

Supporting Information

Controlling Mechanical Properties of 3D Printed Polymer Composites through Photoinduced Reversible Addition-Fragmentation Chain Transfer (RAFT) Polymerization

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Experimental section

Materials.

Fumed silica nanoparticles (Aerosil OX50, 50 nm in diameter) were obtained from Evonik. 3-methacyloxypropyltrimethoxysilane (MPS), *n*-propylamine, 2-hydroxyethyl acrylate (HEA), poly(ethylene glycol) diacrylate (PEGDA 250), and diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO), 1-pyrene methyl methacrylate (PyMMA) were obtained from Sigma-Aldrich and were used without purification. Methyl 2-(*n*-butylthiocarbonothioylthio)propanoate (MBTP) was purchased from Boron Molecular and used as received.

Synthesis and characterization of surface-functionalized silica nanoparticles.

The method reported by Karabela et al. was used to functionalize silica nanoparticles with MPS.¹ In a typical procedure, 20 g of Aerosil OX50 was dispersed in 400 mL cyclohexane by sonication and vigorous string. To the suspension, 0.4 g *n*-propylamine and 2 g MPS were added dropwise. The mixture was stirred for 30 min at room temperature and then transferred to a 65 °C oil bath for another 30 min reaction. After the reaction, solvent and byproducts were removed in a rotary evaporator at 40 °C. The obtained slurry was washed three times by redispersing in ethanol and centrifugation. Finally, the powder was dried at 50 °C for 4 h in a vacuum oven before characterization and use.

Preparation of different photocurable composites.

The initial ratio of HEA, PEGDA and TPO was selected based on our previous work² and was found to provide a serviceable printing speed (20 s/layer). To Prepare 50 mL of a typical FRP resin, the mixture of 34.4 mL HEA and 15.6 mL PEGDA250, corresponding to a weight ratio of 100: 50, were used to dissolve 260 mg TPO (0.5 wt% of the mixture) via 30s of mixing by vortex mixer and 10min bath sonication. For preparing 10mL typical FRP-SNP resin containing 10 wt% MPS-SNPs, 10 mL of prepared FRP resin was used to disperse

1042 mg MPS-SNPs via 20 min probe sonication at 70% amplitude. Similarly, 10 mL RAFT resin (1 wt% MBTP) was obtained by dissolving 104 mg MBTP with 10 mL FRP via 10 min bath sonication. To obtain 10 mL RAFT-SNP resin with 1 wt% MBTP and 10 wt% MPS-SNPs, 10mL typical FRP-SNP resin containing 10 wt% MPS-SNPs was used to dissolve 104 mg MBTP via 10 min bath sonication. Following the above procedure, different resins were prepared by changing the applied weight concentration of MBTP and MPS-SNPs.

