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Stress Memory Materials and Their Fundamental Platform

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1. Symbol List

T_m-SMPU	Shape memory polyurethane with crystalline soft-segment
T_g-SMPU	Shape memory polyurethane with amorphous soft-segment
T_g	glass transition temperature of soft-segment in SMPU
T_m	melting temperature of soft-segment in SMPU
T_{tran}	transition temperature of soft-segment in SMPU
ε_T	total strain
ε_{ps}	plastic strain
ε_v	viscoelastic strain
ε_m	memory strain
ε_e	elastic strain
ε_t	thermal strain ε_t (expansion or contraction)
σ_T	total stress
σ_e	elastic stress
σ_v	viscoelastic stress
σ_m	previously perceived memory stress
σ_t	stress caused by thermo-expansion or contraction
σ_P	pure input programming stress and $\sigma_P=\sigma_R+\sigma_{SR,}$
σ_{RC}	recovery-stress
σ_{SR}	shape recovery stress for recovering the fixed shape only
σ_R	memory stress controlled by rubbery-switch due to entropy change in rubbery matrix
σ_C	memory stress controlled by crystal-switch due to crystal transition
σ_M	temperature sensitive stress or true memory stress

2. Experimental Section

Materials and Sample Preparation

The T_m type shape memory polyurethane (T_m-SMPU) was synthesized in-house by using polycaprolactone (PCL, M_n=4000 g/mol) to form the soft segment and methylene diphenyl diisocyanate (MDI) with its extender butanediol (BDO) to form the hard segment. The ratio of hard segment (MDI+BDO) to soft segment (PCL4000) was 28/72 (weighted ratio). For the T_g type shape memory polyurethane (T_g-SMPU), the soft segment consisted of poly(tetramethylene ether) glycol (PTMEG, Mn=250 g/mol + 650g/mol), with the hard segment being the same with that of the T_m-SMPU. The ratio of hard segment (MDI+BDO) to soft segment (PTMEG250+650) was 67/33 (weighted ratio). The SMPU samples were dissolved into dimethylacetamide (DMAC) and subsequently prepared by film formation in oven at 80^{o}C for at least 24 hours to remove the solvent. The samples were then cut into a rectangular shape with a gauge length of 4.5 mm, a width of 0.8 mm and a thickness ranging from 200 to 300 μm. Rubber specimen was cut from natural rubber tubing and the polyamide 6 film was purchased from Xuan Ge Insulating Materials Company in Dongguan, China.

