Near Infrared Photo-Sensitive Reversible Shape-Memory Polymers Processable Through 4D-Printing

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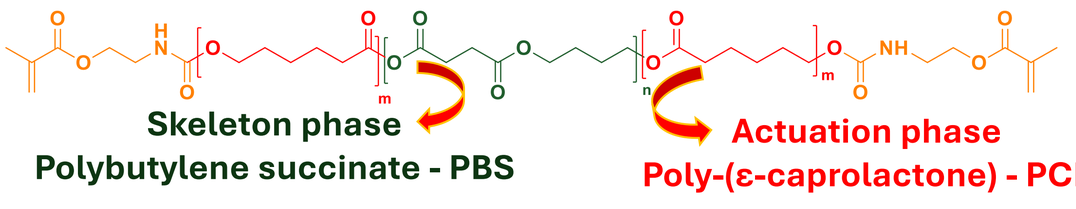
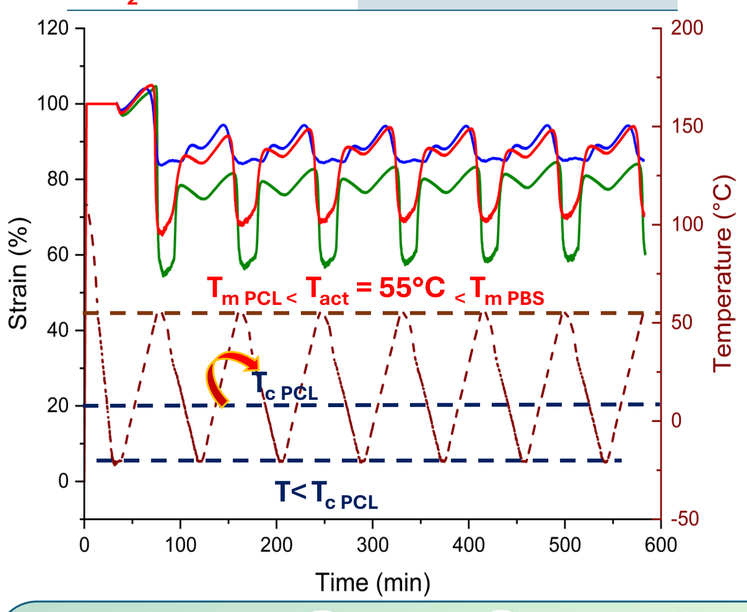
Thermo-responsive shape-memory polymers



These multicrystalline networks can be programmed to change shape by reversibly ***melting*** and ***re-crystallizing*** the ***actuation domain*** through a mechanism of elongation and contraction known as ***CIE*** (crystallization-induced elongation) and ***MIC*** (melt-induced contraction)[1,2].

Code	M_n PCL block	M_n PBS block
S_1	9K	4 K
S_2	3K	



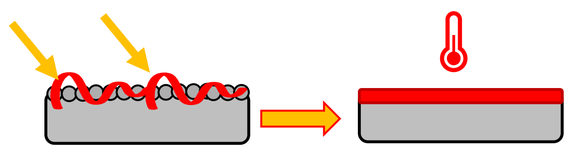
Sample	Composition
Cop_1	75% S_1 – 25% S_2
Cop_2	50% S_1 – 50% S_2
Cop_3	25% S_1 – 75% S_2

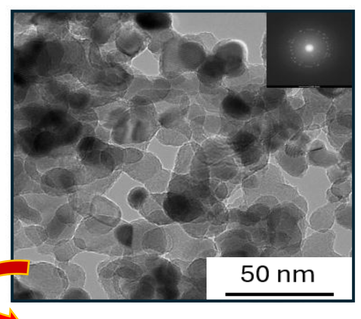
Sample	Actuation	Gel Content
Cop_1	24 %	88 %
Cop_2	18 %	91 %
Cop_3	4 %	90 %

Shape-memory properties of cross-linked copolymers mixtures were evaluated under stress-free conditions, the magnitude of the ***actuation*** represents the amount of elongation registered during the crystallization of PCL phase. Activation temperature was **55°C** to melt just the **PCL** phase and not **PBS**.

Photo-responsive shape-memory polymers

Localized Surface Plasmonic Resonance (LSPR) occurs when an electromagnetic wave interacts with a thin layer of metallic nanoparticles. This interaction leads to localized collective electron oscillations, causing plasmonic nanoparticles to generate significant heat.

