

Supporting Information

Molecular Design Towards Photo-Curable and High-Strength Benzoxazine for 3D Printing

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Experimental Part

Materials. Phenol (99%), 2,2-bis(4-hydroxyphenyl)propane (BPA) (99%), paraformaldehyde (95%), 2-aminoethanol (99%), 5-amino-1-pentanol (95%) and phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO) were purchased from Sigma-Aldrich. A commercial resin (GR20) was provided by BMF Material Technology Inc. (Shen Zhen). All other chemicals were reagent grade and used as received unless stated otherwise.

Instrumentation. ^1H spectra were performed on a JOEL ECA400 nuclear magnetic resonance (NMR) spectrometer in CDCl_3 and tetramethyl silane was used as internal standard. Fourier transform infrared (FT-IR) spectra were recorded by Perkin Elmer Frontier FTNIR/MIR spectrometers, with resolution of 4 cm^{-1} for 16 scans. The UV-vis absorption was conducted on a UV-vis spectrometer (Shimadzu Model: UV2700) in dilute chloroform solution. Flow viscosity experiments were carried out using a TA instruments Discovery Series Hybrid Rheometer DHR-3 with a parallel plate (diameter 25 mm) attachment at $25\text{ }^\circ\text{C}$ with a shear rate ranging from 0.5 to 5 s^{-1} . Differential scanning calorimetry (DSC) (TA Instruments 2010) was performed from room temperature to $300\text{ }^\circ\text{C}$ at a constant heating rate of $10\text{ }^\circ\text{C}/\text{min}$ under nitrogen atmosphere. Thermogravimetric analysis (TGA) measurements were performed on a TA Instruments 2950 under nitrogen atmosphere at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$. Dynamic mechanical analysis (DMA) was carried out with a TA instruments Q800 DMA utilizing the single cantilever mode with temperature ramp from room temperature to $280\text{ }^\circ\text{C}$. The flexural properties were measured by three-point bending tests with loading speed $1\text{ mm}/\text{min}$ using a mechanical tester Instron 5567. The surface morphology of fractured samples was studied by field emission scanning electron microscope (FESEM) (JEOL JSM-7600F).

General preparation of 3-(2-acrylicethyl)-3,4-dihydro-2H-1,3-benzoxazine (BZ-C2), 3-(5-acrylicpentyl)-3,4-dihydro-2H-1,3-benzoxazine (BZ-C5) and bis(3-phenyl-(3-(2-acrylicethyl)-3,4-dihydro-2H-1,3)-benzoxazinyl)isopropane (BZ-BA)

Preparation of hydroxyl-benzoxazine precursors. Paraformaldehyde (2.0 eq) and amino alcohol (1.0 eq) were added to a round bottom flask with stirring for 1 h. Then, chloroform was added and followed by the addition of phenol (1.0 eq). The reaction mixture was heated up 70 °C to and reacted overnight. After cooling to room temperature, an extraction process was conducted with a sodium hydroxide solution (0.1 N). The extracted organic layer was dried over sodium sulphate, filtered and removed under vacuum to get the hydroxyl-benzoxazine. For the synthesis of BZ-BA precursor, BPA instead of phenol was used and the molar ratio of paraformaldehyde, 2-aminoethanol and BPA was 4:2:1.

Preparation of BZ monomers. To a solution of the acrylic acid (1.1 eq) in dry CH₂Cl₂ at 0 °C, oxalyl chloride (COCl)₂ (1.1 eq) was added dropwise followed by adding a catalytic amount of dry DMF (2 drops). When the addition was complete, the solution was allowed to stir at room temperature for 3 h. The solvent was removed under reduce pressure to afford crude acryloyl chloride and directly used for next step. To an ice-bath cooled CH₂Cl₂ solution with previously prepared hydroxyl-benzoxazine (1 eq.) and dried triethyl amine (1.1 eq.), the crude acryloyl chloride was added in slowly. The solution was brought to room temperature and continuously stirred at for another 4 h upon the complete addition. Then the CH₂Cl₂ solution was washed with saturated NaHCO₃ solution for 3 times and DI water for 1 time. The CH₂Cl₂ layer was collected, dried, filtered and CH₂Cl₂ solvent was removed under vacuum to obtain the product. For the synthesis of BZ-BA, the molar ratio of acrylic acid, TEA and BZ-BA hydroxyl precursor was 2.2:2.2:1.

