Loop 3D printing: recyclable photoresins for light-mediated additive manufacturing

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Methods:

Materials

Isophorone diisocyanate (IPDI) (> 99%), isopropylthioxanthone (ITX) (> 98%), Sudan-1 (> 93%), and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (> 98%) were purchased from Tokyo Chemical Industry (TCI) (https://www.tcichemicals.com/ES/en/). Hexamethylene diisocyanate (HDI) (≥ 98.0%), polyethylene glycol (PEG) (M_n: 400 g/mol), polypropylene glycol (PPG) (M_n: 2000 g/mol) and, (M_n: 1000 g/mol) 1,5,7-triazabicyclo[4,4,0]dec-5-ene (TBD), trimethylpropane tris(3-mercaptopropionate) (triSH) (≥ 95.0%),, and 1,1,3,3-tetramethylguanidine (TMG) (99.0%), were obtained from Sigma-Aldrich (https://www.sigmaaldrich.com/ES/es). Sodium tetraphenylborate ($NaBPh_4$) (99%) was purchased from ABCR (https://abcr.com/de_en/). PPG-di-IPDI 2000 was kindly supplied by Cidetec (https://www.cidetec.es). TBD·$HBPh_4$ salt was prepared as specified elsewhere.[1] Isocyanate-terminated prepolymers were prepared by the addition of 2.1 eq. of isocyanate into 1 eq. of polyol previously dried under reduced pressure. The conversion of the reaction monitored by FTIR spectroscopy.

Characterization techniques

Proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy data was collected on a 300 MHz Bruker Advance DPX Spectrometer at 20 ˚C. The samples were dissolved in deuterated solvents and chemical shifts reported in ppms and referenced to solvents peaks.

Fourier Transform Infrared Spectrocopy (FT-IR) spectra were recorded on a Nicolet iS20 Spectrometer using Attenuated Total Reflection (ATR) at a resolution of 2 cm^{-1} and a total of 32 interferograms.

Thermogravimetric analysis (TGA) was carried out on a Q500 Thermogravimetry Analyzer from TA instruments. The system was heated with a heating rate of 10 ˚C/min from room temperature to 600 ˚C under atmospheric conditions.

Differential Scanning Calorimetry (DSC) analysis were performed on a DSC Q2000 from TA Instruments. The analysis was performed in sealed aluminum pans, under dry N_2 atmosphere using a heating rate of 10 ˚C/min a heating ramp from -80 to 160 ˚C.

Size exclusion chromatography (SEC) measurements were carried out on a Waters 1515 GPC chromatograph using chloroform as eluent. Molar masses are referred to PS standards.

Gel content of the samples was determined gravimetrically. At least two specimens of each sample were Soxhlet extracted for 24 h in refluxing THF. The insoluble fraction was dried in the oven. The gel content is expressed as the percentage of insoluble fraction in the sample.

Dynamical Mechanical Thermal Analysis (DMTA) were recorded on a Triton Tritec 2000 DMA instrument. Specimens with dimensions of 15 mm x 5 mm x 0.5 mm were tested in bending mode at a amplitude of 50 µm and a frequency of 1 Hz. A heating ramp of 4 ˚C/min from was used from -70 ˚C to 70 ˚C. The glass transition temperatures (Tg) were calculated from the peak of tanδ.

Rheology measurements were conducted on a AR-G2 rheometer from TA Instruments. For photorheology experiments, a LED UV-curing accessory centered at 365 nm was used together with an acrylic transparent bottom plate. Photorheology experiments were performed at a frequency of 1 Hz and in the linear viscoelasticity region using 20 mm parallel plates and a gap of 400 µm. To determine the viscosity of the formulated resins, a 1° 40 mm cone geometry was used. The shear rate window was from 1 to 100 s^{-1} collecting 11 data points during the experiment. Average values of at least three measurements are shown.

Stress relaxation measurements were performed in a ARES rheometer (Rheometrics) at different temperatures using a film tension fixture and 5 % strain. The samples used for this measurement were in the range of 2.5 to 3 mm wide and 0.5 to 1 mm thick.

