**Preparation and Characterization of Triple Shape Memory Composite Foams**

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Electronic Supplementary Information (ESI)

**Scheme S1.** Step-by-step illustration for preparing the triple shape memory composites. Epoxy monomers and PCL were first mixed at 75 °C for 20 min until a clear, homogenous blends was achieved (A). Then the blend was cooled down to room temperature (RT) after which the crosslinker (JD230) was added (B). The blend was mixed again for another 2-3 min. The product, a low viscosity blend was then poured into a salt template (C) and was kept at ambient for 10 min followed by pulling vacuum at 760 mm.Hg for an additional 10 min in to allow the blend to completely diffuse into the salt template and replace the air. The product was then cured at RT for 24 h followed by curing at 40 °C for 3 days after which the salt was distracted. After drying, the product was a porous interconnected foam (G).

**Figure S1.** SEM micrographs of NaCl templates used to fabricate the foams. To improve pore interconnectivity, salt was fused prior to polymer synthesis, as we now describe. About 6 g of salt with 150-300 μm diameter was added to a 20 high density polyethylene (HDPE) vial. The was then placed in a Styrofoam box (9.25 x 6.25 x 8.25 in) with the lid off in which a 2 L water at 40 °C was placed to provide a humidity saturated environment. The salt was kept in Styrofoam for 24 h during which the humidity of this chamber facilitates the fusion of the salt. The salt was then dried under vacuum at 760 mm.Hg for 24 h. Dashed lines represent some of the regions where salt crystals were welded together.
Figure S2. Representative MicroCT image of a triple shape memory foam. A 6.0 mm diameter and 9.0 mm thick disc was scanned using a Scanco Medical μCT40 scanner at voltage of 45 kV and current of 177 μA. Scanning parameters led to a nominal voxel resolution of 12 μm. Porosity of the foam was obtained to be about 73%. Scale bar represents 1.0 mm.

Figure S3. Thermogram traces of (-) D$_{1\,2\,1.5}$N$_{1\,2\,1.5}$PCL10 film, (--) D$_{1\,2\,1.5}$N$_{1\,2\,1.5}$PCL10 foam, (-) N$_{1\,2\,1.5}$PCL10 film and, (--) N$_{1\,2\,1.5}$PCL10 foam.
**Figure S4.** Thermogram traces of (-) D$_{12}^{1.5}$ film, (-), (-) N$_{21}^{1}$ film, (-) PCL and (-) NaCl template.

**Figure S5.** DSC thermograms (2$^{nd}$ heating cycle) of (i) D$_{12}^{1.5}$ film, (ii) N$_{21}^{1}$ film and, (iii) PCL. It is noted that the heat flow magnitude of the DSC thermogram for PCL was scaled down 5 times. Heating rates were 10 $^\circ$C/min and 5 $^\circ$C/min for heating and cooling, respectively.
Figure S6. Tan Delta traces of (i) D₁₁₂₁,₅PCL10 film, (ii) D₁₁₂₁,₅PCL10 foam, (iii) N₂₁PCL10 film and (iv) N₂₁PCL10 foam.

Figure S7. Tensile storage modulus (E') traces of (-) D₁₁₂₁,₅ film and (-) N₂₁ film.
Figure S8. Videos showing water diffusion into (A) $\text{N}_2\text{J}_1\text{PCL10}$ foam and (2) $\text{D}_1\text{N}_2\text{J}_{1.5}\text{PCL10}$ foam. In latter, water permeates from the surface into the bulk of the foam in less than 30 s while in latter it stays on the surfaces of the foam for over 2 min due to different hydrophobicity of the foams.

Figure S9. Representative contact angle micrograph of (A) $\text{D}_1\text{N}_2\text{J}_{1.5}\text{PCL10}$ foam at RT and (B) $\text{D}_1\text{N}_2\text{J}_{1.5}\text{PCL10}$ foam at 45 °C. A video of water droplet permeating into the foam at RT and 45 °C is available in Figure S10. Scale bar represents 1.0 mm.
Figure S10. Videos showing water permeation into (A) D$_{1\,2\,1.5}$N$_{1\,2\,1.5}$J$_{1.5}$PCL10 foam at RT and (B) D$_{1\,2\,1.5}$N$_{1\,2\,1.5}$J$_{1.5}$PCL10 foam at 45 °C. In both cases, water stays on the surfaces of the foam for over 2 min due to hydrophobicity of the foam.

Figure S11. Representative contact angle micrograph of (A) D$_{1\,2\,1.5}$N$_{1\,2\,1.5}$J$_{1.5}$PCL10 foam at RT and (B) D$_{1\,2\,1.5}$N$_{1\,2\,1.5}$J$_{1.5}$PCL10 foam at 45 °C after 20 min of placing the water droplet on the surfaces of the samples. Scale bar represents 1.0 mm.
Figure S12. Triple shape memory characterization of (A) $D_1N_2J_{1.5}$ film and (B) $N_2J_1$ film using one-step fixing. The beginning of the cycles are marked by the asterisk. Samples were deformed at 65 °C (deformation), cooled to -20 °C and unloaded (fixing), followed by continuous heating to 80 °C (recovery). The arrows denote the various stages, specifically (1) deformation, (2) fixing, (3) unloading, and (4) recovery. One step recovery of both samples indicate dual shape memory behavior.

Figure S13. Triple shape memory characterization of (A) $D_1N_2J_{1.5}$ film and (B) $N_2J_1$ film using a two-step fixing method. Samples were deformed at 65 °C, cooled to -20 °C and unloaded (1st fixing), heated to an intermediate temperature and deformed again, cooled to -10 °C (2nd fixing), followed by continuous heating to 85 °C (recovery). The beginning of the cycles are marked by the asterisk. The arrows denote the various stages of a shape memory cycle; specifically (1) deformation, (2) 1st fixing, (3) 1st unloading, (4) 2nd fixing, (5) 2nd unloading, and (6 and 7) recovery. In both cases, sample completely recovered after heating to an intermediate temperature indicating dual shape memory properties of epoxy films.
Figure S14. (I) A Movie showing the sequential recovery of D_{N} J_{1.5} PCL10 foam from compressed and curled shape (temporary shape (A)) to uncurled shape (temporary shape (B)) at 40 °C (water temperature) and to expanded flat shape (permanent shape) in 80 °C (water temperature). The thermocouple reads the actual temperature of inside of the tank. (II) Photographs of sample revealing the transition from shape (A) to (B) to (C).