

# ON THE MEASUREMENT OF THE WIDTH OF THE DISTRIBUTION OF RELAXATION TIMES IN POLYPROPYLENE

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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, 2].

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.

We adopted a (non-simulative, mainly analytical) truly dynamic molecular modelling approach to general compliance and relaxation behaviour, whereby actual elementary, molecular scale, process-relevant frequencies are derived by adequate (as simple as possible) kinetic formulation. These elementary processes follow an almost exactly Arrhenius behaviour, with a range of activation enthalpies, but their relative contribution to the overall macroscopic behaviour of the materials is adequately quantified, to account for the materials' retardation time spectra and final non-Arrhenius and stretched-exponential behaviour.

Given the wide variety of contributing structural elements that are involved in the entire range of cooperative motions, the logical step to take is to consider an adequate distribution of cluster sizes and corresponding retardation times. A long time ago, Feltham [3] 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 [4], 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 [4, 5] as

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

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

$$D(t) = D_0 + (D_{\infty} - D_0) \frac{\text{erf} \left[ b \ln \left( \frac{\tau^*}{\tau_1} \right) \right] + \text{erf} \left[ b \ln \left( \frac{t}{\tau^*} \right) \right]}{\text{erf} \left[ b \ln \left( \frac{\tau^*}{\tau_1} \right) \right] + 1} \quad (2)$$

The effects of temperature and applied stress on the optimised values of  $b$ ,  $\tau_1$ ,  $\tau^*$ ,  $D_0$  and  $D_{\infty}$  (actual values and physical significance) that best fit the experimental creep strain values are discussed. Figure 1 shows the results of fitting Eq. (2) to the experimental creep compliance curves obtained for PP at 50 °C.

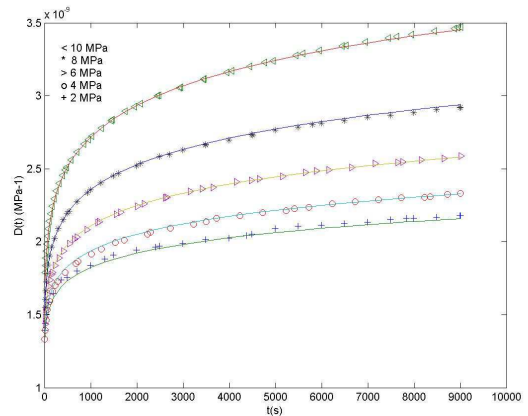


Figure 1. Model Fitting (Eq.2) of the Creep Compliance of PP at 50 °C.

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