Mechanical properties were determined on a Instron 5569 instrument including a 100 N cell at room temperature by uniaxial tensile test. Printed or dye cut samples (20 mm x 7.5 mm x 1 mm) were tested at 2 mm/min strain rate, being the distance between the grips of 10 mm. The Young's modulus (E) was calculated from the initial slope of the stress–strain curve and the deformation at break from the maximum value of stress.

The prepared resins were printed into 3D objects on a commercial Asiga Max-UV DLP 3D printer with a LED source centered at 385 nm. Computer designed 3D objects were prepared for printing in the Asiga Composer software. The optimized printing parameters were 30 s burn-in layer, 20 s exposure time and 50 µm layer thickness at an intensity of 20 mW/cm^2. The material without acetone was printed using 2 payers of 60 s burn-in and 15 s exposure time and 50 µm layer thickness at an intensity of 20 mW/cm^2. The printed objects were washed thoroughly with acetone to remove unreacted monomers and postcured in an oven at 70 ˚C overnight.

Scanning electron microscopy (SEM) measurements were conducted on a Hitachi TM3030Plus microscope at an accelerating voltage of 15 kV. The printed samples were mounted on a specimen stub attached with double-sided carbon adhesive tape and coated with gold before being observed.

Two-photon 3D laser printing (2PLP) was performed using a commercial Photonic Professional GT 2 (Nanoscribe GmbH) direct laser writing system. The fabrication of all microstructures was carried out in oil immersion mode using a 63x oil immersion objective (NA = 1.4). GWL files for desired geometries were generated from STL files of 3D structures employing commercial Describe software (Nanoscribe). Slicing was set to 0.3 µm and hatching to 0.2 µm. Laserpower was 50 mW or 40 mW for the snowflake and smiley respectively, and the scan speed was 2000 µm/s. The laser printed samples were developed in a solution of acetone with excess benzoic acid immediately after printing, then washed with acetone, followed by drying under ambient conditions. The printed samples were stored under ambient conditions. The entire process was performed under yellow light conditions.

Sample preparation

In a typical photopolymerization, equimolar amounts of isocyanate prepolymer and thiol crosslinker were mixed together with TBD·HPBh$_4$ (0.5 wt%) and ITX (0.25 wt%) solution in acetone (30 wt %). The mixture was vortex mixed until homogeneous colorless resin was obtained. This resin was poured into a silicone cast, covered with glass slides and irradiated with a UV-light centered at 365 nm with 60 mW/cm^2 light intensity for 15 minutes. Afterwards, the samples were postcured at 70 °C overnight.

As an example, for the preparation of **PTU1**, 1000.00 mg of PPG-di-IPDI 2000 and 109.00 mg of TMPTMP triSH were mixed in vial. On the other hand, 5.50 mg of TBD·HBPh$_4$ photocatalyst and 2.75 mg of sensitizer (ITX) were dissolved in 300 mg of acetone and added to the monomer mixture. This mixture was vortex agitated until homogeneity was achieved. This resin was freshly used for subsequent studies.

3D printed structures, were washed with acetone to remove unreacted monomer prior the postcuring in an oven at 70 ˚C overnight.

Substrate functionalization for 2PLP: To improve adhesion of 3D printed microstructures, glass slides (Marienfeld, 170 ± 5 µm strength) were washed first with isopropanol, then with acetone and dried using pressurized N_2. Subsequently, the surface was cleaned and activated for one minute by plasma treatment. Following this, the glass slides were immersed in a $4 \cdot 10^{-3}$ M solution of 3-(trimethoxysilyl)propyl acrylate in toluene for 1.5 h. After washing twice in toluene and once in acetone and successive drying with pressurized N_2, the acrylate-functionalized glass slides were used as substrates for 2PLP microfabrication. The entire substrate functionalization was performed under yellow light conditions, along with subsequent storage.

Sample preparation for 2PLP: Using a commercial 2PLP sample holder (Nanoscribe) for oil immersion mode acrylate-functionalized glass slides were attached by tape. Immersion oil was added on the unfunctionalized glass slide surface. A droplet of the functional ink was placed in the center of the slide. The sample was utilized directly for microprinting.

The resin formulation was prepared for 2PLP similarly to the **PTU1** with the addition of octanoic acid ($3 \cdot 10^{-4}$ mmol, 10% w.r.t. the PBG was added to the formulation. The resin mixture was shaken until homogeneity was achieved. The acetone was removed under reduced pressure and the resin was used for printing.