3D printing condition of photocurable composite

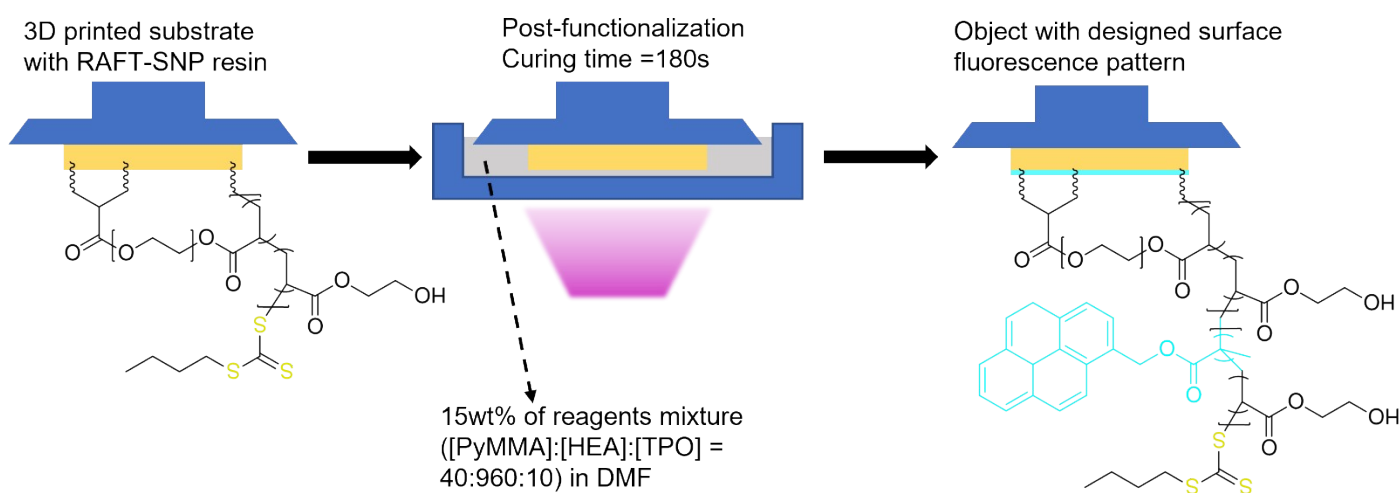
In this study, a commercial 3D printer (Anycubic PhotonS) with blue light (405 nm, 0.4 mWcm⁻²) was utilized to fabricate all specimens and 3D structures. The target printing objects were designed in Autodesk Fusion 360 and exported as .stl files. Printing parameters like layer thickness, exposure time were defined in the Photon workshop and exported as .pws files for 3D printing. All specimens were printed along the direction of their thickness. Two bottom layers with extended curing time were designed for all 3D printings of specimens for mechanical tests. In particular, four bottom layers with 120 s curing time were used for fabrication of complex lattice structures. Detailed conditions are presented in **Table S1**. Unless indicated, all 3D printed specimens in this work were post-cured under 405 nm irradiation for 10 min.

Table S1 Summary of printing conditions for 3D printed objects.

	Formula	wt% MBTP	wt% SNPs	Bottom exposure time (s)	Curing time per layer, t_c (s)
FRP resin	1	0.0	0	90	20
	2	0.5	0	120	30
RAFT resins	3	1.0	0	120	40
	4	1.5	0	120	60
	5	2.0	0	120	90
FRP-SNP resins	6	0.0	5	60	15
	7	0.0	10	30	12
	8	0.0	20	30	11
	9	0.0	30	30	11
RAFT-SNP resins	10	1.0	10	90	30
	11	1.0	30	90	30

Surface functionalization of 3D printing composite materials.

The general procedure for functionalization of the 3D printed objects in this study is shown in **Scheme S1**. A typical procedure is as follows: resin RAFT-SNP 10 was utilized to print a square prism with dimensions of 40× 40×1 mm (l, w, t) as substrate using the printing condition in **Table S1**. A fluorescent resin was prepared by mixing PyMMA, HEA and TPO ([PyMMA]:[HEA]:[TPO] = 40:960:10), then diluted to 15 wt% in DMF for post-functionalization. The printed substrate was kept on the build platform of 3D printer and washed with ethanol and acetone, followed by air dry with compressed air. The dried substrate was then post-cured for 10min under 405 nm light to ensure the conversion of unreacted vinyl bonds prior to surface functionalization. Subsequently, the spatially controlled surface functionalization was realized by conducting a one-layer 3D printing (curing time = 180s, layer thickness = 100 μm) of designed dragon pattern using the dilute fluorescent resin. The obtained surface-functionalized object was then washed with ethanol and acetone, followed by air dry before investigation under 312 nm irradiation.



Scheme S1: Post-printing surface functionalization process with fluorescent monomer PyMMA.

Characterization

Comparison of SNPs and MPS-SNPs

Fourier-transform infrared (FTIR) spectroscopy of unaltered and MPS-modified SNPs was obtained under transmission mode using PerkinElmer Spectrum Two FT-IR Spectrometer. Samples were prepared by grinding 1 wt% of silica nanoparticles with potassium bromide (KBr) and compressing the mixed powder to pellets. Thermogravimetric analyses (TGA) was conducted using a TA Instrument TGA Q5000 thermogravimetric analyzer from 100 °C to 800 °C at a rate of 20 °C/min under nitrogen. FEI Tecnai G2 20 TEM was employed to acquire the morphology of SNPs and MPS-SNPs. Dynamic light scattering (DLS) experiments were carried to compare the size information of SNPs and MPS-SNPs using Zetasizer Nano ZS. 10 mg/mL of SNPs and MPS-SNPs were dispersed in water via sonication to obtain the samples for DLS analysis.

