NON-LINEAR CREEP OF PMMA: SERVICE PERFORMANCE PREDICTION FROM SHORT-TERM TESTS

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INTRODUCTION

In previous literature, empirical models have been applied to describe and predict the viscoelastic behavior of polymer materials. For example, the empirical power-law model seems to fit well, but only for short-term data [1, 2, 3]. Such formulations are of some utility in data reduction and extrapolation, but do not allow meaningful physical interpretations and lack generality.

When we look at the dynamic behavior of polymers, we recognize the presence of a very large variety of possible and specifiable processes (responses), spanning an extremely wide range of frequencies and cluster sizes within the structure, at any given temperature. That range significantly widens and shifts to lower and lower frequencies (and larger and larger cluster sizes) as the temperature is lowered.

CREEP THEORETICAL MODEL

The stress- and temperature-dependent non-linear creep behavior of polymers was quantitatively modeled as a superposition of a range of activated motions at the molecular scale, covering well-defined space and time-scales. Using a recently developed cooperative segmental theory of materials dynamics, CSTMD [4, 5], each characteristic retardation time, τ_n, has been physically and mathematically formulated as

$$\tau_n = a_0\left[\sinh\left(\frac{a_1}{T}\right)\exp\left(\frac{E_1'}{RT}\right)\right]^n \frac{\sigma_0}{\sinh\left(\frac{n\upsilon_1^{\#}\sigma_0}{RT}\right)}$$

a_0, a_1, $\upsilon_1^{\#} = A_1 + B_1 T$ and $E_1^{'}$ are physical parameters, the last two being the minimum activation volume and energy, respectively, associated with the motions of the smallest clusters (n = 1), *i.e.* of single localized chain crankshafts. These characteristic times turn out compatible with the well-known (but as yet unexplained) dynamic crossover [4, 6]. The 1st-order responses of the various clusters (each modeled as a non-linear standard solid) were combined with adequate relative weights (according to an approximately log-normal retardation spectrum) to yield the material's time-, stress- and temperature-dependent creep compliance [5], $D(t,\sigma_0,T)$, with the results below.

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})
.340 10^{-9}	**.738 10^{-6}**	**3.10**	**3.34 10^{-13}**	**7.61 10^{-7}**	**75.2**	**7.96 10^{-5}**	**2.25 10^{-7}**

EXPERIMENTAL

This report focuses on an amorphous polymer – poly (methylmethacrylate), PMMA - 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 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 23°C, and the creep tests 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.

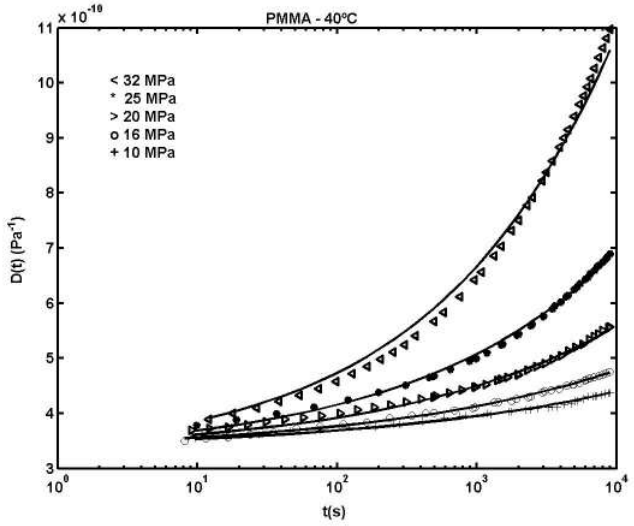

Figure 1 - Experimental and model-predicted creep compliances of PMMA at 40 °C.

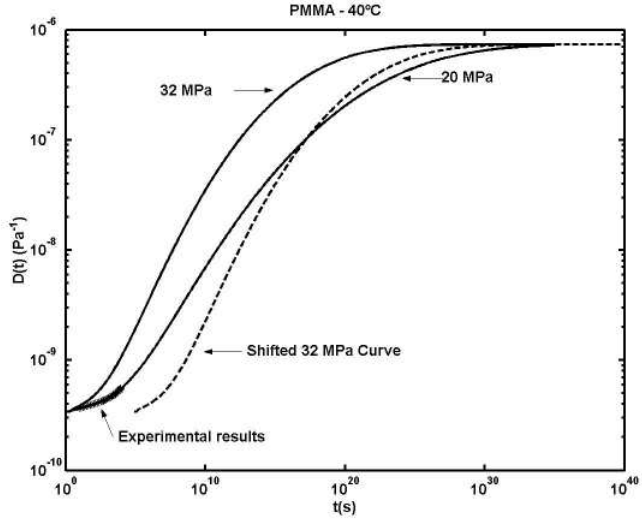

Figure 2 - PMMA model predicted creep curves at 40 ºC, and 20 and 32 MPa, and the latter shifted to longer times.

DISCUSSION

The model successfully predicts the main features of the behavior (Fig. 1), namely its non-linearity, degenerating into full linearity at very low stresses, such that a stress-time superposition results as not strictly valid (Fig. 2). The correct order of magnitude has been predicted for the infinite time compliance, D_∞, despite the limited time-scale of the experiments (< 10^4 s). The calculations for PMMA yielded a crossover temperature, T_c, of 448 K, in agreement with known experimental values [6].

References

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