Characterization

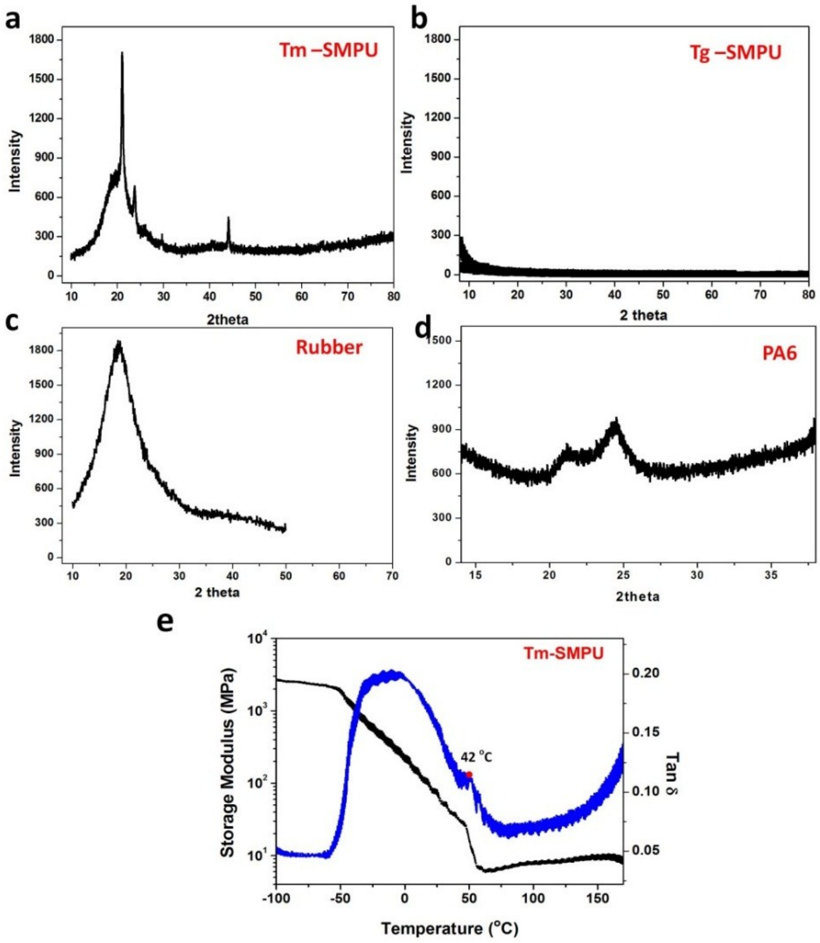

Figure S1. XRD characterization of four samples: (a)T_m-SMPU, (b)T_g-SMPU,(c)rubber and (d)PA6; (e) DMA characterization of T_m-SMPU.

We provide data for the sample structures here which are important for the discussions in the main text. The X-ray diffraction (XRD) were obtained using a Rigaku SmartLab X-Ray Diffractometer. Figure S1 exhibits the XRD curves of the T_m-SMPU, T_g-SMPU, rubber and PA6 separately at room temperature without stretching. It can be seen in Figure S1a, that the T_m-SMPU has two distinct diffraction peaks at 21°and 24 ° originating from reflection of the (110) and (200) planes of PCL,[1] which is a semi-crystalline polymer. The crystallinity of the T_m-SMPU is 23% as quantified from the XRD data while Figure S1e shows the existence of a rubbery-matrix with a very low T_g. For the T_g-SMPU in Figure S1b, there is no crystal signal which accords with its amorphous structure. The XRD result in Figure 1c for a rubber also shows the amorphous nature of the rubber. The XRD pattern of the neat PA6 shows both α- and γ-form crystals reflected by the two peaks located at 2θ values of 21° and 24°is shown in Figure S5d, corresponding to (200) and (002) respectively, which may indicate that PA6 is a non-entropy-dominated polymer.

Preconditioning

Before programming, preconditioning was applied to the specimens, in order to remove plasticity and elasticity, in which successive cycles of shape-memory tests were conducted as shown in Figure S2. The tests were carried out in Instron5566 Testing Machine, which was equipped with a temperature controlled oven, as follows; firstly, heating the specimen to a high temperature above T_{tran} and stretching it to a strain of 100%, then holding the specimen at a constant strain at high temperature for at least 30 min to eliminate the viscous stress and finally cooling it to a low temperature below T_{tran} as well as holding for another 30 min for fixation. Upon cooling the specimen below the transition temperature of the soft segments under the load, the deformation could be fixed. The stress had a significant drop when cooling began followed by unloading the stress to zero. By heating the deformed sample when it was under the unconstrained condition, the original shape could be recovered. In this way, the shape recovery ratio could be calculated and the overlap of the fourth and fifth cycles indicates the structure is unchanging. Upon preconditioning, the strain is large enough to cause an irrecoverable change of the polymer network, namely permanent deformation to the disentanglement or slippage of chains in the polymer network. After repeated cycles, the plasticity is removed through perfecting and stable molecular structures.

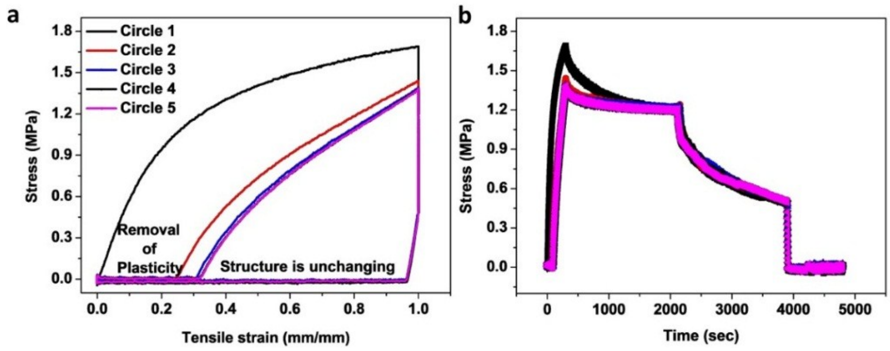

Figure S2. (a)Stress-strain and (b)Stress-time curve of T_m-SMPU during preconditioning.

