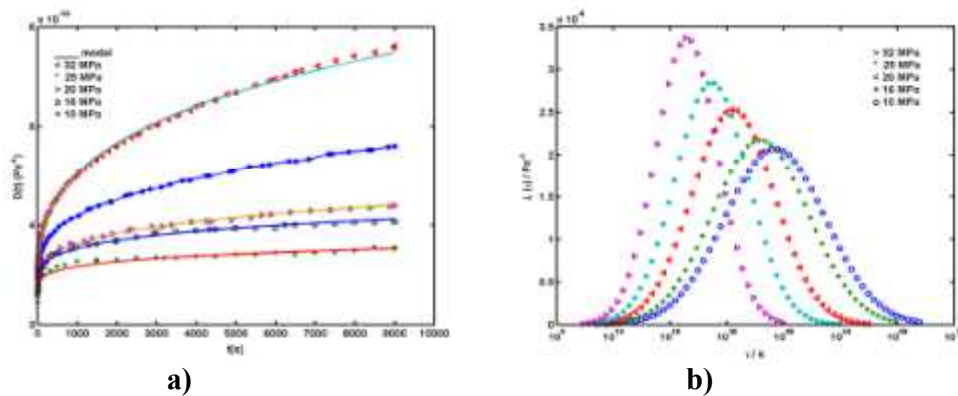


Fig 1a) Model fitting (Eq. 1) of the creep compliance of PMMA at 30°C, for the stress values indicated; **b)** Retardation time spectra of PMMA, at 30°C, for the stress values indicated.

Figure 2 illustrates the model's long-term predictive power (for 20 and 32 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.

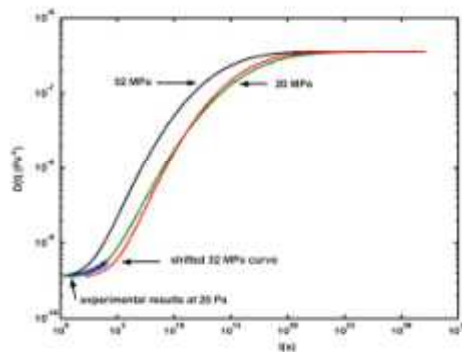


Fig 2. PMMA model-predicted creep curves at 40°C, and 20 and 32 MPa, and the latter shifted to longer times.

Conclusions

The analytical model developed, based on concepts of non-simulative molecular dynamics, accounts for a truncated log-normal retardation time distribution, such that a minimum (τ_1) and an average (τ^*) retardation time are quantitatively predicted, as functions of temperature and applied stress.

The model-predicted shift of the retardation time spectra towards shorter times, when temperature or stress increases, is in agreement with other published results and our own experimental data. In addition, a clear change in the shape (width decrease) of the spectra has been identified and quantified, after increases in the same two operating variables.

References

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