

Supplementary Materials for:

Cyclic Behaviors of Amorphous Shape Memory Polymers

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1. Influence of Deformation on the Shift Factors
2. Influence of loading rates and temperatures to the maximum stress before unloading.

S1. Influence of Deformation on the Shift Factors

Previous studies [1-5] revealed that the stress induced dilatation in polymer network will affect the mobility of molecular chains by changing the free volume, which consequently change the time scale of the polymer response. The combined influence of temperature and stress on the free volume can be formulated as [1]:

$$f = \frac{v_f}{v_0} = f_0 + \alpha_T \Delta T + \varepsilon_v, \quad (\text{S1})$$

where f is the fractional free volume defined in terms of total volume of the solid v_0 and the free volume v_f , f_0 is the fractional free volume at the reference condition, ΔT is the temperature change (from T_0 to T), α_T is the thermal expansion coefficient, and ε_v is the volumetric strain, which is given by $\varepsilon_v = \frac{1}{3} \frac{\sigma_{ii}}{K}$ with σ_{ii} being the first stress invariant.

The free volume can be correlated with the shift factor by [1]:

$$\log \alpha_T(T) = \frac{B}{2.303} \left(\frac{1}{f} - \frac{1}{f_0} \right), \quad (\text{S2})$$

where B is a constant.

Combining Eq. S1 and S2 we have:

$$\log \alpha_T(T) = - \frac{B}{2.303 f_0} \left(\frac{\alpha_T(T - T_0) + \varepsilon_v}{f_0 + \alpha_T(T - T_0) + \varepsilon_v} \right). \quad (\text{S3})$$

It can be noted that under the assumption of small deformation with negligible volumetric strain, Eq. S3 reduces to the Williams-Landel-Ferry (WLF) equation in linear viscoelasticity as applied in the paper:

$$\log \alpha_T(T) = - \frac{C_1 (T - T_M)}{C_2 + (T - T_M)}. \quad (\text{S4})$$

By equalizing Eq. S3 with S4 with $\varepsilon_v = 0$, $T_M = T_0 = 85^\circ C$, $C_1 = 10.44$, $C_2 = 15.6^\circ C$, and $\alpha_T = \alpha_r = 2.893 \times 10^{-4}$, we are able to determine the corresponding parameters: $B = 0.1085$ and $f_0 = 4.513 \times 10^{-3}$.

Eq. S3 indicates that the influence of stress induced dilatation can be quantified by using volumetric strain ε_v . SMPs are usually treated as incompressible materials with Poisson's ratio approximating 0.5. This assumption is reasonable when the polymers are subjected to small deformation, and the associated constitutive models adequately capture the experimental observations [6]. However, when large deformation is encountered, volume strain might be big enough to render noticeable changes in shift factors, and consequently changes the thermodynamical behaviors of SMPs.

In the following, we will examine how the shift factor will be changed when the epoxy SMP is stretched by 60% during the programming step. Since currently there is no critical examination of how the Poisson's ratio of polymers can be affected by the strain amplitude, we perform the following estimation based on the stress state and bulk modulus of SMPs: For the epoxy polymer, the typical bulk modulus is $\sim 6\text{GPa}$ [7], and it exhibits weak temperature dependency [6]. In our previous study [8], the stress-strain behavior of the epoxy SMPs was tested at different temperatures (from $100^\circ C$ to $130^\circ C$), where the maximum tension stress was $\sim 0.9\text{ MPa}$ when the material was stretched by 60%. Thus, the maximum volume strain introduced during the programming step of SMP is $\sim 1.5 \times 10^{-4}$ (according to $\varepsilon_v = \sigma_{ii}/3K$).

Table S1 listed the temperature dependent shift factors calculated by using Eq. S3 and S4, as well as their difference. It is seen that when we consider the influence of programming deformation, the shift factors will be decreased. But the difference between

the two shift factors is minimal, especially at higher temperatures. This means when the SMPs are programmed at high temperatures, the free volume increment contributed from stress dilatation is minimal compared with that from thermal energy. Therefore, we can safely assume the programming deformation (60% used in this study) will not noticeably affect the thermodynamical behaviors of SMPs. However, it is also seen the difference between the two shift factors is increasing as we decrease the temperature. In this case, caution should be taken if the SMP is programmed at low temperatures with large programming deformation, and the associated shift factors should be calculated by Eq. S3.

Table S1. Temperature dependent shift factors calculated from Eq. S3 and S4

T	$\alpha_T(T)$ from Eq. S3	$\alpha_T(T)$ from Eq. S4	Difference
<i>100 °C</i>	7.62×10^{-6}	7.21×10^{-6}	5.37%
<i>110 °C</i>	3.72×10^{-7}	3.61×10^{-7}	3.09%
<i>120 °C</i>	6.00×10^{-8}	5.88×10^{-8}	2.00%
<i>130 °C</i>	1.76×10^{-8}	1.74×10^{-8}	1.41%
<i>140 °C</i>	7.35×10^{-9}	7.28×10^{-9}	1.04%

S2. Influence of loading rates and temperatures to the maximum stress before unloading.

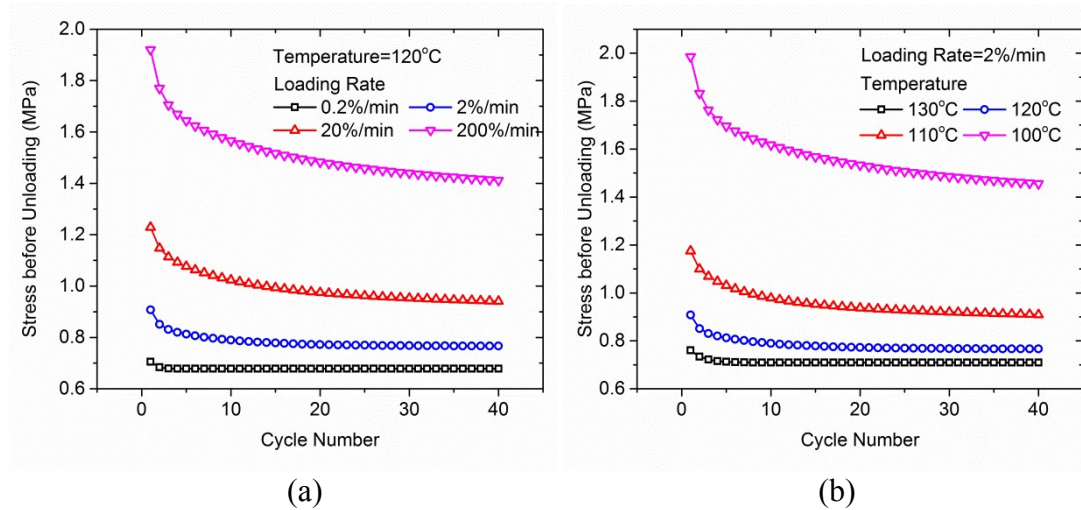


Figure S1. Effects of loading rates (a) and temperatures (b) to the maximum stress before unloading.

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