Healing test

Printed samples of 10 mm x 10 mm x 0.1 mm dimensions were scratched using a blazed blade, placed between two glass slides, and clamped using metal binder clips. The samples were placed in a temperature-controlled microscope stage (Linkam LTS420E) at 120 ˚C temperature while images were taken by an optical microscope (Zeiss AXIO Scope A1) every 30 minutes.

Repairability

Control and tested samples were 3D printed using the **PTU1** formulation and optimized printing conditions. Specimens were 20 mm x 7.5 mm x 1 mm and the tested sample was printed with a 4.5 mm diameter hole in the middle. The repair was carried out by filling the hole with the **PTU1** resin and irradiated with a UV-light centered at 365 nm with 60 mW/cm^2 light intensity for 15 minutes. The samples were postcured at 70 °C for 1 h and at 115 °C for 1 h while applying gentle pressure with binder clips.

Depolymerization of PTU1

For the depolymerization of the crosslinked poly(thio)urethane material, 2.00 g of **PTU1** (1.47 mmol thiourethane [S-CO-NH]) was cut into small pieces and mixed with 2 molar equivalent excess of thiol groups from TMPTMP (0.39 g, 2.95 mmol thiol [SH]), 0.1 wt% of TMG ($2.39 \cdot 10^{-3}$ g, 0.02 mmol) and 20 mL of acetone. The mixture was stirred for 3 h at room temperature until the film was completely dissolved. Solvent was evaporated and the residue redissolved in 20 mL of DCM. This solution was extracted with 1 M HCl solution and with brine solution. The organic phase was dried over anhydrous Na_2SO_4 and solvent evaporated under reduced pressure to yield the recycled thiol terminated oligomer in quantitative yield.

Repolymeriation

The recycled oligomers (2.95 mmol thiol [SH]) were recrosslinked by adding stoichiometric amounts of PPG-diIPDI (M_n: 2444.6 g/mol) (2.95 mmol isocyanate [NCO]), 0.5 wt% of TBD·$HBPh_4$ and 0.25 wt% ITX dissolved in 30 wt% of acetone according to the complete system similarly to the original formulation. The mixture was stirred until homogeneity was achieved. This resin was freshly used for subsequent studies.

Supplementary Figures:

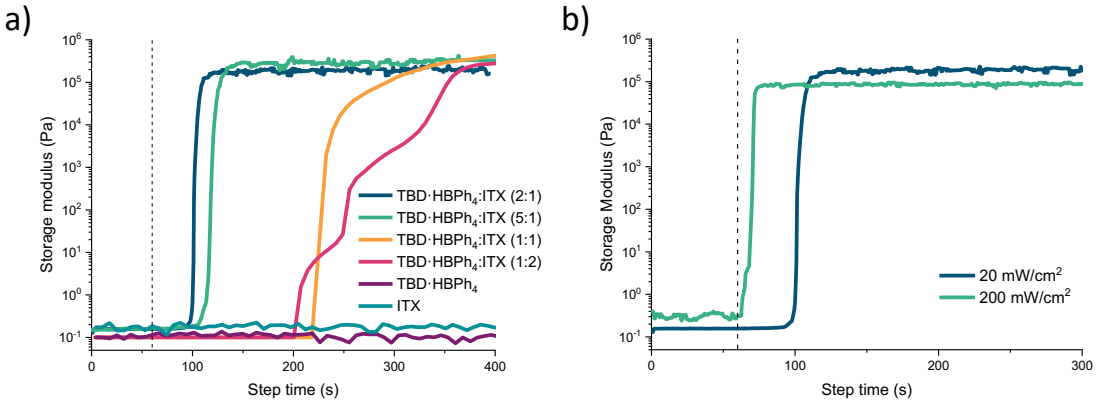


Figure S1: a) Evolution of G' and G'' of PTU1 resin using different catalyst mixtures as function of UV-LED (385 nm) irradiation time at an intensity of 20 mW/cm^2. b) Evolution of G' and G'' of PTU1 resin over time at different irradiation intensities.