Attenuated total reflectance-Fourier-transform infrared (ATR-FTIR) spectroscopy for monitoring polymerization kinetics.

The real-time FTIR spectra of different resins were recorded every 5 s under blue light ($\lambda_{\max} = 405 \text{ nm}$, $I = 3.7 \text{ mW/cm}^2$) using a Bruker Alpha FT-IR spectrometer. The vinyl bond conversion was calculated from the disappearance of the C=C bending peak at 812 cm^{-1} normalized to the C=O stretching peak at 1760 cm^{-1} as an internal standard. As such, the real-time conversion was calculated by **Equation 1**, where α_t is vinyl bond conversion after irradiation of t s, int_0 and std_0 refer to the integration of peak in the range of $788\text{-}822 \text{ cm}^{-1}$ and $1670\text{-}1800 \text{ cm}^{-1}$ for unreacted sample, int_t and std_t refer to these two values after irradiation of t s

$$\alpha_t = 1 - (int_t/std_t)/(int_0/std_0) \quad (1)$$

UV-vis spectroscopy of developed resins

All UV-vis spectra were recorded using a Varian Cary 300 spectrophotometer. Scans were conducted in the range of 800-200 nm at 600 nm/min. 2 mL of FRP, FRP-SNP, RAFT, RAFT-SNP resins were placed in a 1×1 cm glass cuvette for measurements. A spectrum obtained with an empty cuvette was used for baseline correction.

FTNIR Spectroscopy of 3D printed specimens

Fourier Transform Near-Infrared (FTNIR) spectroscopy was performed using a Bruker Vertex 70 Fourier transform spectrometer to determine the vinyl bond conversion of 3D printed objects. 3ml of resins or the 3D printed specimens were placed in a 1×1 cm quartz cuvette for measurement. The conversion was calculated using **Equation 2** by comparing the normalized integral of the C-H vinylic stretching overtone at 6100-6230 cm⁻¹ between the 3D printed specimens and the corresponding photocurable resins.

$$\text{Conversion (\%)} = \left(1 - \left(\frac{\text{int}_f}{\text{int}_0} \times \frac{t_{\text{cuvette}}}{t_{\text{sample}}}\right)\right) \times 100 \quad (2)$$

Where int_f is the integral of the peak from 6100-6230 cm⁻¹ for the 3D printed samples, int_0 is the integral of the peak from 6100-6230 cm⁻¹ for the resins, t_{sample} is the thickness of the sample, and t_{cuvette} is the path length of the cuvette.

Thermomechanical study of 3D printed specimens

Dynamic mechanical analysis (DMA) of 3D printed specimens was conducted under the single cantilever mode using a TA Q800 dynamic mechanical analyzer. Specimens were with the designed dimension of l×w×t = 40×8×3 mm. The actual dimensions were measured with a digital caliper. The experimental method as the following was applied for all specimens: equilibrate at -50 °C and be isothermal for 3 min, ramped up to 80 °C at a rate of 2 °C/min, constant frequency of 1 Hz and displacement of 15 μm.

Tensile tests were performed using an Instron 3369 universal testing system following the ASTM D638-14 standard. The Type V specimen dimension was used for the 3D printing of specimens. The as-printed specimens were measured with a digital caliper to determine the actual dimensions. The travel speed for all tests was 1 mm/min.

Single-edge-notch bending (SENB) tests were performed under 3-point bending mode using an Instron 3369 universal testing system. The standard method and calculation shown in ASTM D5045-14 were applied for all tests. Notched specimens with the dimension of $l \times w \times t = 44 \times 10 \times 5$ mm was designed and applied for 3D printing. The post-cured specimens were measured with a digital caliper to determine the actual dimensions. Afterward, printed samples were intentionally cut with a razor along the notch to induce a weak point, and the corresponding crack length (a) was measured.

Scanning electron microscopy (SEM)

Zeiss AURIGA field emission scanning electron microscope (FESEM) was employed to study the morphology of the fracture surfaces of SENB specimens. Before observation, specimens were set on a double 90° angled stub using conductive type and coated with 5 nm platinum nanoparticles utilizing a Quorum Q3000T sputter coater.