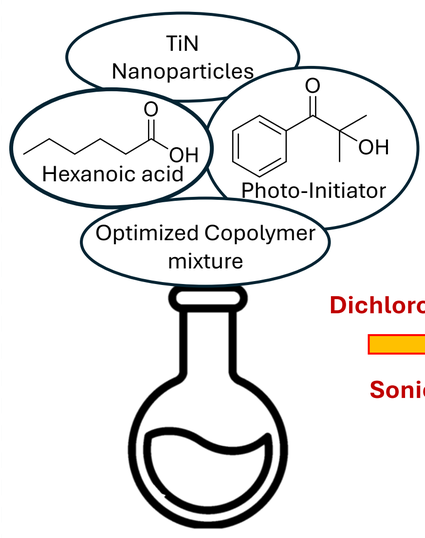




Titanium Nitride cubic nanoparticles
Average dimensions ≈ 20 nm

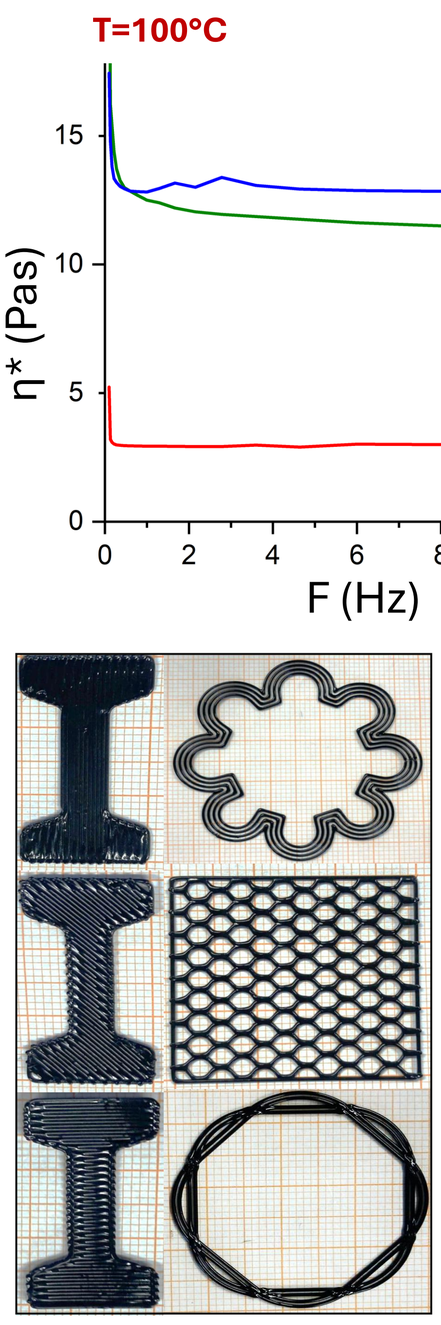
Titanium Nitride (TiN) plasmonic nanoparticles[3] have been incorporated into a polymeric matrix to generate indirect heating[4], which is helpful for activating thermo-sensitive shape memory polymers[5].

Formulation of photo-responsive shape-memory polymers



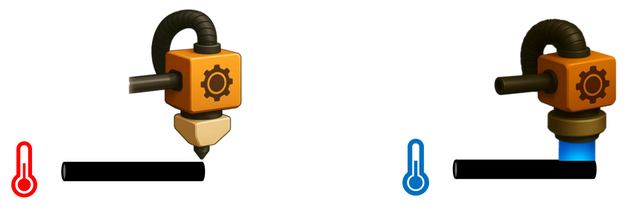
Film doped with 0.5 wt% of TiN nanoparticles

4D-Printing



Neat copolymer mixture
Copolymer + 0.5% TiN + hexanoic acid
Copolymer + 0.5% TiN + after extraction of hexanoic acid

The material has been processed through *Fused Particle Fabrication (FPF)*. The formulation has been firsly dried to remove the hexanoic acid since its presence would drop the viscosity toward too low values.



Optimized Printing conditions

Temperature	100 °C
Pressure	3.5 bar
Speed	7 mm/s

Photo-responsive properties of 4D-printed samples during exposure to solar light simulator.

Sample	Actuation	Gel Content
Sample before extraction	3 %	74 %
Sample after extraction	16 %	/

Properties of photo-crosslinked films

Sample	Actuation	Gel Content
Film before extraction	12 %	75 %
Film after extraction	20 %	/

Thermal activation of shape-memory properties was evaluated cycling the temperature above T_m and below T_C of PCL phase.

