Supporting Information

3D Printed Bioplastics with Shape-Memory Behavior Based on Native Bovine Serum Albumin

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Table S1. Printability of Different Resin Formulations. The two key parameters for a printable resin using a Form 2 stereolithographic commercial printer are a viscosity lower than 10 Pa·s, and a photo-curing rate based on the storage modulus (G') during the first seconds of UV light irradiation higher than 3 kPa/s.

wt % BSA	wt % Co-monomer	Printable	Viscosity (Pa s)	G' rate of change (kPa/s)[a]
30	-	NO	0.08	0
30	1 wt% PEG-DA	NO	0.1	1.3
30	3 wt% PEG-DA	NO	0.12	1.4
30	**5 wt% PEG-DA**	**YES**	**0.22**	**3.8**
30	**7.5 wt% PEG-DA**	**YES**	**0.23**	**5.1**
30	**10 wt% PEG-DA**	**YES**	**1.3**	**7.8**
30	10 wt% PEG-A	NO	-	-
30	10 wt% PEG-DMA	NO	-	-
Formlabs Clear Resin		**YES**	**1.2**	**4.8**

[a]Based on the first 30 s of irradiation, approximately the time to cure a layer in a Form 2 SLA printer.

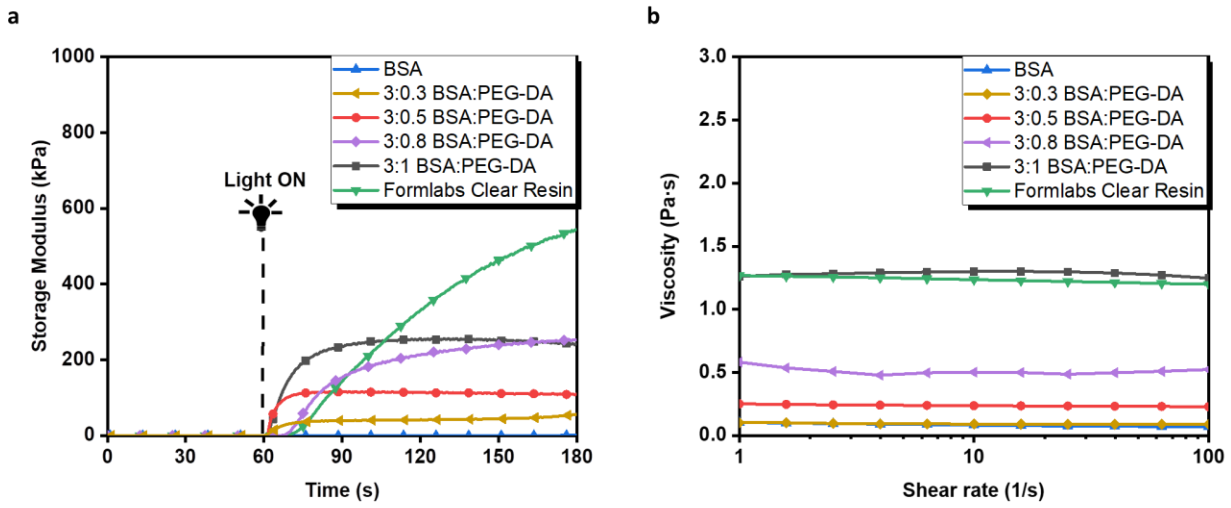


Figure S1. Photo-Curing Rate and Viscosity of Different Resin Formulations. (a) Photo-rheology of the Formlabs clear commercial resin, 30 wt % BSA, 30 wt % BSA with 3 wt % PEG-DA, 5 wt % PEG-DA, 8 wt % PEG-DA, and 10 wt % PEG-DA. All the BSA-based formulations are prepared in DI water, and as last step, the photoinitiating system (0.24 wt % SPS and 0.075 wt % $Ru(bpy)_3Cl$) is added. Light source (365 nm) was turned on after 60 s. (b) Viscosity vs shear rate data for the commercial resin, 30 wt % BSA, and 30 wt % BSA resins with various amounts of co-monomer.