Additional Data

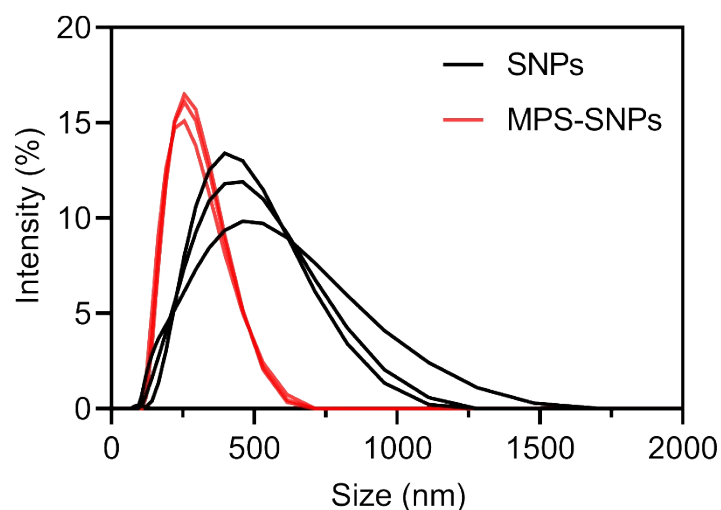


Figure S1. Comparison of DLS results of silica nanoparticles and MPS modified silica nanoparticles. Silica nanoparticles (10 mg/mL) dispersed in water were used in both cases.

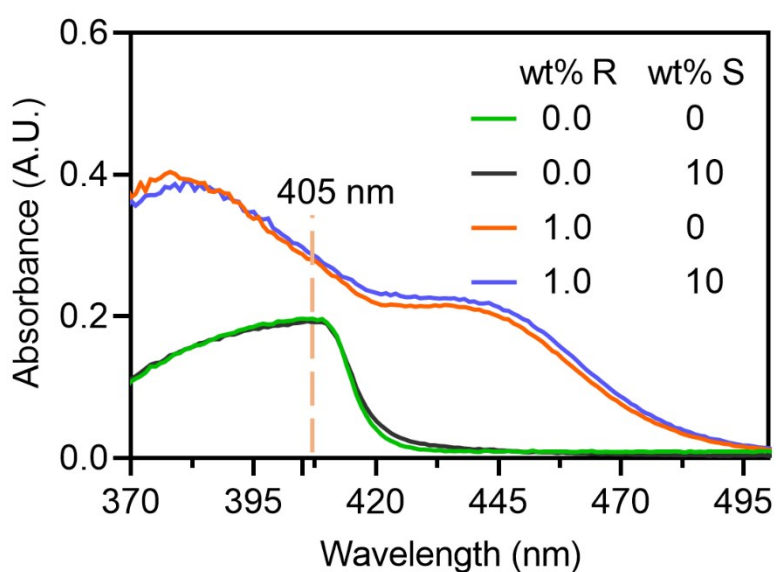


Figure S2. Comparison of UV-vis spectra of FRP resin, RAFT resin (1 wt% MBTP), FRP-SNP resin (10 wt% MPS-SNPs), RAFT-SNP resin (1 wt% MBTP and 10 wt% MPS-SNPs). A fixed weight ratio of [HEA]:[PEGDA]:[TPO] = 100:50:0.75 was applied in all cases.

