Advanced Modeling of Polymer Non-Linear Stress Relaxation – Poly(methylmethacrylate) and Polycarbonate

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Abstract. Sound models of temperature- and strain-dependent non-linear stress relaxation are still lacking. Very recent work has shown that focusing on polymers' local, non-affine, strains and stresses provides an adequate basis for developing such models and accurately predicting experimental stress relaxation moduli, the values of meaningful physical parameters and long time behavior, from experiments spanning only a few hours. A new modeling strategy that explicitly considers such non-affine local stresses and strains was applied to two amorphous polymers – a poly(methylmethacrylate), PMMA, and a bisphenol-A polycarbonate, PC. The results support a view of the stress relaxation process where a temperature-dependent, truncated, approximately log-normal distribution of local cooperative (or clustering) transitions are involved, at and above a minimum (or primitive) relaxor size. Within this view, cooperativity (via the average and maximum cluster sizes) increases with decreasing temperatures. Beyond the reasonable agreement with the experiments, the model succeeds in predicting (1) the effect of increases in the fully relaxed modulus, E_∞, as in semi-crystalline or strongly cross-linked polymers, (2) the strict inapplicability of time-temperature and strain-time super-positions, (3) an extended, Kohlrausch-Williams-Watts, type of relaxation response, spanning 12 or more time decades, and (4) specific, meaningful, physical parameters: a minimum activation energy (close to those of corresponding β-type transitions), the (occupied + free) volume of the primitive relaxor, and the approximate crossover temperature, T_c, and frequency, ν_c, both of critical importance in condensed matter dynamics. The model also has the potential of incorporating the effect of changes in free volume and allows very fast computations, irrespective of the experimental time scale.

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SCOPE

Focusing on the material's *non-affine local strains and stresses* provides a sound basis for modeling *stress relaxation* in a physically realistic way and accurately predicting decreasing (from E_0 to E_∞) experimental *stress relaxation moduli* (to within 1% or lower relative errors), the values of meaningful physical parameters and very long time behavior, from experiments spanning less than 3 hours.

MODEL AND DATA ANALYSIS

Reference 1 develops the modeling strategy in full detail in its simplest form (Model I), which reasonably agrees with PMMA experimental data[1] and already accounts for the highly cooperative nature of the material's response, whereby specific *primitive relaxors* (like *e.g.* small chain crankshafts) are able to respond in *clusters* of increasing sizes and longer response times with decreasing temperatures. This behavior entirely agrees with a recent *cooperative segmental theory of materials' dynamics* (CSTMD)[1,2] and is also fully consistent with earlier simplified formulations of cooperative behavior[3,4]. The relevant resulting equations were

$$\theta_n = \frac{1}{c_0} \cdot \exp\left(\frac{E_{a,n}}{k_B T}\right) \cdot \exp\left(-\alpha_{1,n}\right), \quad \alpha_{1,n} = \frac{\upsilon_{0,n}}{8 k_B T} \cdot \frac{\left(E_0 - E_\infty\right)\left(3E_0 + E_\infty\right)}{E_0} \cdot \varepsilon_0^{\,2} \qquad (1)$$

with $E_{a,n} = nE_{a,1}$ and $\upsilon_{0,n} = n\upsilon_{01}$, where ε_0 is the applied constant overall strain, and υ_{01}, $\upsilon_{0,n}$, $E_{a,1}$ and $E_{a,n}$ are the (occupied plus free) volumes and effective activation energies of each primitive relaxor and of their varying clusters (n integer), respectively.

