Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Materials for:

Temperature Memory Effect in Amorphous Shape Memory Polymers

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1. Multi-branch Rheological Model and the Material Parameters Identification

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The thermomechanical properties of a thermo-rheologically simple polymer is described by a multi-branch rheological model, as shown in Figure S1. A detailed description of the multi-branch model for SMP application can be found in Yu et al [1], and its extension for 3D nonlinear model can be found in Westbrook et al [2]. As shown in the figure, the model consists of one equilibrium branch and several thermoviscoelastic nonequilibrium branches (number of *n*) to represent the multiple relaxation processes (for example, Rouse modes) of the polymer.

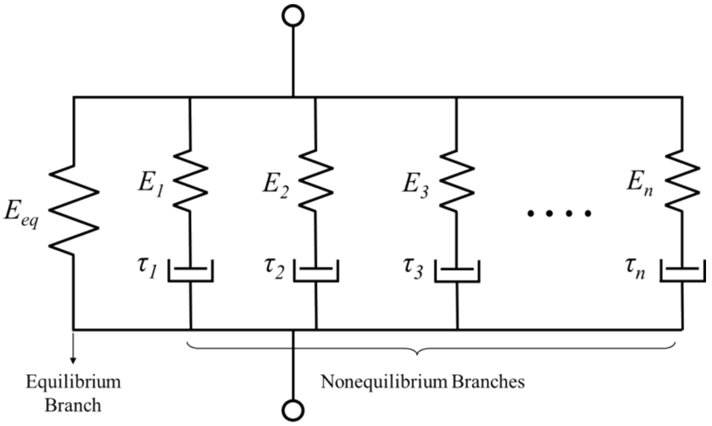

Figure. S1. 1D rheological representation of the used 1D multi-branch model

By applying the Boltzmann's superposition principle [3], the total stress $\sigma(t)$ of the model is:

$$\sigma(t) = E_{eq} e_m(t) + \sum_{i=1}^{n} E_i e_i^e \tag{S1a}$$

with

$$e_i^e = \int_0^t \frac{de_m(s)}{dt} \exp\left(-\int_s^t \frac{dt'}{\tau_i\left(T, t'\right)}\right) ds\,, \tag{S1b}$$

to describe the elastic strain evolution in each nonequilibrium branches. In Eq. S1a and S1b, $e_m(t)$ is the total strain. E_{eq} and E_i is the elastic modulus in the equilibrium and nonequilibrium branches, respectively. $\tau_i(T)$ denotes the temperature dependent relaxation time in the dashpots. Here, it is assumed that the time-temperature shift for each branch follows the same rule. According to the well-established "thermorheological simplicity" principle [3] under a non-isothermal condition, the relaxation times (or viscosity) of each nonequilibrium branch vary as the temperature changes:

$$\tau_i = \alpha_T(T)\tau_i^0 , \tag{S2}$$

where $\alpha_T(T)$ is a time-temperature superposition (TTSP) shifting factor, and τ_i^0 is the reference relaxation time at the temperature when $\alpha_T(T) = 1$.

Following O'Connell and McKenna [4], the method for calculating the temperature influence on the viscoelastic behavior depends on whether the material temperature is above or below a shifting temperature T_s. For temperatures above and near T_s, the (Williams-Landel-Ferry) WLF equation is used to calculate $\alpha_T(T)$ [5]:

$$log\alpha_T(T) = -\frac{C_1\left(T - T_r\right)}{C_2 + \left(T - T_r\right)} , \tag{S3a}$$

where T_r is the WLF reference temperature, and C_1 and C_2 are material constants that depend on the choice of T_r. In comparison, for temperature below T_s, $\alpha_T(T)$ follows the Arrhenius-Type behavior [6]:

$$ln\alpha_T(T) = -\frac{AF_c}{k_b}\left(\frac{1}{T} - \frac{1}{T_g}\right), \tag{S3b}$$

where A is a material constant, F_c is the configurational energy and k_b is Boltzmann's constant. T_s is the crossing point of two curves representing Eqs. S3a and S3b on a $\alpha_T(T)$ vs T plot.

The model parameters were determined by using the tan δ and storage modulus of the SMP obtained in the DMA tests. A detailed model parameters identification method of the multi-branch model can be found in our previous study [1, 7]. As shown in Figure 3, the acrylate SMPs possesses a storage modulus of 3.05 *MPa* when the temperature is 95°C. This modulus could be considered as the equilibrium modulus of the material as the relaxation time in each nonequilibrium branch at this temperature is minimal. Under the temperature of 5°C, the SMP composite has a storage modulus of 2349.1*MPa*. So we have $E_{eq}^{0}+\sum_{i=1}^{n}E_i=2349.1MPa$.

By using the nonlinear regression (NLREG) method [8, 9], the parameters for TTSP, the number of nonequilibrium branches, as well as the modulus and relaxation time in each individual branch, can be determined by fitting the model prediction with the experimental DMA results shown in Figure 3 [7]. For the 1D multi-branch linear model, the temperature dependent storage modulus $E_s(T)$, loss modulus $E_l(T)$ and $\tan\delta(T)$ are respectively expressed as:

$$E_s(T)=E_{eq}+\sum_{i=1}^{n}\frac{E_i w^2\tau_i^2}{1+w^2\tau_i^2}, \tag{S4a}$$

$$E_l(T)=\sum_{i=1}^{n}\frac{E_i w\tau_i}{1+w^2\tau_i^2}, \tag{S4b}$$

$$\tan\delta(T)=\frac{E_l(T)}{E_s(T)}, \tag{S4c}$$

where w is the testing frequency. For the convenience of operation, we assume that the relaxation times in the rubbery branch increase in a tenfold sequential. During the NLREG analysis, nonequilibrium branches are gradually added into the model to improve the prediction, and the branch number is finally determined when the NLREG estimations (shown as dash lines in Figure 3) could capture the experimental storage and tanδ curves within the entire testing temperature range (5° C-95° C). By using the determined TTSP parameters, the shift factors were calculated by using Eq. S3 and plotted in Figure 3b as a function of temperature. The final set of model parameters are then listed in Table 1.

References

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