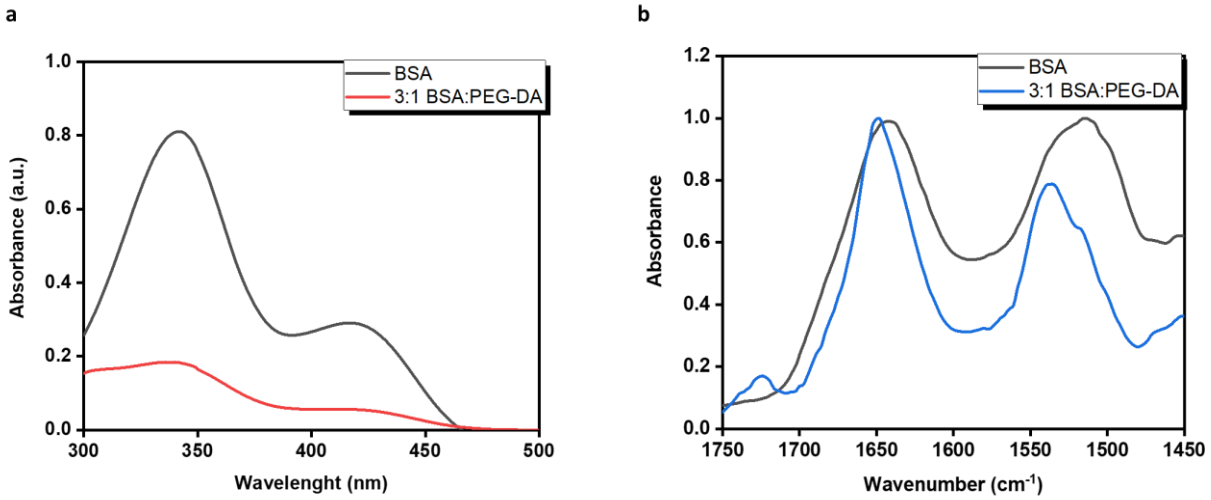


Figure S2. Primary Amine Reaction with the Acrylate Groups. (a) The functionalization was demonstrated using a 2,4,6-trinitrobenzenesulfonic acid (TNBS) assay where primary amines react with TNBS to form a compound that absorbs strongly at 342 nm. It was prepared a resin composed of 30 wt % of BSA, 10 wt % of PEG-DA and 60 wt % of DI water, and after 3 days of dialysis, it was freeze dried to obtain a 3:1 BSA:PEG-DA powder. BSA and 3:1 BSA:PEG-DA were each dissolved in CB buffer at a concentration of 20 µg/mL. 0.25 mL of 0.01 % (w/v) solution of TNBS was added to 0.5 mL of each protein solution. The samples were incubated at 37 °C for 2 hours. To quench the reaction, 0.25 mL of 10 % SDS and 0.125 mL of 1N HCl were added to each sample. The absorbance of each solution was measured at 342 nm, and it could be concluded that the 78 % of the lysine residues present in the BSA had reacted with the PEG-DA (b) The appearance of a peak at 1540 cm^{-1} in the ATR-FTIR spectrum of the 3:1 BSA:PEG-DA formulation, corresponds to the secondary amines formed when the lysine residues on the surface of BSA react with the acrylates of PEG-DA via an *aza*-Michael addition.

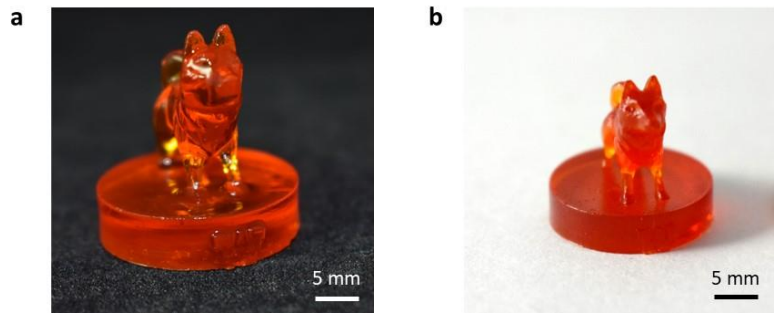


Figure S3. Isotropic De-Swelling of the Printed Hydrogels. The bioplastic retained the same geometries and shapes as the printed hydrogel but with 30 % smaller dimensions after drying. (a) A husky shaped hydrogel just 3D printed. (b) The same husky shape air dried overnight (bioplastic).

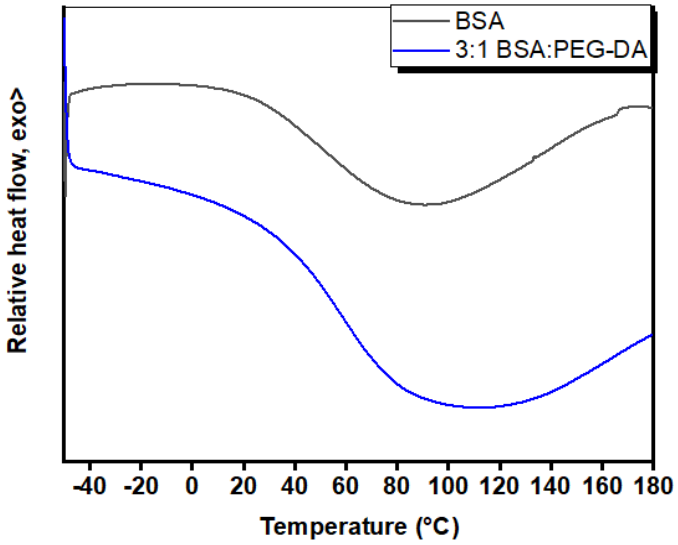


Figure S4. DSC Thermograms Representing the Thermal Denaturation of the BSA. Both BSA in the native state and the BSA-based bioplastics suffer a denaturation process at a temperature above 90 °C. It should be mentioned that the transition temperature was determined using DMTA, due to a superior sensitivity compared to the differential scanning calorimetry (DSC) in materials where the glass transition is so broad.

