Supporting Information

Porous polymeric materials by 3D printing of photocurable resin

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Rheological behavior of the ink

Although the three base resins were measured successfully but the current setup cannot measure the viscosity of the ink properly as shown in Fig. S1. Future study on the rheological behavior of the ink may require a rheometer with a sandblasted cylinder measuring system that can reduce wall slipping effects and is designed for measuring slurry.

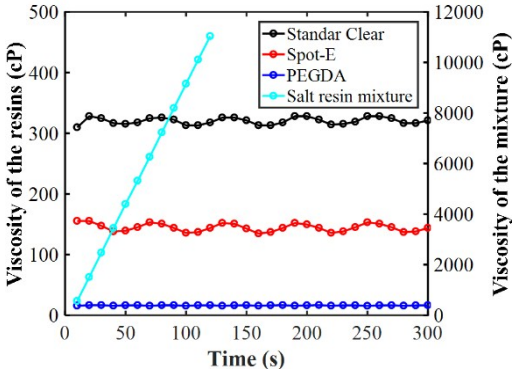


Fig. S1. Rheological testing results showing the viscosity of Standard Clear resin, Spot-E resin and PEGDA resin are 320 cP, 145 cP and 16 cP, respectively. Salt resin mixture (volume ratio 10% salt to 90% Spot-E) is out of the range of our rheometer.

Photo-DSC tests

The photo-DSC tests were conducted by using DSC Q200 as introduced in the main text and the heat flow curves are plotted in Fig. S2. The peak represents the heat flow from the tested sample during light irradiation, and an integral of the curve gives the heat released during polymerization. After integral, the heat released from Standard Clear resin, PEGDA resin and Spot-E resin are 336 J/g, 513 J/g and 343 J/g, respectively. The heat released from Standard Clear ink, PEGDA ink and Spot-E ink are 58 J/g, 87 J/g and 51 J/g, respectively. Since the ink has salt particulates in its composition so that the measured heat released per mass need to be converted according to the mass ratio between salt and resin. After conversion, the heat released from the resins in Standard Clear ink, PEGDA ink and Spot-E ink value are 318 J/g, 495 J/g and 328 J/g, respectively. The extent of crosslinking for each ink is calculated by comparing

the heat released from the pure resin and the heat released from the resin in the ink. As a result, the extent of crosslinking for Standard Clear ink, PEGDA ink and Spot-E ink are 94.6%, 96.4% and 95.6%, respectively. Therefore, we assume the influence of salts on the extent of photocrosslinking can be neglected.

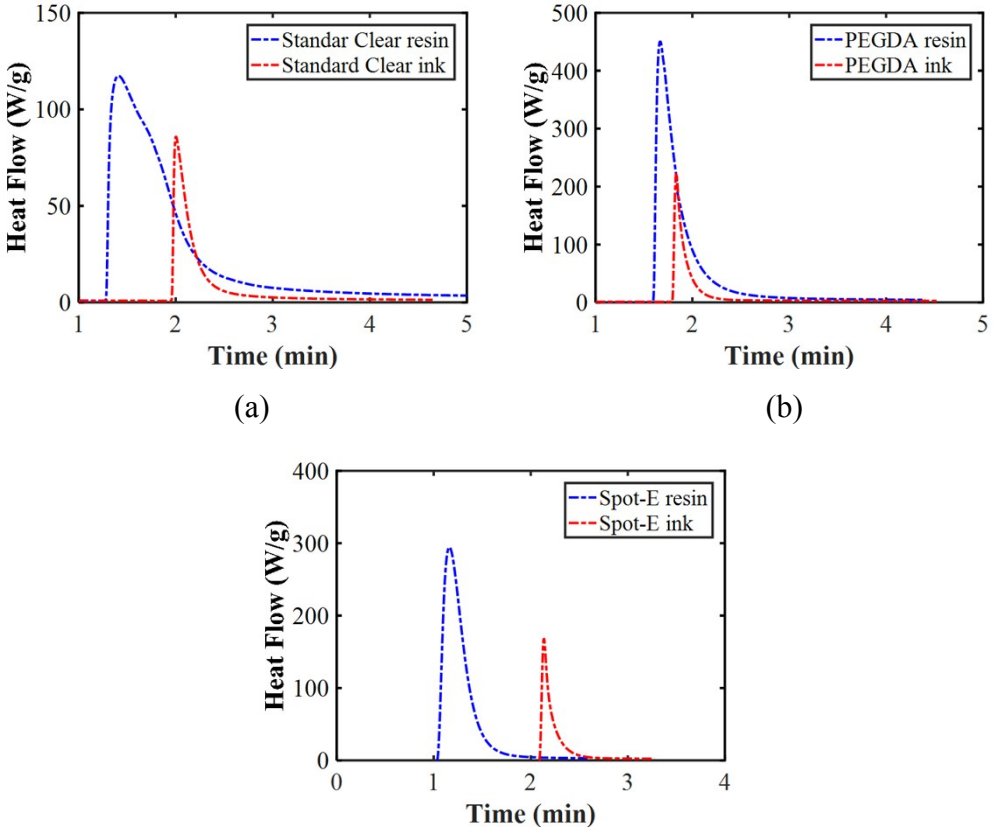
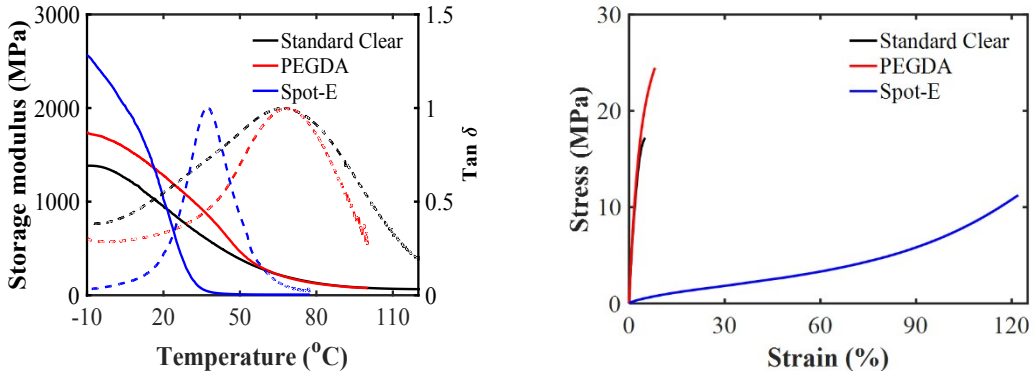