BZ-C2 (yellow liquid, yield: 82%): ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.13 - 6.77 (m, 4H, aromatics), 6.42 (dd, 1H), 6.14 (q, 1H), 5.85 (dd, 1H), 4.85 (s, 2H), 4.32 (t, 2H), 4.05 (s, 2H), 3.07 (t, 2H). FTIR (KBr, cm⁻¹): 1720 (C=O st), 1638 (C=C st), 1490 (C-C Ar st), 1224 (C-O-C st asymmetric), 1063 (C-O-C st symmetric), 933 (N-C-O st).

BZ-C5 (yellow liquid, yield: 86%): ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.09 - 6.75 (m, 4H, aromatics), 6.38 (dd, 1H), 6.10 (q, 1H), 5.79 (dd, 1H), 4.83 (s, 2H), 4.14 (t, 2H), 3.96 (s, 2H), 2.73 (t, 2H), 1.71-1.41 (m, 6H). FTIR (KBr, cm^{-1}): 1723 (C=O st), 1635 (C=C st), 1487 (C-C Ar st), 1226 (C-O-C st asymmetric), 1059 (C-O-C st symmetric), 928 (N-C-O st).

BZ-BA (highly viscous orange liquid, yield: 78%): ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.27 - 6.93 (m, 6H, aromatics), 6.56 (dd, 2H), 6.25 (q, 2H), 6.02 (dd, 2H), 4.88 (s, 4H), 4.37 (t, 4H), 4.10 (s, 4H), 3.11 (t, 4H), 1.57 (s, 6H).

Resin formulation based on BZ-C2 and BZ-C5 monomers.

Resin formulation based on BZ-C2 monomer: BZ-C2, BAPO (0.45 wt%) and THF (30 wt%) were mixed together and homogenized with a vortex mixer for 30 s. The resultant mixture was subsequently allowed to stand at room temperature for 2 h to ensure the absence of bubbles.

Resin formulation based on BZ-C5 monomer: BAPO (0.6 wt%) was dissolved in a miniscule amount of THF and then added to BZ-C5. The mixture was mixed homogeneously using a vortex mixer for 30 s and stand for 2h to ensure the absence of bubbles.

Sample preparation by photo and thermal cure. Samples for FT-IR, DSC, TGA, DMA and 3-point bending test were prepared by UV photocuring uniform samples firstly, followed by thermal curing with a progressive heat treatment. Typically, liquid BZ-C2 or BZ-C5 and photo initiator BAPO were mixed vigorously. The resin was added into silicone moulds with round or rectangular cavity and photocured within a UV chamber (2 mW/cm^2) for 3 min. The specimens were demoulded, flipped over and photocured within the UV chamber for another 3 min. The specimen thickness was controlled by the resin adding volume. The thermal curing was subsequently carried out by subjecting the photocured samples to the following heating schedule: 140 °C (1 h), 160 °C (1 h), 180 °C (1 h), 200 °C (1h), 220 °C (1 h) and 240 °C (1 h).

P μ SL printing with BZ-C2 or BZ-C5 based resin formulation. The P μ SL printing process was performed with a commercially available 3D printer (nanoArch S140, BMF). A UV-LED (405 nm) was utilized as the light resource. The intensity of 17.5 mW cm⁻² was used during all printing. Computer aided design (CAD) of the print structures were designed in the software of Autodesk fusion 360. The resulting STL files were sliced for a 2D file output using BMF P μ SL printing software with different slicing thickness. After printing, the acquired objects were washed thoroughly with isopropanol to remove any residual unreacted resin, left to dry for 5 min and then placed into a UV curing chamber for further photopolymerization for 5 min. The printed 3D structures were placed into a vacuum oven at 60 °C overnight to remove residual solvent.