Programming and Stress Memory Behaviors Testing

- Clamping the sample with two ends by holders and heating at 80°C for at least 15 mins to eliminate thermal history.
- Heating the samples to the prescribed temperature (programming temperature, T_p) which is above the transition temperature (T_{tran}) of soft segments (65°C for the T_m-SMPU, rubber, and polyamide 6 (PA6), 75 °C for the T_g-SMPU).
- Stretching the sample to certain strains of 20% with an extension rate of 1 mm/min.
- Cooling the sample to room temperature 20°C after a period of relaxation (the sample was held isothermally) at T_p.
- Conducting the cyclic confined shape recovery tests by only changing temperature, which means all the stress memory tests were under constant strain~~s~~, following a hot programming process and a period of stress relaxation.

Direct observation of Stress Memory Behaviour

Rubber can store energy as demonstrated in the famous Rubber-Band-Engine. Direct comparison of stress storage power of the T_m-SMPU with rubber can be seen in the Supplementary Movies 1 and 2. Two samples of the same size were with stretched and fixed shapes are under the same load of 50g and 500g respectively. It can be seen that the memory-stress difference between the rubber and T_m-SMPU is very obvious. In fact is about 70 times different as calculated using the data in the main text as shown Figure 1c. The magnified stress-memory effect of the T_m-SMPU can be seen in Supplementary Movie 3.

3. Definitions and relationships of stresses in SMPs

Derived from previous work,[2] there are five components in a thermally-responsive SMP during a thermomechanical process: (1) plastic strain ε_{ps}, (2) viscoelastic strain ε_v, (3) memory strain ε_m, (4) elastic strain ε_e and (5) the thermal strain ε_t (expansion or contraction upon heating or cooling). Hence, the total strain ε_T can be expressed as:

$$\varepsilon_T = \varepsilon_{ps} + \varepsilon_v + \varepsilon_m + \varepsilon_e \pm \varepsilon_t \tag{S1}$$

Since plastic strain ε_{ps} has no stress term, correspondingly, the total stress σ_T for a specimen in a cyclic thermomechanical process can be:

$$\sigma_T=\sigma_e+\sigma_v+\sigma_m\pm\sigma_t \tag{S2}$$

$$\sigma_P=\sigma_T-\sigma_e-\sigma_v\pm\sigma_t=\sigma_m \tag{S3}$$

where σ_e is the elastic stress, σ_v is the viscoelastic stress, σ_m is the previously perceived-memory-stress, and σ_t is the stress caused by thermo-expansion. σ_e was eliminated by programing and σ_v by stress relaxation, thermo-expansion stress $\pm\sigma_t$ were very small (9.8% in Tg-SMPU and 3.6% in Tm-SMPU of maximum memory stress) and can be neglected [2]. Thus, σ_P represents pure input programming stress for stress-memory or shape-fixing. We define $\sigma_{SR,}$ the stress to recover the fixed shape, thus called shape-recovery-stress, as shown in Figure 1a. With these treatments, we can focus on the analysis of $\sigma_{m,}$ the perceived-memory-stress. If all pure input programming stress for fixing the shape can be memorized in a SMP, $\sigma_m=\sigma_{SR}=\sigma_{P.}$ However, in our results, σ_m is not equal, but related to shape-recovery-stress σ_{SR} as illustrated in Figure 1a:

$$\sigma_m=\sigma_{RC}=\sigma_R+\sigma_{SR}=\sigma_P \tag{S4}$$

Even the recovery-stress, $\sigma_{RC,}$ which is the stress measured for shape-recovery, is not equal to shape-recovery-stress, $\sigma_{SR,}$ which is what is actually required to recover the fixed shape, due to the existence of a rubbery component, smaller than σ_{RC}. For easy examination, σ_M is utilized to present the true-memory-stress, that is, temperature-sensitive-stress we define in the current paper, differentiating from the perceived one σ_m. For the T_m-SMPU,

$$\sigma_M=\sigma_m=\sigma_R+\sigma_{SR}=\sigma_C+\sigma_R=\sigma_P \tag{S5}$$,

where σ_C is from the crystal-switch. If $\sigma_C=\sigma_{SR}$, the shape-recovery-stress σ_{SR} can be totally memorized by the crystal transition. As a result, the memory-stress equals to the input programming stress as well as the sum of the memory-stress from the rubbery and crystal switch controls in the T_m-SMPU.

It may be intuitive to reason that the T_g-SMPU should have similar stress behavior as the T_m-SMPU since there is a shape-fixation-stress for both the T_g-SMPU and T_m-SMPU whose shape-memory effects are equally as good. However, from our observations as shown in Figure 1c, in the T_g-SMPU, even though σ_{SR} can fix a shape, this part of the input programming stress cannot be responsive to temperature at all, thus is not memorized. Instead, there is only a small $\sigma_M=\sigma_{R,}$ which is from the rubbery matrix controlled by an entropy change responsive to temperature. From Figure 1c and Figure 3e, surprisingly and first time, it is discovered that the T_g has nothing to do with stress memory. Moreover, even though the T_g cannot lead to stress-memory, there is still a temperature-sensitive stress, an extra stress component, namely, $\sigma_{R,}$ from the rubbery entropy change in the rubbery-matrix, existing during cyclic thermomechanical process in the T_g-SMPU. Thus the relationship $\sigma_m=\sigma_{SR}=\sigma_P$ does not hold. For the T_g-SMPU, σ_{SR} may be controlled by kinetic energy from the glass transition and chain Brownian movement and the equation

$$\sigma_P=\sigma_{SR}+\sigma_R=\sigma_{RC} \tag{S6}$$

means that in the T_g-SMPU, the pure input programming stress is used to memorize a shape and a small amount of stress respectively. The key component, $\sigma_{SR,}$ can differentiate shape-memory from stress-memory. When we measure the recovery stress, $\sigma_{RC,}$ the memory-stress is included in addition to the stress required to recover the fixed shape, σ_{SR}.