Fig. S2. Photo-DSC results showing the resin in (a) Standard Clear ink, (b) PEGDA ink and (c) Spot-E ink have an extent of crosslinking higher about 95%.

Thermomechanical and tension tests

The procedures of the thermomechanical and the uniaxial tension tests are introduced in the experimental section of the manuscript. The solid lines in Fig. S1 represents storage modulus of each resin and the dash lines are the corresponding normalized tan δ curves. Stretchability of Standard Clear and PEGDA is obviously smaller than Spot-E which is the reason Spot-E was chosen for printing most of the samples including shape memory foams.



(a) (b)

Fig. S3. (a) Thermomechanical testing results showing the T_g of Standard Clear, PEGDA and Spot-E are 66.5 °C, 69.2 °C and 37.5 °C, respectively. (b) Tension testing results measured the modulus of Standard Clear, PEGDA and Spot-E are 640 MPa, 670 MPa and 4.5 MPa, respectively.

Shape memory test

To quantitatively study the shape memory properties of 3D printed porous materials, such as recovery time and shape fixity, DMA tests have been conducted on both solid sample and porous sample for comparison. The first test was done by uniaxially stretching a solid strip made of Spot-E resin as shown in Fig. S4(a). The strip was first loaded to 30% strain at 50 °C that is above its T_g and then the temperature was decreased to -10 °C at a rate of 3 °C min^{-1} while maintaining the displacement. After cooling down to -10 °C for 2 min, the applied load was released and the deformed shape was fixed at almost 100%. The temperature was then rapidly jumped to 70 °C and the original shape was recovered within 2 min. The second test was designed similarly but was conducted by compressing a porous cube (3D printed by fine ink). As shown in Fig. S4(b), the porous cube was programmed by a 50% compression at 50 °C. The applied load was maintained the same while temperature was dropped down to -10 °C at the same rate as the first test. The shape fixity of porous cube after unloading at -10 °C was approximately 96% and the recovery time was shorter than 1 min after heating. The observation of a faster response time for the porous cube can be explained by the fact that the porous cube has a much larger surface area thus can be heated up much faster than the solid strip. As a comparison between Fig. S4(a) and (b), the beginning trending

of both recovery curves are almost the same before 15 °C but the curve of the porous cube keeps decreasing until fully recovery. This phenomenon may be caused by the growing pore volume during recovery that accelerates the heating of the material. To test the repeatability of shape memory foam, the same porous cube was tested for 8 cycles as shown in Fig. S4(c). No obvious shape fixity change nor shape recovery loss was observed during the test. Interestingly, Fig. S4 show that the porous cube recover faster than the solid strip. This might be due to that the porous cube can be heated faster then the solid strip.