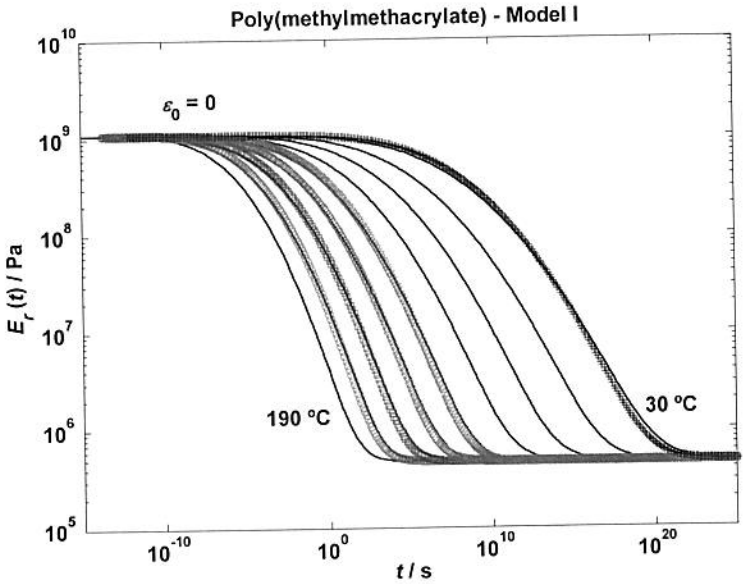

FIGURE 1. — Calculated Relaxation Modulus at 20 °C Intervals from 30 to 190 °C at 0% Strain; – $t_{190} \times 20$; ∀ $t_{170} \times 30$; M $t_{150} \times 40$; X $t_{130} \times 50$; □ $t_{50} \times 800$.

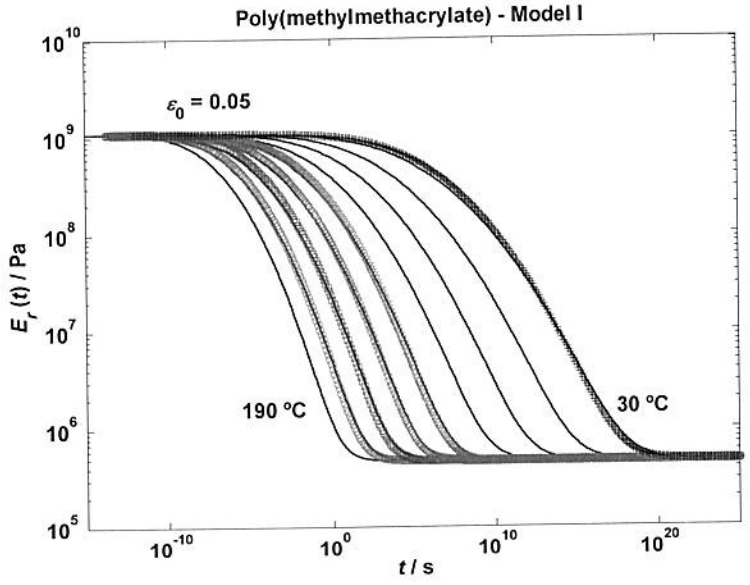

FIGURE 2. — Calculated Relaxation Modulus at 20 °C Intervals from 30 to 190 °C at 5% Strain; – $t_{190} \times 20$; ∀ $t_{170} \times 30$; M $t_{150} \times 40$; X $t_{130} \times 50$; □ $t_{50} \times 800$.

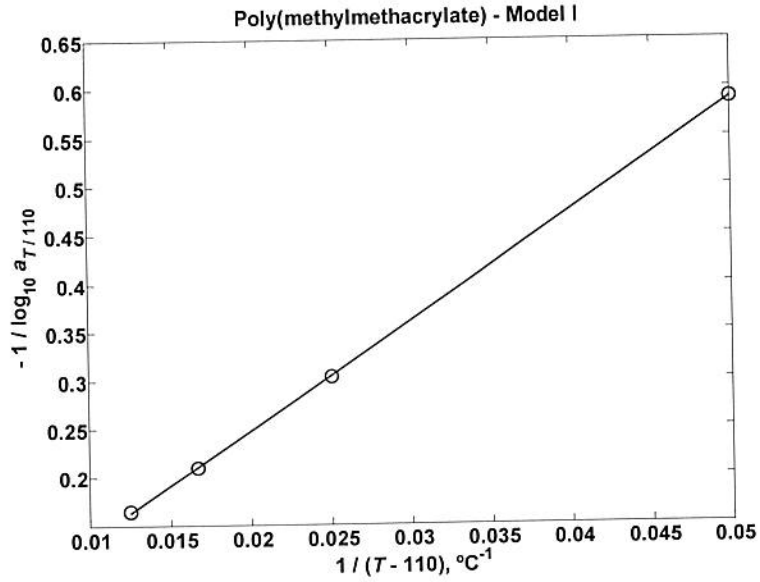

FIGURE 3. Calculated WLF Plot for PMMA at 0% Strain above 110 °C, with 110 °C as Reference Temperature.

