Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Fabrication of Tough Epoxy with Shape Memory Effects by UV-assisted Direct-ink Write Printing

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S1. The direct ink write (DIW) set up

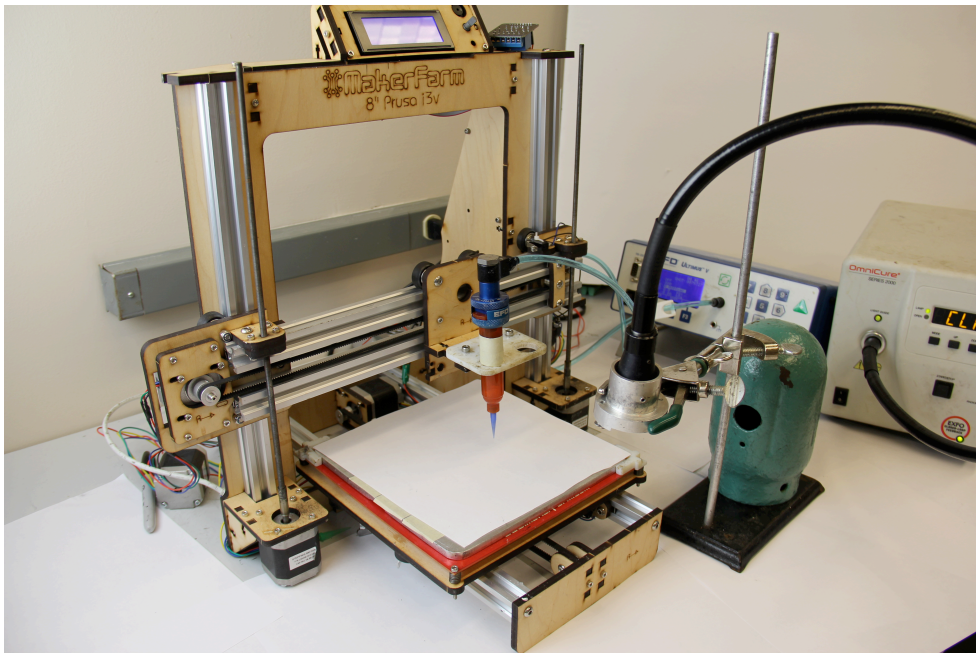

Figure S1. The direct ink write (DIW) set up

S2. Photo-differential scanning calorimetry (DSC) tests

The photo-differential scanning calorimetry (DSC) tests were conducted on the epoxy composites with 40% weight fraction of photopolymer, but with different contents of silica and the heat flow curves are plotted in Fig. S2. It can be observed that these two heat flow cures almost overlap. Besides, the heat generation, which can be calculated by an integral of the curve, is 126 and 105J/g for the ink with 0% and 8% weight fraction of silica, respectively. Since the ink has epoxy and silica in its composition so that the measured heat per mass need to be converted. After conversion, the heat generation from the ink with 0 and 8% weight fraction of silica are 315 and 283.5J/g, respectively. The difference of heat generation for the ink with 0 and 8% weight fraction of silica are very small (less than 10%). Therefore, we assume the influence of the silica on the photo cure reaction can be neglected.

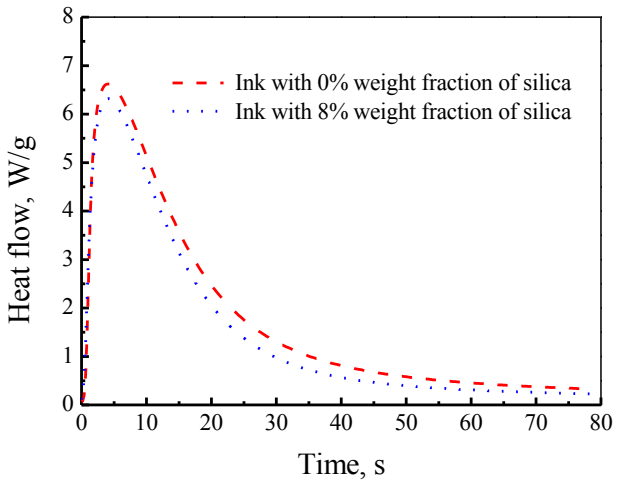

Figure S2. Photo-DSC curve of ink (epoxy composites with 40% weight fraction of photopolymer) with different weight fraction silica

