Shape Memory Polymers

Functional and Smart Materials course
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Shape memory polymers (SMP)

- Shape memory principles
- Applications
- Production and polymer types
Shape memory polymers

- Polymers show elastic moduli that range from bakelite (similar to a silica-glass) to the softer rubbers.
- Shape Memory Polymers (SMP) both characteristics
- They show a glass transition temperature (Tg) with an abrupt change of the elasticity modulus
- At high temperature they are softer and can be deformed (shape change)
- Decreasing the temperature below the Tg they become rigid but keep the deformed shape
- Returning at high temperature they recover the original shape
Elastic modulus variation with temperature

- Glass zone
- Glass transition zone
- Rubber zone
- Fluid zone

Elasticity modulus

$T_g$ Temperature
SMP characteristics

- Radical change from a rigid to an elastomeric polymer
- We can deform the polymer over the Tg up to 200% and freeze the shape below the Tg
- Heating the polymer over the so-called switching temperature (Ts) the polymer without constraints recovers to the original shape
- The Tg can vary between -30°C and +260°C
- Unlimited number of cycles
Example

- **Switching temperature:** 46 °C
- **Recovery at:** 70 °C

\[
\text{butylacrylate + poly(\varepsilon\text{-caprolactone}) dimethacrylate}
\]
SMP working principle

• We need a functionalized polymer to block the deformation to a certain level

• Thermosensitive polymers are used normally

• Shape memory thermoplastic polymers are composed by two distinct blocks or phases
  • One with higher transition temperature ($T_{perm}$) that stabilizes the permanent shape like a physical network
  • the second with a lower $T_{trans}$ (can be a $T_g$ or a melting temperature) that will work as a switch
  • $T_{trans} < T_{perm}$, they deform between $T_{trans}$ and $T_{perm}$
  • $T_{switch}$ is the intermediate temperature at which we can deform them and is determined by a thermomechanical test
The molecular mechanism of the shape-memory effect is described, with a focus on the programming of the temporary shape. The energy for the stretching of a standard volume is given by Equation (3). The segments should be a function of the temperature, and one kind of molecular switch can be used for the fixation of the permanent shape. This can be reached by using the network chains as a thermoplastic shape-memory polymer, as schematically shown in Figure 5 for a linear multiblock copolymer.

The temporary shape is a melting point, strain-induced crystallization, and the permanent shape is fixed by thermal transition. The material can be stabilized in the deformed state in a temperature range that is relevant for the particular application. In this experiment, different test protocols were performed by means of a tensile tester equipped with a thermochamber. The measurements are thermomechanical investigations.

The shape-memory effect can be quantified by cyclic, thermomechanical characterization. The phase with the highest thermal transition at glass transition of the amorphous material is in the temperature range of interest for the particular application. At temperatures above the glass transition of the amorphous material, the polymer re-forms its original shape. Such polymers exhibit a shape-memory functionality if the thermal transition chosen for the fixation of the permanent shape is stabilized by covalent netpoints, whereas the crystallization achieved is always incomplete, which means that a certain amount of the chains remains amorphous. The crystallites formed prevent the segments from spontaneously recovering the permanent shape that is defined by the netpoints. The permanent shape of shape-memory thermoplasts is fixed by the netpoints.
Deformation and recovery

\[\sigma \rightarrow \varepsilon \rightarrow \varepsilon_p, \varepsilon_u, \varepsilon_m\]

\[\sigma \rightarrow \varepsilon \rightarrow \varepsilon_m, T_{\text{trans}}\]