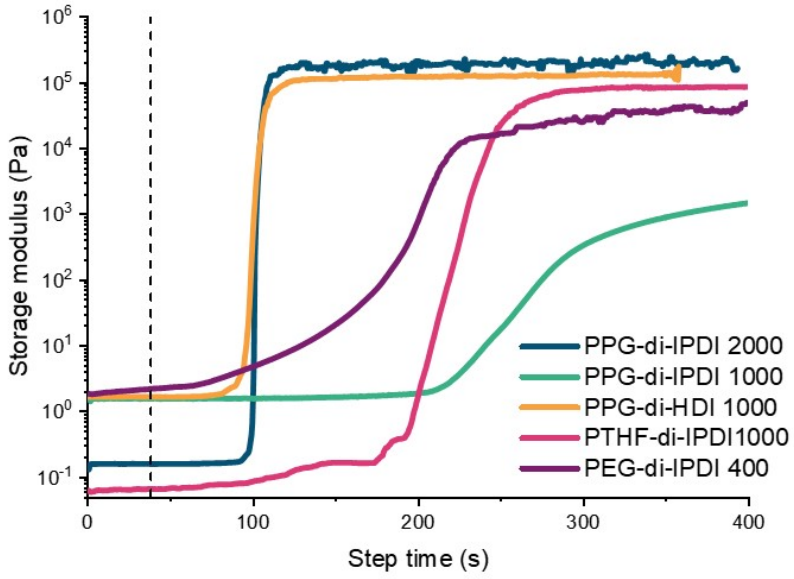


Figure S2: Evolution of G' and G'' of for PTU resins containing different isocyanate prepolymer.

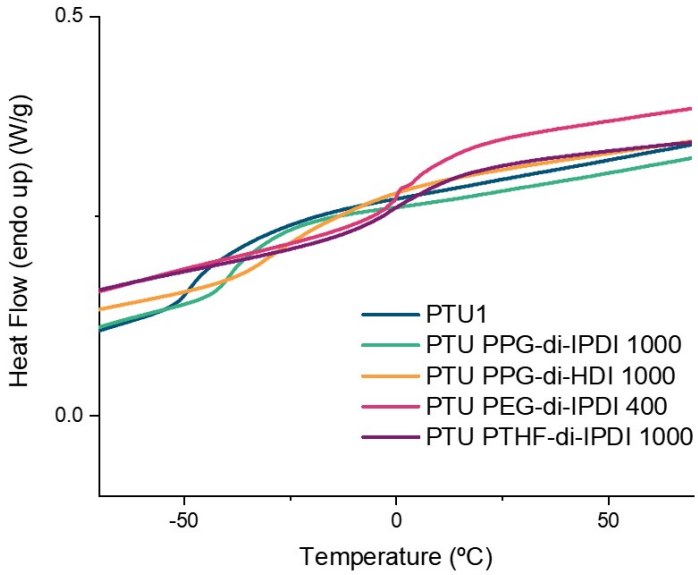


Figure S3: DSC traces for different PTU formulations.

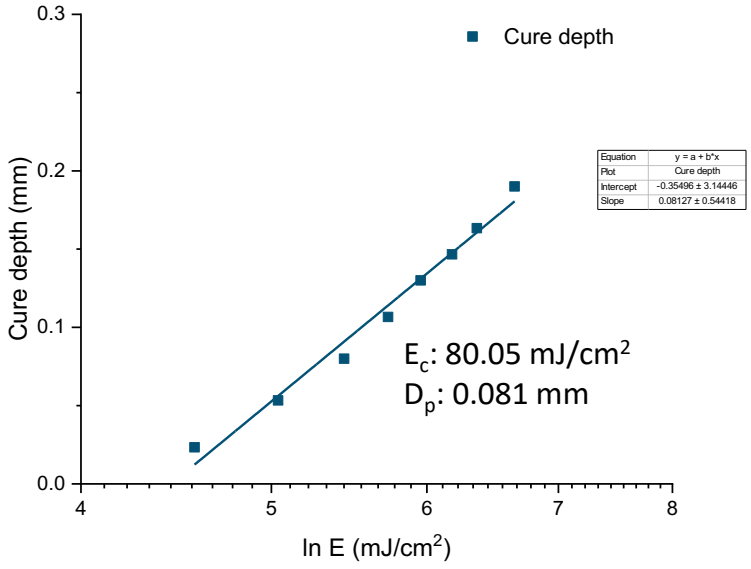


Figure S4: Jacobs working curves for PTU1 formulation at a constant intensity of 20 mW/cm^2.