Preparation of PBZ 3D structured objects. The fully dried 3D structured objects were then undergone thermal treatment as described above to achieve the final PBZ products. The heights of the 3D structured objects were measured using a micrometre for 3 times before and after the thermal treatment.

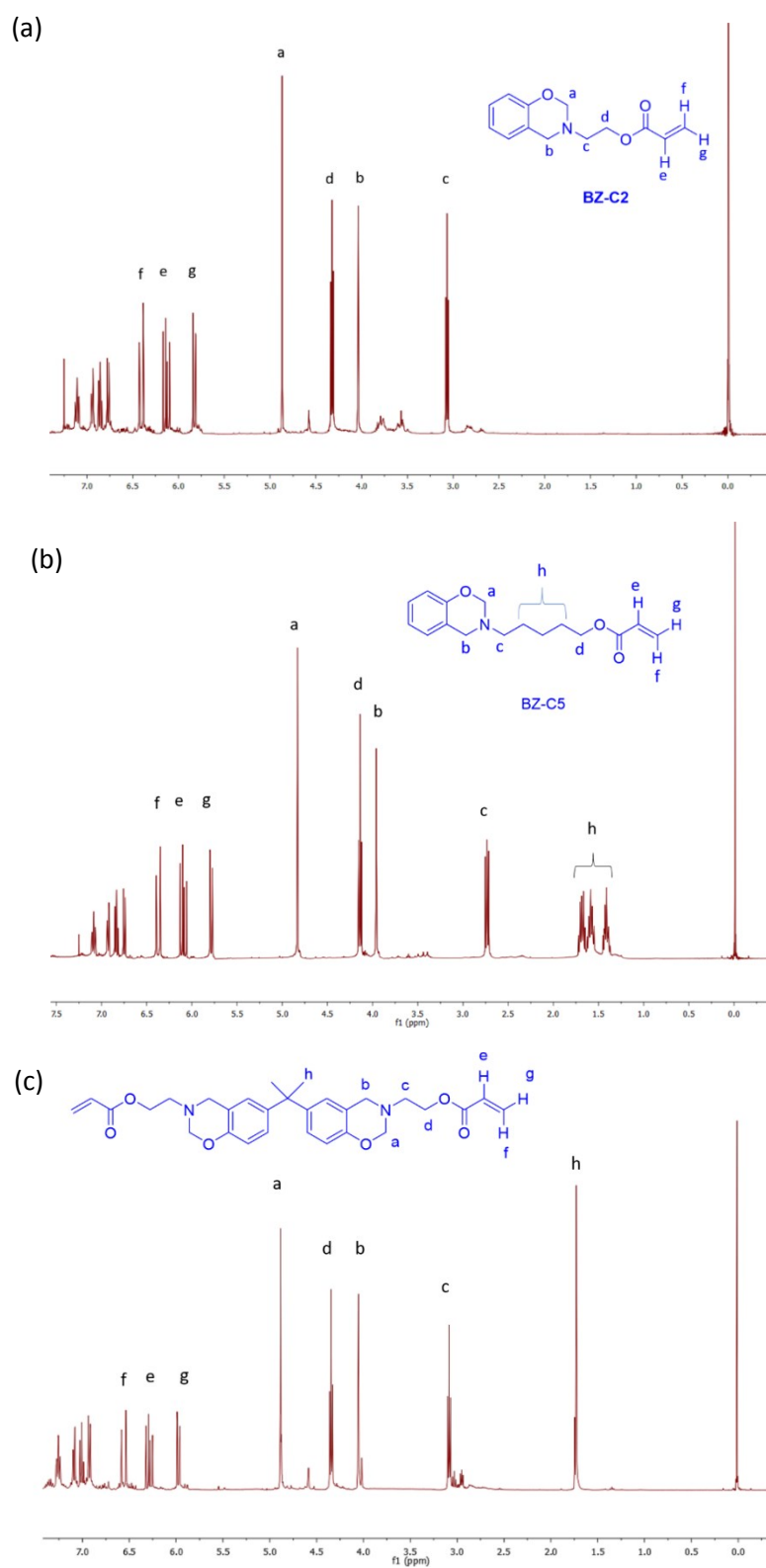