4. Comparison of the Stress memory of the SMPUs and the Rubber

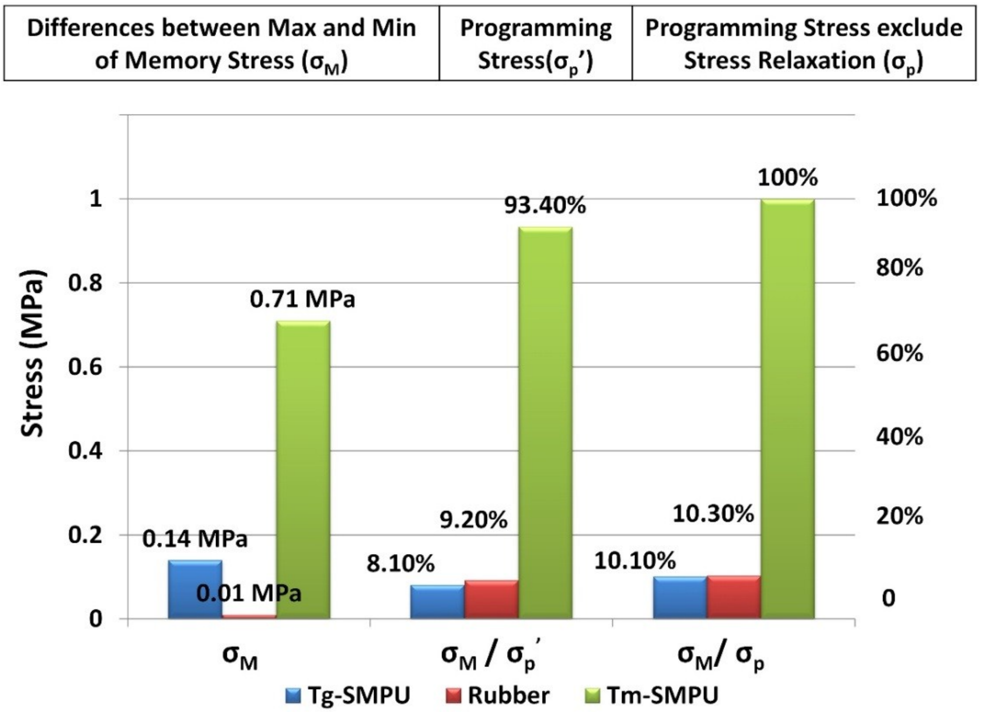

Figure S3. Comparison of the stress-memory ability of the T_g-SMPU, T_m-SMPU and Rubber: σ_M represents the difference between the maximum and minimum of temperature-sensitive stress in the cycles. The σ_p' denotes the programming stress before the relaxation.

Calculated from the results in Figure 1c and shown in Figure S3, 100% of σ_M/σ_p indicates that the stress can be completely memorized from programming. In fact, the memory-stress of T_m-SMPU is 70 times that of the rubber, thus the PCL soft segment T_m-SMPU is a very effective energy storage material due to its semi-crystalline nature, which can memorize a large stress, sensitive to temperature.

5. Thermomechanical stress-strain relationship of the SMPs in the Rubbery and Plastic States

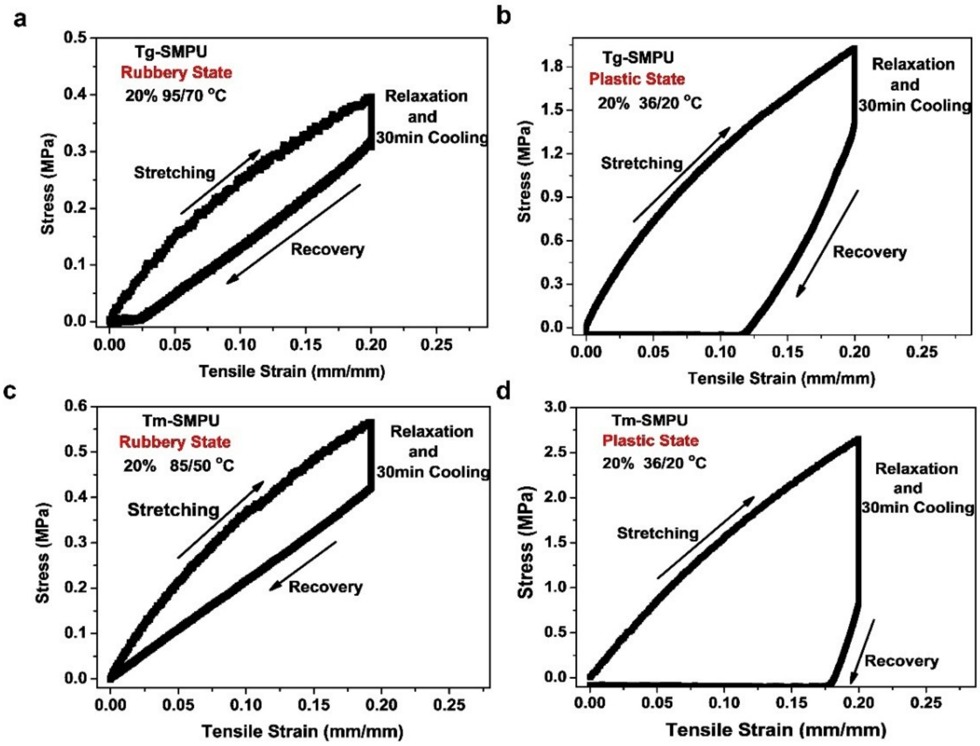

Figure S4. Stress-strain relationship of the T_g-SMPU and the T_m-SMPU with 20% strain in different processing and memory testing states: (a) and (c) in the rubbery state. (b) and (d) in the plastic state.

