Shape memory epoxy: Composition, structure, properties and shape memory performances

Ingrid A. Rousseau* and Tao Xie*

*Corresponding Author: ingrid.rousseau@gm.com, Tel: 586-986-0638

Supplementary Equations

\[ L_d^d(N) = L_o(N) + \Delta L_{\text{def}}(N) \]  
\[ L_m^m(N) = L_o(N) + \Delta L_{\text{def}}(N) - \Delta CLTE_{\varepsilon_m} - \Delta L_{\text{rel}}(N) \]  
\[ L_u^u(N) = L_o(N) + \Delta L_{\text{def}}(N) - \Delta CLTE_{\varepsilon_m} - \Delta L_{\text{rel}}(N) - \Delta L_{u\text{rel}}(N) \]  
\[ L_r^r(N) = L_o(N) + \Delta L_{\text{def}}(N) - \Delta CLTE_{\varepsilon_m} - \Delta L_{\text{rel}}(N) - \Delta L_{u\text{rel}}(N) + \Delta CLTE_{\varepsilon_m} + \Delta L_{\text{rec}}(N) \]

In Eqs. (S1) through (S4), \( \Delta L_{\text{def}} \) denotes the change in length of the sample imposed by the deformation. \( \Delta L_{c\text{rel}} \) and \( \Delta L_{u\text{rel}} \) represent the change in length of the sample due to strain relaxation upon cooling and unloading, respectively. Finally, \( \Delta L_{\text{rec}} \) stands for the change in sample length occurring during strain recovery in the last step of the SMC. The apparent CLTE of our epoxies was shown to be a function of \( \varepsilon_m^d \). Therefore, the CLTE adopts specific values at \( \varepsilon_u \) and \( \varepsilon_m^d \): CLTE_{\varepsilon_u} or CLTE_{\varepsilon_m}, respectively. Furthermore, \( \Delta L_{\text{def}} \) can be expressed as follows:

\[ \Delta L_{\text{def}}(N) = L_o \left( \varepsilon_m^d(N) - \varepsilon_o(N) \right). \]  

During a shape memory cycle, the strains adopted by the samples can be defined by:

\[ \varepsilon_o(N) = \frac{L_o(N) - L_o}{L_o}, \]  
\[ \varepsilon_m^d(N) = \frac{L_m^d(N) - L_o}{L_o}, \]
\[ \varepsilon_u(N) = \frac{L_u(N) - L_o}{L_o}, \quad (S8) \]

and,

\[ \varepsilon_p(N) = \frac{L_p(N) - L_o}{L_o}. \quad (S9) \]

By substituting Eqs. (S8) and (S9) in Eq. (3) for the shape fixity and by substituting with Eqs. (S1) and (S3), \( R_f \) becomes:

\[ \frac{R_f}{100} = \frac{L_m^d(N) - L_o - \Delta T \cdot CLTE_{\varepsilon_m} - \Delta L_{rel}^c - \Delta L_{rel}^u}{L_m(N) - L_o}. \quad (S10) \]

Eq. (S7) allows for \( R_f \) to be rewritten:

\[ \frac{R_f}{100} = 1 - \frac{\Delta L_{rel}^c + \Delta L_{rel}^u}{L_o e_m^{d}(N)} - \frac{\Delta T \cdot CLTE_{\varepsilon_m}}{L_o e_m^{d}(N)}, \quad (S11) \]

where the second term in the right hand side is negligible (<<1).

**Supplementary Figures**

Figure S1  Schematic representation of the evaluation of the shape memory variables (deformation temperature \( T_d \), setting temperature \( T_s \), storage moduli at \( T_d \) and \( T_s \) (\( E'_d \) and \( E'_s \), respectively), and transformation temperature \( T_{trans} \)) determined from the equilibrium mechanical data (storage modulus \( E' \), loss modulus \( E'' \) and loss angle (\( \delta \)), glass transition temperature \( T_g \)) measured for each epoxy SMP.
Figure S 2  Effect of increasing the number of consecutive shape memory cycles (N) on (a) the shape fixity ($R_f$), (b) and (c) the shape recovery ($R_{\text{r min}}$) and ($R_{\text{r} u}$), respectively, of our epoxy SMPs. The shape recovery and shape fixity reach stable values after the first cycle is completed except for E-C10, which incorporates flexible pendant decyl chains. This is likely due to a rearrangement of the decyl chains during the deformation stage which disables them from
recovering their original state during the recovery stage.
Figure S 3  Effect of the deformation strain $\varepsilon_u(N)-\varepsilon_o(N)$ on (a) the recovery speed ($V_r$) and (b) the recovery time ($t_r$) for the shape memory epoxies. Four successive shape memory cycles were performed on each sample, each under increasing deformation strains. $V_r$ varies linearly with the recoverable strain ($\varepsilon_u(N)-\varepsilon_o(N)$), and $t_r$ varies accordingly.
Figure S 4 Influence of the recovery heating rate on (a) the temperatures at which 10 and 90% strain recovery are achieved (T_{10%} and T_{90%}, respectively) and (b) the response temperature (T_r).
Figure S 5  Influence of the recovery heating rate on (a) the recovery speed and (b) the recovery time of the epoxy SMPs. Above 10 °C/min, $V_r$ and $t_r$ leveled off most likely as a result of low heat transfer which became the limiting factor for the shape memory response.