Figures 1-3 illustrate, for PMMA, the effect of temperature on predicted $E_r(t)$, showing that WLF time-temperature superposition is only followed within a narrow (less than 100 °C) temperature range above the material's glass transition temperature, T_g, as known from experiment. Further detailed theoretical analysis of the c_0 parameter in θ_n, in the light of CSTMD[1,2], now establishes (Model II) that c_0 is in fact also size-dependent, such that

$$c_{0,n} = \nu_c \left(\frac{c_{0,1}}{\nu_c} \right)^n \quad , \quad c_{01} = \nu_c \exp\left(\frac{E_{a,1}}{k_B T_c} \right) \frac{\sinh\left(\frac{h\nu_c}{2k_B T_c} \right)}{\sinh\left(\frac{h\nu_c}{2k_B T} \right)} \exp\left[\frac{h\nu_c}{2k_B} \left(\frac{1}{T} - \frac{1}{T_c} \right) \right] \quad , \quad (2)$$

with ν_c and T_c the *crossover* frequency and temperature, two important material-specific parameters, reasonably well established for a limited number of material structures[5], namely PMMA. It may be checked that $\theta_n = (\nu_c \theta_1)^n / \nu_c$, and shown that this yields a discrete relaxation spectrum, whose contour may be approximated to continuous and truncated log-normal[1,2], $L'(\theta)$. Finally, the relaxation modulus may be obtained by

$$E_r(t) = E_\infty + (E_0 - E_\infty) \int_0^\infty L'(\theta) d \ln \theta \quad . \quad (3)$$

This formulation is equivalent to a cooperative two-level Ising model[1], but ongoing theoretical work[6] proves that the various relaxors may be in up to four different levels of local strain and stress, thus rendering the future updated formulation equivalent to a four-level Ising one.

Figure 4 shows the predicted $E_r(t)$ curves for PMMA at 40 (black) and 50 °C (red) at 3, 4 and 5% strains, together with the short term (< 3 hours) experimental measurements. Figure 5 shows presently available predicted and experimental data for a bisphenol-A polycarbonate (PC), and Figure 6 illustrates the effect of temperature (and, additionally, of E_∞ at 40 °C) on the behavior of this same PC. The optimized parameter values are shown in Table 1, pending eventual future adjustments, after ongoing longer time experiments. Future full application of CSTMD[2] will explicitly and directly yield the complete relaxation spectrum, reducing the number of parameters to five – E_0, E_∞, $E_{a,1}$, ν_c and T_c.

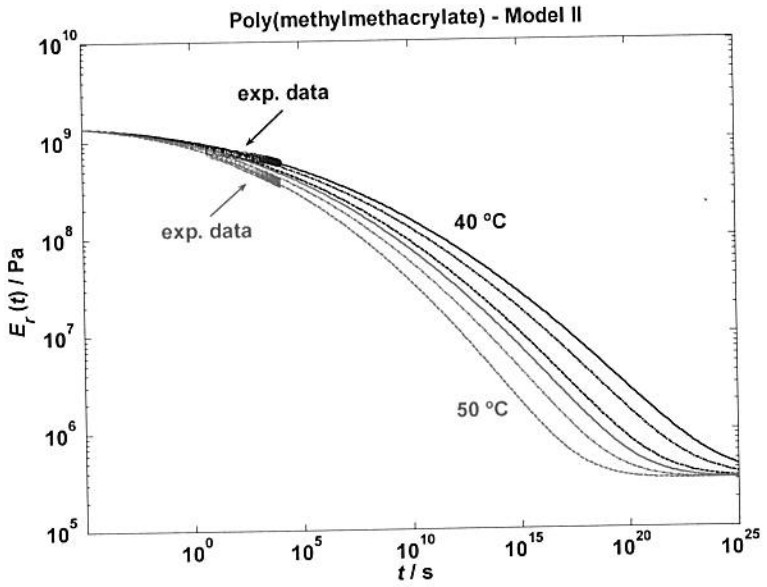

FIGURE 4. Calculated and Experimental Stress Relaxation Modulus for PMMA: —, — 3% Strain; – ⊙, – ⊙ 4%; – –, – – 5%