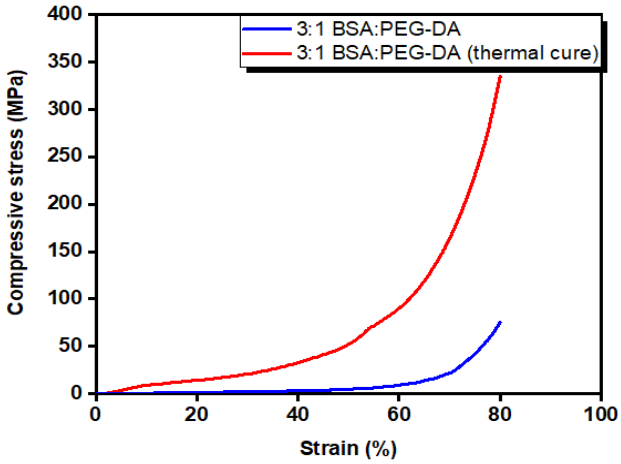
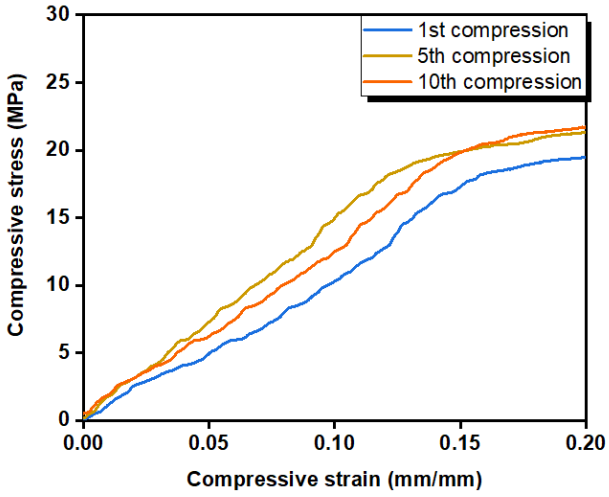


Figure S5. Compression Tests Comparing Heated and Non-Heated Samples. The compressive elastic modulus varies from 10.5 MPa for non-heated samples to 103.5 to heated samples. Likewise, the compressive strength at the 80 % of deformation raises from 75.5 MPa for the dehydrated samples to 334.9 MPa for thermally cured samples.



Compression Cycle Number	Thickness (mm)	Diameter (mm)	Compressive Modulus (MPa)[a]
1	4.4	7.93	83.07
2	4.3	7.93	101.69
3	4.26	7.86	106.29
4	4.11	7.83	130.17
5	4.15	7.82	136.11
6	4.17	7.88	146.02
7	4.25	7.8	152.84
8	4.22	7.85	157.04
9	4.19	7.86	160.22
10	4.16	7.86	162.32

[a]Compressive modulus was determined from the slope of the elastic region of the stress–strain curve.

Figure S6. Mechanical Properties after Various Number of Compression & Thermo-Recovery Cycles. After 10 cycles of compression and recovery of the compression samples (4 mm x 8 mm; thickness x diameter) using heat, the same sample retains the initial compressive modulus with small increases to the compressive modulus with each cycle.

DESCRIPTION OF SUPPORTING VIDEO MATERIAL

Video S1. Shape Recovery of a Compressed Cylinder with Heat. A 3D printed husky dog is on the top of four-dollar quarters, and these, in turn, are on the top of a cylindrical puck that was 3D printed and compressed a 50 % of its initial height. This group is placed on the top of a heating plate that it is at 120 °C, and the shape is able to recover the shape, as well as lift an overall weight of 25 grams in roughly 3 minutes.

Video S2. Shape Recovery of a Compressed Spherical Lattice with Hydration. The 3D printed hollow spherical lattice is compressed a 50 % of its original diameter. Then, this compressed shape is submerged in water, and thanks to the hydration, the spherical lattice regains its printed architecture. The complete recover of the original hydrogel occurs after 30 minutes of hydration.

Video S3. Changing the Shape of a Solid Sphere to Pass through a Rectangular Cavity. The 3D printed solid sphere with an initial diameter of 14 mm is compressed until the height is 9 mm to pass through a rectangular cavity 10 mm in height. After crossing the gate, the ball recovers the shape with the help of a heat gun and goes down the ramp.

Video S4. Shape Recovery of a Stretched W Shape with Heat. The 3D printed w-shaped object that initially has a length of 40 mm, is stretched by hand until a length of 55 mm and then, the shape can be recovered in just 15 seconds when it is placed onto a heating plate at 120 °C.