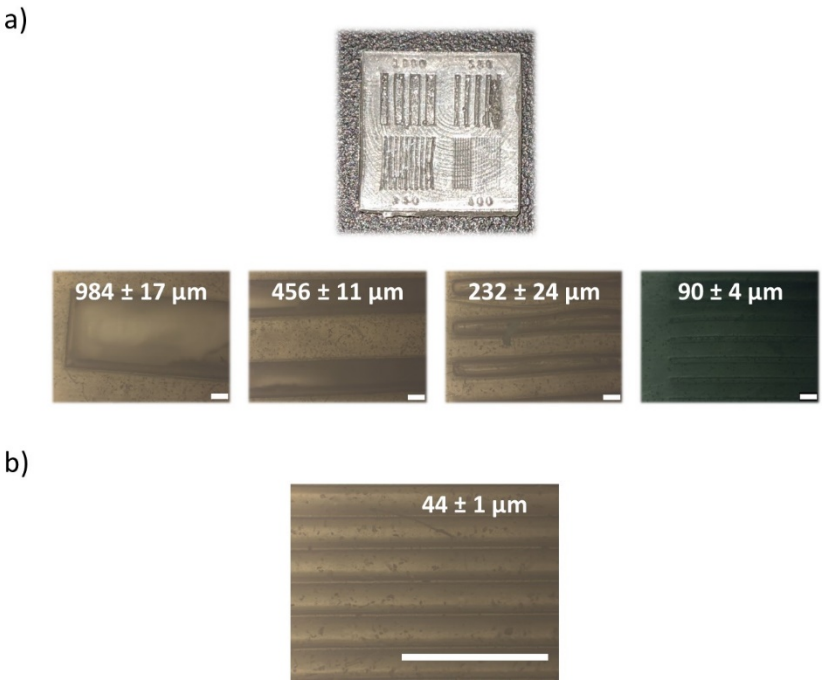


Figure S5. a) Top: Photograph of the XY resolution test 3D object with PTU1 resin. Bottom: Zoom-in microscope images of 1000 µm, 500 µm, 250 µm, and 100 µm outline shapes for resolution demonstration, the number above shows the average measured feature length. b) Zoom-in microscope image of the Z axis of the printed sample showing the layer thickness, the number on the top of the image shows the average measured layer thickness. Scale bar 200 µm.

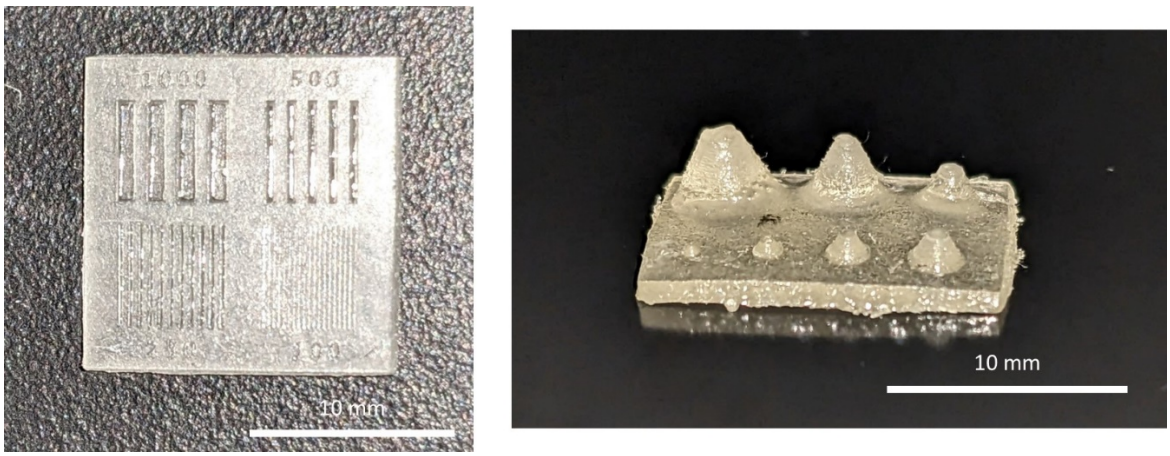


Figure S6. Photograph of 3D printed objects printed without acetone.