In order to understand whether the SMPs have rubbery behaviour, we obtained their stress-strain relationship as above in their rubbery-states in a thermodynamic cycle. For the T_g-SMPU, in temperature range between 70 and 95°C in Figure S4a, the sample stays in the rubbery-state all of the time where the shape fixity is close to zero. For the T_m-SMPU, fixity is even more so, that is, zero at 50 °C shown in Figure S4c. Even though they are not always perfect, these data give indications that they have little fixity which is the normal behavior of a rubber. On the other hand, in the plastic-state, the thermomechanical process is within the temperature range of 36 °C and 20°C, and the two materials demonstrated plastic deformation which cannot be recovered with temperature below their respective transition temperature, T_m=45 °C and T_g=50 °C shown in Figure S4b and d.

6. Thermodynamic analyses on Programming and Stress-Memory of the SMPs

As shown in Figure S5, external heating Q and stretching W are two ways of adding energy to the polymer system. Firstly, heating around the memory-state temperatures makes network transfer from the plastic-state to the rubbery-state, either through a Tg transition or crystal transition in SMPUs, so there is an increase in the conformational entropy or/and enthalpy respectively. In this original shape after heating, the molecular chains of the SMPUs adopt the highest entropy state. Then stretching during programming adds external work to the polymer system leading to a potential energy increase, but this induces chain orientation and entropy loss in turn. The potential energy above the T_{trans} is later kinetically trapped due to freezing molecular chains in the soft segments and is used as a strain constraint for stress-memory while there is a lower entropy energy state in rubbery chains, $T\Delta S_1$, and/or enthalpy, ΔH_2 from crystal melting when available,[3] are also stored in the SMPs by cooling for later use.

As the temperature increases, retraction of the elastic network controlled by hard segments and recoil of chains in soft segments will be driven by entropic energy. Thus polymer chains in rubbery-state of soft segments release the stored entropic energy $T\Delta S_1$ companied with ΔH_1 from the rubbery-matrix, then the enthalpic energy, ΔH_2 from crystal melting. When relaxation and thermal expansion are excluded, as the sample will not perform any work due to its confined shape, the stress-temperature effect can be understood by energy transformation between programming and stress memory. Figure S5 is a schematic to present the equivalency of programming and stress-memory. It should be noted that, in this present work, the stress-memory is demonstrated essentially from rubbery chains in the SMPs. Thus the thermodynamics of elastomers should apply. At the top of this balance is the equation showing the relationship between the entropy change at constant temperature with respect to length change and the stress change with respect to temperature. The sources of the changes are due to the energy terms under these two arms respectively.

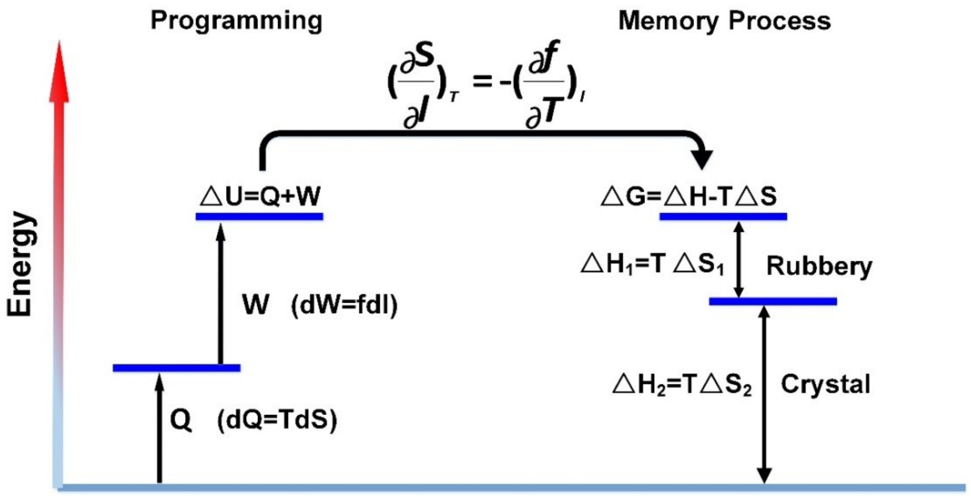

Figure S5. Schematic of the energy transformation from the programming to the memory-process