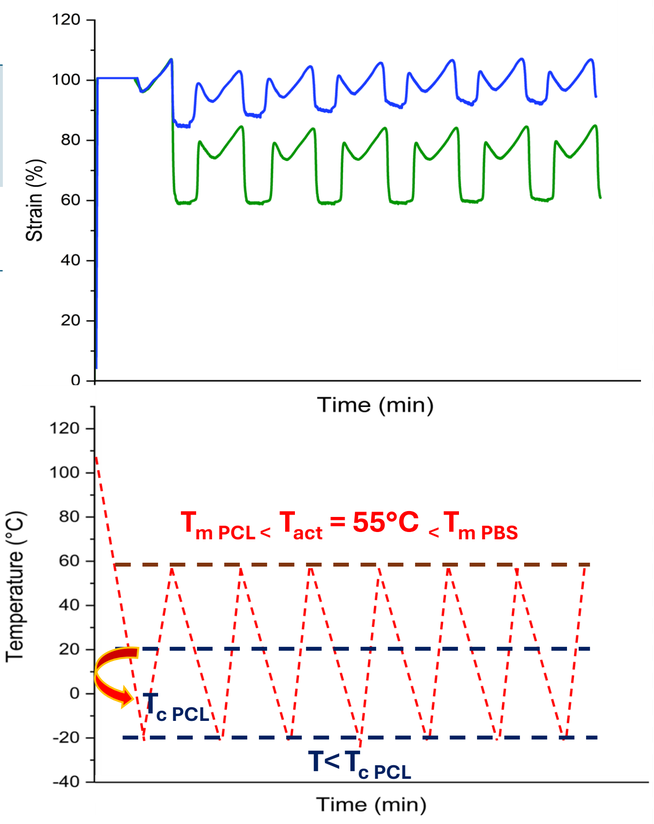
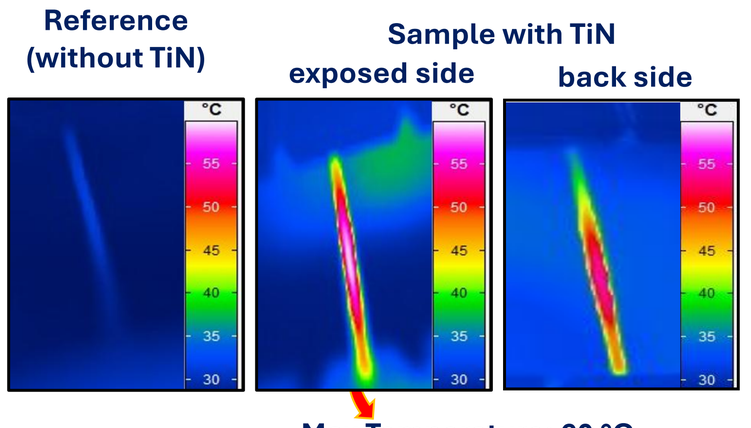
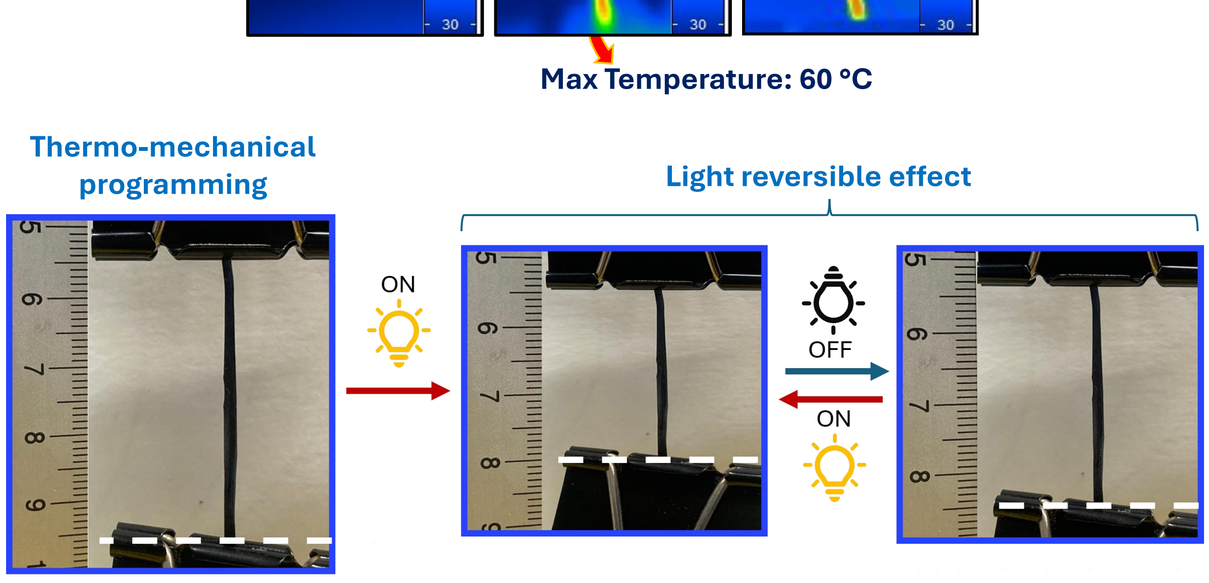


Photo-activation was achieved through a solar light simulator. When ON, the generated heating melted PCL. When OFF, the material equilibrated at RT and PCL re-crystallized.

Heating during exposure to solar light simulator of photo-sensitive formulation cointaning 0.5% wt TiN nanoparticles.





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