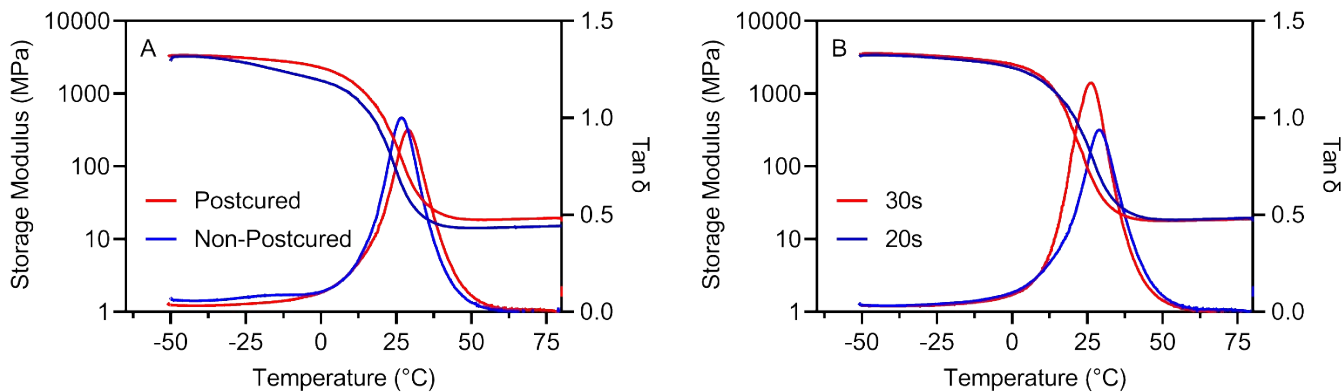


Figure S3. DMA study of the effect of printing conditions. A) Effect of post-cure on the storage modulus and tan δ . B) Effect of curing time per layer (t_c) on the storage modulus and tan δ of post-cured samples. Neat resin with fixed weight ratio of [HEA]:[PEGDA]:[TPO] = 100:50:0.75 was applied in all cases.

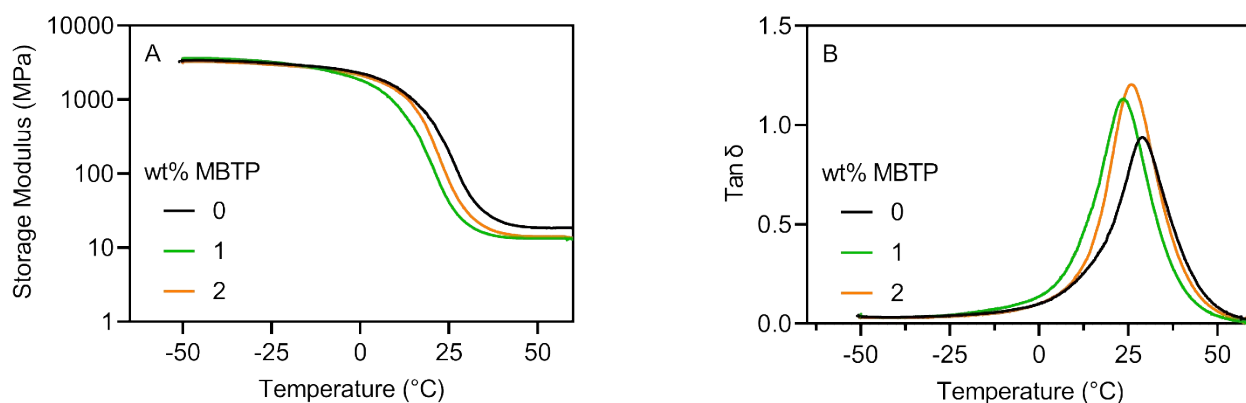


Figure S4. DMA study of the effect of RAFT agent (MBTP). A) Effect of weight ratio of RAFT agent in RAFT resin on storage modulus. B) Effect of weight ratio of RAFT agent in RAFT resin on tan δ curve. A fixed ratio of [HEA]:[PEGDA]:[TPO] = 100:50:0.75 was applied in all cases. All samples were post-cured before characterization.