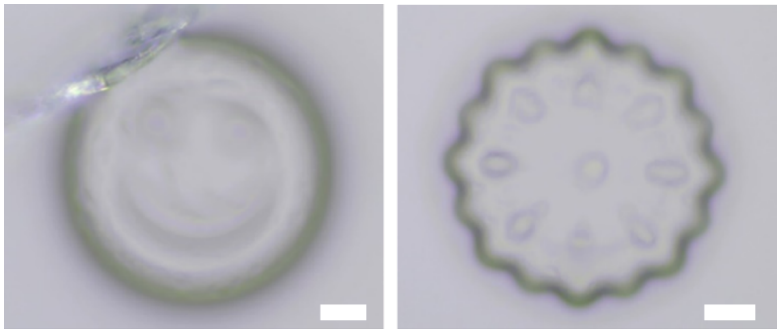


Figure S 7: Microscope images of lower resolution DLW printed smiley (left) and sunflower (right) without the addition of octanoic acid as a quencher, scale bar 15 µm.

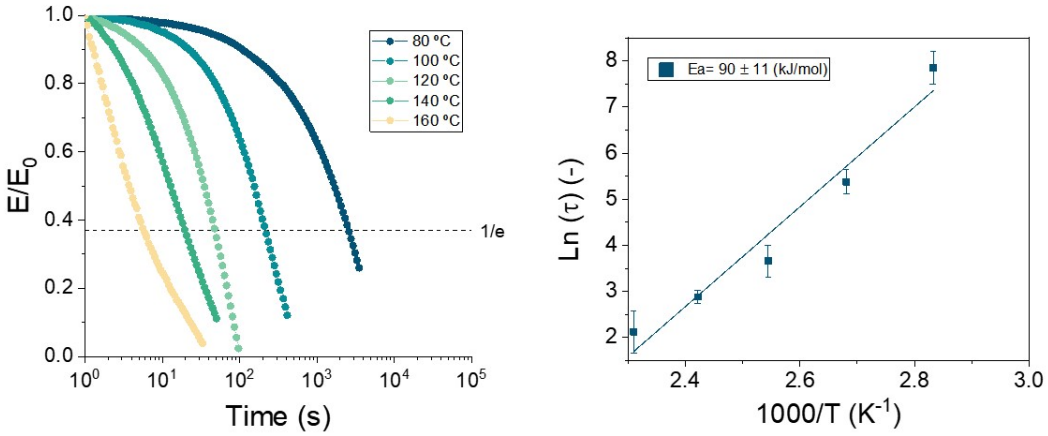
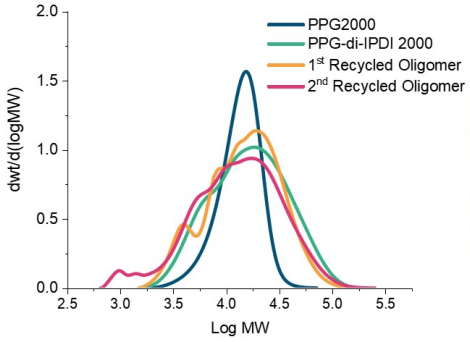


Figure S8: Stress-relaxation measurements for **PTU1** a different temperatures (left) Arrhenius plots of characteristic relaxation time of **PTU1** (right).



Sample	Mn (kDa)	PDI
PPG 2000	2.8	1.08
PPG-di-IPDI 2000	5.4	1.41
1st Recycled Oligomer	11.7	1.94
2nd Recycled Oligomer	7.5	2.52

Figure S9: SEC traces for PPG 2000 (blue), PPG-di-IPDI 200 (green), 1st Recycled Oligomer (orange) and 2nd Recycled Oligomer (pink).