Fig. S1 ^1H NMR spectra of (a) BZ-C2, (b) BZ-C5 and (c) BZ-BA compounds.

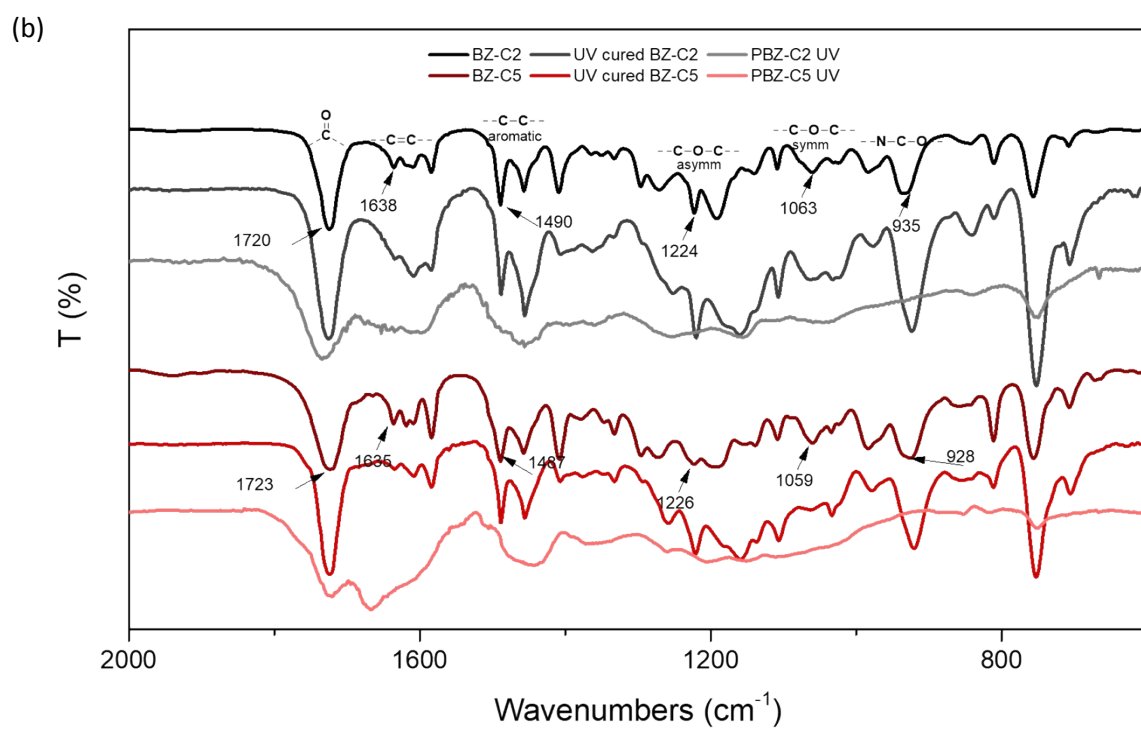
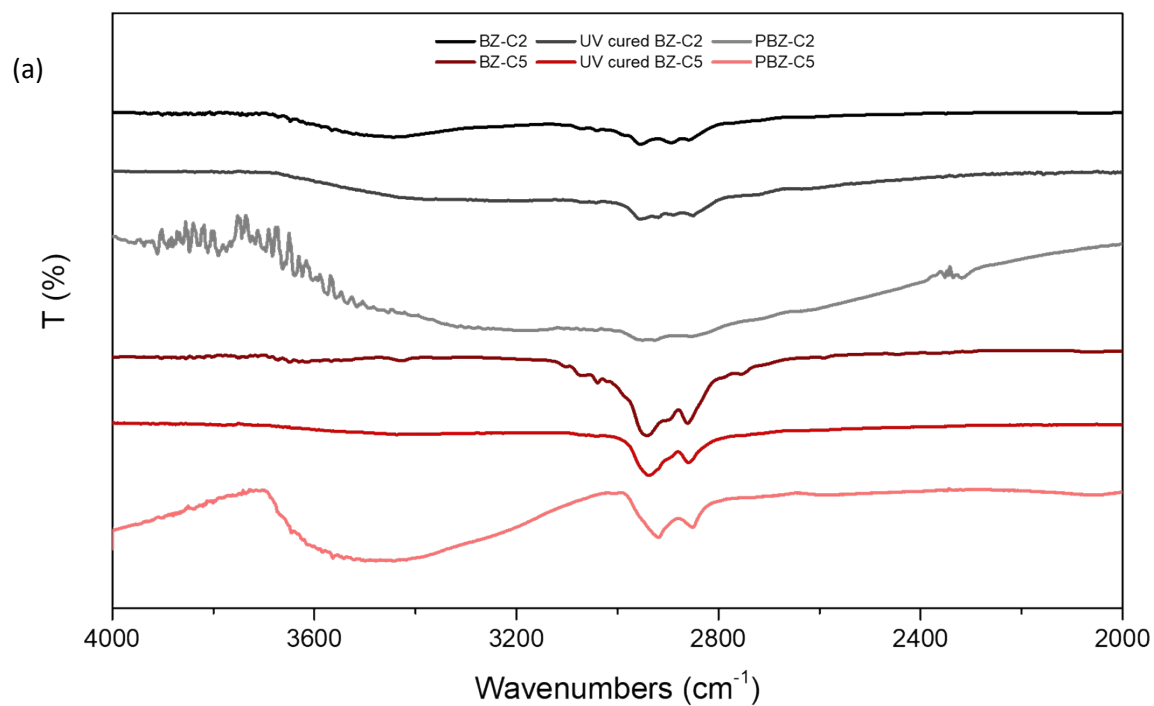