Based on the first law of thermodynamics, since SMPs deformation in our work can be roughly regarded as taking place at constant volume, the relationships of $\mathrm{dW} = -f\mathrm{d}l$ and $\mathrm{dQ} = T\mathrm{d}S$ can be obtained, where T is the thermodynamic temperature and dS is the change in entropy of the system. When rubbery chains in SMPs are considered only during programming and memory processes, the Maxwell relation applies:

$$(\frac{\partial \mathrm{S}}{\partial l})_T = -(\frac{\partial f}{\partial T})_l \qquad \text{(S7).}$$

The Equation S7 first shows that entropy change caused by deformation is the main way to store stress into rubbery chains in SMPs. Secondly, the entropy change with length at the constant temperature is equivalent to the temperature-responsive stress at a constant length. This guarantees that the memory-stress can be induced by the entropy change in the rubbery chains of the SMPs.

7. Memory-stress in SMPs is from entropic energy of rubbery chains

When a SMP is in rubbery-state, which is above its T_g or T_m, the stress with strain constraint will drop as the temperature decreases or vice versa. This phenomenon can be directly related to the formula below. [4] Applied stress to specimen can be expressed by combining internal energy and entropy

$$f=\left(\frac{\partial U}{\partial l}\right)_T-T\left(\frac{\partial \mathrm{S}}{\partial l}\right)_T \tag{S8}.$$

Under a certain temperature, in the Equation S8, the first term represents the change in internal energy with extension and the second refers to the change in entropy with extension. From Equation S7, we can obtain

$$f=\left(\frac{\partial U}{\partial l}\right)_T+T\left(\frac{\partial f}{\partial T}\right)_l \tag{S9},$$

which is used to calculate the stress required to hold the sample under strain constraint at different temperature conditions. In rubbery-matrix, rubbery and near-rubbery state of a SMP, entropy plays a dominant role in stress decision, the value of (∂U/∂l) should be small and negligible, then

$$f\approx T\left(\frac{\partial f}{\partial T}\right)_l \tag{S10}$$

The Equation S10 is the constitutive relation for stress-memory in SMPs where rubbery chains exist in soft segments and are sensitive to temperature due to entropic energy change. This conclusion is from rubber, which has the behavior of cooling induces stress to decrease and heating causes stress to increase, and called thermo-elastic effect.[4] It needs to clarify that in most polymer materials, internal energy contributes the most to the stress, particularly semi-crystalline polymers, [5] which is applicable probably more to non-entropy dominated cases. Here we treat the crystal transition as an intrinsic behavior of rubbery chains in SMPs as reported on shape-memory effect in rubbers, [6] then we ignore the internal energy term $\left(\frac{\partial U}{\partial 1}\right)_T$ in Equation S9 and use Equation S10 to represent the stress-memory. This internal energy term is actually included in ΔH_2, enthalpy from crystal transition, which contains ΔU according to the definition of enthalpy itself, namely H=U+PV. Our treatment can simplify the analyses enormously and it is true as shown in our experiments and literature.[4] More interestingly, it can be observed from Figure 3d, that the stress-strain curve of Tm-SMPU in memory-state is very similar to rubbery-state. This gives us more confidence to use elastomer theory to SMPs. Besides, it has been proved that fast heating promotes instant increase of the entropy in rubbery-switch, while slow heating gives the chance and time for molecular chains to escape from crystal domains.[7] Due to the hinder of crystals, extra movements are restricted until further increasing temperature and most of energy is released. That is why the rubbery-switch is quicker than crystal-switch in T_m-SMPU. Thus the fast decreasing straight line with 0.1 MPa in Figure 3g in memory-stress indicates the entropy change while subsequent decrease implies the fold, rearrangement and crystallization. All these changes are still the behavior of rubbery chains at different states in SMPs.

Supplementary Information References

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