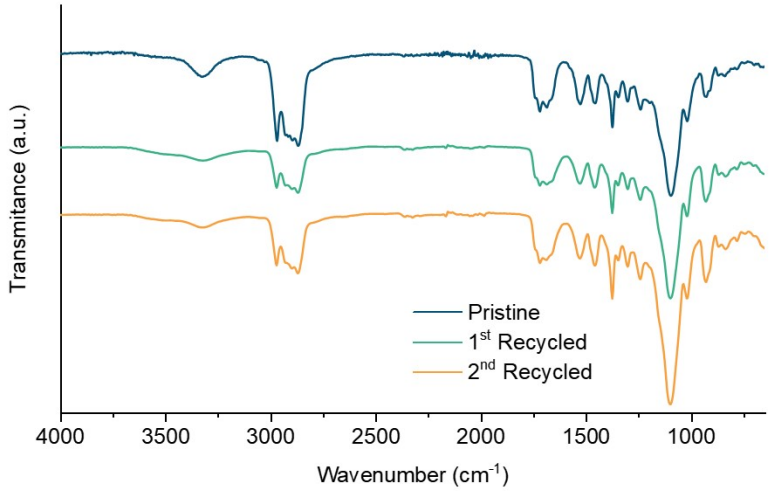
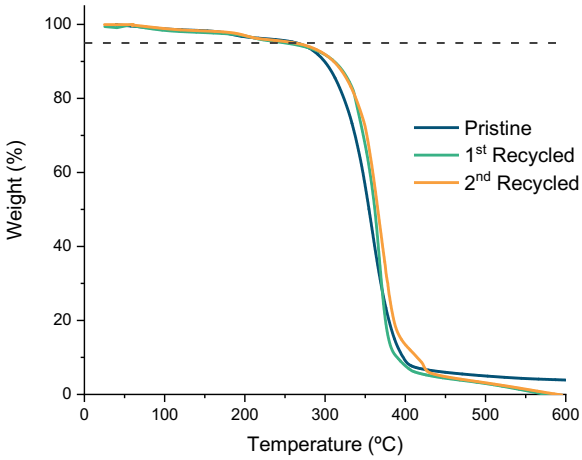


Figure S10: FTIR spectra of pristine (blue), 1st (green) and 2nd (orange) recycled PTU material.



Sample	$T_{5\%}$ (˚C)
Pristine	265
1st Recycled	250
2nd Recycled	261

Figure S11: Thermogravimetric analysis of pristine (blue), 1st recycled (green) and 2nd recycled (orange) materials. Dashed line determines de 5 % of weight loss. In the table the onset temperatures (T 5%).

Table S1: Gel content values for PTU printed materials.

Sample	Gel content (%)
Pristine	97 ± 3
1st Recycled	95 ± 3
2nd Recycled	97 ± 2

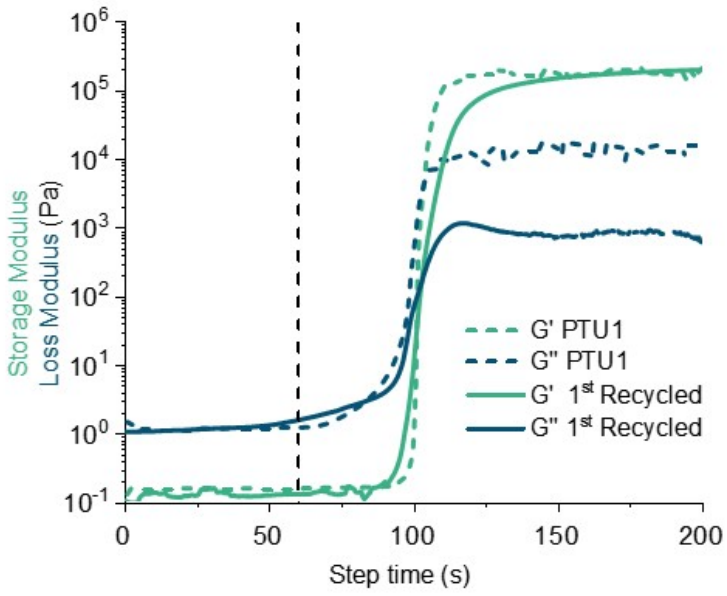
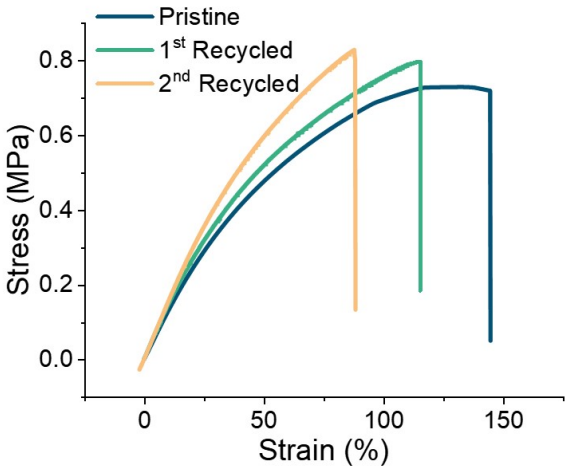


Figure S12: Evolution of storage modulus (G') (green) and loss modulus (G'') (blue) as function of UV-LED (385 nm) irradiation time at an intensity of 20 mW/cm². Dashed lines **PTU1** resin, solid line recycled PTU1 resin.