Fig. S2 FT-IR spectra of monomers, photo cured BZ-C2/C5 and PBZ-C2/C5.

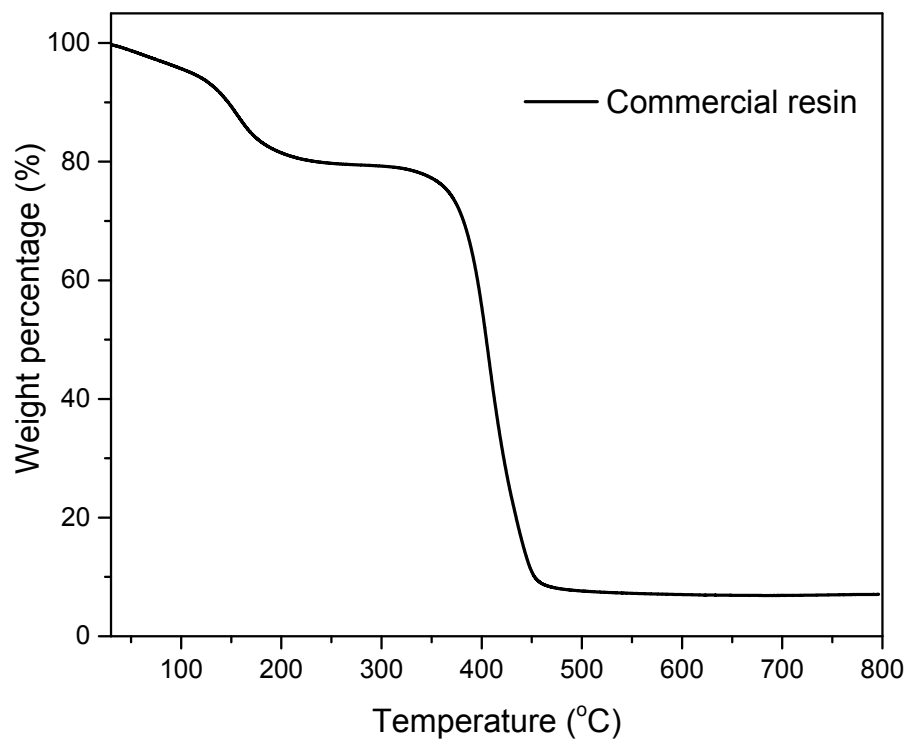


Fig. S3 TGA curve of a commercial resin (GR20) in N_2 atmosphere.

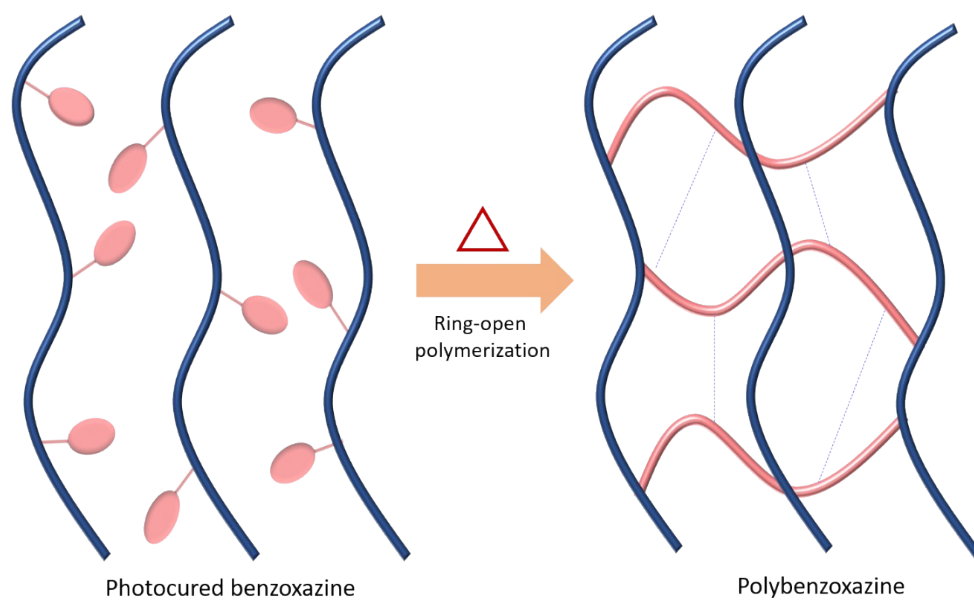


Fig. S4 Schematic illustration of the triple networks formed in the PBZs.