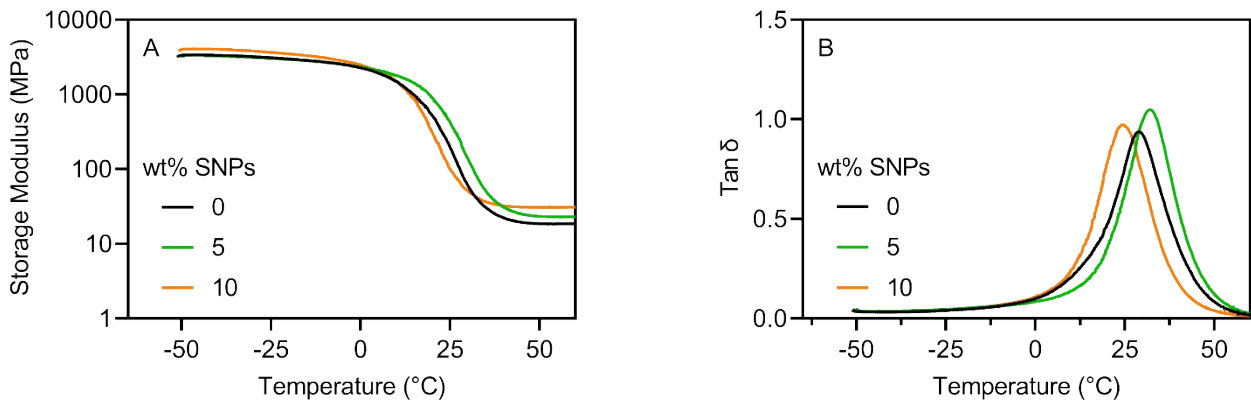


Figure S5. DMA study of the effect of MPS-SNPs. A) Effect of weight ratio of MPS-SNPs in FRP-SNP resin on storage modulus. B) Effect of weight ratio of MPS-SNPs in FRP-SNP resin on $\tan \delta$ curve. A fixed ratio of [HEA]:[PEGDA]:[TPO] = 100:50:0.75 was applied in all cases. All samples were post-cured before characterization.

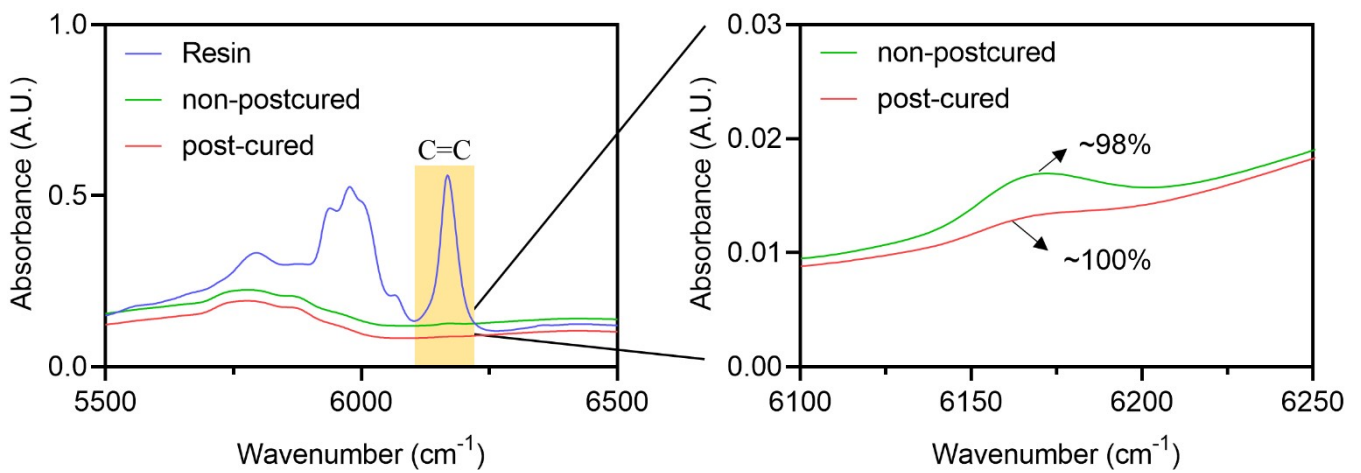


Figure S6. Representative FT-NIR spectra of FRP resin and the 3D printed objects for calculation of vinyl group conversion of 3D printed objects.