S3. Schematic illustration of chemical reaction of the ink used in this work

For this ink, the acrylate monomers were cured by photo induced free radicals polymerization, and the epoxy resin was thermally cured with organic-base catalyzed ring-opening polymerization. The ink was exposed to UV irradiation leading to form a network by the acrylates. Afterwards, the above material was thermally cured in oven to generate a 2nd network. As these two kinds of components are polymerized through different mechanisms individually, the two cross-linked network are locked together noncovalently which is also called interpenetrated polymer network (IPN).

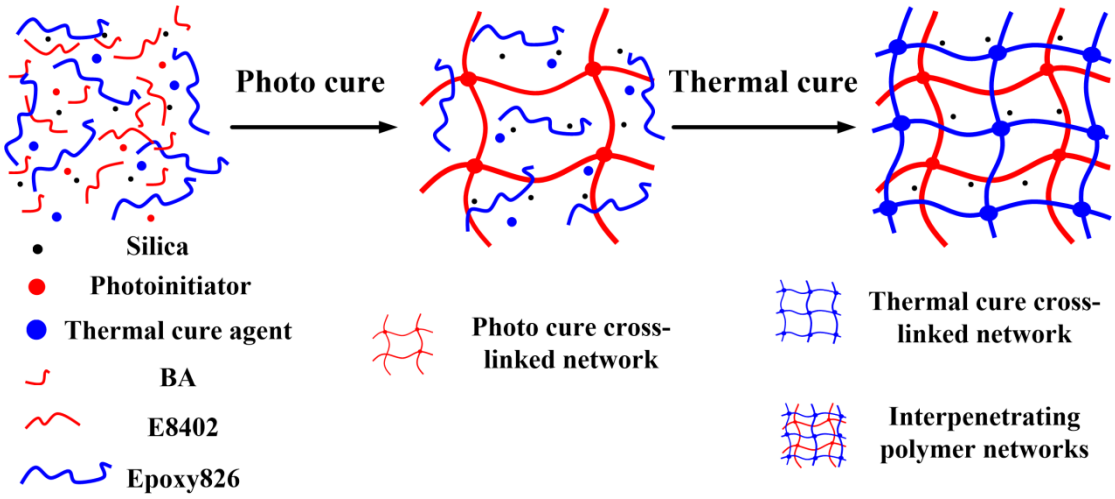

Figure S3. Schematic illustration of chemical reaction of the ink with two-stage cure process.

S4. The schematic illustration of fabricated dog-bone shaped samples with different printing paths and the corresponding printed results