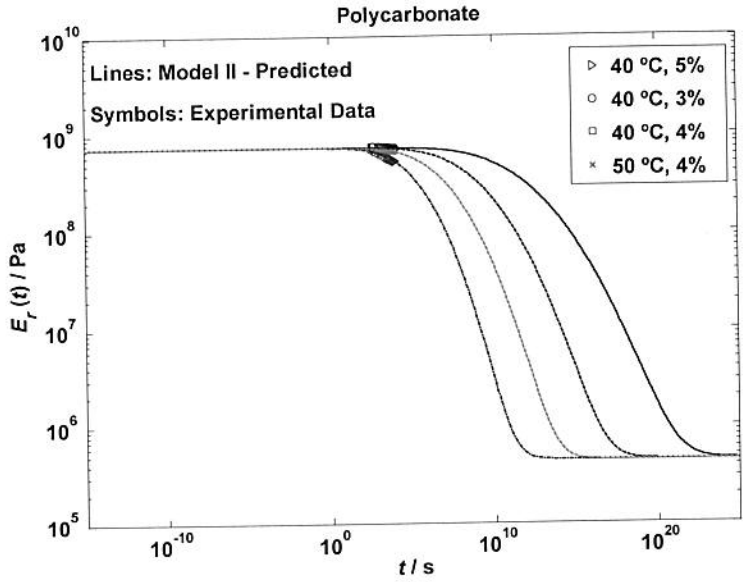

FIGURE 5. Calculated and Presently Available Experimental Stress Relaxation Modulus for PC: — 3% Strain; – –, – – 4%; – ⊙ 5%

TABLE 1. Model Parameters' Predicted Values.

PMMA	Physical Parameter	PC
1.2869	E_0 (GPa)	0.7269
0.3133	E_∞ (MPa)	0.4453
33.314	$E_{a,1}$ (kJ/mol)	108.97
1.3634	υ_{01} (10^{-3} m^3/mol)	29.221
2.2388	ν_c (10^5 Hz)	4.6959
456.2	T_c (K)	495.9

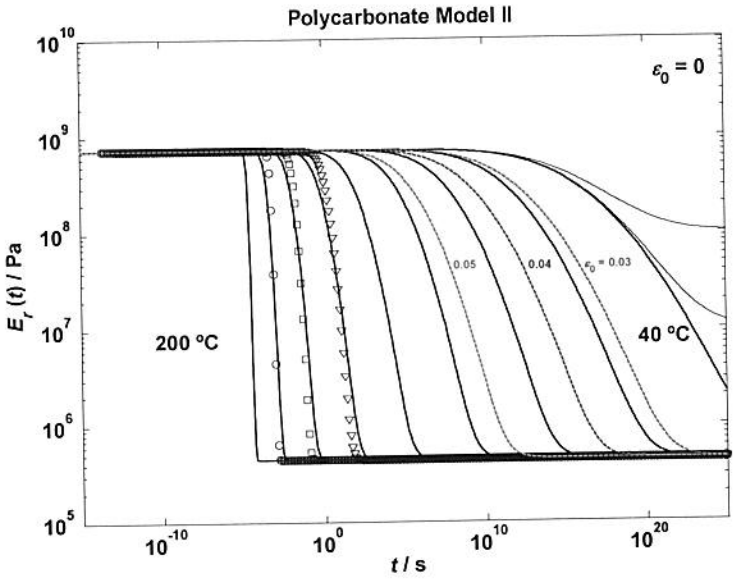

FIGURE 6. — Calculated Relaxation Modulus at 20 °C Intervals from 40 to 200 °C at 0% Strain for PC (including the effect of increasing E_e at 40 °C); – $t_{200} \times 25$; ∀ $t_{180} \times 50$; X $t_{160} \times 150$; Broken Colored Curves: varying strains at 40 °C.

CONCLUDING REMARKS

As in Reference 1, the above set of parameter values may be physically interpreted and will be separately discussed[6] in detail but, in the present limited space, it is important to note that the present crossover parameters, v_c and T_c, very closely agree with their known values for PMMA[5] and, as far as we know, they stand as the first reported estimates for PC. Further, given that for all well known cases[5] $T_c \sim 1.1$ to $1.2\ T_g$ (in K), one easily recognizes that the crossover temperatures obtained are fully consistent with the known glass transition temperatures of both materials. Finally, this work and Reference 1 show that analytical modeling of non-linear stress relaxation and other physical response behavior remains a viable, productive, and computationally efficient alternative (seconds- *vs.* "ages"-long calculations) to molecular dynamics algorithms, to gain physical insight and real predictive capability (of both actual behavior and relevant physical parameters), in the context of the dynamics of real (not simulated) materials, with which computation times become completely independent of experimental time scale.

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