Sample	Deformation at break (%)	Stress at break (MPa)	Young Modulus (kPa)
Control	140 ± 10	0.73	1.21 ± 0.04
1st Recycled	115	0.79	1.39
2nd Recycled	88	0.82	1.50

Figure S13: Left: Uniaxial stress–strain curves for the pristine material (blue), 1st recycled material (green) and 2nd recycled material (orange). Right: Table summarizing the most relevant mechanical properties of the materials.

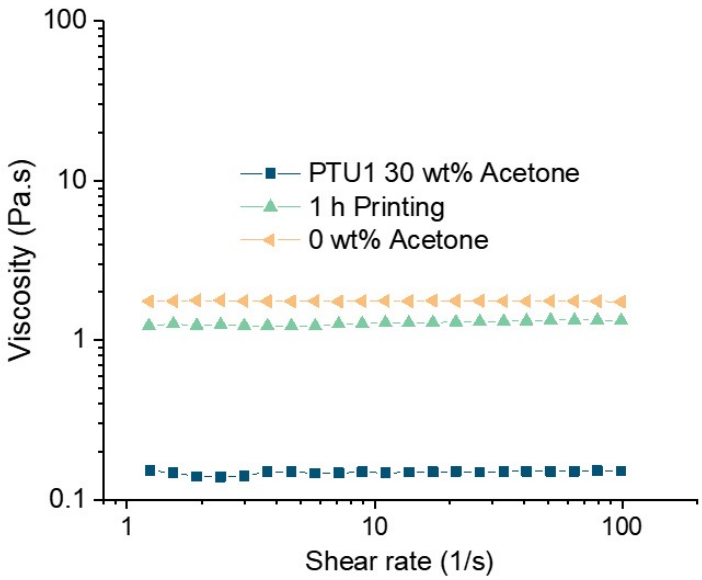


Figure S14: Viscosity curves of the PTU1 resin formulation (blue), PTU1 resin formulation after 1 h printing (green), and the resin formulation without acetone (orange).

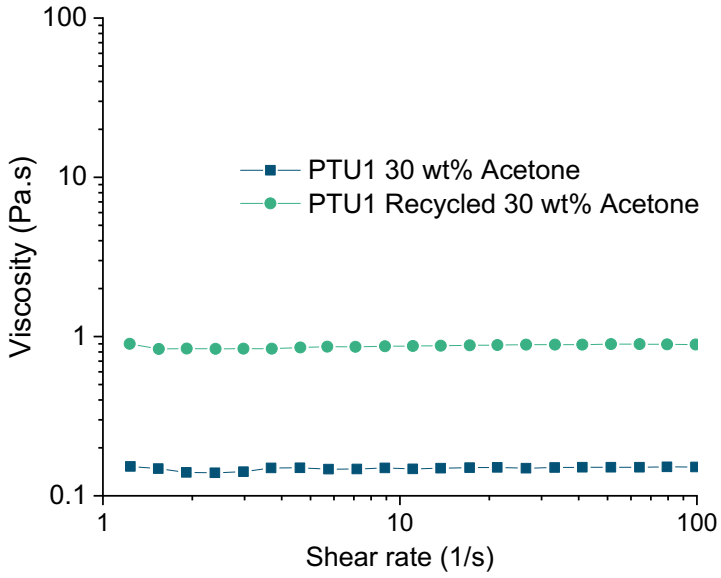


Figure S15: Viscosity curves of the PTU1 resin formulation (blue) and recycled PTU1 formulation (green), both containing 30 wt% of acetone as diluent.

Bibliography:

[1] X. Sun, J. P. Gao, Z. Y. Wang, *J. Am. Chem. Soc.* **2008**, *130*, 8130–8131.