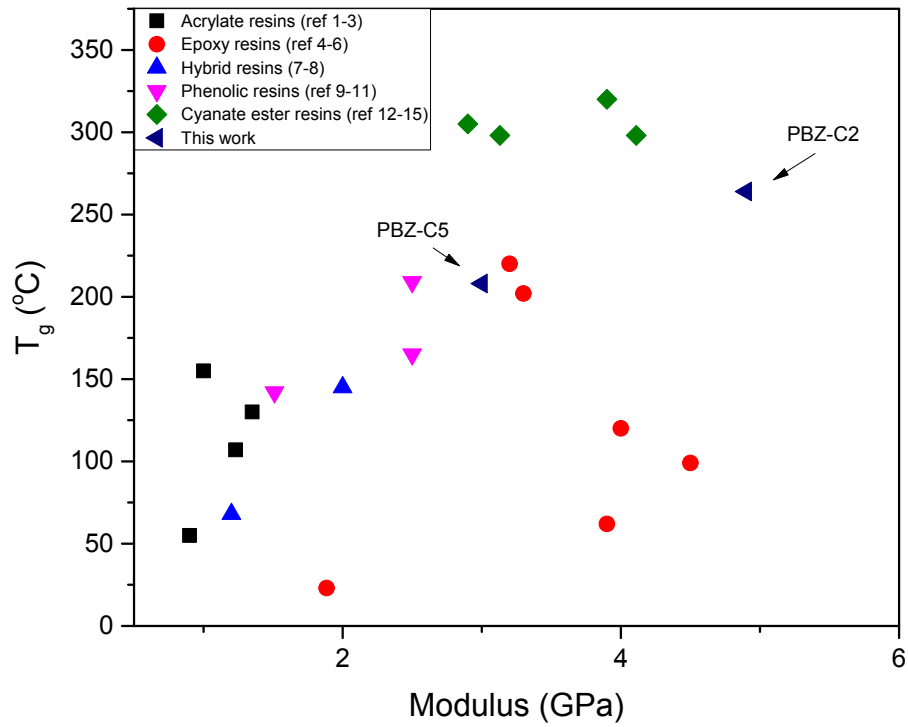


Fig. S5 T_g and modulus of PBZ-C2 and PBZ-C5 compared with literature results.

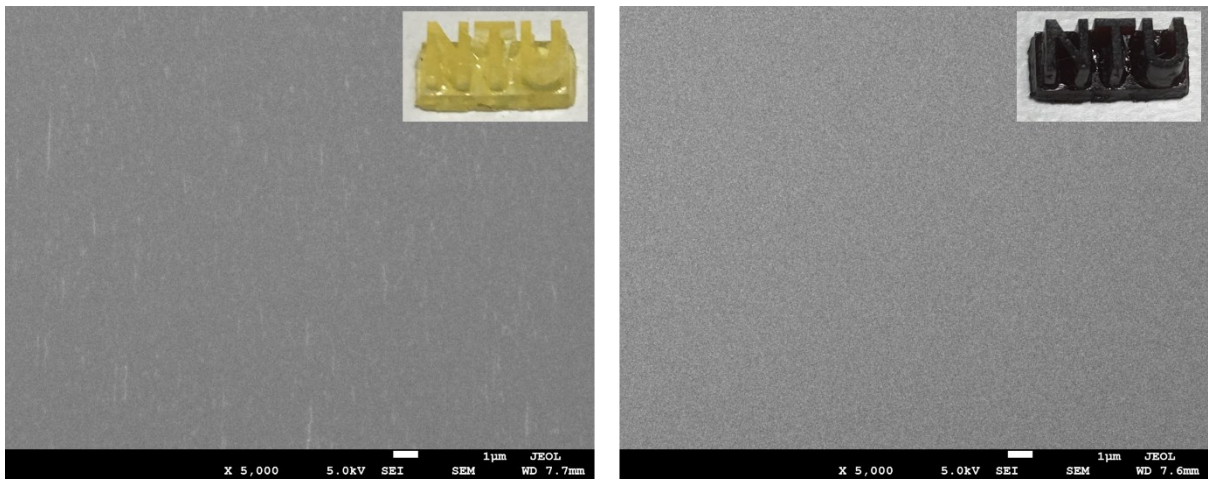


Fig. S6 SEM images of fracture surface of printed NTU logo before (left) and after thermal treatment (right). (BZ-C2 based resin, insets: photos of as-printed NTU logo before and after thermal curing).

Table S1 Mechanical performances determined by 3-point bending test

BZ resins	Thermally cured temperature (°C)	Modulus (GPa)	Flexure stress (MPa)*	Flexure strain (%)*
BZ-C2	180	3.90 ± 0.22	98.4 ± 10.0	2.5 ± 0.2
	240	4.91 ± 0.21	154.3 ± 15.7	3.2 ± 0.2
BZ-C5	180	2.32 ± 0.15	94.0 ± 7.8	3.7 ± 0.2
	240	3.00 ± 0.21	133.4 ± 10.6	4.4 ± 0.3

* Average flexure stress and strain at yield point

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