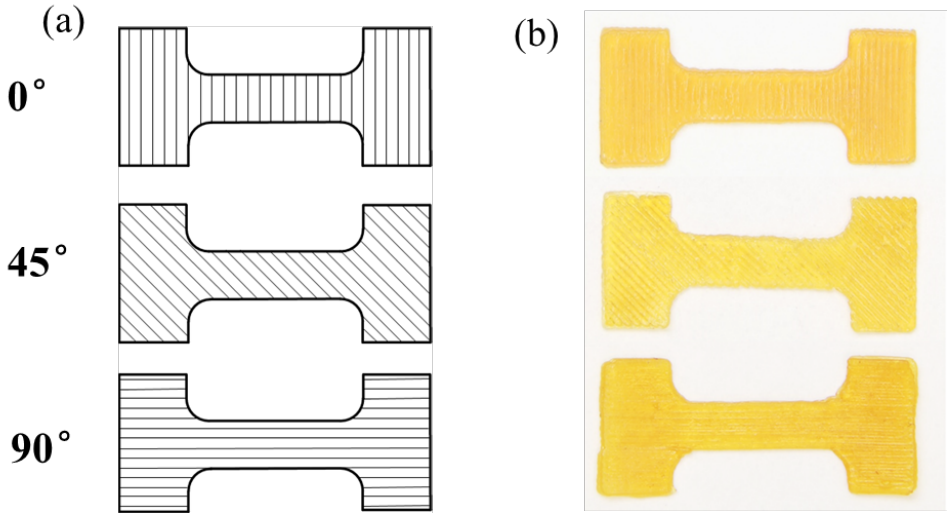

Figure S4. (a) and (b) the schematic illustration and the corresponding printed results of fabricated dog-bone shaped samples with different printing paths, respectively.

S5. The mechanical and thermal mechanical properties of epoxy composites with different weight fraction of photopolymer.

The mechanical properties of IPN epoxy composites with different of photo polymer was tested. The uniaxial tension tests were conducted in the displacement-controlled mode with a loading rate of 1.5mm/min at room temperature by using a MTS tester. The dog-bone samples were fabricated using PDMS moulds via a two stage curing, i.e., photo curing with a UV light density of 28mW/cm^2 for 10 s followed by thermal curing with pre-curing at 100 ^{o}C for 2 h and and post curing at 150 ^{o}C for 1 h.

The thermal mechanical properties of IPN epoxy composites with different of photo polymer was tested. The glass transition temperature (T_g) was determined by DMA. Rectangular sample with dimension of 20.0mm×4.0mm×0.4mm were used. The DMA test results show that there is only one T_g for the neat materials and IPN composites. The glass modulus, rubbery modulus and T_g increase with decreasing the weight fraction of photopolymer. The T_g can be tuned from 7.0 ^{o}C to 95.2^{o}C (Fig. S5 b).

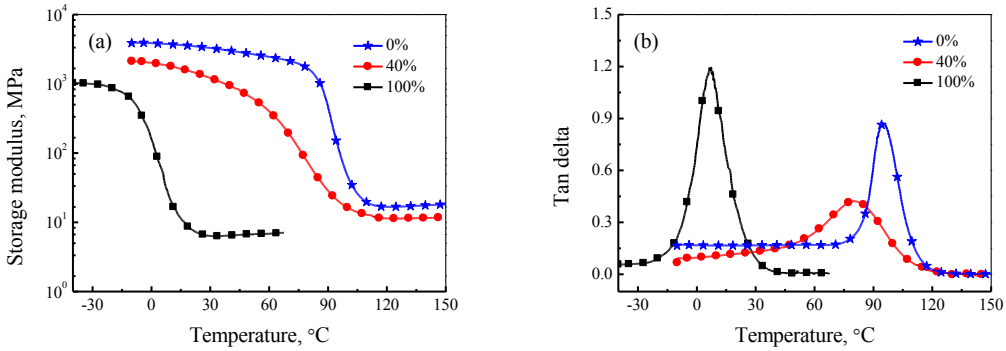

Figure S5. The results of DMA test on the epoxy composites with different weight fraction of photopolymer: (a) the storage modulus vs. temperature; (b) the Tan delta vs. temperature

S6. The thermomechanical test on the printed material

The procedures of the thermomechanical test are introduced in the above-mentioned (at the S5 in the supported information). The solid line is storage modulus and the dash line is the corresponding tan delta curves, as shown in Fig. S6. It shows that the T_g of the printed material is 76.4 ℃.