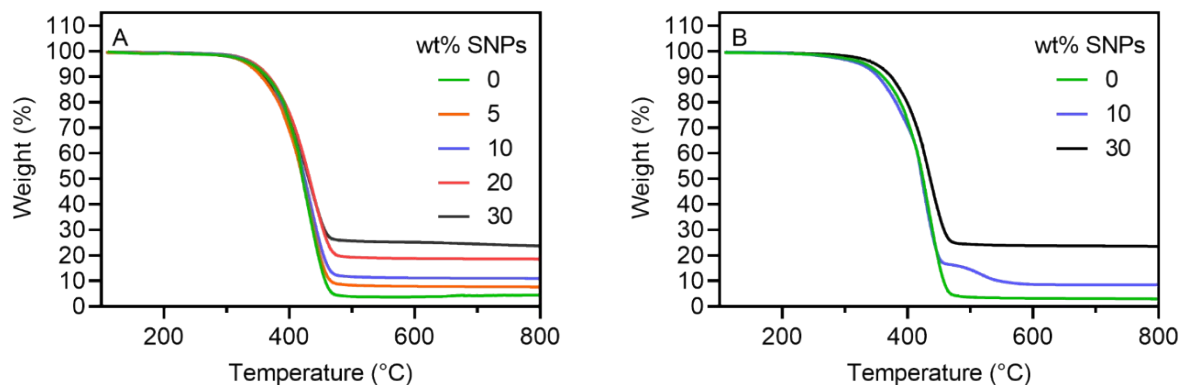


Figure S7. TGA results of 3D printed composite materials with different resins. A) Composites 3D printed using FRP-SNP resin with increasing weight ratio of MPS-SNPs. B) Composites 3D printed using RAFT-SNP resin with 1 wt% MBTP and increasing weight ratio of MPS-SNPs. A fixed weight ratio of [HEA]:[PEGDA]:[TPO] = 100:50:0.75 was applied in all cases.

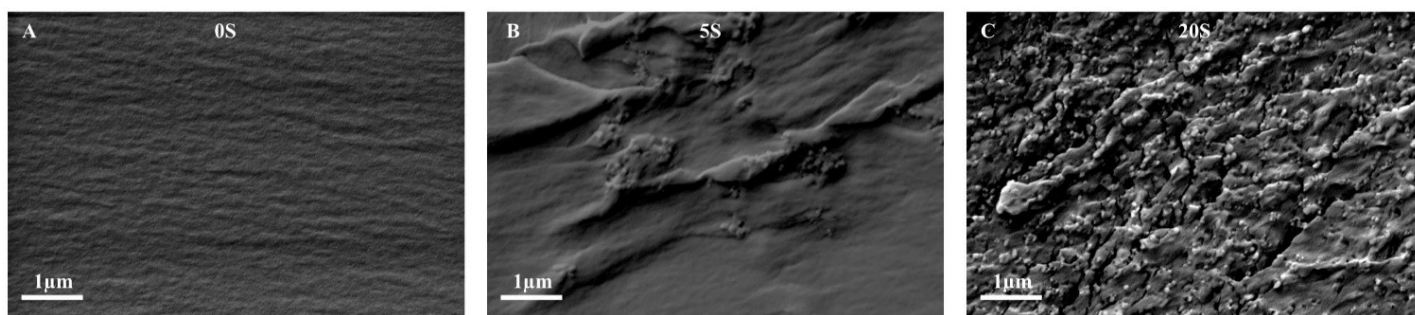


Figure S8. SEM images of the fracture surface of 3D printed specimens using A) FRP resin. B) FRP-SNP resin with 5 wt% MPS-SNPs. C) FRP-SNP resin with 20 wt% MPS-SNPs. A fixed ratio of [HEA]:[PEGDA]:[TPO] = 100:50:0.75 was applied in all cases.

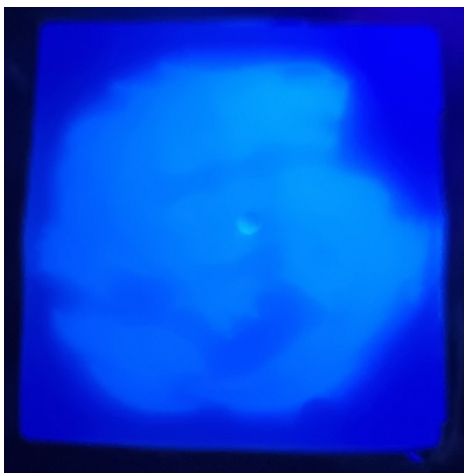


Figure S9. Surface modified 3D printed parts from FRP-SNP resin with 10 wt% MPS-SNPs. Fixed ratio of [HEA]:[PEGDA]:[TPO] = 100:50:0.75 was applied in the resin for 3D printing of substrate. 15 wt% [PyMMA]:[HEA]:[TPO]= 40:960:10 mixture in DMF for modification.

Supporting Information - References

1. Sideridou, I. D.; Karabela, M. M., Effect of the amount of 3-methacyloxypropyltrimethoxysilane coupling agent on physical properties of dental resin nanocomposites. *Dent. Mater.* **2009**, *25* (11), 1315-1324.
2. Lee, K.; Corrigan, N.; Boyer, C., Rapid High-Resolution 3D Printing and Surface Functionalization via Type I Photoinitiated RAFT Polymerization. *Angew. Chem., Int. Ed.* **2021**, *60* (16), 8839-8850.