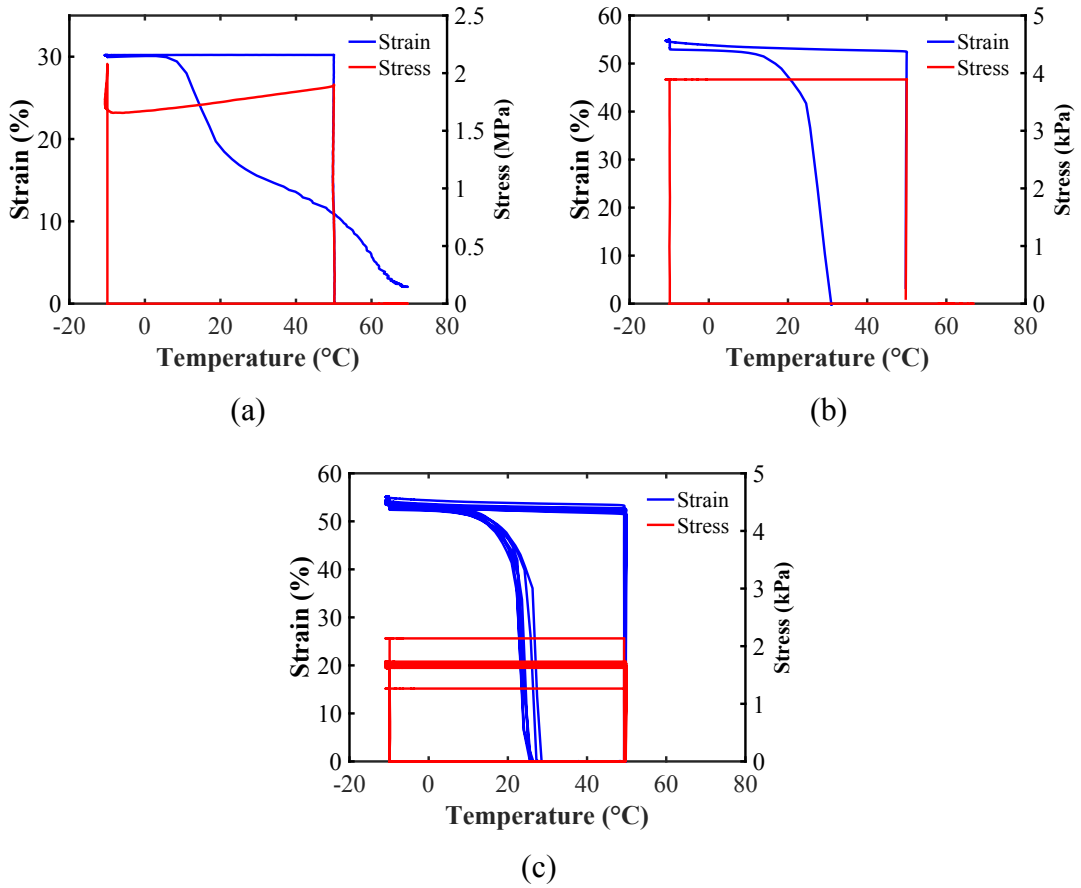


Fig. S4. Shape memory testing results for (a) solid strip, (b) porous cube and (c) its cyclic testing results.

Infiltrated conductive sample surface profile

In order to check the conductive ink infiltration and coating quality, SEM images were taken on the infiltrated porous samples. However, comparing to the SEM images in Fig.

2, the SEM images of the infiltrated sample show no difference, indicating relatively completely wetting of PEDOT:PSS to the surface of the pores of the printed sample.

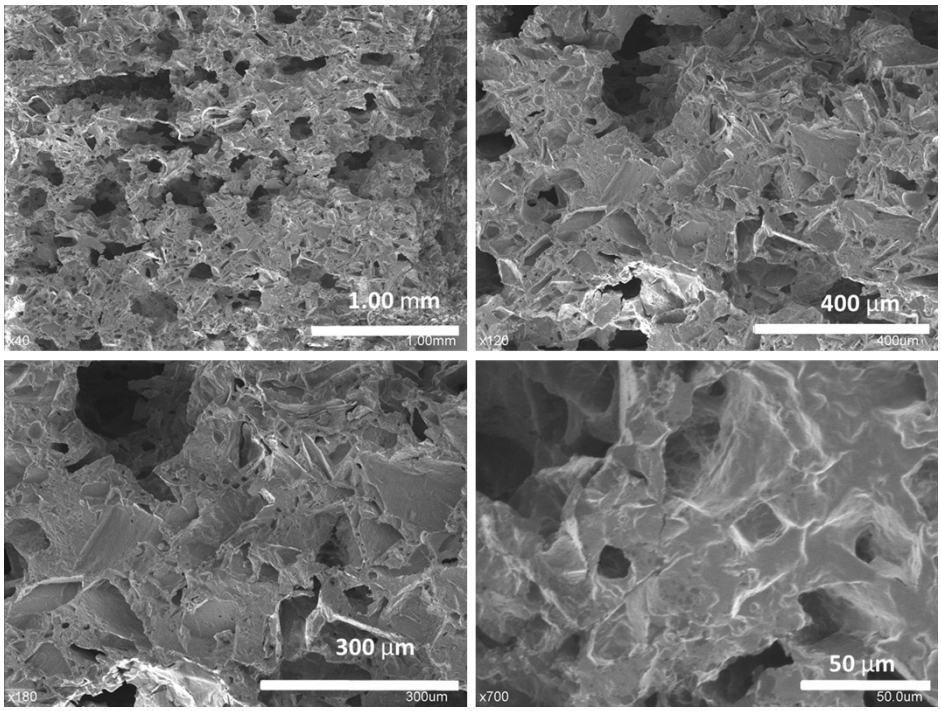


Figure S5. SEM images of PEDOT:PSS infiltrated samples.

Supplementary Movies

Movie S1. Porous printing process

Movie S2. Sphere in hollow cube

Movie S3. 3D printed shape memory foam

Movie S4. Conductivity test