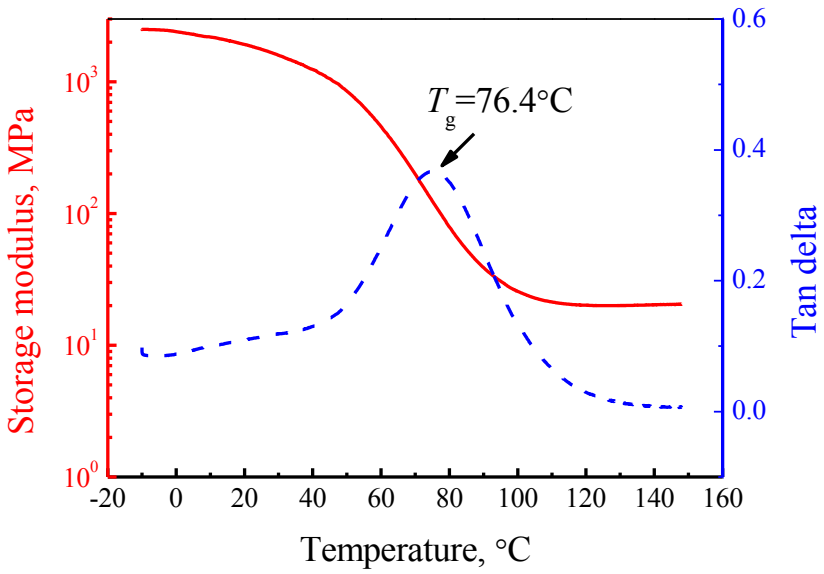

Figure S6. The results of thermomechanical test on the printed material.

S7. The temperature field of oil bath for shape memory test

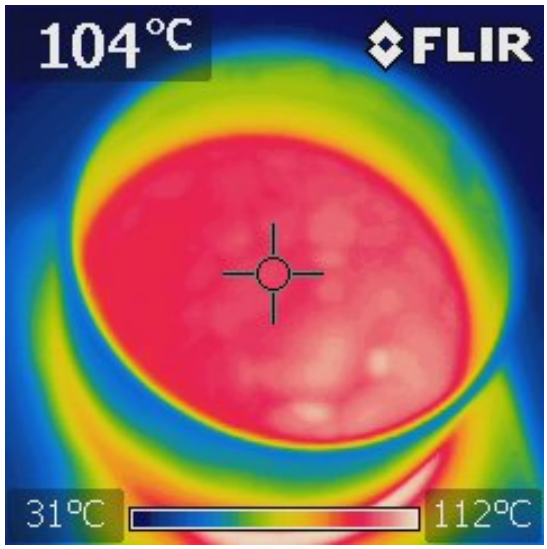

Figure S7. Test temperature field of pump oil bath equipped with hotplate

S8. Shape memory test

To quantitatively investigate the repeated shape memory properties of the printed epoxy composites, DMA tests were performed. The strip samples with dimension of 20mm×5.0mm×0.8mm was cut from the printing films. The sample was first kept in the 110 ^{o}C temperature for 5 min and then stretched to 10% of strain (ε_{load}). Maintaining the deformation, the temperature was decreased to 20 ^{o}C at a rate of 5 ^{o}C /min followed by holding at 20 ^{o}C for 10 min. Afterwards, the sample was unloaded and the fixed strain (ε_{f}) was determined. For shape recovery, the temperature increases 110 ^{o}C and the recovery deformation (ε_{r}) also can be observed within 5 min. This shape memory process was repeated for 3 times.

The shape fixity ratio (R_f) and shape recovery ratio (R_r) were defined as $R_f(N)=\varepsilon_f(N)/\varepsilon_{load}(N)\times 100\%$ and $R_r(N)=\dfrac{\varepsilon_f(N)-\varepsilon_r(N)}{\varepsilon_f(N)-\varepsilon_r(N\text{-}1)}\times 100\%$, respectively.

Where, $\varepsilon_{load}(N)$, $\varepsilon_f(N)$ and $\varepsilon_r(N)$ represent the strain after loading, the strain after removed loading and the strain after recovery in the N_{th} cycle, respectively.